Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supplementary Information

Synthesis, optical and electrochemical properties of propeller-type 3,5,8-trithienyl-BODIPY dyes

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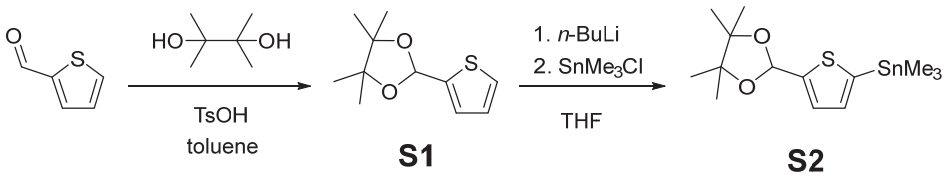
Experimental Section

Synthesis of 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3-dioxolane (S1): A solution of thiophene-2-carbaldehyde (20.0 g, 178 mmol), pinacol (42.2 g, 357 mmol), and *p*-toluenesulfonic acid monohydrate (1.57 mg, 8.96 mmol) in toluene (500 mL) was refluxed by using Dean-Stark apparatus under a nitrogen atmosphere. After 2 h, the reaction mixture was concentrated under reduced pressure. The residue was chromatographed on alumina (hexane ethyl acetate = 9 : 1 as eluent) to give **S1** (36.3 g, yield 96 %) as a light yellow oil; ^{1}H NMR (400 MHz, acetone-d_6) δ = 1.27 (d, 12H), 6.16 (s, 1H), 6.98 (dd, J = 3.5 and 5.0 Hz, 1H), 7.14–7.16 (m, 1H), 7.44 (dd, J = 0.9 and 5.0 Hz, 1H); ^{13}C NMR (100 MHz, acetone-d_6): δ = 22.30, 22.39, 24.54, 24.62, 83.43, 97.25, 97.44, 126.71, 126.80, 126.90, 126.96, 127.09, 127.25, 145.38 ppm; HRMS (ESI): m/z (%): $[M+H]^+$ Calcd for $C_{11}H_{17}O_2S$, 213.09438; found 213.09399.

Synthesis of trimethyl(5-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)thiophen-2-yl)stannane (S2): A solution of **S1** (2.00 g, 9.42 mmol) in THF (50 mL) was prepared under a nitrogen atmosphere and stirred at –78 °C. 1.55 M *n*-BuLi in hexane (6.68 mL, 10.4 mmol) was slowly dropped into the solution, and the mixture was stirred at –78 °C for 1 h. Then, trimethylthin (IV) chloride (2.06 g, 10.4 mmol) was added to the solution, and the mixture was stirred at room temperature for 11 h. After concentrating under reduced pressure, the resulting residue was dissolved in DCM, and washed with water. The DCM extract were evaporated under reduced pressure to give **S2** as a brown oil (2.95 g, 84% yield); ^{1}H NMR (400 MHz, acetone-d_6) δ = 0.35 (s, 9H), 1.27 (dd, 12H), 6.19 (s, 1H), 7.09 (d, J = 3.3 Hz, 1H), 7.23 (dd, J = 0.5 and 3.3 Hz, 1H); ^{13}C NMR (100 MHz, acetone-d_6): δ = –8.34, –8.46, 22.32, 22.39, 24.58, 24.66, 83.33, 97.21, 97.39, 128.01, 128.18, 135.29, 135.46, 139.23, 150.87 ppm; HRMS (ESI): m/z (%): $[M+Na]^+$ Calcd for $C_{14}H_{24}O_2NaSSn$, 399.04112; found 399.04117.



Scheme S1 Synthesis of **S2**.

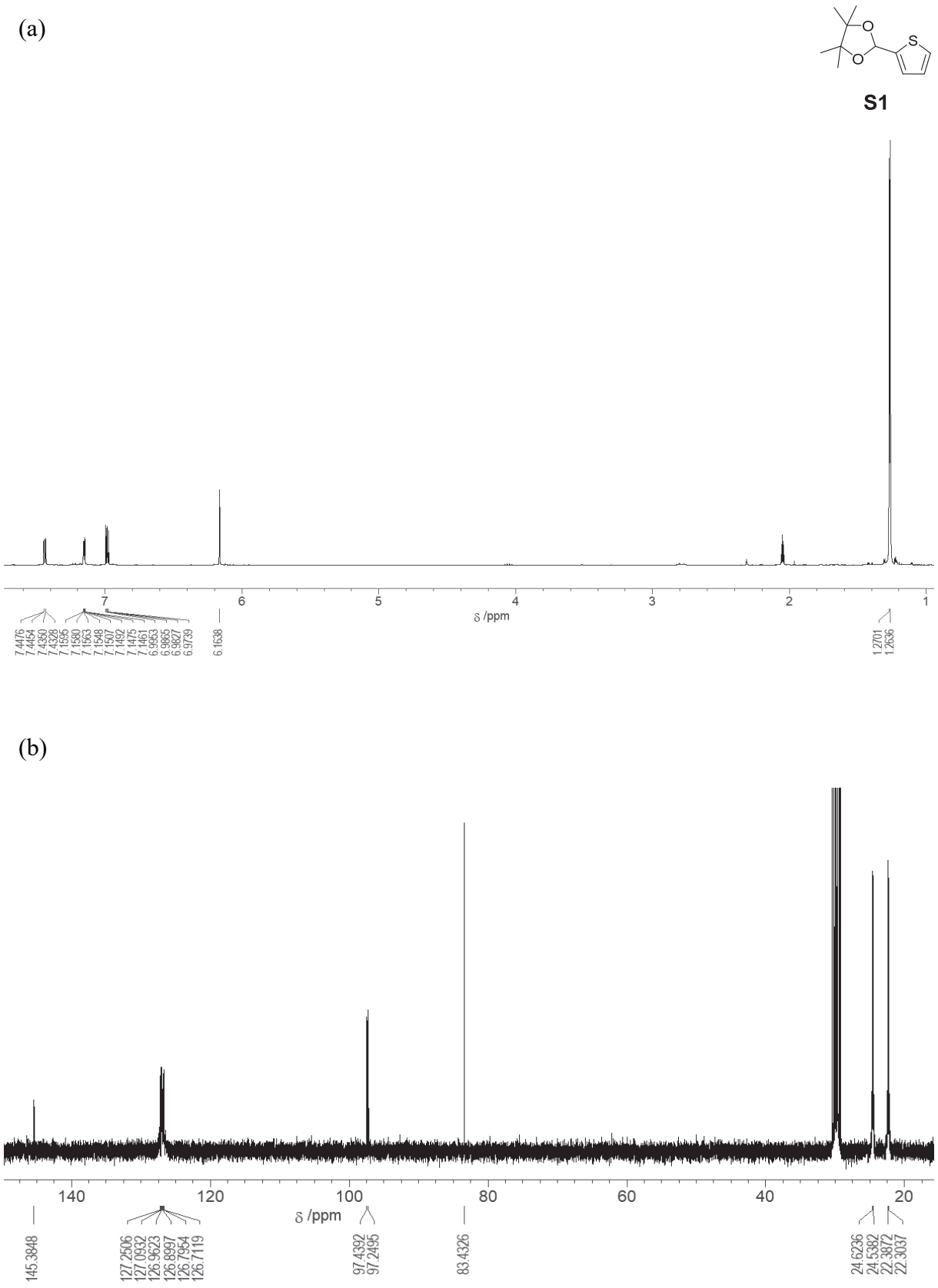
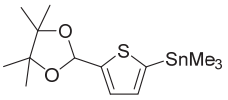
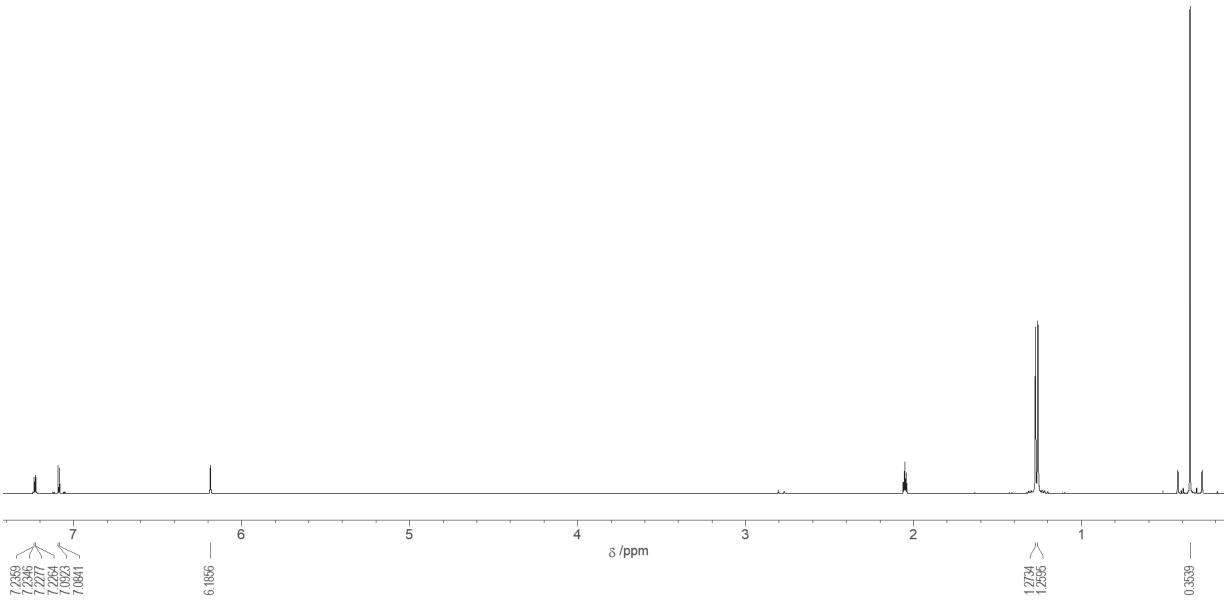


Fig. S1 (a) ^{1}H NMR (400 MHz) and (b) ^{13}C NMR (100 MHz) spectra of **S1** in acetone-d_6.

(a)



S2



(b)

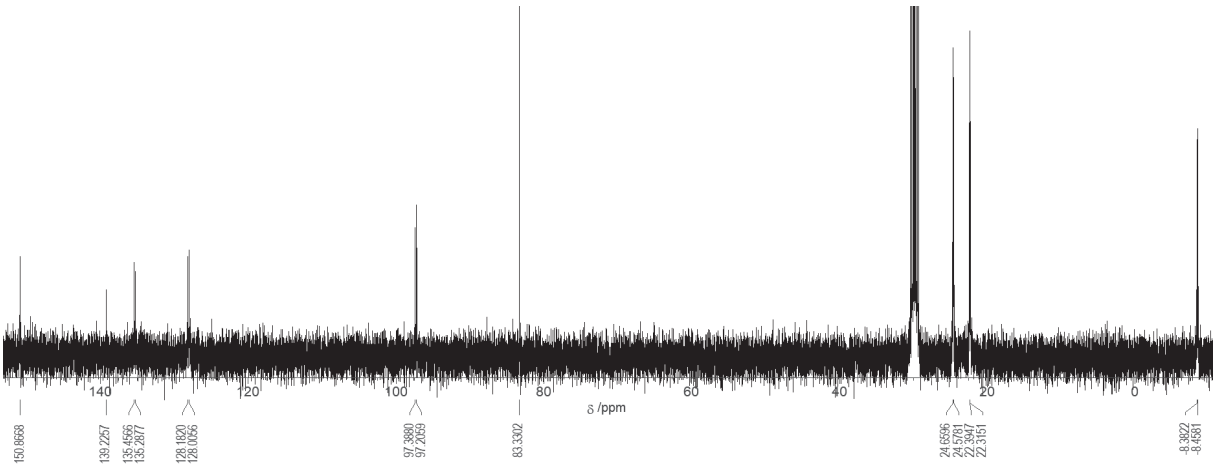


Fig. S2 (a) ^{1}H NMR (400 MHz) and (b) ^{13}C NMR (100 MHz) spectra of **S2** in acetone-d_6.

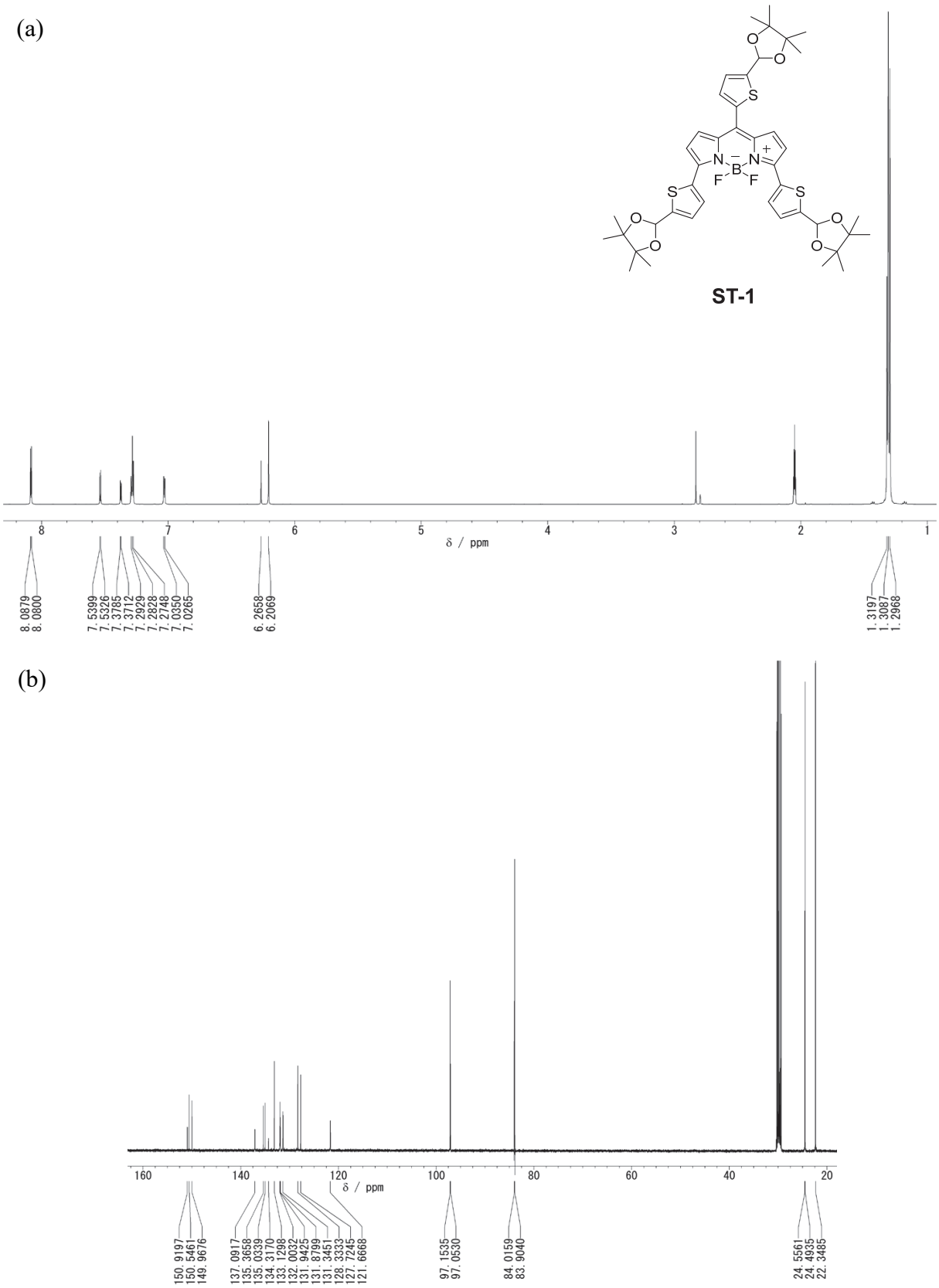
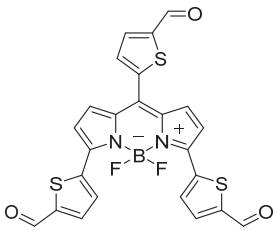
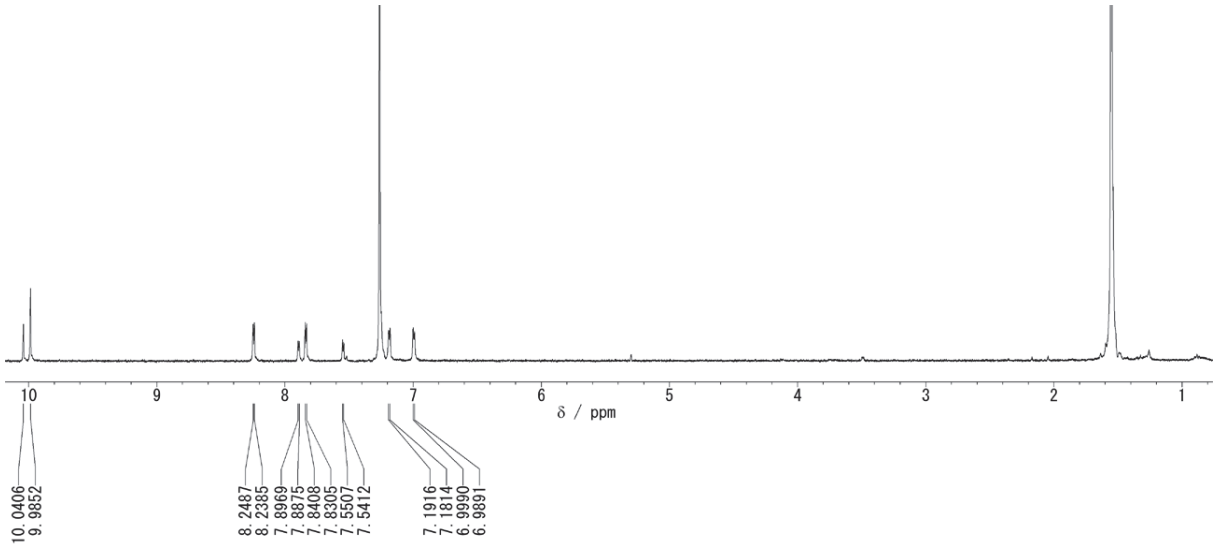


Fig. S3 (a) ^{1}H NMR (500 MHz) and (b) ^{13}C NMR (125 MHz) spectra of **ST-1** in acetone-d_6.

(a)



ST-2



(b)

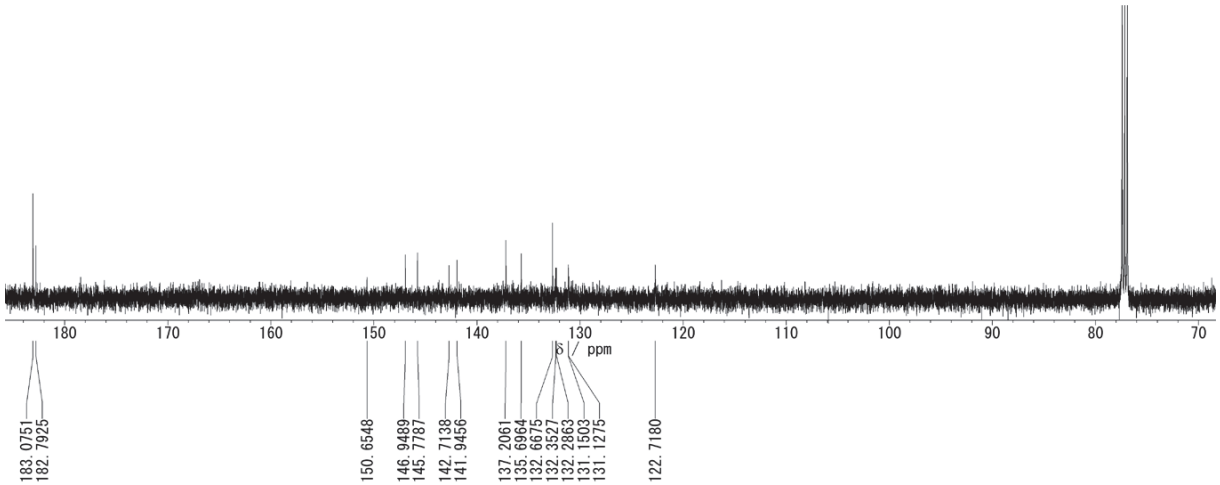


Fig. S4 (a) ^{1}H NMR (400 MHz) and (b) ^{13}C NMR (125 MHz) spectra of **ST-2** in $CDCl_3$.

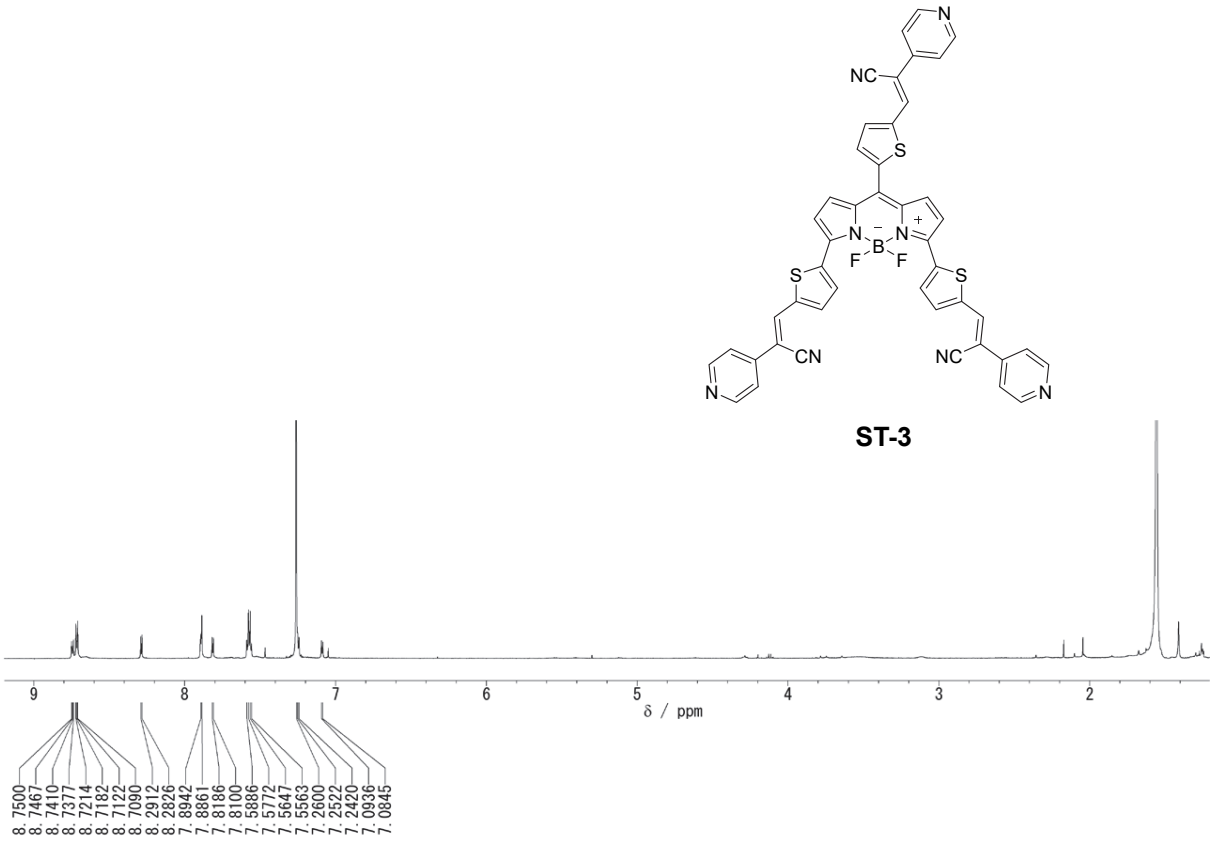


Fig. S5 ^{1}H NMR (500 MHz) spectrum of **ST-3** in $CDCl_3$.