

## Supporting Information

### **Color Tuning of Alternating Conjugated Polymers Composed of Pentaazaphenylene by Modulating Their Unique Electronic Structures Involving Isolated-LUMOs**

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## General

<sup>1</sup>H (400 MHz) and <sup>13</sup>C (100 MHz) NMR spectra were recorded on JEOL JNM-EX400 or JNM-AL400 spectrometers. <sup>1</sup>H and <sup>13</sup>C spectra used tetramethylsilane (TMS) as an internal standard in CDCl<sub>3</sub>. High-resolution mass spectra (HRMS) were obtained on a Thermo Fisher EXACTIVE for electron spray ionization (ESI). UV-vis absorption spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Fluorescence emission spectra were recorded on a HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer. Gel permeation chromatography (GPC) was carried out on a TOSOH 8020 (TSKgel G3000HXL column) instrument using chloroform as an eluent after calibration with standard polystyrene samples. Cyclic voltammetry (CV) was carried out on a BAS ALS-Electrochemical-Analyzer Model 600D with a glassy carbon working electrode, a Pt counter electrode, an Ag/Ag<sup>+</sup> reference electrode, and the ferrocene/ferrocenium external reference at a scan rate of 0.05 Vs<sup>-1</sup>. All reactions were performed under argon. The films for UV-vis absorption measurement were prepared by spin-coat method using MIKASA Spincoater 1H-D7.

## Materials

All reagents were obtained from commercial sources and used without further purification. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-didodecylfluorene<sup>1</sup>, 4,4'-didodecyl-2,2'-bithiophene-5,5'-diboronic acid bis(pinacol)ester<sup>2</sup>, 2,5-didodecyloxybenzene-1,4-diboronic acid bis (pinacol)ester<sup>3</sup>, 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,1,3-benzothiadiazole<sup>4</sup>, and 1-perfluorooctyl-4-trifluoromethyl-2,5-dibromobenzene<sup>5</sup> were prepared according to the literatures.

## Synthesis

The copies of the NMR spectra are shown in Figure S1–S10.

*N*-Cyano-*N'*-(6-amino-2-pyridyl)acetamide (1).

A solution of 2,6-diaminopyridine (25 g, 0.23 mol) and methyl *N*-cyanoacetimidate (25 g, 0.26 mol) in 100 mL of degassed glyme was stirred at room temperature for 24 h. A part of the product was precipitated after stirring overnight. After filtration, the precipitate was washed repeatedly with chloroform and ethanol. The filtrate was evaporated *in vacuo*. Then, the residue was washed repeatedly with chloroform and ethanol. The crude was obtained as an off-white powder (27.0 g, 0.15 mol, 67%). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm): 10.62 (s, 1H, NH), 7.45 (t, *J* = 8.0 Hz, 1H, Ar), 7.27 (d, *J* = 7.9 Hz, 1H, Ar), 6.33 (d, *J* = 7.9 Hz, 1H, Ar), 5.96 (s, 2H, NH<sub>2</sub>), 2.47 (s, 3H, Me). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, ppm): 170.7, 158.6, 148.8, 138.9, 116.5, 105.1, 103.0, 21.6. HRMS (p-ESI) calcd. for C<sub>8</sub>H<sub>9</sub>N<sub>5</sub>+H [M+H]<sup>+</sup> 176.0932, found 176.0931.

Tridecanoyl chloride (2).

This compound was synthesized according to the literature with tridecanoic acid (25 g, 117 mmol).<sup>6</sup> The reaction proceeded quantitatively from the <sup>1</sup>H NMR analyses, and the product was used for the subsequent reaction without purification. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 2.80 (t, 7.3 Hz, 2H, RCH<sub>2</sub>COCl), 1.63 (p, *J* = 7.5 Hz, 2H, R'CH<sub>2</sub>CH<sub>2</sub>COCl), 1.1–1.3 (br m, 18H), 0.80 (t, *J* = 6.5 Hz, 3H, CH<sub>3</sub>).

### 2-Dodecyl-5-methyl-1,3,4,6,9b-pentaazaphenalene (**3**, **5AP-C12**).

The synthesis was performed according to the previous literature<sup>7</sup>. A cold slurry (0 °C) of **1** (4.38 g, 25 mmol) and dehydrated pyridine (1.98 g, 2 mL, 25 mmol) in 35 mL of degassed glyme was stirred. Then, **2** (15 mL, 60 mmol) was added dropwise. After the mixture was refluxed for 4 h, the reaction was quenched by slowly adding methanol and subsequent saturated aqueous sodium hydrogen carbonate. The mixture was extracted with 3 × 50 mL of chloroform. The combined organic layers were washed with water (3 × 100 mL) and brine, and then dried over magnesium sulfate. After filtration, the solvent was removed *in vacuo*. Recrystallization from chloroform and methanol gave **3** as a pink powder (4.92 g, 14 mmol, 56%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, ppm): 7.16 (t, 1H, Ar), 5.95 (m, 2H, Ar), 1.87 (s, 3H, Ar-CH<sub>3</sub>), 2.08 (t, 2H, Ar-CH<sub>2</sub>), 1.51 (p, *J* = 7.4 Hz, 2H, Ar-CH<sub>2</sub>CH<sub>2</sub>), 1.1–1.3 (m, 18H), 0.80 (t, *J* = 7.1 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, ppm): 181.2, 178.0, 160.5, 155.2, 155.1, 146.1, 146.0, 111.2, 110.9, 39.3, 32.3, 30.1, 30.0, 29.9, 29.78, 29.76, 29.6, 26.9, 25.9, 25.8, 23.1, 14.2. HRMS (p-ESI) calc. for C<sub>21</sub>H<sub>31</sub>N<sub>5</sub>+H [M+H]<sup>+</sup> 354.2652, found 354.2649.

### 7,9-Dibromo-2-dodecyl-5-methyl-1,3,4,6,9b-pentaazaphenalene (**4**, **5AP-C12-Br2**).

A solution of **3** (3.35 g, 9 mmol) and of *N*-bromosuccinimide (5.36 g, 30 mmol) in 150 mL of degassed chloroform was refluxed for 3 d. The residual solution was evaporated under vacuum. After column chromatography on silica gel using chloroform as an eluent, followed by recrystallization from chloroform / methanol, the product (2.07 g, 4.05 mmol, 41%) was obtained as a purple powder. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, ppm): 7.85 (s, 1H, Ar), 2.30 (t, *J* = 7.6 Hz, 2H, Ar-CH<sub>2</sub>), 2.09 (s, 3H, Ar-CH<sub>3</sub>), 1.62 (p, *J* = 7.7 Hz, 2H, Ar-CH<sub>2</sub>CH<sub>2</sub>), 1.2–1.4 (m, 18H), 0.88 (t, *J* = 7.2 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, ppm): 182.5, 179.3, 160.1, 151.64, 151.56, 151.0, 102.8, 102.4, 39.4, 32.4, 30.08, 30.07, 30.05, 29.9, 29.8, 29.6, 26.8, 26.21, 26.18, 14.3. HRMS (p-ESI) calcd. for C<sub>21</sub>H<sub>29</sub>Br<sub>2</sub>N<sub>5</sub>+H [M+H]<sup>+</sup> 512.0842, found 512.0837.

### 1-Perfluorooctyl-4-trifluoromethylbenzene-2,5-diboronic acid bis(pinacol)ester (**5**).

To a THF (30 mL) solution of 1-perfluorooctyl-4-trifluoromethyl-2,5-dibromobenzene (1.44g, 2 mmol) was slowly added *tert*-BuLi (1.54 M in *n*-pentane, 10.4 mL, 16 mmol) at –78 °C. After stirred for 20 min, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.72 g, 20 mmol) was slowly added to the mixture. The reaction mixture was stirred for an additional 1 h, then allowed to warm to room temperature. After stirring for 22 h at room temperature, the reaction was carefully quenched by water. The mixture was diluted with chloroform, washed with brine and dried over sodium sulfate, and then the solvent was removed under reduced pressure. The crude product was purified with column chromatography on silica gel using hexane/ethyl acetate (40:1) as an eluent. Recrystallization from chloroform/methanol gave the desired product as an off-white solid (0.80 mmol, 40%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 7.89 (s, 2H, Ar), 1.37 (s, 12H, Me), 1.36 (s, 12H, Me). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): 136.2 (q, *J* = 32 Hz, C(Ar)-CF<sub>3</sub>), 134.3 (t, *J* = 23 Hz, C(Ar)-CF<sub>2</sub>-), 133.7 (br t, C(Ar)-B, adjacent to C(Ar)-CF<sub>2</sub>-), 130.7 (br q, C(Ar)-B, adjacent to C(Ar)-CF<sub>3</sub>), 125.1 (s, C(Ar)-H), 122.4 (s, C(Ar)-H), 85.0, 84.9, 24.7, 24.6. Other peaks of the fluoroalkyl chains were

not detectable because of the  $^{13}\text{C}$ - $^{19}\text{F}$  coupling. HRMS (p-ESI) calcd. for  $\text{C}_{27}\text{H}_{26}\text{B}_2\text{F}_{20}\text{O}_4+\text{Na}$   $[\text{M}+\text{Na}]^+$  839.1590, found 839.1592.

General polymerization procedure.

Compound **4** (51.13 mg, 0.1 mmol), aryl diboronic acid bis (pinacol)ester (0.1 mmol), tris(dibenzylideneacetone)dipalladium(0) ( $\text{Pd}_2(\text{dba})_3$ , 4.58 mg, 5  $\mu\text{mol}$ ), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-Phos, 8.21 mg, 0.02 mmol) and cesium carbonate (325 mg, 1.0 mmol) were dissolved in toluene (2.0 mL) and  $\text{H}_2\text{O}$  (2.0 mL). After stirred at 85 °C for 3 d, the mixture was diluted with toluene, and the polymeric products were isolated by reprecipitation into methanol.

5AP-co-FL.

A purple solid, 89% yield.  $M_n = 8,600$ ,  $M_w / M_n = 3.7$ .

$^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , ppm): 7.73–7.71 (br d, 2H, Ar-*H* of fluorene(FL)), 7.67–7.64 (br d, 2H, Ar-*H* of FL), 7.60 (br, 2H, Ar-*H* of FL), 7.43 (br, 1H, Ar-*H* of 5AP), 2.19 (br, 2H, Ar- $\text{CH}_2$  of 5AP), 1.97 (br, 3H, Ar- $\text{CH}_3$  of 5AP), 1.9 (br, 4H, Ar- $\text{CH}_2$  of FL), 1.5 (br, 2H, Ar- $\text{CH}_2\text{-CH}_2$  of 5AP), 1.3–0.9 (br, 58H, alkyl chains of FL and 5AP), 0.86 (br t, 6H,  $-\text{CH}_3$  of FL), 0.74 (br, 3H,  $-\text{CH}_3$  of 5AP). Coupling constants were not calculated due to severely broadened peaks.

5AP-co-Bithio.

A green solid was obtained quantitatively.  $M_n = 5,800$ ,  $M_w / M_n = 1.9$ .

$^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , ppm): 7.49 (br, 2H Ar-*H* of bithiophene(Bithio)), 7.32 (br, 1H, Ar-*H* of 5AP), 2.54 (br, 4H Ar- $\text{CH}_2$  of Bithio), 2.38 (br, 2H, Ar- $\text{CH}_2$  of 5AP), 2.13 (br, 3H, Ar- $\text{CH}_3$  of 5AP), 1.71 (br, 2H, Ar- $\text{CH}_2\text{-CH}_2$  of 5AP), 1.3–1.0 (br, 58H, alkyl chains of Bithio and 5AP), 0.86 (br, 9H,  $-\text{CH}_3$  of Bithio and 5AP).

5AP-co-OC10.

A purple solid, 89% yield.  $M_n = 6,200$ ,  $M_w / M_n = 1.9$ .

$^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , ppm): 7.46 (br, 1H, Ar-*H* of 5AP), 6.8 (br m, 2H, Ar-*H* of 1,4-didecyloxybenzene( $\text{OC}_{10}$ )), 3.86 (br, 4H, Ar- $\text{CH}_2$  of  $\text{OC}_{10}$ ), 2.17 (br, 2H, Ar- $\text{CH}_2$  of 5AP), 1.97 (br, 3H, Ar- $\text{CH}_3$  of 5AP), 1.71 (br, 4H, Ar- $\text{CH}_2\text{-CH}_2$  of  $\text{OC}_{10}$ ), 1.5 (br, 2H, Ar- $\text{CH}_2\text{-CH}_2$  of 5AP), 1.4–1.0 (br, 46H, alkyl chains of  $\text{OC}_{10}$  and 5AP), 0.86 (br, 9H,  $-\text{CH}_3$  of  $\text{OC}_{10}$  and 5AP).

5AP-co-BThZ.

A brown solid, 90% yield.  $M_n = 3,800$ ,  $M_w / M_n = 1.5$ .

$^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , ppm): 7.90 (br, 2H, Ar-*H* of 2,1,3-benzothiadiazole), 7.37 (br, 1H, Ar-*H* of 5AP), 2.15 (br, 2H, Ar- $\text{CH}_2$  of 5AP), 1.95 (br, 3H, Ar- $\text{CH}_3$  of 5AP), 1.6 (br, 2H, Ar- $\text{CH}_2\text{-CH}_2$  of 5AP), 1.2–1.0 (br, 18H, alkyl chain of 5AP), 0.87 (br, 3H,  $-\text{CH}_3$  of 5AP).

5AP-co-CF3.

A purple solid, 62% yield.  $M_n = 8,100$ ,  $M_w / M_n = 3.0$ .

$^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ , ppm): 7.60 (br, 2H, Ar-*H* of fluoroalkylbenzene), 7.21 (br, 1H, Ar-*H* of 5AP), 2.1–1.7 (br, 5H, Ar- $\text{CH}_3$  of 5AP and Ar- $\text{CH}_2$  of 5AP), 1.42 (br, 2H, Ar- $\text{CH}_2$ - $\text{CH}_2$  of 5AP), 1.3–1.0 (br, 18H, alkyl chain of 5AP), 0.87 (br, 3H, - $\text{CH}_3$  of 5AP).

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**Table S1.** TD-DFT calculation<sup>a</sup> result of FL

Excited State	Excitation Energy (Wavelength)	Assignment with Weight <sup>b</sup>	Oscillator Strength <i>f</i>
1	2.1955 eV (564.73 nm)	HOMO-2 → LUMO 0.018550	0.0383
		HOMO → LUMO 0.468184	
2	3.0892 eV (401.34 nm)	HOMO-1 → LUMO 0.487735	0.0054
3	3.3481 eV (370.31 nm)	HOMO → LUMO+1 0.492593	0.4961
4	3.3636 eV (368.61 nm)	HOMO-2 → LUMO 0.457544	0.0451
		HOMO → LUMO 0.021913	
5	3.4871 eV (355.55 nm)	HOMO-2 → LUMO 0.010254	0.2775
		HOMO → LUMO+2 0.470226	
6	3.6627 eV (338.50 nm)	HOMO-7 → LUMO 0.180447	0.0019
		HOMO-5 → LUMO 0.094735	
		HOMO-3 → LUMO 0.185959	
7	3.7648 eV (329.33 nm)	HOMO-8 → LUMO 0.048435	0.4094
		HOMO-6 → LUMO 0.014390	
		HOMO-4 → LUMO 0.019379	
		HOMO-1 → LUMO+1 0.079332	
		HOMO → LUMO+3 0.317792	
8	3.7710 eV (328.78 nm)	HOMO-8 → LUMO 0.164349	0.0033
		HOMO-6 → LUMO 0.055089	
		HOMO-4 → LUMO 0.071353	
		HOMO-1 → LUMO+1 0.029070	
		HOMO → LUMO+3 0.145687	
9	3.8128 eV (325.18 nm)	HOMO-8 → LUMO 0.037465	0.3030
		HOMO-6 → LUMO 0.020521	
		HOMO-4 → LUMO 0.027872	

		HOMO-1 → LUMO+1	
		0.378643	
		HOMO → LUMO+3	0.022100
10	3.9815 eV	HOMO-8 → LUMO	0.196373
	(311.40 nm)	HOMO-6 → LUMO	0.059370
		HOMO-4 → LUMO	0.208493

<sup>a</sup> All TD-DFT calculations were performed at B3LYP/6-31G++(d) level using Gaussian 09 software package<sup>8</sup>.

<sup>b</sup> Square of CI expansion coefficient.

**Table S2.** TD-DFT calculation result of **Bithio**

Excited State	Excitation Energy (Wavelength)	Assignment with Weight	Oscillator Strength $f$
1	2.0686 eV (599.37 nm)	HOMO → LUMO 0.474005	0.0464
		HOMO → LUMO+2 0.011396	
2	3.0476 eV (406.82 nm)	HOMO-1 → LUMO 0.486060	0.0065
3	3.1871 eV (389.01 nm)	HOMO → LUMO+1 0.455787	0.5467
		HOMO → LUMO+2 0.031195	
4	3.1955 eV (388.00 nm)	HOMO → LUMO+1 0.032227	0.2190
		HOMO → LUMO+2 0.441401	
5	3.4181 eV (362.69 nm)	HOMO-8 → LUMO 0.032368	0.0092
		HOMO-2 → LUMO 0.448203	
6	3.6076 eV (343.67 nm)	HOMO-9 → LUMO 0.095339	0.0108
		HOMO-7 → LUMO 0.086648	
		HOMO-6 → LUMO 0.047428	
		HOMO-5 → LUMO 0.093697	
		HOMO-4 → LUMO 0.149994	
7	3.6213 eV (342.37 nm)	HOMO-10 → LUMO 0.015540	0.0374
		HOMO-8 → LUMO 0.023180	
		HOMO-7 → LUMO 0.020658	
		HOMO-6 → LUMO 0.024643	
		HOMO-5 → LUMO 0.107741	
		HOMO-4 → LUMO 0.080055	
		HOMO-3 → LUMO 0.060974	
		HOMO-1 → LUMO+1 0.143732	
8	3.6272 eV (341.82 nm)	HOMO-5 → LUMO 0.014144	0.0216
		HOMO-3 → LUMO 0.390838	
		HOMO-1 → LUMO+1 0.056103	
9	3.6838 eV	HOMO-7 → LUMO 0.012168	0.2013



	(336.56 nm)	HOMO-6 → LUMO 0.042308	
		HOMO-5 → LUMO 0.076469	
		HOMO-4 → LUMO 0.082329	
		HOMO-1 → LUMO+1	
		0.256532	
10	3.8015 eV (326.14 nm)	HOMO-9 → LUMO 0.253603	0.0323
		HOMO-8 → LUMO 0.049093	
		HOMO-5 → LUMO 0.081179	
		HOMO-4 → LUMO 0.058404	
		HOMO-3 → LUMO 0.013426	
		HOMO → LUMO+3 0.012419	

**Table S3.** TD-DFT calculation result of **OC10**

Excited State	Excitation Energy (Wavelength)	Assignment with Weight	Oscillator Strength $f$
1	2.3210 eV (534.19 nm)	HOMO-2 $\rightarrow$ LUMO 0.018635 HOMO $\rightarrow$ LUMO 0.469362	0.0152
2	2.9919 eV (414.40 nm)	HOMO-1 $\rightarrow$ LUMO 0.496546	0.0007
3	3.0414 eV (407.66 nm)	HOMO-2 $\rightarrow$ LUMO 0.475741 HOMO $\rightarrow$ LUMO 0.019971	0.0015
4	3.6380 eV (340.80 nm)	HOMO-5 $\rightarrow$ LUMO 0.076049 HOMO-3 $\rightarrow$ LUMO 0.347074 HOMO $\rightarrow$ LUMO+1 0.062565	0.0328
5	3.6902 eV (335.99 nm)	HOMO-5 $\rightarrow$ LUMO 0.028839 HOMO-3 $\rightarrow$ LUMO 0.038632 HOMO $\rightarrow$ LUMO+1 0.406840	0.2835
6	3.7048 eV (334.66 nm)	HOMO $\rightarrow$ LUMO+2 0.471406	0.1143
7	3.8575 eV (321.41 nm)	HOMO-6 $\rightarrow$ LUMO 0.168995 HOMO-4 $\rightarrow$ LUMO 0.300896	0.0002
8	3.8672 eV (320.61 nm)	HOMO-1 $\rightarrow$ LUMO+1 0.489272	0.0451
9	3.9674 eV (312.51 nm)	HOMO-2 $\rightarrow$ LUMO+1 0.385902 HOMO-1 $\rightarrow$ LUMO+2 0.097888	0.0059
10	3.9846 eV (311.16 nm)	HOMO-2 $\rightarrow$ LUMO+1 0.089413 HOMO-1 $\rightarrow$ LUMO+2 0.395176	0.0121

**Table S4.** TD-DFT calculation result of **BThZ**

Excited State	Excitation Energy (Wavelength)	Assignment with Weight	Oscillator Strength $f$
1	2.3241 eV (533.47 nm)	HOMO → LUMO 0.056017	0.0340
		HOMO → LUMO+1 0.093673	
		HOMO → LUMO+2 0.334535	
2	2.4981 eV (496.32 nm)	HOMO → LUMO 0.432780	0.0821
		HOMO → LUMO+1 0.034969	
		HOMO → LUMO+2 0.028328	
3	2.5498 eV (486.25 nm)	HOMO → LUMO+1 0.367551	0.0199
		HOMO → LUMO+2 0.122038	
4	3.5340 eV (350.83 nm)	HOMO-1 → LUMO 0.438072	0.0348
		HOMO-1 → LUMO+2 0.032580	
5	3.5874 eV (345.61 nm)	HOMO-3 → LUMO+2 0.040913	0.0358
		HOMO-2 → LUMO+2 0.020301	
		HOMO-1 → LUMO 0.042770	
		HOMO-1 → LUMO+1 0.185614	
		HOMO-1 → LUMO+2 0.169736	
6	3.6735 eV (337.51 nm)	HOMO-3 → LUMO+2 0.022082	0.0723
		HOMO-1 → LUMO+1 0.268272	
		HOMO-1 → LUMO+2 0.142793	
		HOMO → LUMO+3 0.030909	
7	3.7023 eV (334.89 nm)	HOMO-2 → LUMO 0.010994	0.0864
		HOMO-2 → LUMO+2 0.027400	
		HOMO-1 → LUMO+1 0.025370	
		HOMO → LUMO+3 0.340764	
		HOMO → LUMO+4 0.055079	
8	3.7720 eV (328.70 nm)	HOMO-3 → LUMO+2 0.026507	0.0958
		HOMO-2 → LUMO 0.253643	
		HOMO-2 → LUMO+1 0.022350	
		HOMO-2 → LUMO+2 0.043152	
		HOMO-1 → LUMO+2 0.044243	
		HOMO → LUMO+3 0.057576	
HOMO → LUMO+4 0.016025			
9	3.8058 eV (325.78 nm)	HOMO-5 → LUMO+2 0.032512	0.1674
		HOMO-4 → LUMO+2 0.015969	

		HOMO-3 → LUMO 0.011662	
		HOMO-3 → LUMO+1 0.010028	
		HOMO-3 → LUMO+2 0.086084	
		HOMO-2 → LUMO 0.011453	
		HOMO-1 → LUMO+2 0.030695	
		HOMO → LUMO+3 0.014578	
		HOMO → LUMO+4 0.245491	
10	3.8250 eV	HOMO-6 → LUMO+2 0.029255	0.0530
	(324.14 nm)	HOMO-5 → LUMO+2 0.070135	
		HOMO-4 → LUMO+1 0.020079	
		HOMO-4 → LUMO+2 0.128357	
		HOMO-3 → LUMO 0.019488	
		HOMO-2 → LUMO+1 0.065669	
		HOMO-2 → LUMO+2 0.035153	
		HOMO → LUMO+4 0.057730	

**Table S5.** TD-DFT calculation result of **CF3**

Excited State	Excitation Energy (Wavelength)	Assignment with Weight	Oscillator Strength $f$
1	2.4260 eV (511.07 nm)	HOMO $\rightarrow$ LUMO 0.487679	0.0102
2	3.4937 eV (354.88 nm)	HOMO $\rightarrow$ LUMO+1 0.476445 HOMO $\rightarrow$ LUMO+4 0.011535	0.0703
3	3.5976 eV (344.63 nm)	HOMO $\rightarrow$ LUMO+2 0.493239	0.0123
4	3.6981 eV (335.26 nm)	HOMO-3 $\rightarrow$ LUMO 0.020575 HOMO-1 $\rightarrow$ LUMO 0.459223	0
5	3.8107 eV (325.36 nm)	HOMO-2 $\rightarrow$ LUMO 0.466434	0.0005
6	3.9130 eV (316.85 nm)	HOMO-7 $\rightarrow$ LUMO 0.015528 HOMO $\rightarrow$ LUMO+3 0.464020	0.1626
7	4.0066 eV (309.45 nm)	HOMO $\rightarrow$ LUMO+4 0.307637 HOMO $\rightarrow$ LUMO+5 0.186477	0.0389
8	4.1319 eV (300.06 nm)	HOMO $\rightarrow$ LUMO+6 0.493731	0.0015
9	4.2417 eV (292.30 nm)	HOMO $\rightarrow$ LUMO+1 0.016471 HOMO $\rightarrow$ LUMO+4 0.161942 HOMO $\rightarrow$ LUMO+5 0.293233	0.2040
10	4.5596 eV (271.92 nm)	HOMO-3 $\rightarrow$ LUMO 0.306429 HOMO-1 $\rightarrow$ LUMO 0.028016 HOMO-1 $\rightarrow$ LUMO+3 0.132110	0.0168

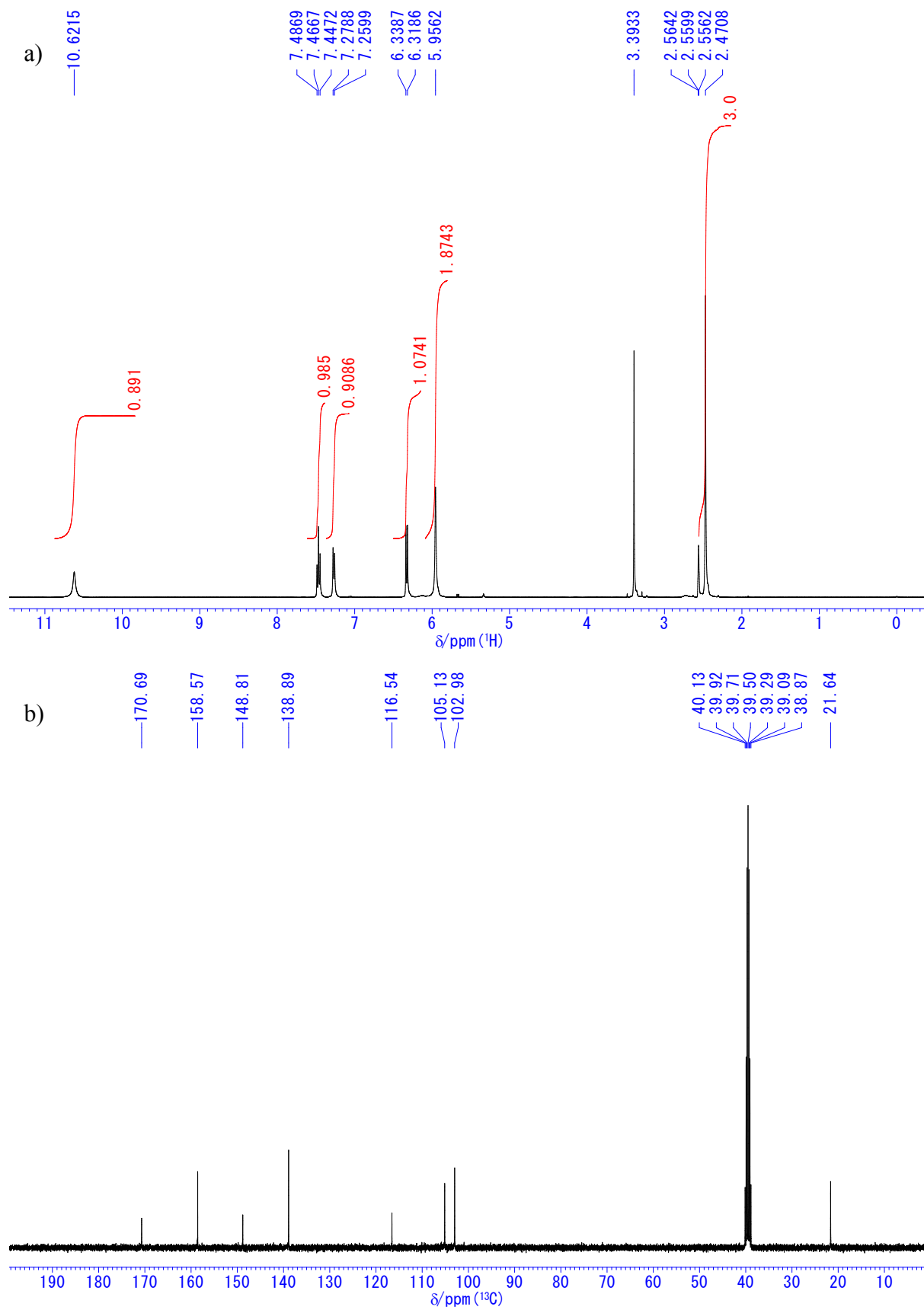


Figure S1. a)  $^1\text{H}$  and b)  $^{13}\text{C}$  NMR spectra of **1**.

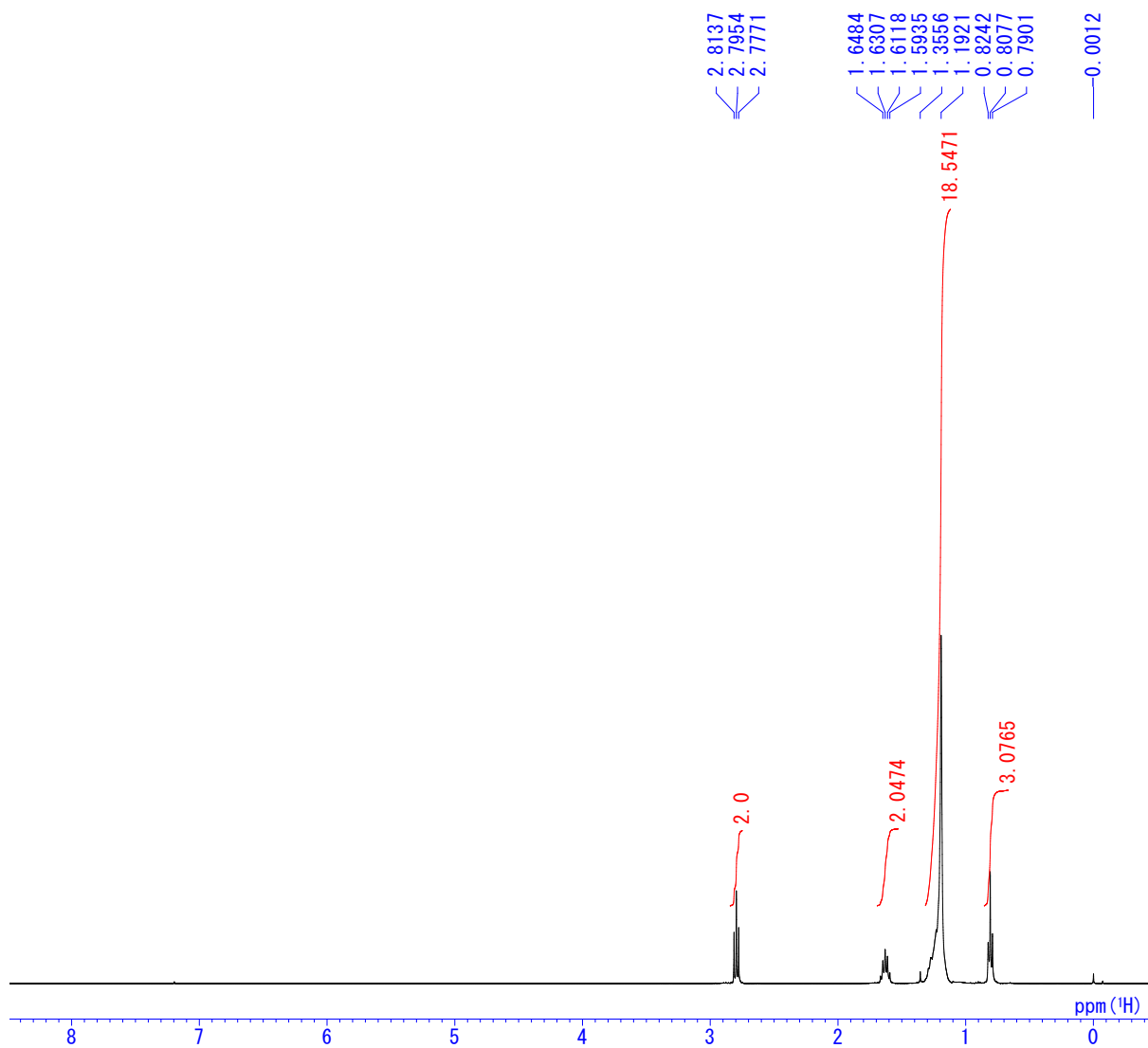


Figure S2.  $^1\text{H}$  NMR spectrum of **2**.

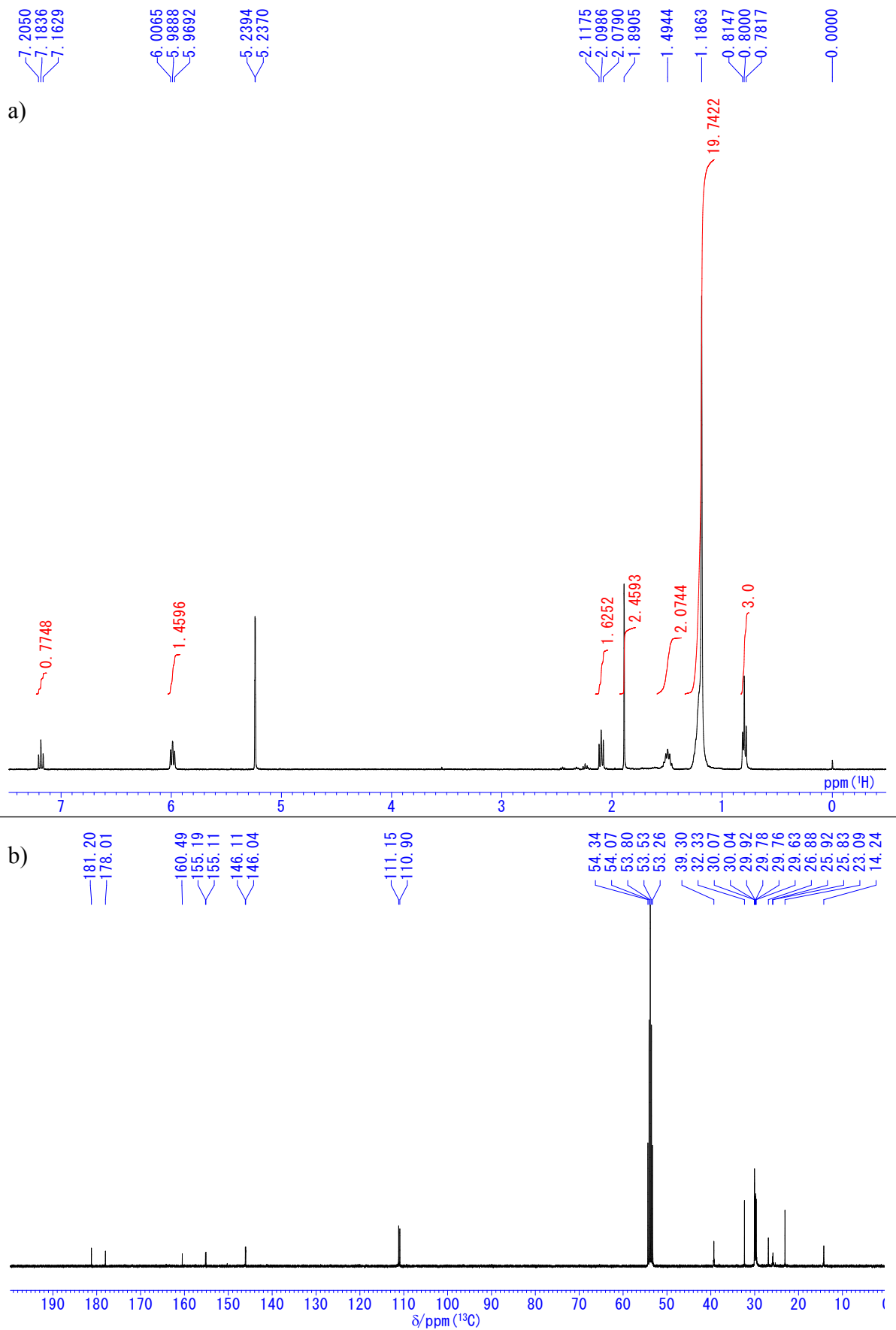
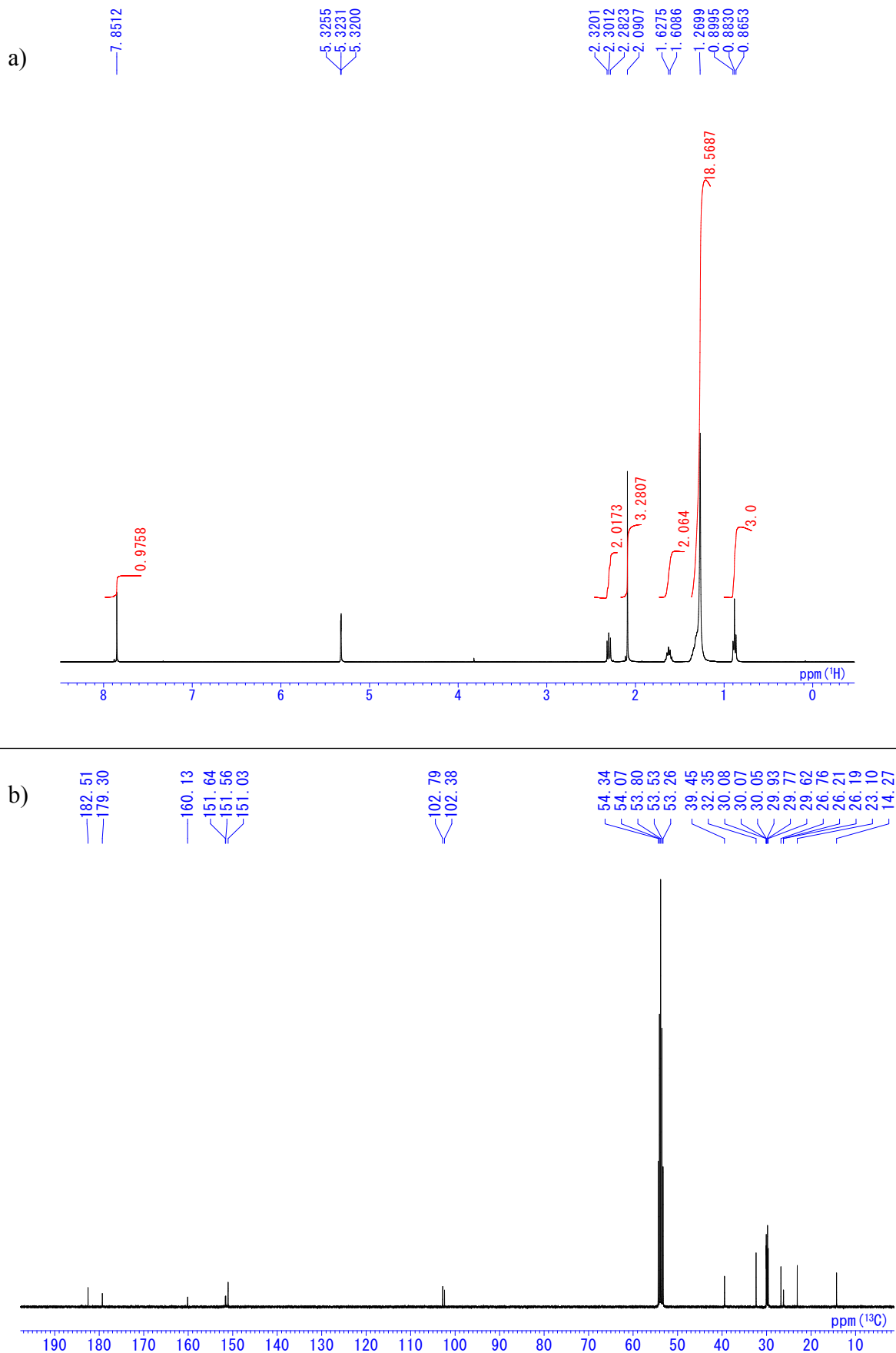
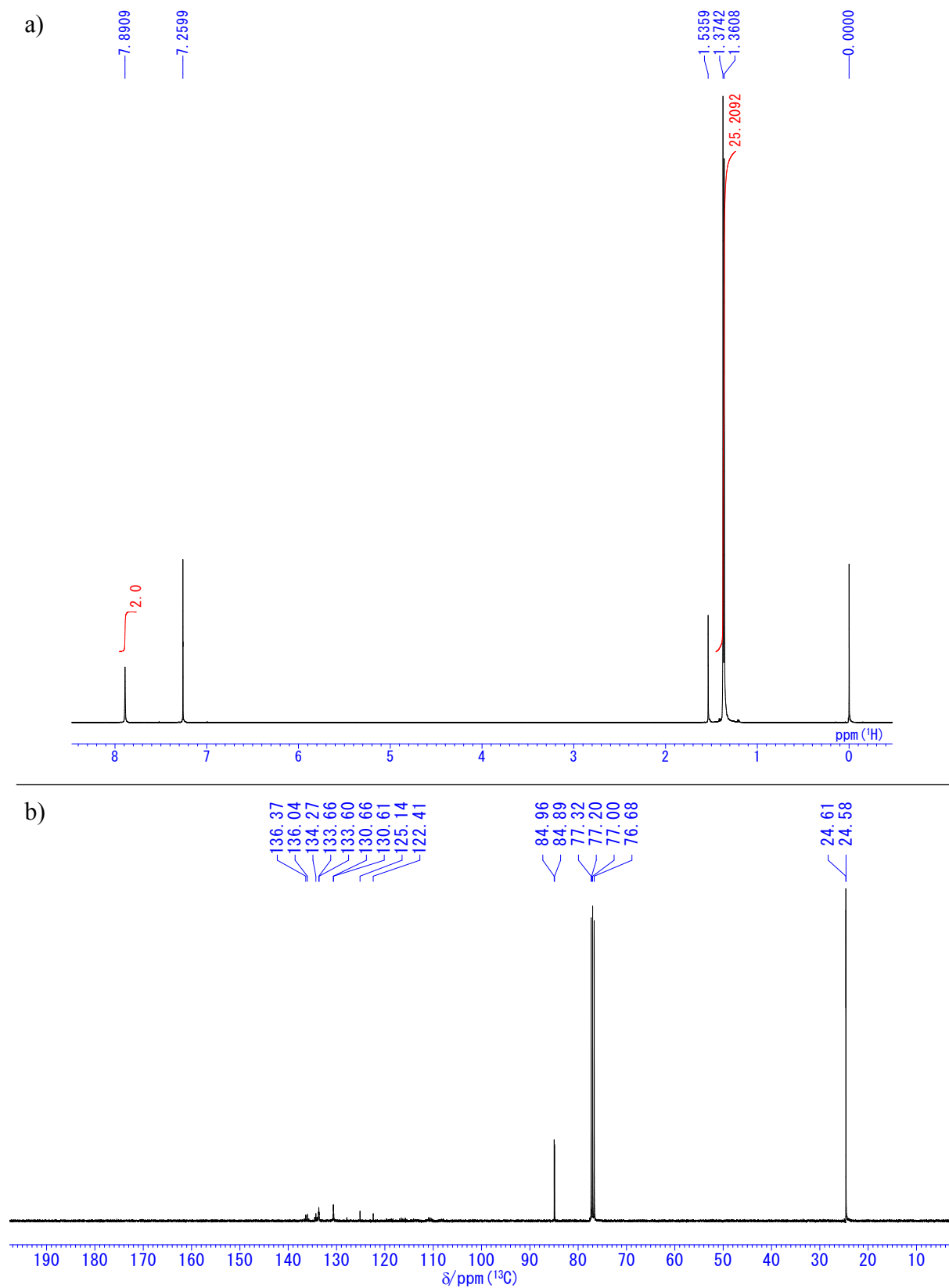


Figure S3. a)  $^1\text{H}$  and b)  $^{13}\text{C}$  NMR spectra of **3**.







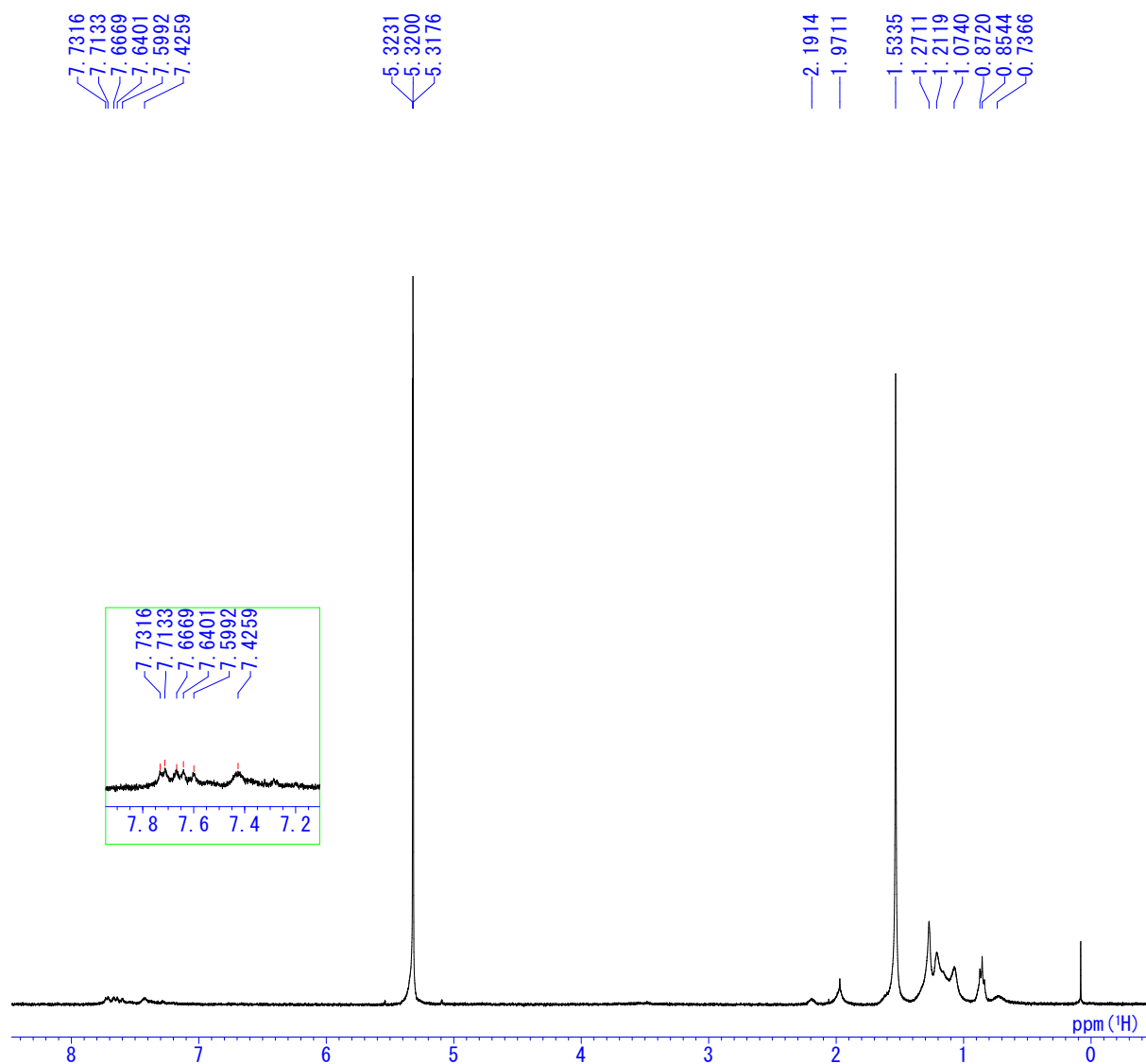


Figure S6. <sup>1</sup>H NMR spectrum of 5AP-co-FL.

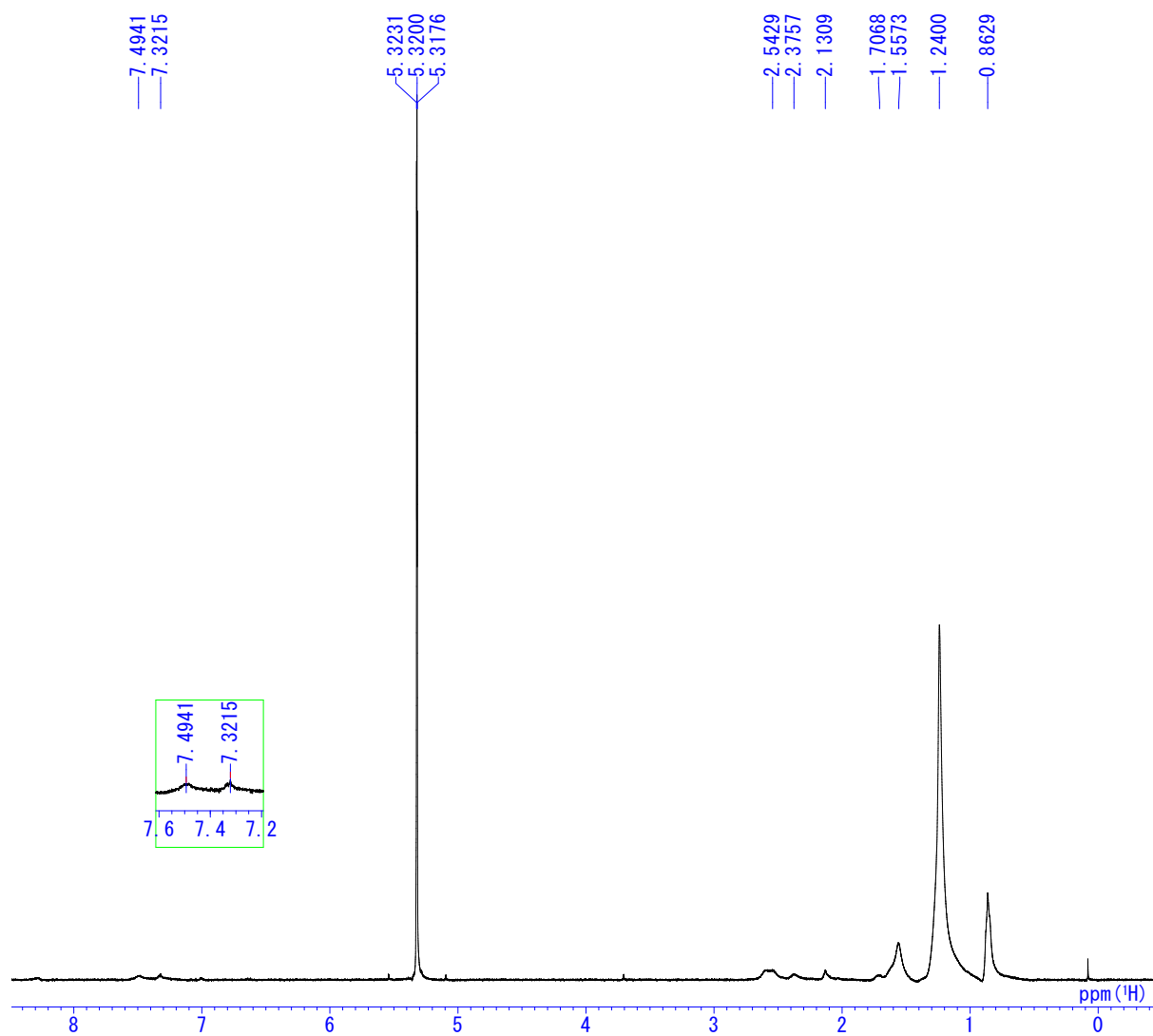


Figure S7.  $^1\text{H}$  NMR spectrum of 5AP-co-Bithio.

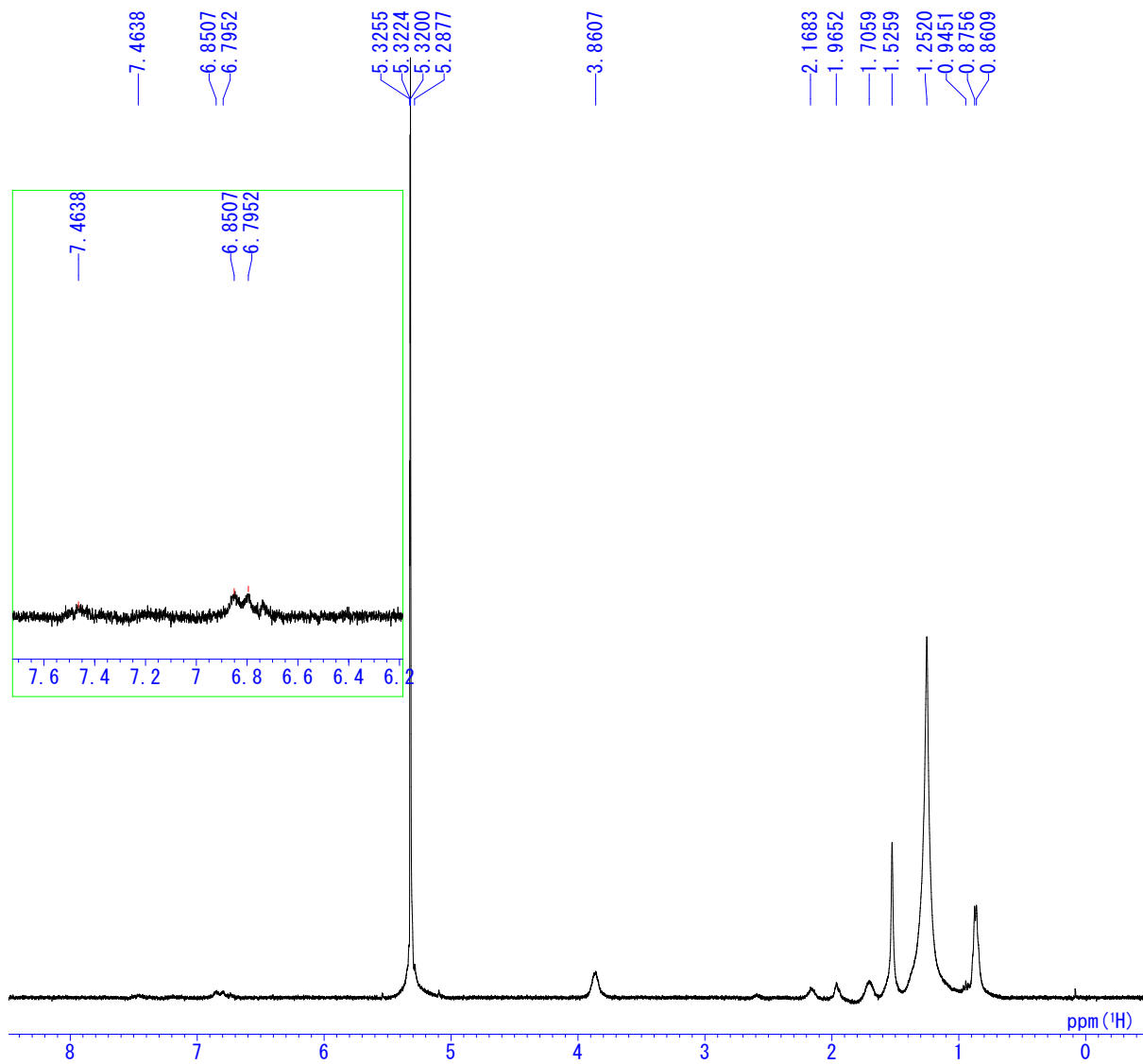
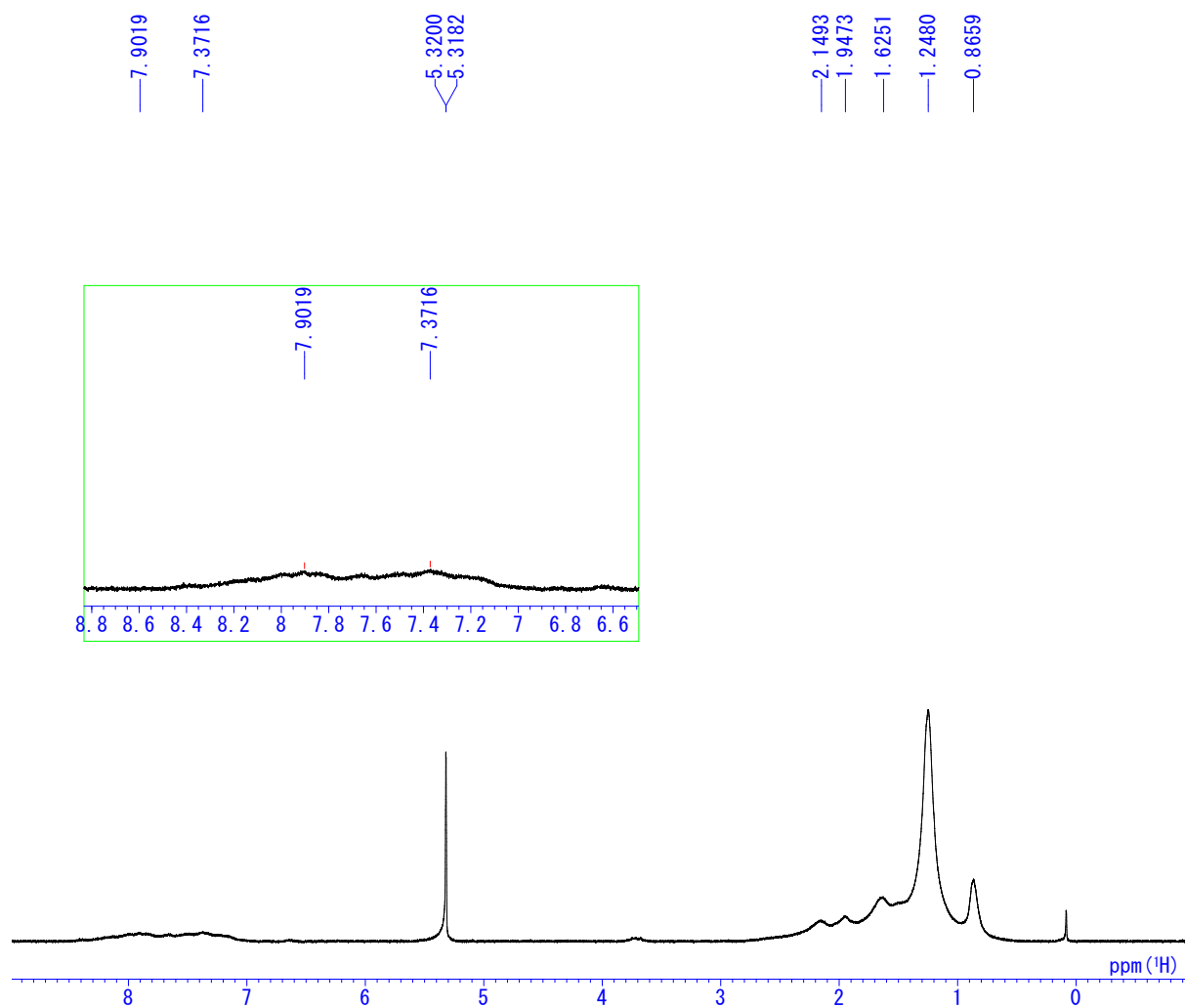


Figure S8.  $^1\text{H}$  NMR spectrum of 5AP-co-OC10.



**Figure S9.**  $^1\text{H}$  NMR spectrum of 5AP-co-BThZ.

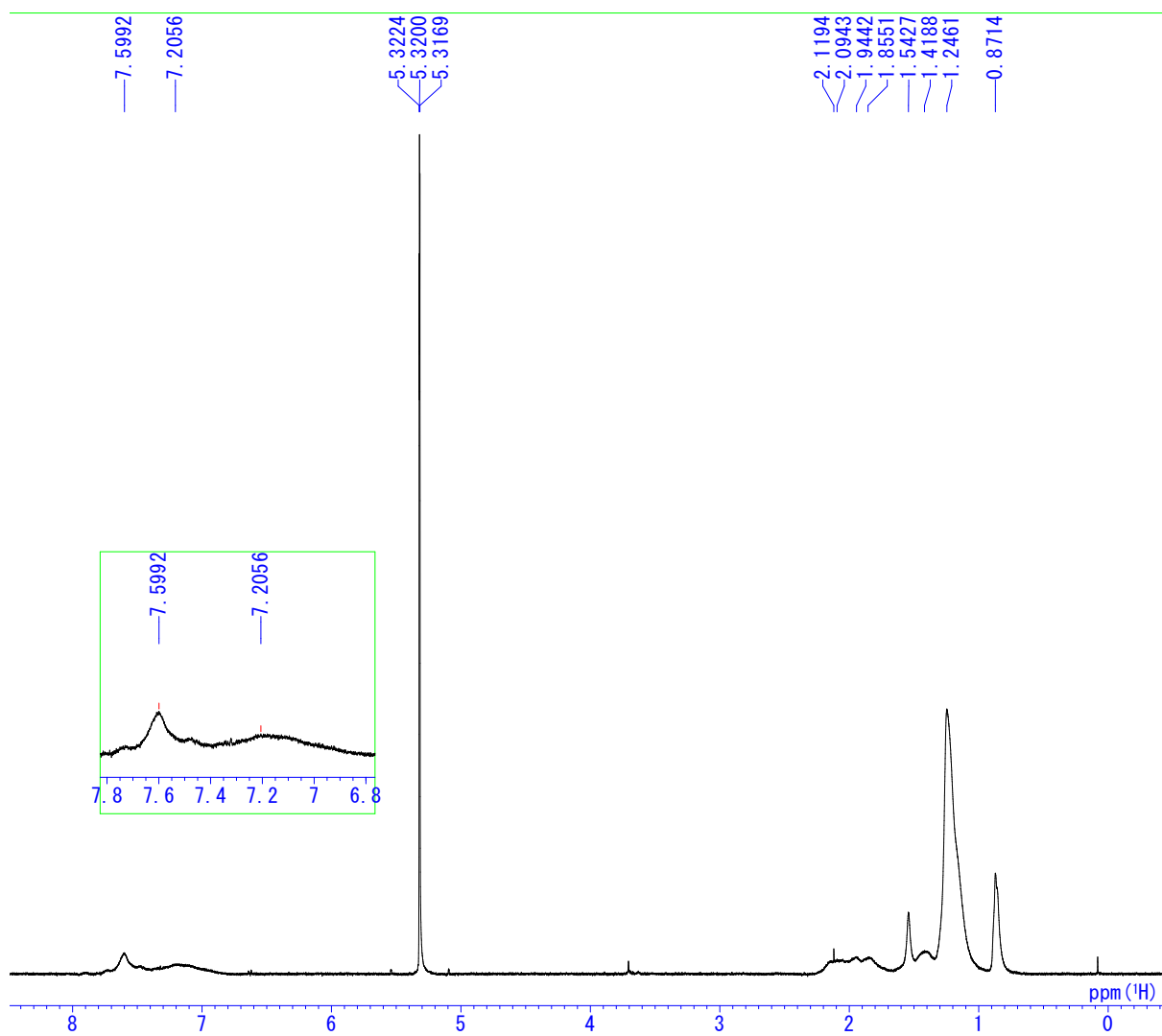
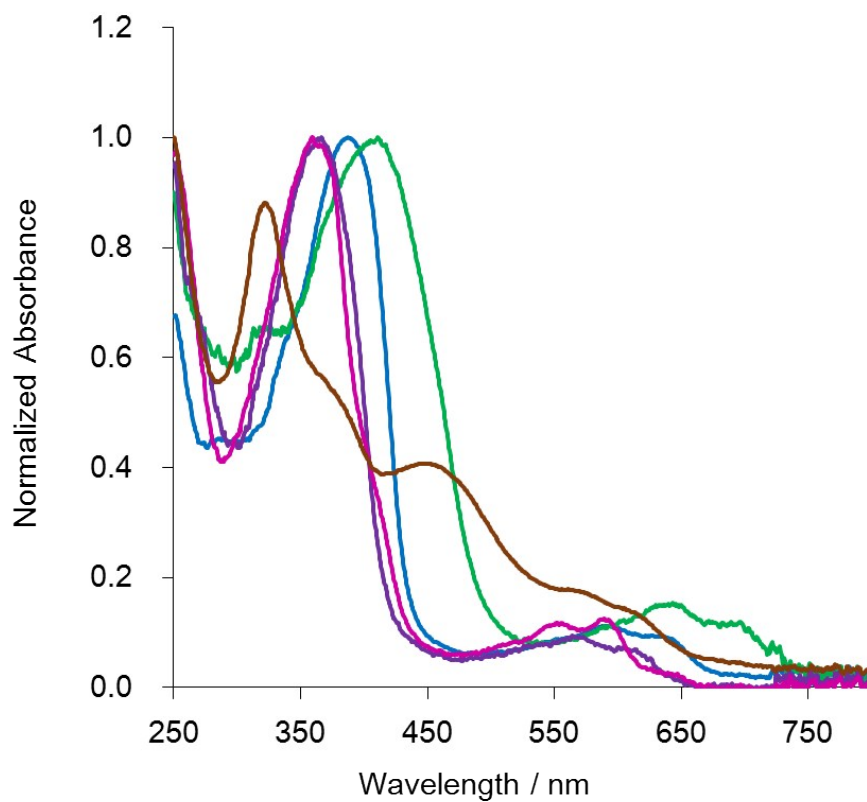
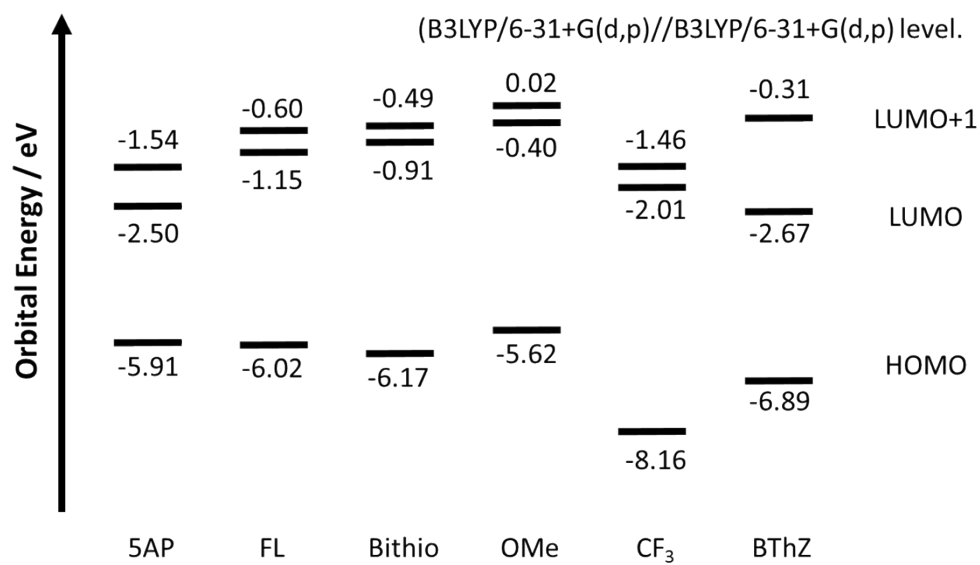


Figure S10.  $^1\text{H}$  NMR spectrum of 5AP-co-CF<sub>3</sub>.



**Figure S11.** UV-vis absorption spectra of the polymers in the film states (prepared by spin-coat method from  $1.0 \times 10^{-3}$  M chloroform solutions).





**Figure S12.** Calculated energy levels of 5AP and each comonomer unit. Long alkyl chains were replaced by methyl groups.