

Supporting Information

Modulation of Sensitivity to Mechanical Stimulus in
Mechanofluorochromic Properties by Altering Substituent
Positions in Solid-State Emissive Diiodo Boron Diiminates

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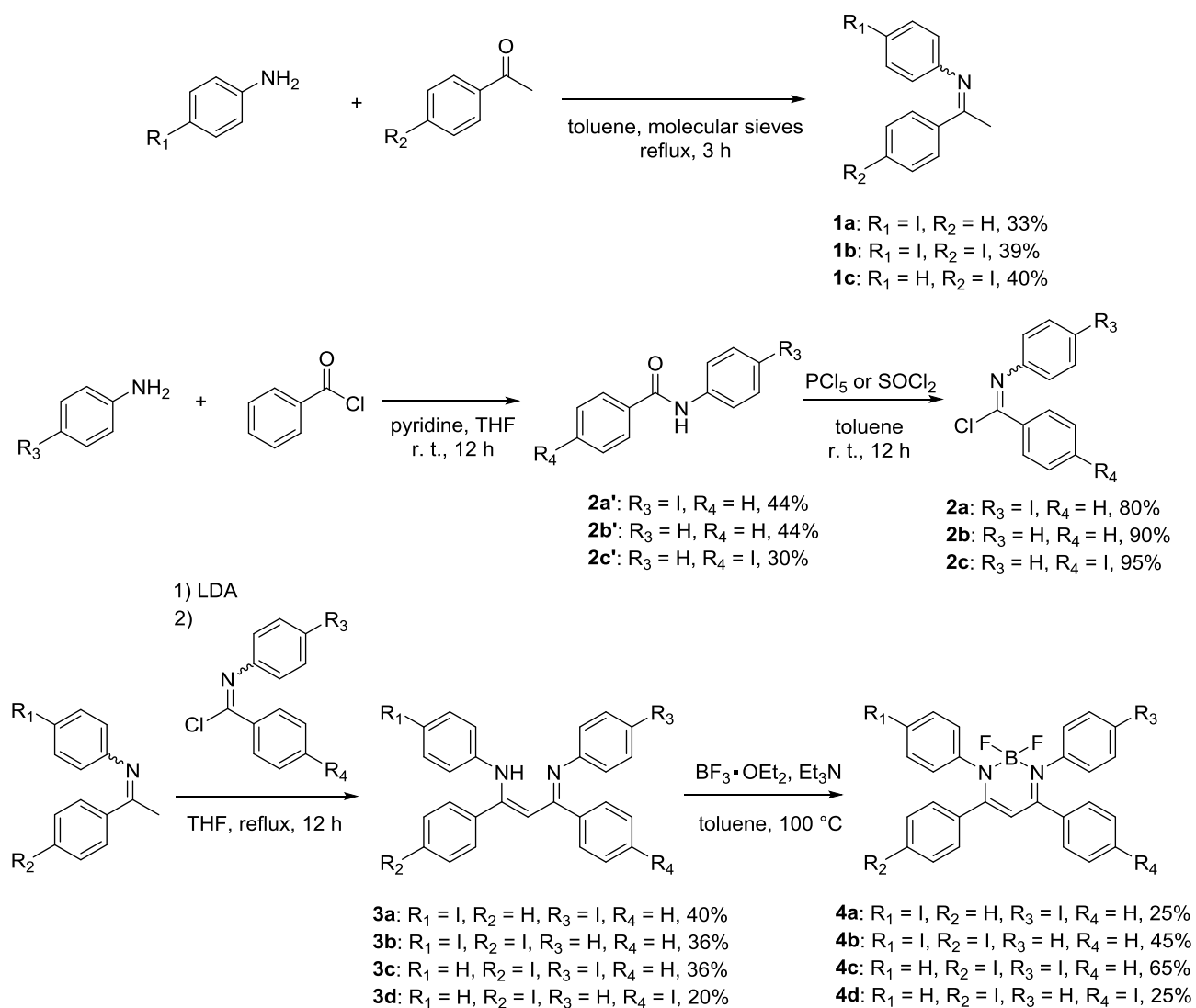
Experimental Section

Measurements: ^1H (400 MHz), ^{13}C (100 MHz), and ^{11}B (128 MHz) NMR spectra were recorded on JEOL JNM-EX400 spectrometers. In ^1H and ^{13}C NMR spectra, tetramethylsilane (TMS) was used as an internal standard in CDCl_3 , and ^{11}B NMR spectra were referenced externally to $\text{BF}_3\cdot\text{OEt}_2$ (sealed capillary). ^{19}F (376 MHz) NMR spectra were recorded on JEOL JNM-ECX400P spectrometer. Ethyl trifluoroacetate ($\delta = -78$ ppm) was used as an internal standard. Thermogravimetric analyses (TGA) were performed on an EXSTAR TG/DTA6220, Seiko Instrument, Inc., with the heating rate of 10 °C/min under nitrogen flowing (200 mL/min). UV–vis spectra were recorded on a SHIMADZU UV-3600 spectrophotometer. Fluorescence emission spectra were measured with a HORIBA JOBIN YVON Fluoromax-4P spectrofluorometer. Absolute PL quantum efficiencies (Φ_{PL}) were determined using a Horiba FL-3018 Integrating Sphere with the minimum detection limit at 0.01. Powder X-ray diffraction (XRD) patterns were taken by using $\text{CuK}\alpha$ radiation with a Rigaku Miniflex. X-ray crystallographic analysis was carried out by a Rigaku R-AXIS RAPID-F graphite-monochromated $\text{Mo K}\alpha$ radiation diffractometer with an imaging plate. A symmetry-related absorption correction was carried out by using the program ABSCOR. The analysis was carried out with direct methods (SHELX97 or SIR92) using Yadokari-XG. The program ORTEP35 was used to generate the X-ray structural diagram. Differential scanning calorimetry (DSC) thermograms were carried out on a SII DSC 6220 instrument. The sample on the aluminum pan was heated at the rate of 10 °C/min under nitrogen flowing (30 mL/min).

Materials: Aniline (Wako Chemical, Co.), *p*-iodoaniline (Tokyo Kasei Kogyo, Co.), benzoyl chloride (Tokyo Kasei Kogyo, Co.), *p*-iodobenzoyl chloride (Tokyo Kasei Kogyo, Co.), acetophenone (Tokyo Kasei Kogyo, Co.), *p*-iodoacetophenone (Tokyo Kasei Kogyo, Co.), acetic acid (Wako Chemical, Co.), pyridine (Wako Chemical, Co.), thionyl chloride (Wako Chemical, Co.), phosphorus pentachloride (Tokyo Kasei Kogyo, Co.), lithium diisopropylamide 3S (1 mol/L in mixed solvent of hexane and THF, Kanto Chemical, Co., Inc.) and boron trifluoride diethyl etherate ($\text{BF}_3\cdot\text{OEt}_2$, Aldrich Chemical,

Co.) were used as received. Tetrahydrofuran (THF) and triethylamine were purified using a two-column solid-state purification system (Glasscoutour System, Joerg Meyer, Irvine, CA).

Scheme S1. Synthesis of boron diiminates



Synthesis of 1a

p-Iodoaniline (25 g, 114 mmol) and molecular sieve were added to the solution of acetophenone (13.7 g, 13.3 mL, 114 mmol) in toluene (175 mL). The reaction mixture was stirred under argon atmosphere at reflux temperature for 3 h. After the sieves were removed by filtration, the solvent was removed by a rotary evaporator. The product was purified by recrystallization from methanol. The precipitate collected by filtration was dried in vacuum to give pure **1a** as a yellow crystal (12.4 g, 33%). ¹H NMR (CDCl₃): δ = 7.95 (2H, d, *J* = 6.71 Hz, Ar-*H*), 7.64 (2H, d, *J* = 8.30 Hz, Ar-*H*), 7.48–7.43 (3H, dd, *J* = 13.98 Hz, 6.47 Hz, Ar-*H*), 6.57 (2H, t, *J* = 8.12 Hz, Ar-*H*), 2.23 (3H, s, -CH₃) ppm. ¹³C NMR (CDCl₃): δ = 166.03, 151.39, 139.22, 137.93, 130.69, 128.40, 127.20, 121.66, 86.57, 17.39 ppm. HRMS (ESI): Calcd for [M+H]⁺, 322.0084; found, *m/z* 322.0087.

Synthesis of 1b

p-Iodoaniline (11.5 g, 52.5 mmol) and molecular sieves and *p*-iodoacetophenone (12.9 g, 52.5 mmol) and acetic acid (5 mL) were added in toluene (150 mL). The reaction mixture was stirred under argon atmosphere at reflux temperature for 3 h. After the sieves were removed by filtration, the solvent was removed by a rotary evaporator. The obtained product was washed with methanol, and the solid collected by filtration was dried in vacuum to give pure **1b** as a yellow powder (9.2 g, 39%). ¹H NMR (CDCl₃): δ = 7.79 (2H, d, *J* = 8.36 Hz, Ar-*H*), 7.69–7.64 (4H, Ar-*H*), 6.55 (2H, d, *J* = 8.30 Hz, Ar-*H*), 2.19 (3H, s, -CH₃) ppm. ¹³C NMR (CDCl₃): δ = 165.14, 151.00, 138.60, 137.98, 137.60, 128.87, 121.54, 97.58, 86.88, 17.13 ppm. HRMS (ESI): Calcd for [M+H]⁺, 447.9054; found, *m/z* 447.9051.

Synthesis of 1c

Compound **1c** was prepared from aniline (7.5 g, 7.35 mL, 80.53 mmol) and *p*-iodoacetophenone (19.8 g, 80.5 mmol) in 40% yield (10.4 g, pale yellow solid) according to the same method with **1a**. ¹H NMR (CDCl₃): δ = 7.75 (4H, dd, *J* = 34.8 Hz, 8.61 Hz, Ar-*H*), 7.35 (2H, t, *J* = 15.7 Hz, Ar-*H*), 7.09 (1H, t, 14.9 Hz, Ar-*H*), 6.78 (2H, d, *J* = 7.14 Hz, Ar-*H*), 2.20 (3H, s, -CH₃) ppm. ¹³C NMR (CDCl₃): δ = 164.47, 151.38, 138.98, 137.52, 128.97, 128.86, 123.41, 119.25, 97.21, 17.06 ppm.

HRMS (ESI): Calcd for $[M+H]^+$, 322.0087; found, m/z 322.0085.

Synthesis of 2a'

Benzoyl chloride (19.3 g, 15.9 mL, 137 mmol) and pyridine (10.8 g, 11.1 mL, 137 mmol) were added to *p*-iodoaniline (20.0 g, 91.3 mmol) in THF (180 mL). The reaction mixture was stirred under argon at ambient temperature for 12 h. After the generated salt was removed by filtration, the solvent was removed by a rotary evaporator. The obtained product was washed with methanol, and the solid collected by filtration was dried in vacuum to give pure **2a'** as a white solid (13.2 g, 44%). ^1H NMR (CDCl_3): δ = 7.86 (2H, d, J = 7.35 Hz, Ar-*H*), 7.75 (1H, br s, -NH-), 7.68 (2H, d, J = 8.79 Hz, Ar-*H*), 7.57 (1H, t, J = 14.5, Ar-*H*), 7.50 (2H, t, J = 15.2, Ar-*H*), 7.44 (2H, d, J = 8.48 Hz, Ar-*H*) ppm. Because of poor solubility, ^{13}C NMR spectrum was not detectable. HRMS (ESI): Calcd for $[M+H]^+$, 323.9880; found, m/z 323.9877.

Synthesis of 2b'

Compound **2b'** was prepared from aniline (10.0 g, 9.8 mL, 107 mmol) and benzoyl chloride (2.6 g, 18.8 mmol) in 44% yield (9.3 g, white solid) according to the same method with **2a'**. ^1H NMR (CDCl_3): δ = 7.87 (2H, d, J = 7.87 Hz, Ar-*H*), 7.79 (1H, br s, -NH-), 7.65 (2H, d, J = 8.06 Hz, Ar-*H*), 7.58-7.48 (3H, Ar-*H*), 7.38 (2H, t, J = 14.5 Hz, Ar-*H*), 7.16 (1H, t, J = 14.6 Hz, Ar-*H*) ppm. ^{13}C NMR (CDCl_3): δ = 165.69, 137.97, 135.10, 131.82, 129.11, 128.81, 127.01, 124.59, 120.22 ppm. HRMS (ESI): Calcd for $[M+H]^+$, 198.0913; found, m/z 198.0914.

Synthesis of 2c'

Compound **2c'** was prepared from aniline (8.75 g, 8.58 mL, 94.0 mmol) and *p*-iodobenzoyl chloride (25.0 g, 94.0 mmol) in 30% yield (3.0 g, pale yellow solid) according to the same method with **2a'**. ^1H NMR (CDCl_3): δ = 7.85 (2H, d, J = 8.42 Hz, Ar-*H*), 7.72 (1H, br s, -NH-), 7.61 (4H, dd, J = 17.1 Hz, 8.61 Hz, Ar-*H*), 7.38 (2H, t, J = 15.9 Hz, Ar-*H*), 7.17 (1H, t, J = 15.0 Hz, Ar-*H*) ppm. Because of

poor solubility, ^{13}C NMR spectrum was not detectable. HRMS (ESI): Calcd for $[\text{M-H}]^-$, 321.9734; found, m/z 321.9732.

Synthesis of 2a

Phosphorus pentachloride (6.4 g, 30.6 mmol) was added to the solution of **2a'** (9.0 g, 27.9 mmol) in toluene (100 mL). The reaction mixture was stirred under argon atmosphere at reflux temperature for 12 h. After the solution was cooled to ambient temperature, the solvent was removed by vacuum distillation. Sodium hydrogen carbonate was added to the residue for neutralization. Precipitates were removed by filtration, and then the solvent was removed by a rotary evaporator to give the desired product **2a** as a pale yellow solid (7.7 g, 80%). The product was used for the next reaction without further purification.

Synthesis of 2b

Thionyl chloride (42.2 g, 25.7 mL, 0.35 mol) was added to the solution of **2b'** (10.0 g, 42.2 mmol) in toluene (150 mL). The reaction mixture was stirred under argon atmosphere at reflux temperature for 12 h. After the solution was cooled to ambient temperature, the solvent and the remaining thionyl chloride were removed by vacuum distillation. Sodium hydrogen carbonate and toluene were added to the residue for neutralization. Precipitates were removed by filtration, and then the solvent was removed by a rotary evaporator to give the desired product **2b** as a pale yellow solid (9.9 g, 90%). The product was used for the next reaction without further purification.

Synthesis of 2c

Compound **2c** was prepared from **2c'** (2.5 g, 7.7 mmol) in 95% yield (2.5 g, pale yellow solid) according to the same method with **2b**.

Synthesis of 3a

Lithium diisopropylamide (10.9 mL, 11.9 mmol) was added dropwise to the solution of **1a** (3.5 g,

10.9 mmol) in THF (75 mL) at $-10\text{ }^{\circ}\text{C}$. The reaction mixture was stirred at $-10\text{ }^{\circ}\text{C}$ for 30 min under argon atmosphere, and then **2a** (3.72 g, 10.9 mmol) in THF (75 mL) was added to the reaction solution at $-10\text{ }^{\circ}\text{C}$. After stirred the solution at reflux temperature for 12 h, the solution was poured into a large amount of CH_2Cl_2 . The solution was washed with brine three times and dried over anhydrous magnesium sulfate. After the solvent was removed by a rotary evaporator, the obtained product was dissolved in a small amount of CHCl_3 , and then the product was reprecipitated from methanol. The precipitate collected by filtration was dried in vacuum to give pure **3a** as a yellow powder. (2.92 g, 40%). ^1H NMR (CDCl_3): $\delta = 12.9$ (1H, s, $-\text{NH}-$), 7.39 (4H, d, $J = 8.42$ Hz, Ar- H), 7.32–7.27 (12H, Ar- H), 6.48 (4H, d, $J = 8.42$ Hz), 5.38 (1H, s, $-\text{CH}=\text{}$) ppm. HRMS (ESI): Calcd for $[\text{M}+\text{H}]^+$, 626.9789; found, m/z 626.9777.

Synthesis of 3b

Compound **3b** was prepared from **1b** (2.5 g, 5.6 mmol) and **3b** (1.2 g, 5.6 mmol) in 36% yield (1.1 g, a yellow powder) according to the same method with **3a**. ^1H NMR (CDCl_3): $\delta = 12.9$ (1H, s, $-\text{NH}-$), 7.36–7.26 (10H, Ar- H), 7.62 (2H, d, $J = 8.24$ Hz, Ar- H), 7.42 (2H, d, $J = 8.36$ Hz, Ar- H), 7.33–7.28 (6H, Ar- H), 7.11 (2H, t, $J = 15.3$ Hz, Ar- H), 7.03 (2H, d, $J = 8.18$ Hz, Ar- H), 6.92 (1H, t, $J = 15.1$ Hz, Ar- H), 5.31 (1H, s, $-\text{CH}=\text{}$) ppm. HRMS (ESI): Calcd for $[\text{M}+\text{H}]^+$, 626.9789; found, m/z 626.9776.

Synthesis of 3c

Compound **3c** was prepared from **1c** (3.5 g, 10.9 mmol) and **2a** (3.7 g, 10.9 mmol) in 36% yield (3.2 g, a yellow powder) according to the same method with **3a**. ^1H NMR (CDCl_3): $\delta = 12.9$ (1H, s, $-\text{NH}-$), 7.60 (2H, d, $J = 8.24$ Hz, Ar- H), 7.38 (2H, d, $J = 8.48$ Hz, Ar- H), 7.32–7.27 (5H, Ar- H), 7.14 (2H, t, $J = 15.8$ Hz, Ar- H), 7.07 (2H, d, $J = 8.30$ Hz, Ar- H), 6.94 (1H, t, $J = 14.5$ Hz, Ar- H), 6.72 (2H, d, $J = 7.51$ Hz, Ar- H), 6.48 (2H, d, $J = 8.42$ Hz, Ar- H), 5.32 (1H, s, $-\text{CH}=\text{}$) ppm. HRMS (ESI): Calcd for $[\text{M}+\text{H}]^+$, 626.9789; found, m/z 626.9777.

Synthesis of 3d

Lithium diisopropylamide (9.34 mL, 10.3 mmol) was added dropwise to the solution of **1c** (3.0 g, 9.3 mmol) in THF (75 mL) at $-10\text{ }^{\circ}\text{C}$. The reaction mixture was stirred at $-10\text{ }^{\circ}\text{C}$ for 30 minutes under argon atmosphere, and then **3c** (3.1 g, 9.3 mmol) in THF (75 mL) was added to the solution at $-10\text{ }^{\circ}\text{C}$. After stirred the solution at ambient temperature for 12 h, the solution was poured into a large amount of CH_2Cl_2 . The solution was washed with brine three times and dried over anhydrous magnesium sulfate. After the solvent was removed by a rotary evaporator, the obtained product was dissolved in a small amount of CHCl_3 , and then the product was reprecipitated from methanol. The precipitate collected by filtration was dried in vacuum to the desired product of **3d** as an orange powder. The product was used for next reaction without further purification because of extremely low stability (0.25 g, 20%).

Synthesis of 4a

$\text{BF}_3\cdot\text{OEt}_2$ (3.0 mL, 3.4 g, 24.0 mmol) and triethylamine (3.3 mL, 2.4 g, 24.0 mmol) were added to the solution of **3a** (1.5 g, 2.4 mmol) in toluene (60 mL) at ambient temperature, and the solution was stirred at $100\text{ }^{\circ}\text{C}$ for 6 h. After precipitates were removed by filtration, the solvent was removed by a rotary evaporator. The obtained product was dissolved in a small amount of CHCl_3 , and then the product was reprecipitated from methanol. After the precipitate collected by filtration was dried in vacuum the product was purified by silica gel column chromatography (eluted with hexane/ethyl acetate = 2.5/1). The product was purified by recrystallization from methanol. The precipitate collected by filtration was dried in vacuum to give pure **4a** as a yellow crystal (0.4 g, 25%). ^1H NMR (CDCl_3): $\delta = 7.48$ (4H, tt, $J = 8.65$ Hz, 4.51 Hz, Ar-*H*), 7.33–7.23 (10H, Ar-*H*), 6.91 (4H, d, $J = 8.53$ Hz), 5.64 (1H, s, -*CH=*) ppm. ^{13}C NMR (CDCl_3): $\delta = 164.60, 141.47, 137.52, 135.96, 129.84, 129.65, 129.02, 128.41, 100.11, 91.53$ ppm. ^{11}B NMR (CDCl_3): $\delta = 1.56$ (t, $J = 37.5$ Hz) ppm. ^{19}F NMR (CDCl_3): $\delta = -130.3$ (q, $J = 34.6$ Hz) ppm. HRMS (ESI): Calcd for $[\text{M}+\text{Na}]^+$, 696.9591; found, m/z 696.9583.

Synthesis of 4b

$\text{BF}_3\cdot\text{OEt}_2$ (3.0 mL, 3.4 g, 24.0 mmol) and triethylamine (3.3 mL, 2.4 g, 24.0 mmol) were added to

the solution of **3b** (1.5 g, 2.4 mmol) in toluene (60 mL) at ambient temperature, and the solution was stirred at 100 °C for 6 h. After precipitates were removed by filtration, the solvent was removed by a rotary evaporator. The obtained product was dissolved in a small amount of CHCl₃, and then the product was reprecipitated from methanol. After the precipitate collected by filtration was dried in vacuum, the product was purified by recrystallization from methanol. The precipitate collected by filtration was dried in vacuum to give pure **4b** as a yellow crystal (0.7 g, 45%) . ¹H NMR (CDCl₃): δ = 7.61 (2H, d, *J* = 8.22 Hz, Ar-*H*), 7.50 (2H, d, *J* = 7.92 Hz, Ar-*H*), 7.28–7.08 (10H, Ar-*H*), 7.03 (2H, d, *J* = 7.92 Hz, Ar-*H*), 6.92 (2H, d, *J* = 8.53 Hz, Ar-*H*), 5.58 (1H, s, -CH=) ppm. ¹³C NMR (CDCl₃): δ = 165.21, 162.79, 141.41, 141.40, 137.68, 137.64, 136.09, 135.63, 130.60, 129.66, 129.61, 128.98, 128.37, 128.20, 127.70, 126.60, 99.63, 96.30, 91.96 ppm. ¹¹B NMR (CDCl₃): δ = 1.56 (t, *J* = 25.1 Hz) ppm. ¹⁹F NMR (CDCl₃): δ = -130.3 (q, *J* = 24.4 Hz) ppm. HRMS (ESI): Calcd for [M+Na]⁺, 696.9591; found, m/z 696.9582.

Synthesis of 4c

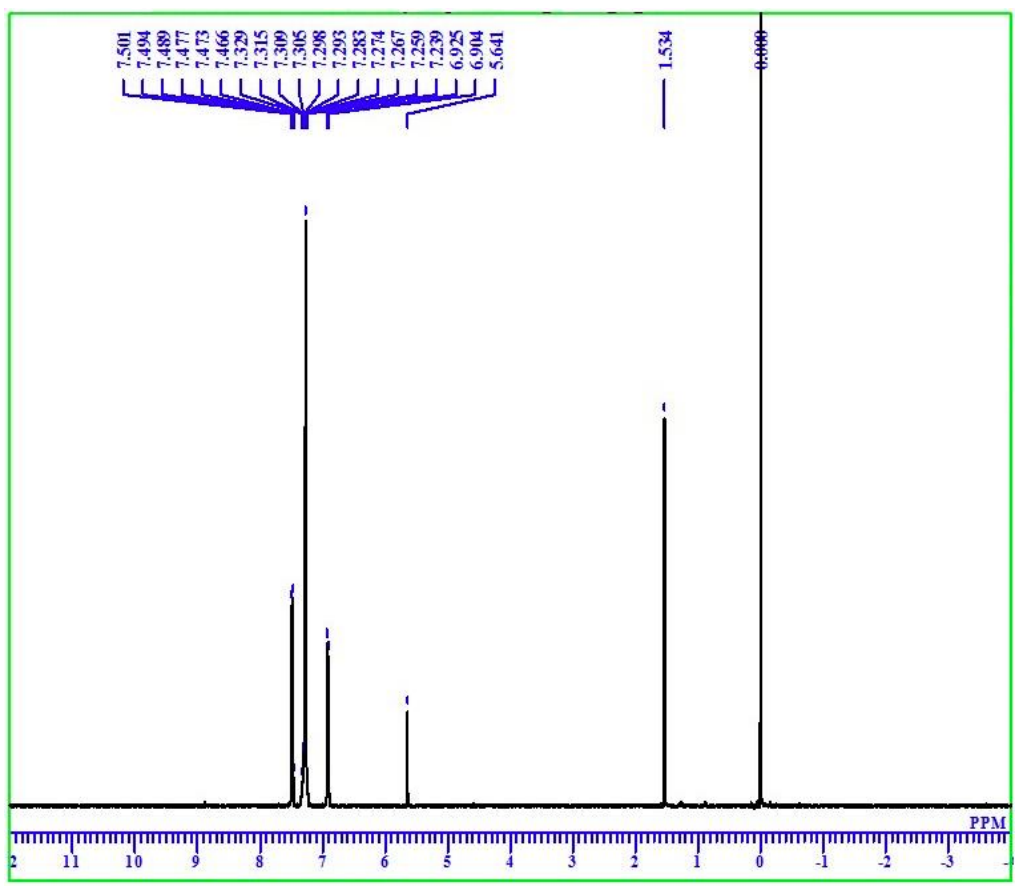
Compound **4c** was prepared from **3c** (1.7 g, 2.6 mmol) in 65% yield (3.2 g, a yellow powder) according to the same method with **4b**. ¹H NMR (CDCl₃): δ = 7.57 (4H, tt, *J* = 8.53 Hz, 4.02 Hz, Ar-*H*), 7.33–7.11 (10H, Ar-*H*), 7.03 (2H, tt, *J* = 8.53 Hz, 3.84 Hz, Ar-*H*), 6.91 (2H, d, *J* = 8.65 Hz, Ar-*H*) 5.57 (1H, s, -CH=) ppm. ¹³C NMR (CDCl₃): δ = 164.44, 163.66, 141.53, 141.33, 137.48, 137.44, 135.98, 135.77, 130.59, 129.81, 129.66, 129.00, 128.56, 128.40, 127.69, 126.70, 99.56, 96.10, 91.45 ppm. ¹¹B NMR (CDCl₃): δ = 1.56 (t, *J* = 25.0 Hz) ppm. ¹⁹F NMR (CDCl₃): δ = -130.3 (q, *J* = 24.4 Hz) ppm. HRMS (ESI): Calcd for [M+Na]⁺, 696.9591; found, m/z 696.9581.

Synthesis of 4d

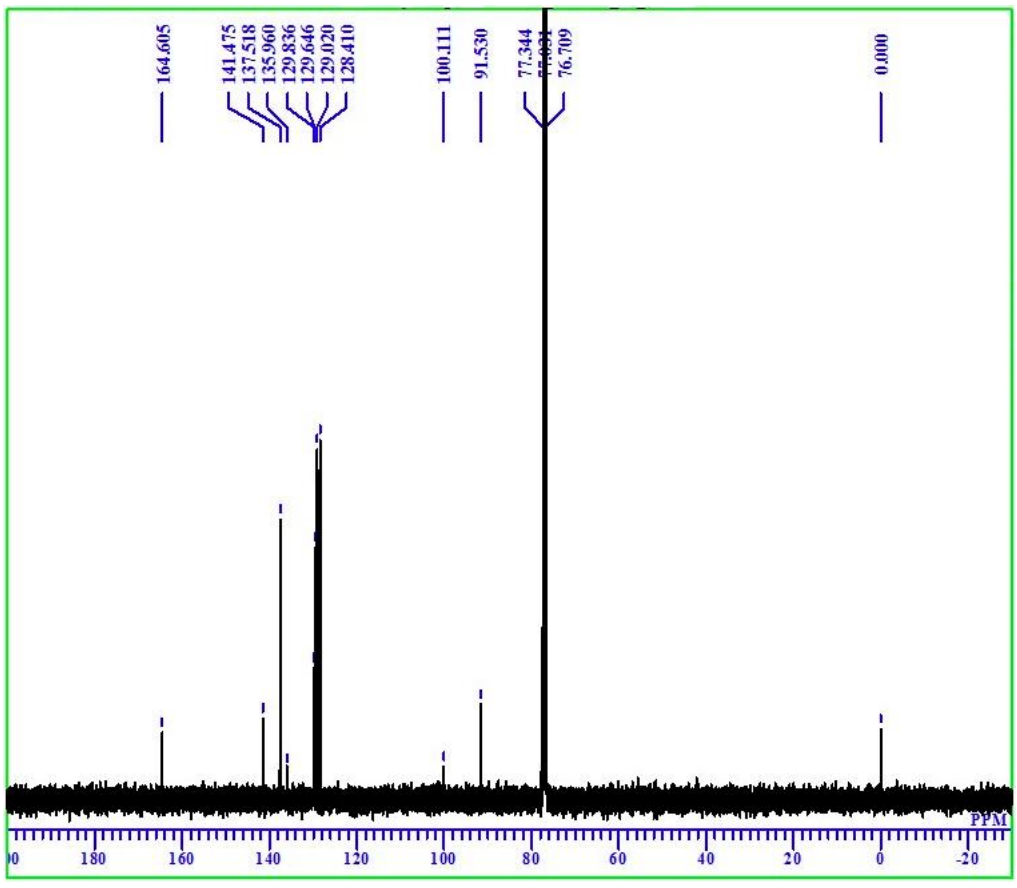
BF₃•OEt₂ (4.9 mL, 5.7 g, 39.9 mmol) and triethylamine (5.6 mL, 4.0 g, 39.9 mmol) were added to the solution of **3c** (2.5 g, 4.0 mmol) in toluene (60 mL) at ambient temperature, and the solution was stirred at 100 °C for 6 h. After precipitates were removed by filtration, the solvent was removed by a rotary evaporator. The obtained product was dissolved in a small amount of CHCl₃, and then the

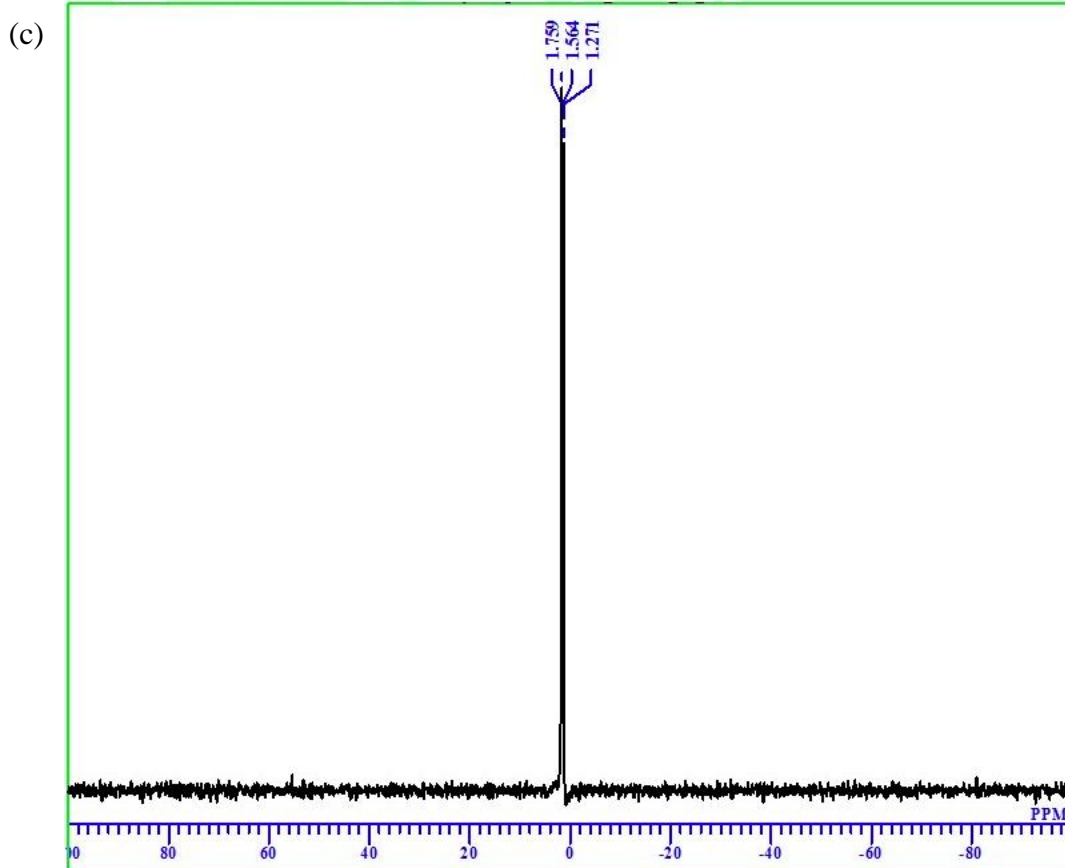
product was reprecipitated from methanol. After the precipitate collected by filtration was dried in vacuum the product was purified by silica gel column chromatography (eluted with hexane/ethyl acetate = 5/1). The product was purified by recrystallization from methanol. The precipitate collected by filtration was dried in vacuum to give pure **4d** as a yellow crystal (0.4 g, 25%). ^1H NMR (CDCl_3): $\delta = 7.58$ (4H, tt, $J = 8.30$ Hz, 4.09 Hz, Ar-*H*), 7.21–7.11 (10H, Ar-*H*), 7.02 (4H, tt, $J = 8.42$ Hz, 4.09 Hz, Ar-*H*), 5.52 (1H, s, -CH=) ppm. ^{13}C NMR (CDCl_3): $\delta = 163.48, 141.36, 137.43, 135.79, 130.59, 128.52, 127.69, 126.65, 98.94, 96.09$ ppm. ^{11}B NMR (CDCl_3): $\delta = 1.66$ (t, $J = 25.1$ Hz) ppm. ^{19}F NMR (CDCl_3): $\delta = -130.4$ (q, $J = 28.6$ Hz) ppm. HRMS (ESI): Calcd for $[\text{M}+\text{H}]^+$, 674.9771; found, m/z 674.9767.

(a)



(b)





(d)

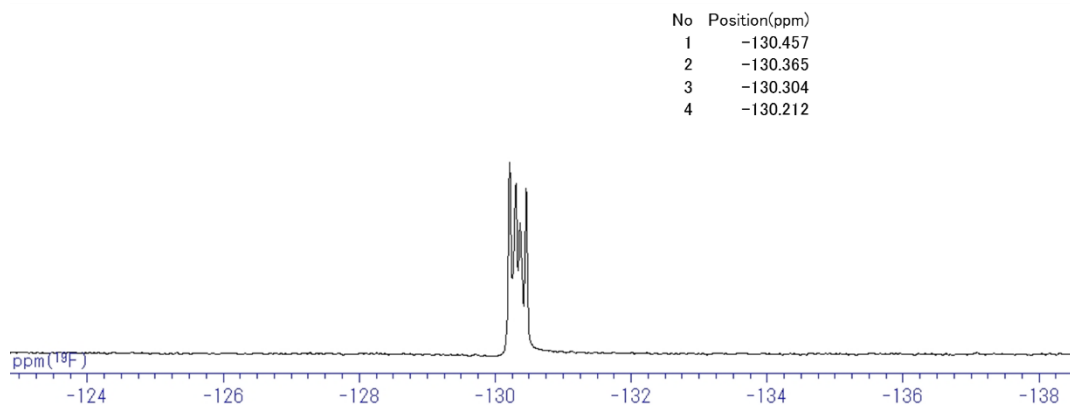
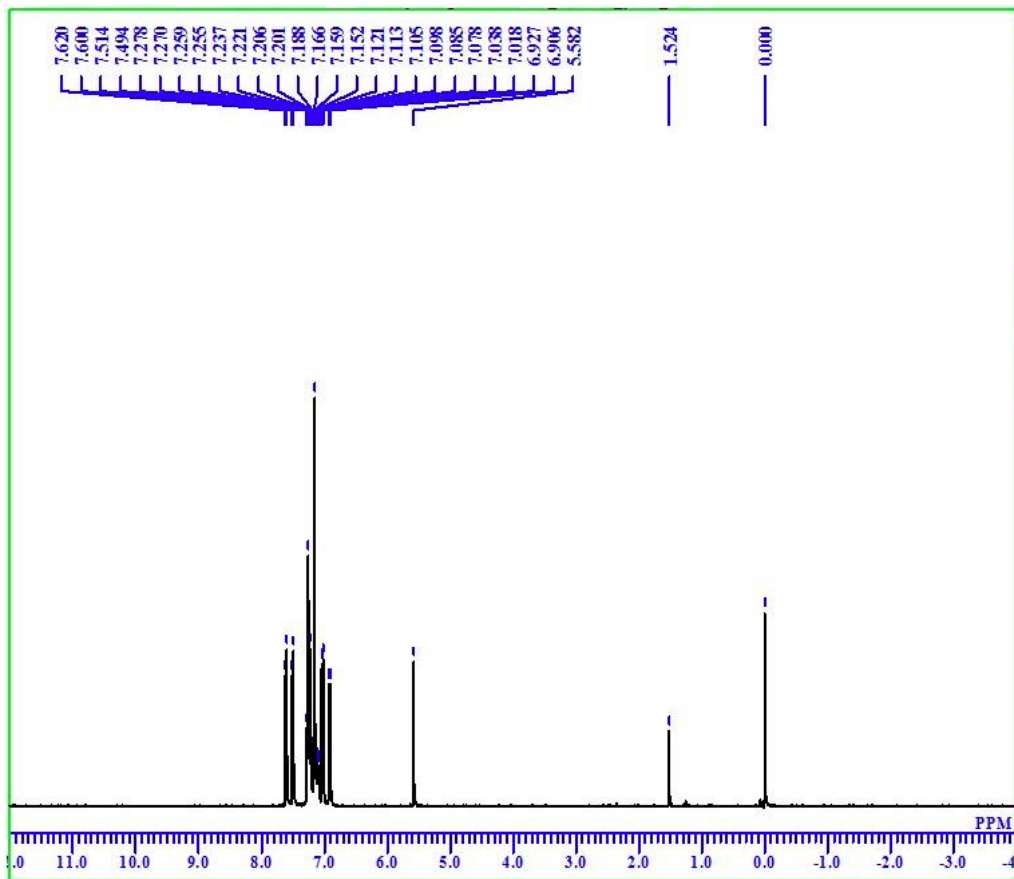
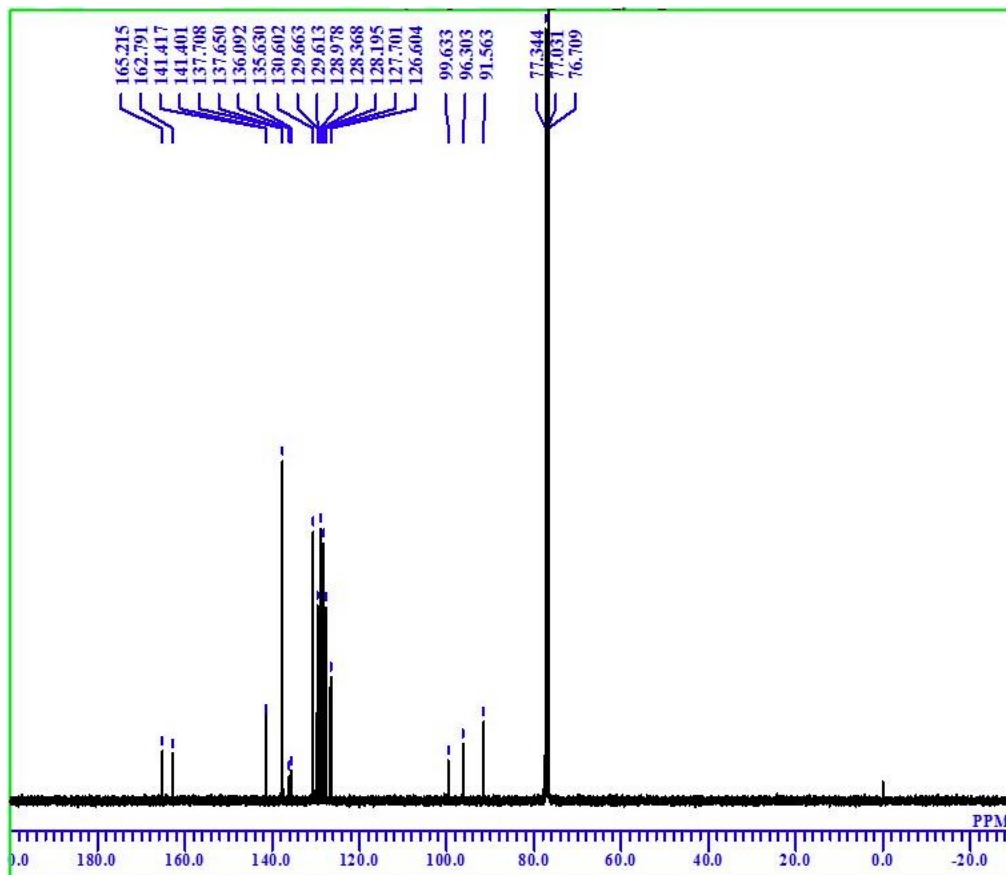


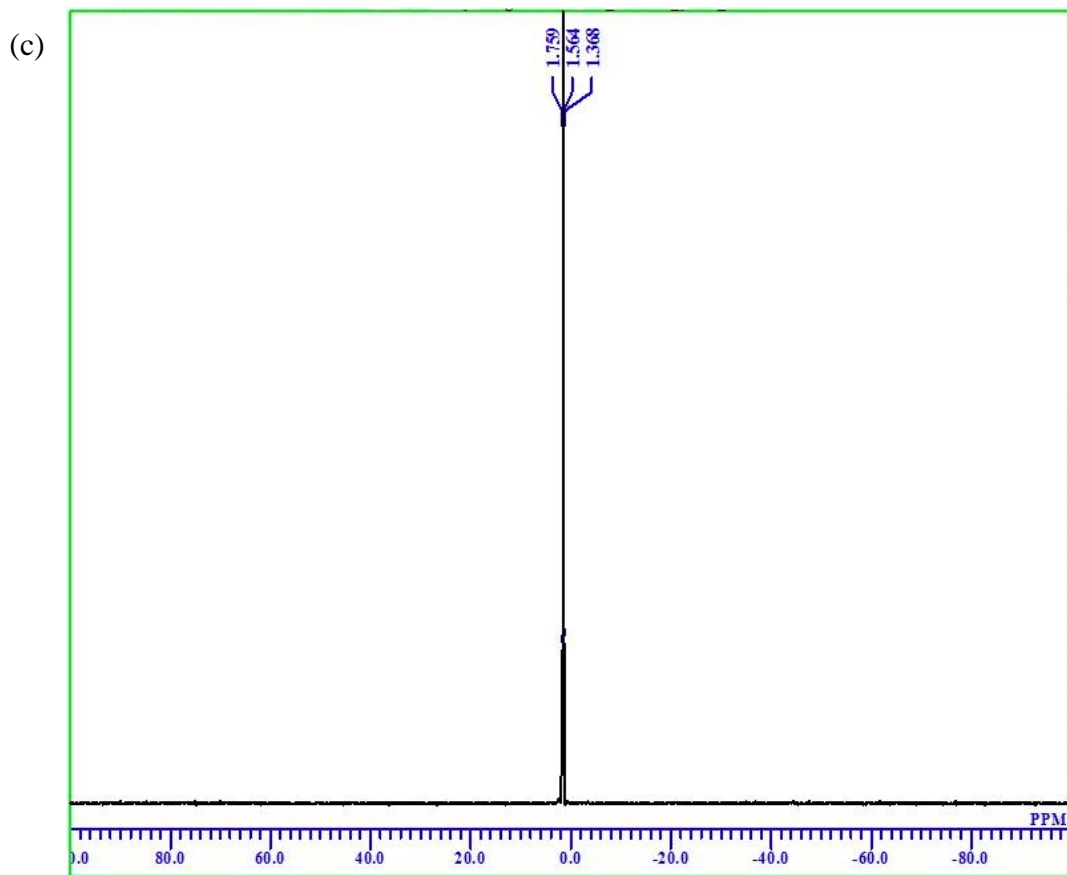
Figure S1. (a) ^1H , (b) ^{13}C , (c) ^{11}B and (d) ^{19}F NMR spectra of **4a** in CDCl_3 .

(a)



(b)





(d)

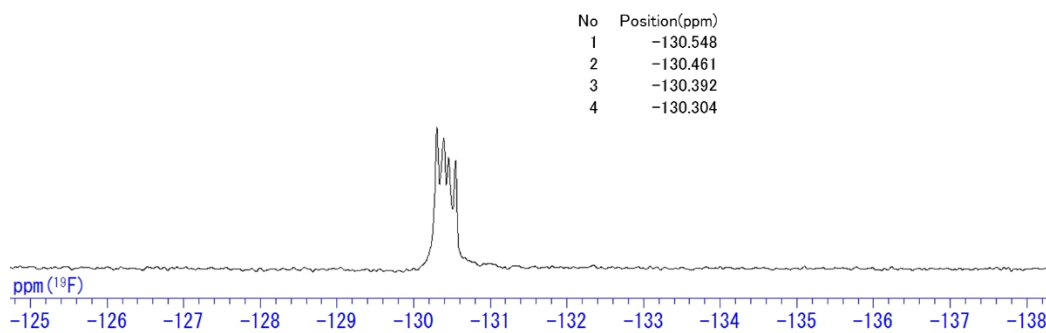
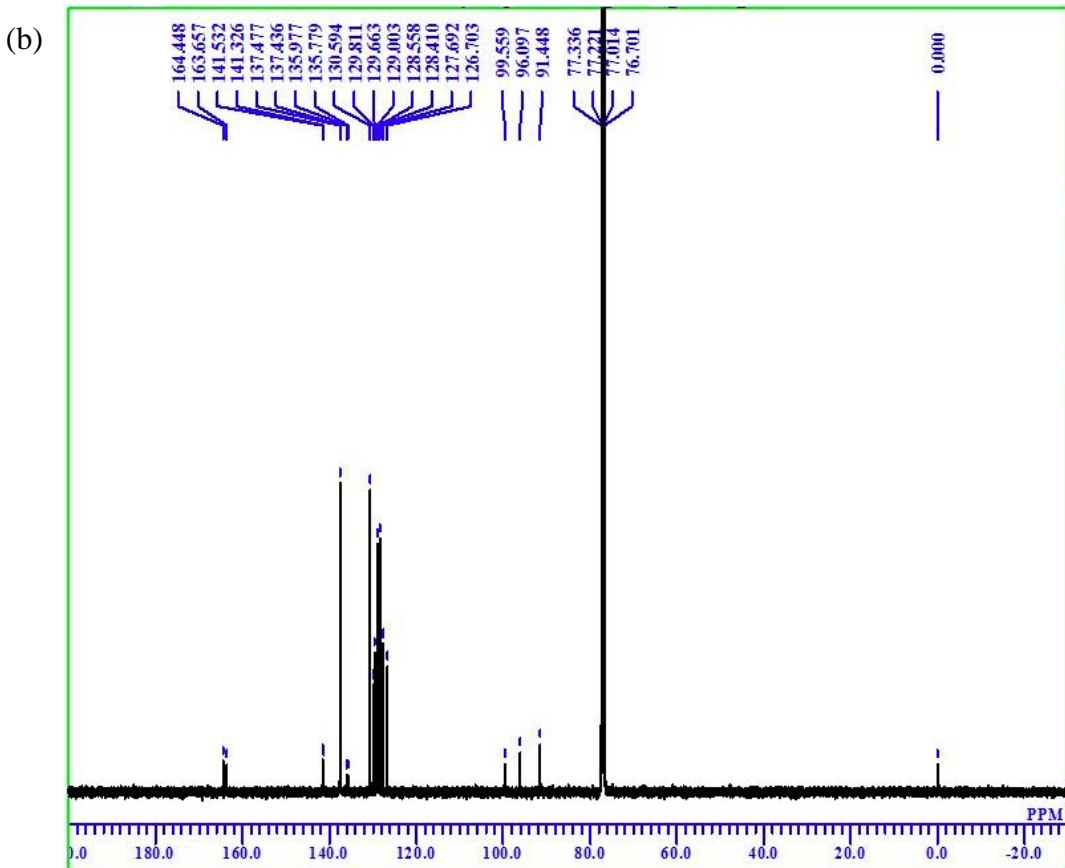
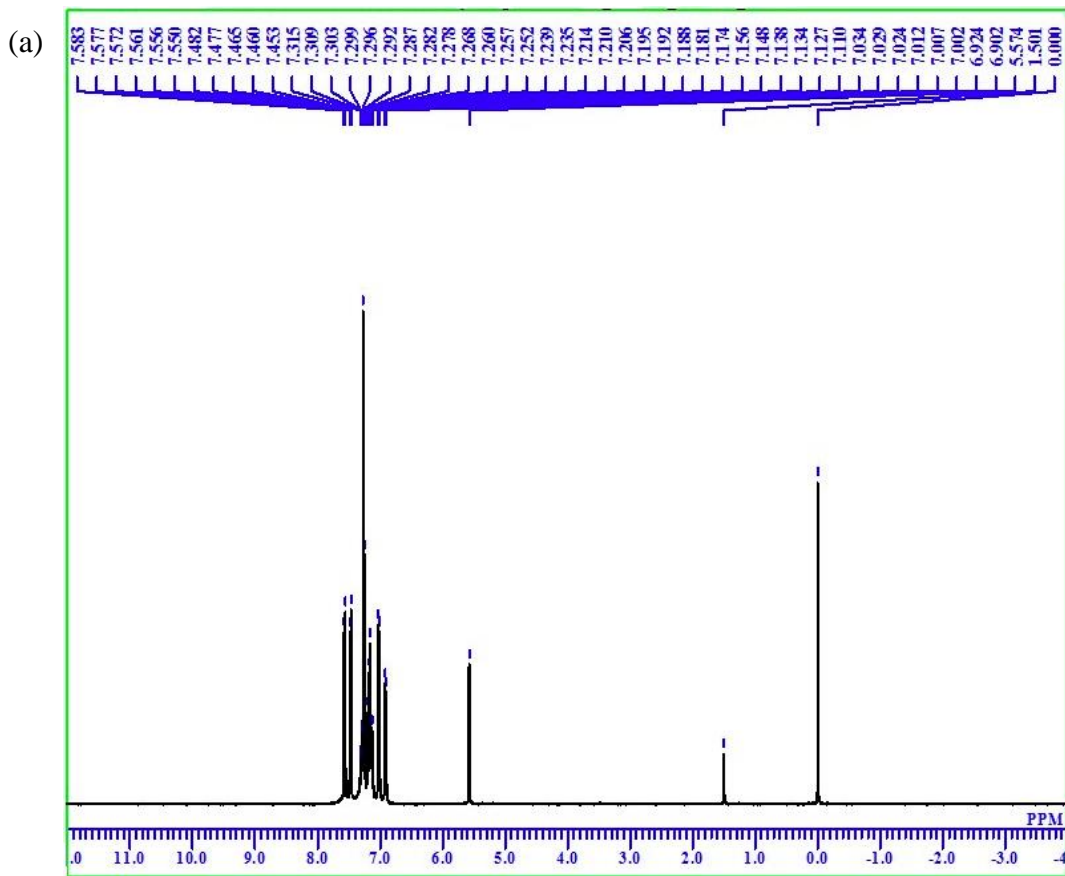
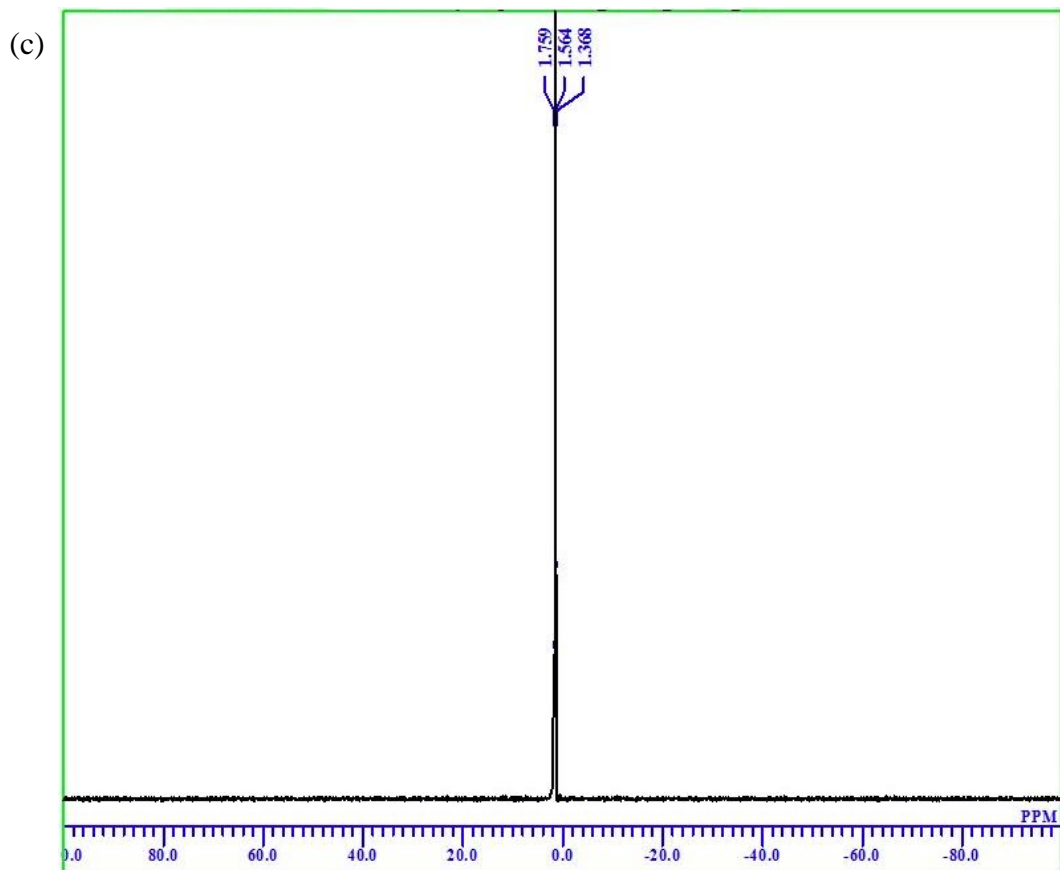


Figure S2. (a) ¹H, (b) ¹³C, (c) ¹¹B and (d) ¹⁹F NMR spectra of **4b** in CDCl₃.





(d)

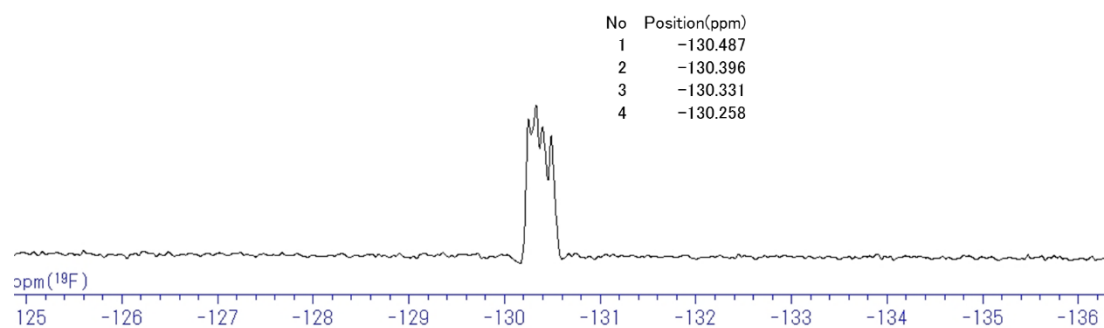
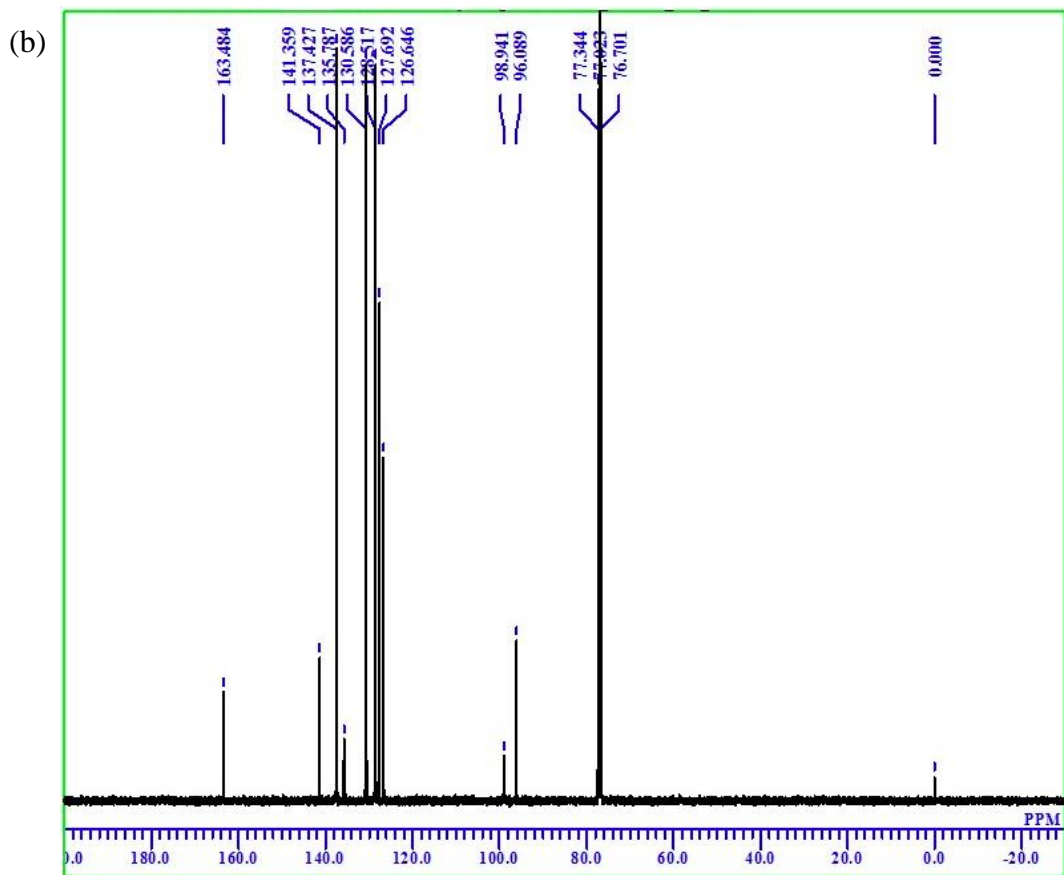
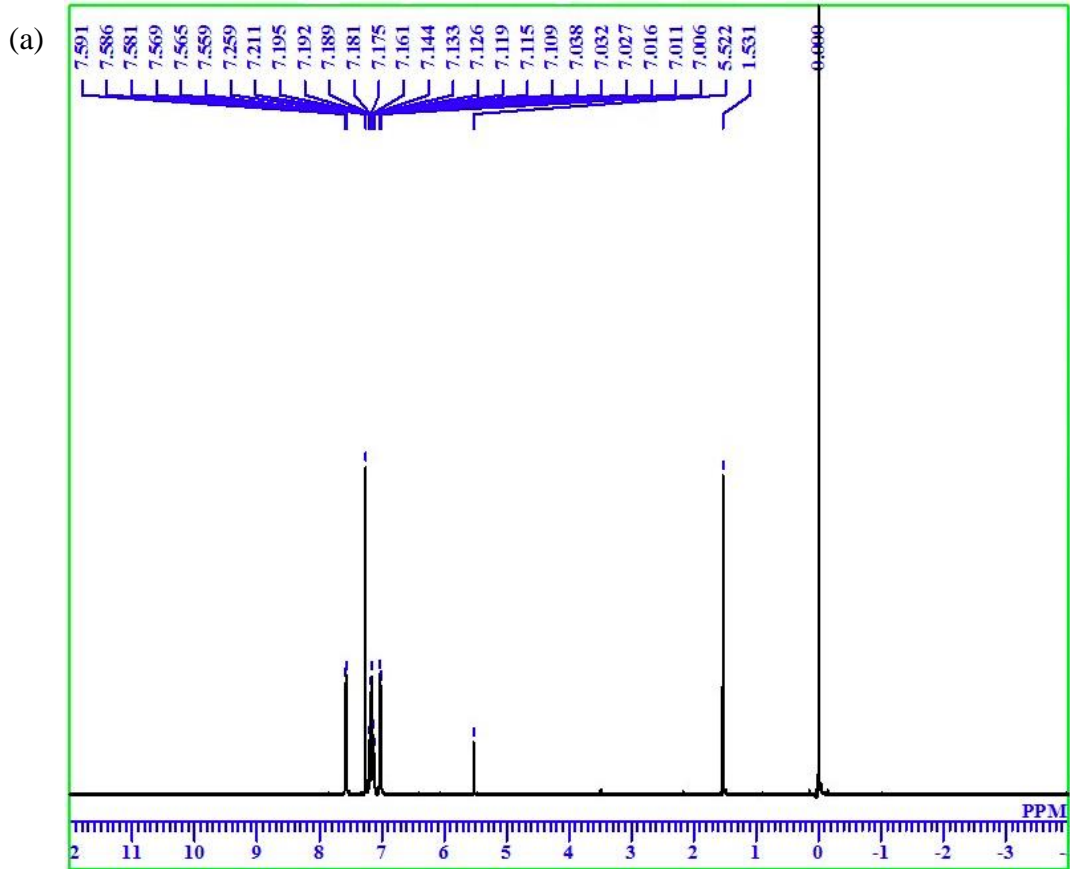
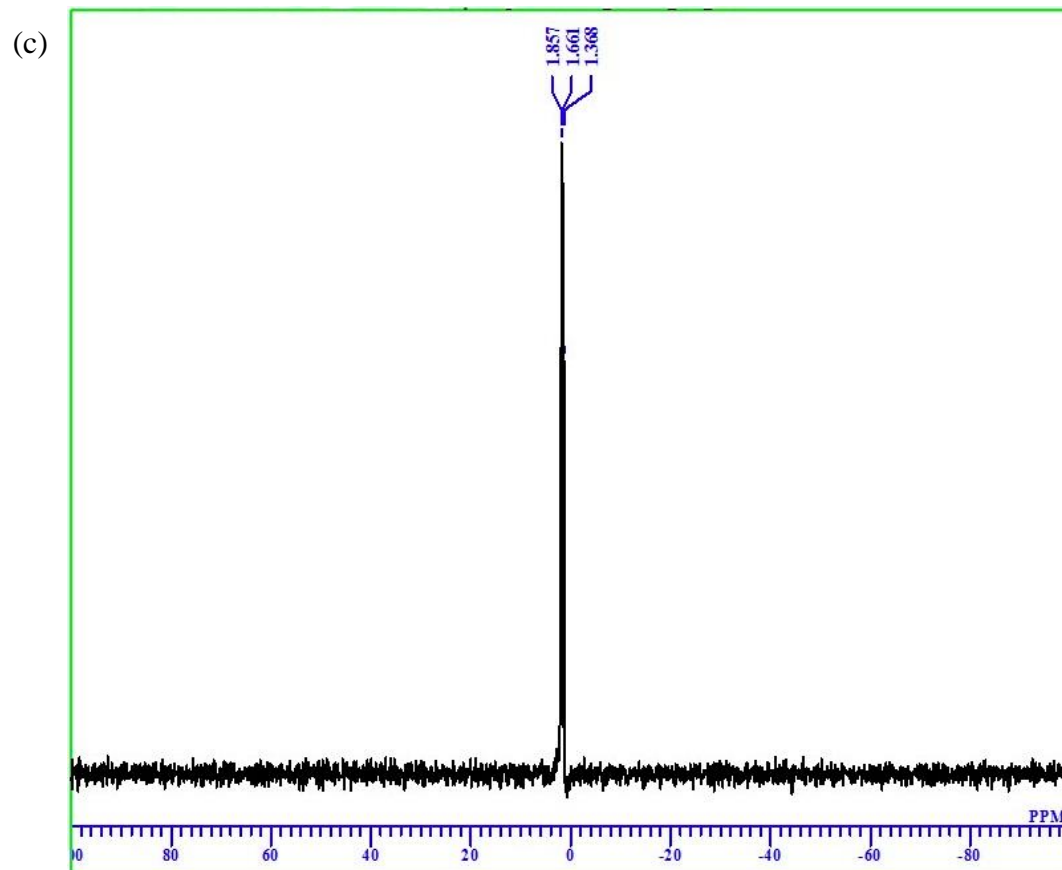


Figure S3. (a) ^1H , (b) ^{13}C , (c) ^{11}B and (d) ^{19}F NMR spectra of **4c** in CDCl_3 .





(d)

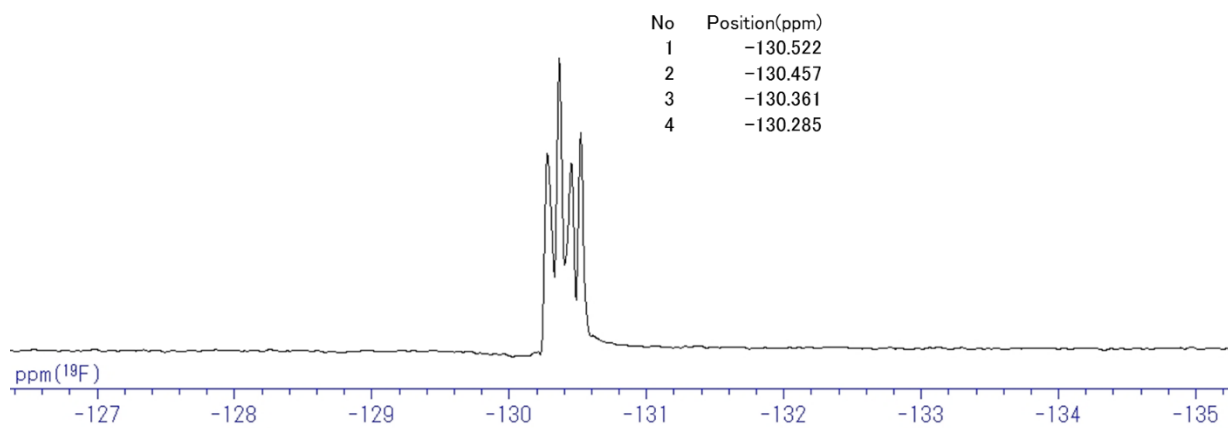


Figure S4. (a) ¹H, (b) ¹³C, (c) ¹¹B and (d) ¹⁹F NMR spectra of **4d** in CDCl₃.

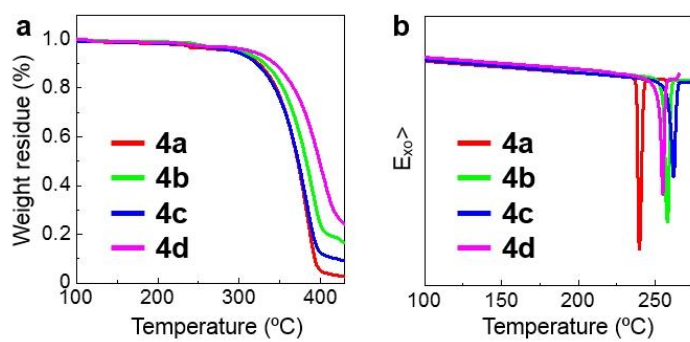


Figure S5. (a) TGA and (b) DSC profiles of **4**.

Table S1. Thermal properties of **4**

	T_{d5}^a	T_m^b
4a	296	240
4b	304	258
4c	295	262
4d	316	255

^aDecomposition temperature with 5% weight losses.

^bMelting temperature.

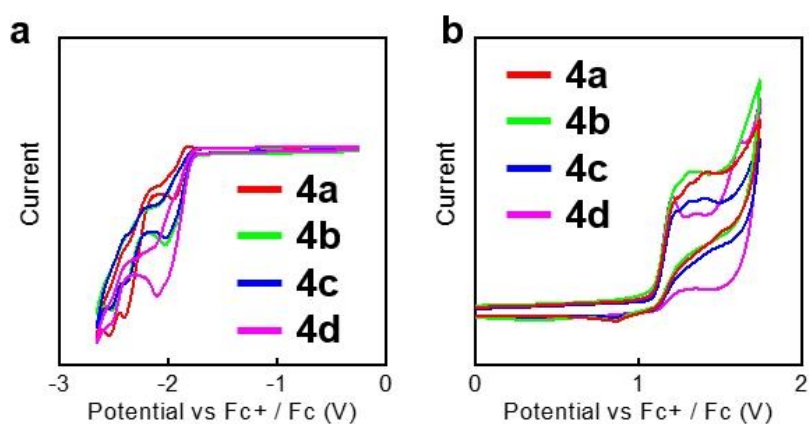


Figure S6. Cyclic voltammograms of **4** from (a) 0 V to -2.4 V and (b) 0 V to 1.2 V in dichloromethane ($c = 1 \times 10^{-3}$ M) with 0.1 M Bu_4NPF_6 as a supporting electrolyte, AgCl/Ag as a reference electrode, and Pt wire as working and counter electrodes, and scan rate at 100 mV/s.

Table S2. UV-vis absorption and electrochemical properties of **4**

	λ_{abs}^a	ϵ^b	$E_{\text{ox}}^{c,d}$	$E_{\text{red}}^{c,e}$	HOMO ^f	LUMO ^g
	[nm]	[$\text{M}^{-1}\text{cm}^{-1}$]	[eV]	[V]	[eV]	[eV]
4a	381	28700	1.09	-1.80	-5.89	-3.00
4b	382	23500	1.09	-1.79	-5.89	-3.01
4c	382	24500	1.09	-1.79	-5.89	-3.01
4d	381	26200	1.09	-1.79	-5.89	-3.01

^a UV-vis spectra were measured in CHCl_3 (1.0×10^{-5} M). ^b Molar absorption coefficients of the absorption maxima at longer wavelength region. ^c CV measurements were carried out in CH_2Cl_2 with 0.1 M Bu_4NPF_6 as supporting electrolyte. ^d E_{ox} is the onset potential of first oxidation wave. ^e E_{red} is the onset potential of first reduction wave. ^f Calculated from the empirical formula, $\text{HOMO} = -E_{\text{ox}} - 4.80$ (eV). ^g Calculated from the empirical formula, $\text{LUMO} = -E_{\text{red}} - 4.80$ (eV).

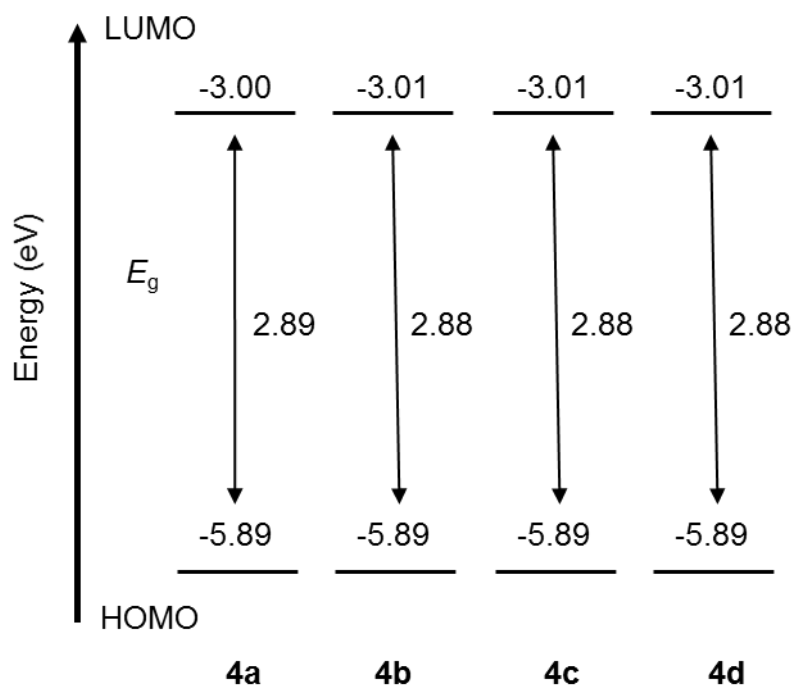


Figure S7. Energy diagrams of **4** calculated from the CV data.

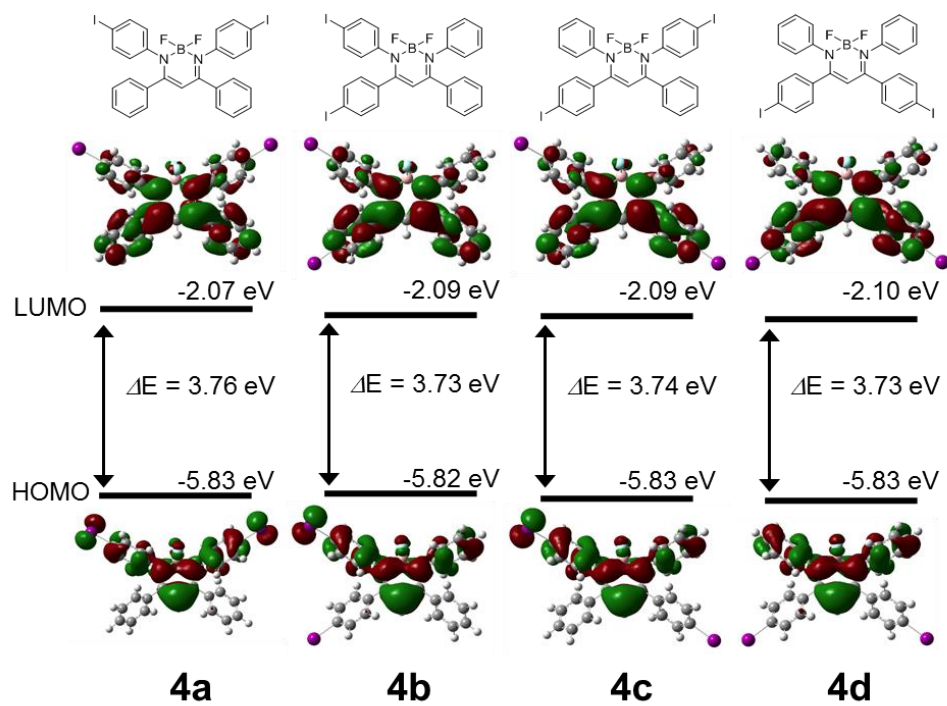


Figure S8. Structures and molecular orbital diagrams for LUMOs and HOMOs of **4** (B3LYP/6-31G (d))/B3LYP/6-31G (d)).

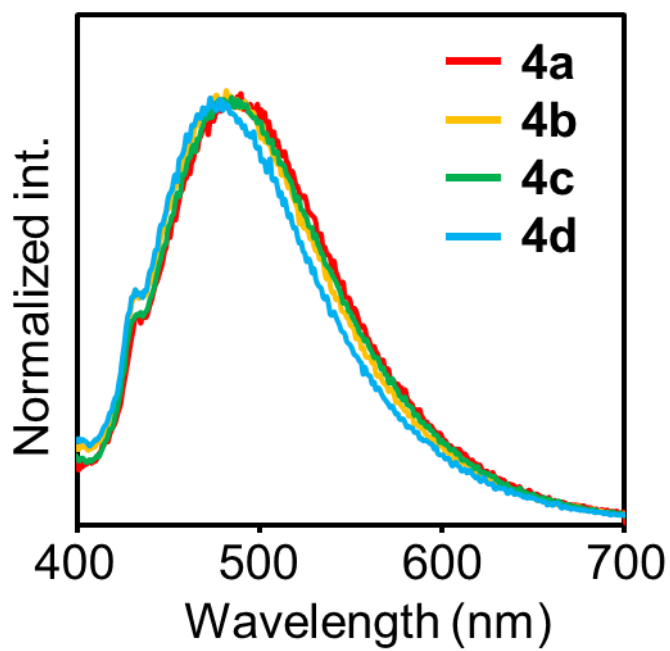


Figure S9. PL spectra of **4** in CHCl_3 (1.0×10^{-5}).

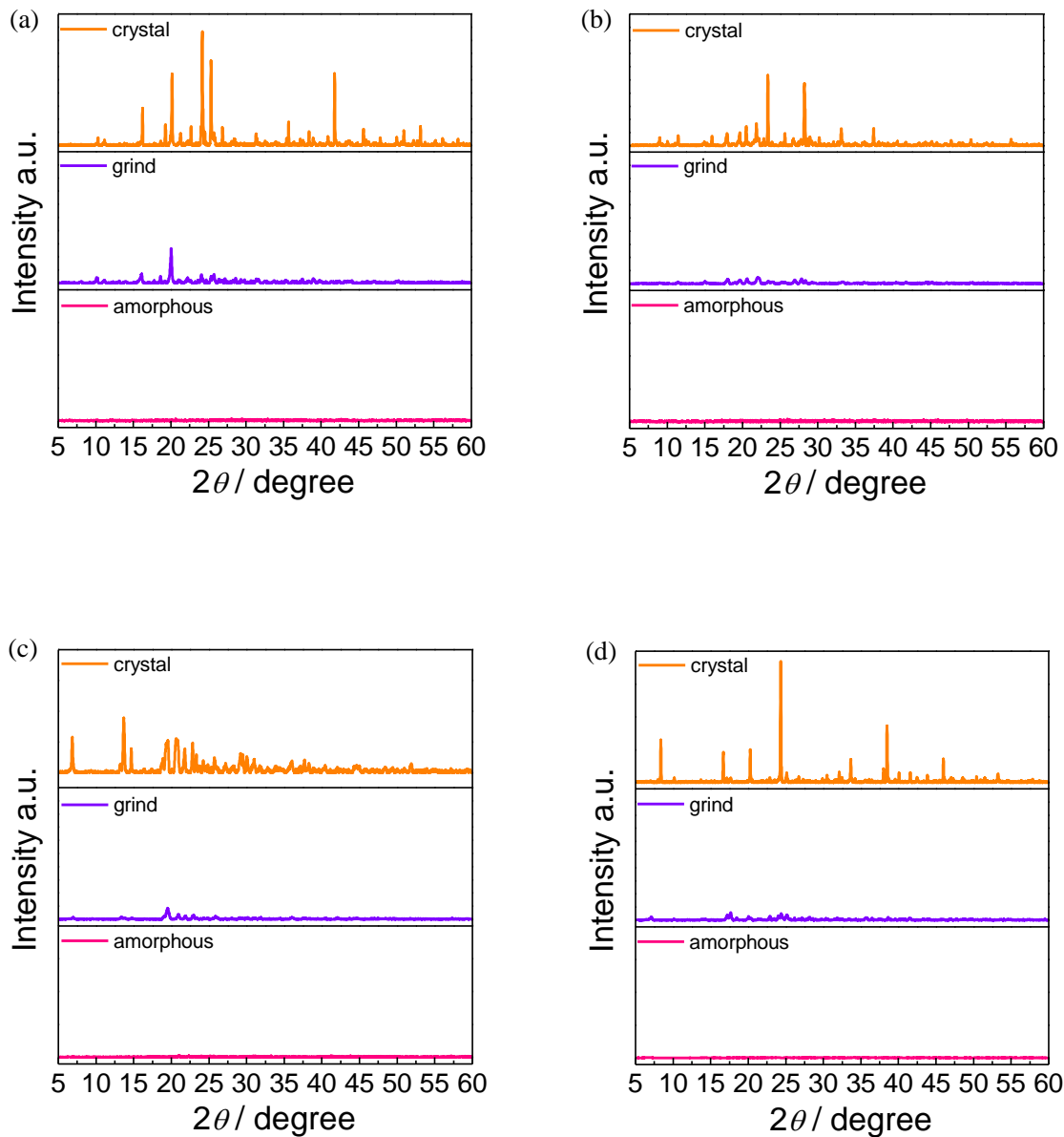


Figure S10. XRD patterns of (a) **4a**, (b) **4b**, (c) **4c**, and (d) **4d** in crystal, grind, and amorphous states.

Table S3. Crystallographic data of **4a^a**

Empirical formula	C ₂₇ H ₁₉ BF ₂ I ₂ N ₂
Formula weight	674.05
Temperature (K)	93(2)
Wavelength (Å)	0.71075
Crystal system, space group	monoclinic, <i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions	<i>a</i> = 9.8811(8) <i>b</i> = 21.9613(11) <i>c</i> = 11.8955(7) <i>α</i> = 90 <i>β</i> = 106.396(7) <i>γ</i> = 90
<i>V</i> (Å ³)	2476.4(3)
Z, calculated density (Mg m ⁻³)	4, 1.808
Absorption coefficient	2.573
<i>F</i> (000)	1296
Crystal size (mm)	0.10 × 0.10 × 0.10
<i>θ</i> range for data collection	3.01 –27.48
Limiting indices	–12 ≤ <i>h</i> ≤ 12, –28 ≤ <i>k</i> ≤ 28, –15 ≤ <i>l</i> ≤ 15
Reflections collected (unique)	23042/5674 [<i>R</i> (int) = 0.0399]
Completeness to theta = 27.48	0.999
Goodness-of-fit on <i>F</i> ²	0.923
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] ^b	<i>R</i> ₁ = 0.0347, w <i>R</i> ₂ = 0.1108
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0402, w <i>R</i> ₂ = 0.1159

^a The structures were solved by direct method (SIR97)^[9] and refined by full-matrix least-squares procedures based on *F*² (SHELX-97).^[10] ^b *R*₁ = Σ(|*F*₀ – *F*_c|)/Σ|*F*₀|. w*R*₂ = [Σw(*F*₀² – *F*_c²)/Σw(*F*₀²)²]^{1/2}. w

$$= 1/[\sigma^2(F^2_0)+[(ap)^2+bp]], \text{ where } p = [\max(F^2_0,0)+2F^2_c]/3.$$

Table S4. Crystallographic data of **4b**^a

Empirical formula	C ₂₇ H ₁₉ BF ₂ I ₂ N ₂
Formula weight	674.05
Temperature (K)	93(2)
Wavelength (Å)	0.71075
Crystal system, space group	triclinic, <i>P</i> -1
Unit cell dimensions	<i>a</i> = 10.1509(19) <i>b</i> = 10.2761(19) <i>c</i> = 13.098(2) α = 73.482(5) β = 71.610(5) γ = 76.301(5)
<i>V</i> (Å ³)	1226.7(4)
<i>Z</i> , calculated density (Mg m ⁻³)	2, 1.825
Absorption coefficient	2.597
<i>F</i> (000)	648
Crystal size (mm)	0.10 × 0.10 × 0.10
θ range for data collection	3.06 –27.48
Limiting indices	-13 ≤ <i>h</i> ≤ 13, -13 ≤ <i>k</i> ≤ 13, -16 ≤ <i>l</i> ≤ 16
Reflections collected (unique)	11928/5587 [<i>R</i> (int) = 0.0782]
Completeness to theta = 27.48	0.992
Goodness-of-fit on <i>F</i> ²	1.031
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] ^b	<i>R</i> ₁ = 0.0441, w <i>R</i> ₂ = 0.1352
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0549, w <i>R</i> ₂ = 0.1506

^a The structures were solved by direct method (SIR97)^[9] and refined by full-matrix least-squares procedures based on *F*² (SHELX-97).^[10] ^b $R_1 = \Sigma(|F_0|-|F_c|)/\Sigma|F_0|$. $wR_2 = [\Sigma w(F^2_0-F^2_c)^2/\Sigma w(F^2_0)^2]^{1/2}$. *w*

$$= 1/[\sigma^2(F^2_0)+[(ap)^2+bp]], \text{ where } p = [\max(F^2_0,0)+2F^2_c]/3.$$

Table S5. Crystallographic data of **4c^a**

Empirical formula	C ₂₇ H ₁₉ BF ₂ I ₂ N ₂
Formula weight	674.05
Temperature (K)	93(2)
Wavelength (Å)	0.71075
Crystal system, space group	triclinic, <i>P</i> -1
Unit cell dimensions	<i>a</i> = 9.714(2) <i>b</i> = 10.007(2) <i>c</i> = 13.415(3) α = 104.363(7) β = 99.942(7) γ = 99.426(7)
<i>V</i> (Å ³)	1214.8(5)
Z, calculated density (Mg m ⁻³)	2, 1.843
Absorption coefficient	2.623
<i>F</i> (000)	648
Crystal size (mm)	0.10 × 0.10 × 0.10
θ range for data collection	3.03 –27.48
Limiting indices	-12 ≤ <i>h</i> ≤ 12, -12 ≤ <i>k</i> ≤ 11, -17 ≤ <i>l</i> ≤ 17
Reflections collected (unique)	11188/5505 [<i>R</i> (int) = 0.1166]
Completeness to θ = 27.48	0.989
Goodness-of-fit on <i>F</i> ²	1.187
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] ^b	<i>R</i> ₁ = 0.0810, w <i>R</i> ₂ = 0.2002
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1048, w <i>R</i> ₂ = 0.2198

^a The structures were solved by direct method (SIR97)^[9] and refined by full-matrix least-squares procedures based on *F*² (SHELX-97).^[10] ^b $R_1 = \Sigma(|F_0| - |F_c|) / \Sigma|F_0|$. $wR_2 = [\Sigma w(F^2_0 - F^2_c)^2 / \Sigma w(F^2_0)^2]^{1/2}$. *w*

$$= 1/[\sigma^2(F^2_0)+[(ap)^2+bp]], \text{ where } p = [\max(F^2_0,0)+2F^2_c]/3.$$

Table S6. Crystallographic data of **4d**^a

Empirical formula	C ₂₇ H ₁₉ BF ₂ I ₂ N ₂
Formula weight	674.05
Temperature (K)	93(2)
Wavelength (Å)	0.71075
Crystal system, space group	monoclinic, <i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	<i>a</i> = 7.4834(8) <i>b</i> = 20.9614(19) <i>c</i> = 15.6517(15) α = 90 β = 94.901(7) γ = 90
<i>V</i> (Å ³)	2446.2(4)
<i>Z</i> , calculated density (Mg m ⁻³)	4, 1.830
Absorption coefficient	2.605
<i>F</i> (000)	1296
Crystal size (mm)	0.10 × 0.10 × 0.10
θ range for data collection	3.08 –27.45
Limiting indices	–9 ≤ <i>h</i> ≤ 9, –27 ≤ <i>k</i> ≤ 26, –15 ≤ <i>l</i> ≤ 20
Reflections collected (unique)	22048/5559 [<i>R</i> (int) = 0.0699]
Completeness to theta = 27.48	0.995
Goodness-of-fit on <i>F</i> ²	1.003
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] ^b	<i>R</i> ₁ = 0.0477, w <i>R</i> ₂ = 0.1377
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0597, w <i>R</i> ₂ = 0.1496

^a The structures were solved by direct method (SIR97)^[9] and refined by full-matrix least-squares procedures based on *F*² (SHELX-97).^[10] ^b $R_1 = \Sigma(|F_0| - |F_c|) / \Sigma|F_0|$. $wR_2 = [\Sigma w(F^2_0 - F^2_c)^2 / \Sigma w(F^2_0)^2]^{1/2}$. $w = 1/[\sigma^2(F^2_0)+[(ap)^2+bp]]$, where $p = [\max(F^2_0,0)+2F^2_c]/3$.

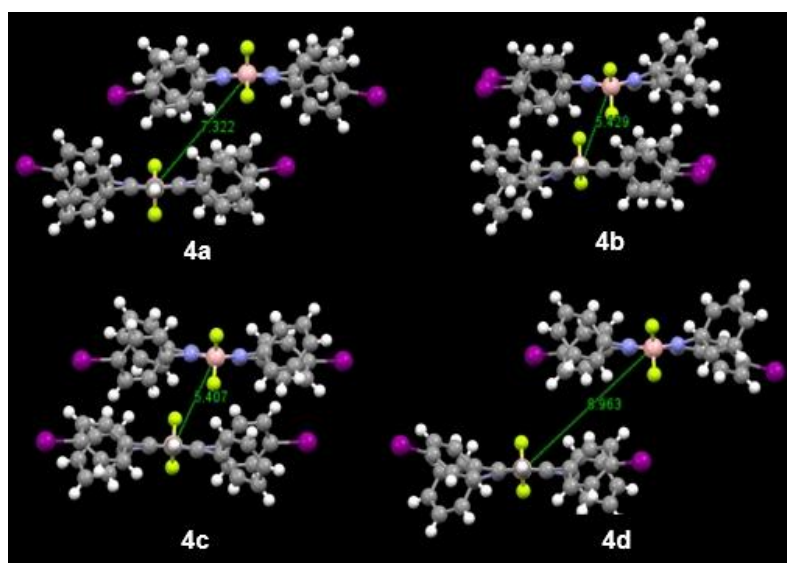


Figure S11. Packing structures of **4**.

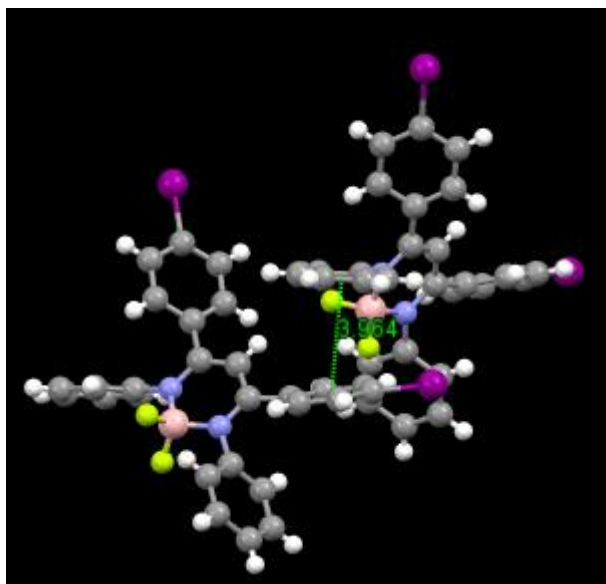


Figure S12. Packing structure of **4d**.

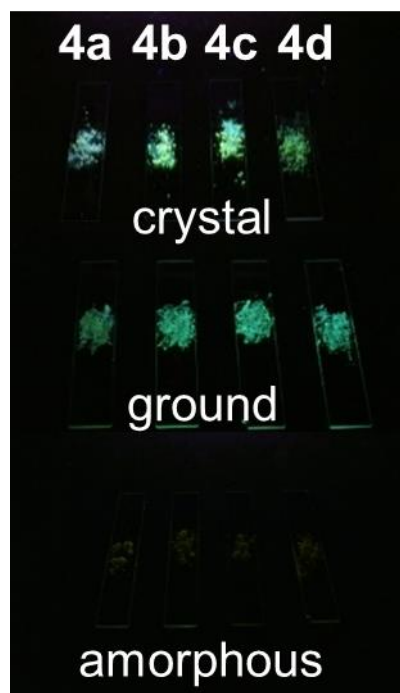


Figure S13. Appearances of the powder samples under UV irradiation (365 nm).

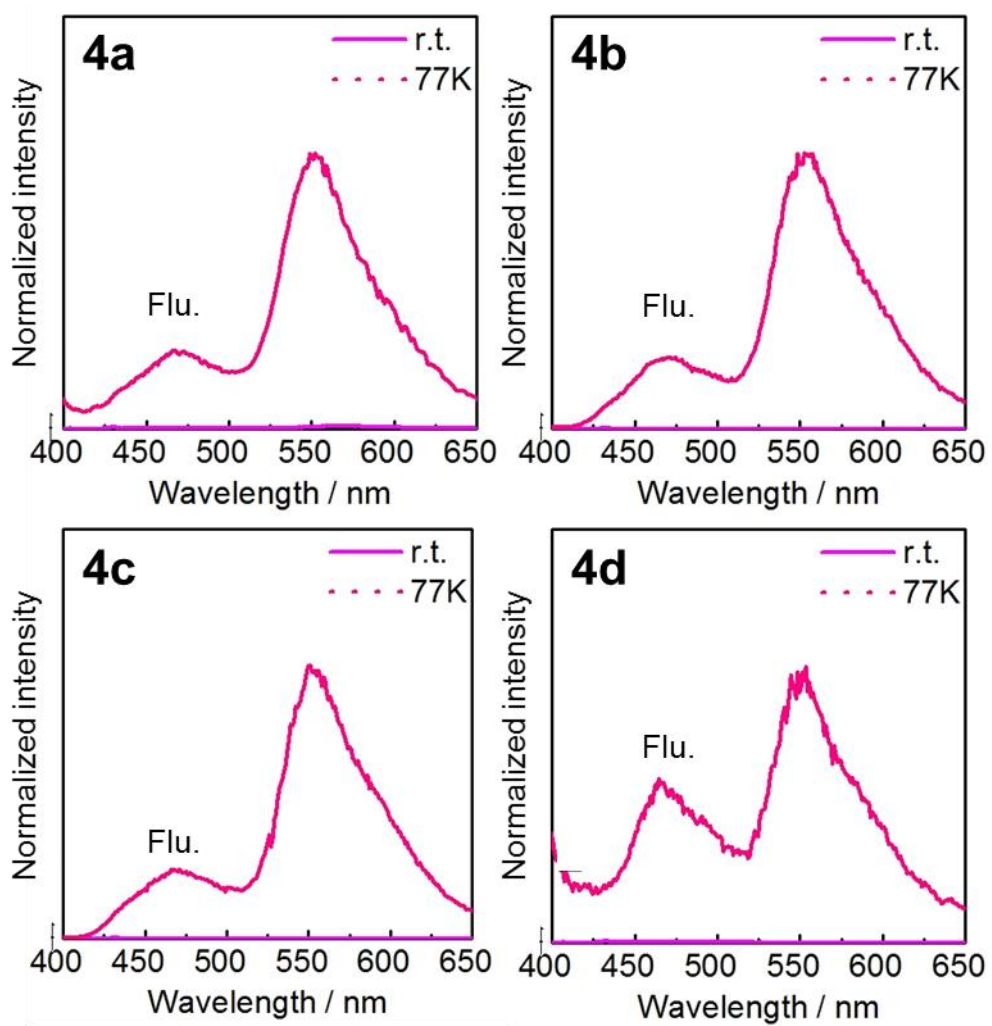


Figure S14. PL spectra of boron diiminates in 2-methyl THF at room temperature and 77 K.