

## Electronic Supplementary Material (ESI) for Naphtho[2,1-*b*:3,4-*b'*]bisthieno[3,2-*b*][1]benzothiophene-Based Semiconductors for Organic Field-Effect Transistors

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## 1. General Information

### Materials and methods:

All chemicals used in this chapter were purchased from Sigma-Aldrich Corporation or Dieckmann (HK) Chemical Company Ltd without further purification. All the solvents of reagent-grade used for the synthesis were dried by the standard procedures.  $^1\text{H}$  NMR spectra and  $^{13}\text{C}$  NMR spectra were recorded using Bruker Ultrashield 400 Plus NMR spectrometer and calibrated by the residual undeuterated solvent ( $\text{CHCl}_3$  7.26 ppm, for  $^1\text{H}$  NMR and 77.15 ppm for  $^{13}\text{C}$  NMR; DMSO 2.50 ppm for  $^1\text{H}$  NMR and 39.5 ppm for  $^{13}\text{C}$  NMR). High-Resolution Mass spectrometer (HRMS) was recorded with matrix-assisted laser desorption ionization-time-of-flight (MALDI-TOF) technique. Thermal stabilities were estimated on Perkin-Elmer Thermal analyzer (PE-TGA6) with a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$  under  $\text{N}_2$  from room temperature to  $900\text{ }^\circ\text{C}$ . Differential scanning calorimetry was recorded on PE Pyris Diamond DSC. Melting points were estimated on Barnstead Electrothermal 9100. All UV-vis absorption measurements were carried out on Varian Cary 100 Scan Spectrophotometer in dry dichloromethane with a concentration of  $10^{-5}\text{ mol/L}$ . The X-ray diffraction (XRD) measurements were carried out using D/max 2500 X-Ray Diffractometer, with scan scale from  $3^\circ$  to  $30^\circ$ ,  $3^\circ/\text{min}$ . The atomic force microscope (AFM) measurements were carried out using Bruke Multimode 8, tapping mode. The element analysis was carried out using Flash EA 1112 elemental analyzer.

### TFT device fabrication and measurement:

OTFT devices were fabricated in a bottom-gate bottom-contact (BGBC) configuration (gold electrode on  $\text{Si}/\text{SiO}_2$  substrates). The gold source-drain electrodes were prepared by photolithography, and then OTS treatment was performed on the gate dielectrics which were placed in a vacuum oven with OTS at a temperature of  $120\text{ }^\circ\text{C}$  for 3 hours to form an OTS self-assembled layer, followed by cleaning with n-hexane, alcohol and chloroform for 6 min in ultrasonic cleaner to remove the redundant OTS molecules or the hydrolysate physically absorbed on the electrode and

OTS layer. Subsequently, the thin films were evaporated on the OTS modified SiO<sub>2</sub>/Si substrates from the solutions. The OTFTs devices were annealed successively at 80, 120, 160, 180, 200, 220, 240, and 260 °C for 6 min in air, and measured after each annealing step at room temperature in air by using a Keithley 4200 Semiconductor Characterization System.

The mobility of the devices was calculated in the saturation regime. The equation is listed as follows:

$$I_{DS} = (W / 2L) C_i \mu (V_{GS} - V_{th})^2$$

where W/L is the channel width / length, C<sub>i</sub> is the insulator capacitance per unit area, and V<sub>GS</sub> and V<sub>th</sub> are the gate voltage and threshold voltage, respectively.

## 2. Experimental Procedures

**3-Bromobenzo[*b*]thiophene-2-carbaldehyde (1a).** To a solution of diisopropylamine (11.6 mL, 82.87 mmol) in dry THF (150 mL) at 0 °C was added 2.4 M *n*-BuLi (29.6 mL, 71.03 mmol) dropwise under N<sub>2</sub>. The mixture was stirred for 30 min at 0 °C, then cooled to -78 °C and added a solution of 3-bromobenzo[*b*]thiophene (12.61 g, 59.19 mmol) in dry THF (25 mL) dropwise. The mixture was stirred for another 1 h at -78 °C, and added *N*-formylmorpholine (10.21 g, 88.80 mmol) in one portion. The mixture was allowed to warm up to RT slowly and stirred overnight. After quenched with water (150 mL), the solution mixture was extracted with ethyl acetate (100 mL × 3), washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography affording the title product as a light yellow solid (12.13 g, 85%). Mp: 118-119 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 10.28 (s, 1H), 8.02 (d, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.59-7.51 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 184.82, 140.47, 138.04, 136.48, 129.33, 126.00, 125.05, 123.43, 118.92. EI-MS: *m/z* 239 (M-H, 85%), 240 (M<sup>+</sup>, 100%), 241 (95%), 242 (93%).

**Thieno[3,2-*b*][1]benzothiophene-2-carboxylate ethyl (1b).** To a mixture of compound **1a** (12 g, 49.77 mmol), K<sub>2</sub>CO<sub>3</sub> (13.74 g, 99.54 mmol) in DMF (80 mL) at

0 °C was added ethyl 2-mercaptoacetate (5.93 g, 49.77 mmol) dropwise. The mixture was stirred for 3 days at RT. After poured into ice-water (200 mL), the solid was collected by filtration, washed with H<sub>2</sub>O (50 mL), and dried in vacuum at 60 °C affording the title product as a light yellow solid (12.01 g, 92%). Mp: 123-124 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.01 (s, 1H), 7.89-7.84 (m, 2H), 4.55-4.38 (m, 2H), 4.41 (q, *J* = 7.20 Hz, 2H), 1.42 (t, *J* = 7.20 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 162.32, 143.84, 139.96, 137.36, 135.56, 132.06, 126.31, 125.99, 125.01, 123.98, 121.82, 61.57, 14.42. EI-MS: *m/z* 262 (M<sup>+</sup>, 100%), 234 (M-CH<sub>2</sub>CH<sub>3</sub>, 38%), 217 (M-OCH<sub>2</sub>CH<sub>3</sub>, 52%), 189 (M-COOCH<sub>2</sub>CH<sub>3</sub>, 16%).

**Thieno[3,2-*b*][1]benzothiophene-2-carboxylic acid (1c).** To a solution of compound **1b** (10 g, 38.12 mmol) in THF (50 mL) at room temperature was added a solution of NaOH (4.57 g, 114.36 mmol) in water (25 mL). The mixture was refluxed for 5 h at 80 °C. After cooled to room temperature, the mixture was poured into 3 M HCl (60 mL) at 0 °C. The solid was collected by filtration, washed with H<sub>2</sub>O (50 mL), and dried in vacuum at 60 °C affording the title product as a light yellow solid (7.95 g, 89%). Mp: 258-260 °C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 8.20 (s, 1H), 8.11-8.07 (m, 2H), 7.52-7.47 (m, 2H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ: 163.00, 143.08, 138.56, 137.44, 136.63, 131.38, 126.96, 126.21, 125.29, 124.31, 121.95. EI-MS: *m/z* 234 (M<sup>+</sup>, 100%), 217 (M-OH, 20%), 190 (M-COOH, 29%).

**Thieno[3,2-*b*][1]benzothiophene (1d).** To a mixture of compound **1c** (3.1 g, 13.2 mmol) in quinoline (20 mL) at room temperature was added copper powder (0.83 g, 13.2 mmol) in one portion. The mixture was refluxed for 6 h at 230 °C. After cooled to room temperature, the reaction mixture was extracted with hexane (50 mL × 3), washed with brine, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography affording the title product as a white solid (1.63 g, 65%). Mp: 90-91 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.88-7.85 (m, 2H), 7.51 (d, *J* = 5.1 Hz, 1H), 7.45-7.41 (m, 1H), 7.38-7.36 (m, 1H), 7.33 (d, *J* = 5.1 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 142.78, 137.99, 134.89, 132.63, 127.98, 124.68, 124.47, 123.97, 121.02, 120.35. EI-MS: *m/z*

190 (M<sup>+</sup>, 100%).

**2-Bromothieno[3,2-*b*][1]benzothiophene (1e).** To a solution of compound **1d** (2.4 g, 12.63 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) at -35 °C was added a solution of bromine (2.02 g, 12.63 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) dropwise. The mixture was allowed to warm up to room temperature slowly and stirred overnight. After quenched with 2M K<sub>2</sub>CO<sub>3</sub>, the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (30 mL × 3), washed with brine, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed by rotary evaporation and the residue by silica gel column chromatography affording the title product as a white solid (2.78 g, 82%). Mp: 99-100 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.85-7.83 (m, 1H), 7.77-7.74 (m, 1H), 7.41 (td, *J* = 7.2 Hz, *J* = 1.2 Hz, 1H), 7.36 (td, *J* = 7.2 Hz, *J* = 1.5 Hz, 1H), 7.31 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 141.47, 136.70, 134.90, 132.23, 124.91, 124.67, 123.82, 123.09, 120.83, 114.20. EI-MS: *m/z* 268 (M<sup>+</sup>, 90%), 270 (M+2, 100%), 189 (M-Br, 15%).

**3-Bromothieno[3,2-*b*][1]benzothiophene (1f).** To a solution of diisopropylamine (2.2 mL, 15.46 mmol) in dry THF (50 mL) at 0 °C was added 2.5 M *n*-BuLi (5.8 mL, 14.86 mmol) dropwise under N<sub>2</sub>. The mixture was stirred for 30 min at 0 °C, then cooled to -78 °C and added a solution of compound **1d** (3.2 g, 11.89 mmol) in dry THF (20 mL) dropwise. The mixture was stirred for 5 h at -78 °C, allowed to warm up to room temperature slowly and stirred overnight at RT. After quenched with water (100 mL), the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (50 mL × 3), washed with brine, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography affording the title product as a white solid (2.11 g, 66%). Mp: 98-99 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.88-7.87 (m, 1H), 7.83-7.80 (m, 1H), 7.44 (td, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.41-7.36 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 142.32, 139.46, 134.30, 133.14, 125.08, 124.97, 124.39, 124.16, 121.05, 103.54. EI-MS: *m/z* 268 (M<sup>+</sup>, 94%), 270 (M+2, 100%), 189 (M-Br, 14%).

**3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)thieno[3,2-*b*][1]benzothiophene (1g).** To a solution of **1f** (1 g, 3.71 mmol), bis(pinacolato)diboron (1.88 g, 7.42 mmol),

KOAc (1.8 g, 18.55 mmol) in 1,4-dioxane (15 mL) was added Pd(dppf)Cl<sub>2</sub> (60 mg). The mixture was stirred overnight at 80 °C under N<sub>2</sub>. After cooled to RT, the reaction mixture was extracted with ethyl acetate (50 mL × 3), washed with brine, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography affording the title product as a white solid (0.80 g, 68%). Mp: 89-93 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.10 (s, 1H), 7.90 (t, *J* = 7.0 Hz, 2H), 7.46-7.42 (m, 1H), 7.39-7.35 (m, 1H), 1.44 (s, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 143.58, 143.47, 138.77, 134.65, 132.46, 124.44, 124.23, 123.90, 121.00, 84.27, 24.96. HRMS (MALDI-TOF): calcd for C<sub>16</sub>H<sub>17</sub>BO<sub>2</sub>S<sub>2</sub>: 316.0763; found: 316.0754 (M<sup>+</sup>).

**3-Bromo-5-fluorobenzo[*b*]thiophene-2-carbaldehyde (2a).** To a solution of diisopropylamine (4 mL, 28 mmol) in dry THF (80 mL) at 0 °C was added 2.4 M *n*-BuLi (10 mL, 24 mmol) dropwise under N<sub>2</sub>. The mixture was stirred for 30 min at 0 °C, then cooled to -78 °C, and added a solution of 3-bromo-5-fluorobenzo[*b*]thiophene (4.62 g, 20 mmol) in dry THF (25 mL) dropwise. The mixture was stirred for another 1 h at -78 °C and then added *N*-formylmorpholine (3.43 g, 30 mmol) in one portion which was allowed it to warm up to RT slowly and stirred overnight. After quenched with water (150 mL), the reaction mixture was extracted with ethyl acetate (100 mL × 3), washed with brine, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography affording the title product as a light yellow solid. (4.51 g, 87%). Mp: 138-139 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 10.26 (s, 1H), 7.84 (ddd, *J* = 8.9 Hz, *J* = 4.6 Hz, *J* = 0.28 Hz, 1H), 7.68 (ddd, *J* = 8.8 Hz, *J* = 2.5 Hz, *J* = 0.28 Hz, 1H), 7.34 (td, *J* = 8.7 Hz, *J* = 2.5 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 184.56, 161.56 (d, *J* = 244 Hz), , 139.39 (d, *J* = 10 Hz), 138.68, 135.96, 125.05 (d, *J* = 9 Hz), 118.67 (d, *J* = 26 Hz), 117.61 (d, *J* = 5.0 Hz), 110.39 (d, *J* = 25 Hz). HRMS (MALDI-TOF): calcd for C<sub>9</sub>H<sub>4</sub>BrFOS: 259.9186; found: 259.9198 (M<sup>+</sup>).

**7-Fluorothieno[3,2-*b*][1]benzothiophene-2-carboxylate ethyl (2b).** To a mixture of compound **2a** (4.25 g, 16.4 mmol), K<sub>2</sub>CO<sub>3</sub> (4.5 g, 32.8 mmol) in DMF (30 mL) at 0

°C was added ethyl 2-mercaptoacetate (1.97 g, 16.4 mmol) dropwise. The mixture was stirred for 3 days at RT and then poured into ice-water (200 mL). The solid was collected by filtration, washed with H<sub>2</sub>O (50 mL), and dried in vacuum at 60 °C affording the title product as a light yellow solid (4.14 g, 90%). Mp: 145-146 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.01 (s, 1H), 7.80 (dd, *J* = 8.9 Hz, *J* = 4.7 Hz, 1H), 7.57 (dd, *J* = 8.9 Hz, *J* = 2.5 Hz, 1H), 7.18 (td, *J* = 8.9 Hz, *J* = 2.5 Hz, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 162.19, 160.95 (d, *J* = 235 Hz), 139.28, 139.10, 139.04 (d, *J* = 4.0 Hz), 136.46, 133.08 (d, *J* = 10.0 Hz), 126.27, 125.13 (d, *J* = 9.0 Hz), 114.52 (d, *J* = 25 Hz), 107.87 (d, *J* = 24 Hz), 61.65, 14.34. HRMS (MALDI-TOF): calcd for C<sub>13</sub>H<sub>9</sub>FO<sub>2</sub>S<sub>2</sub>: 280.0028; found: 280.0031 (M<sup>+</sup>).

**7-Fluorothieno[3,2-*b*][1]benzothiophene-2-carboxylic acid (2c).** To a solution of compound **2b** (4 g, 14.27 mmol) in THF (30 mL) at room temperature was added a solution of NaOH (1.71 g, 42.81 mmol) in H<sub>2</sub>O (25 mL). The mixture was refluxed for 5 h at 80 °C. After cooled to RT, the reaction mixture was poured into 2 M HCl (40 mL) at 0 °C. The solid was collected by filtration, washed with H<sub>2</sub>O (25 mL), and dried in vacuum at 60 °C affording the title product as a light yellow solid (3.24 g, 90%). Mp: 288-289 °C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 8.19 (s, 1H), 8.14 (dd, *J* = 8.9 Hz, *J* = 5.0 Hz, 1H), 8.04 (dd, *J* = 9.5 Hz, *J* = 2.5 Hz, 1H), 7.38 (td, *J* = 9.0 Hz, *J* = 2.5 Hz, 1H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ: 162.97, 160.35 (d, *J* = 240 Hz), 139.45, 138.56 (d, *J* = 2.0 Hz), 138.41, 137.53 (d, *J* = 4.0 Hz), 132.55 (d, *J* = 10.0 Hz), 126.45, 125.89 (d, *J* = 10.0 Hz), 114.23 (d, *J* = 25 Hz), 107.97 (d, *J* = 25 Hz). HRMS (MALDI-TOF): calcd for C<sub>11</sub>H<sub>5</sub>FO<sub>2</sub>S<sub>2</sub>: 251.9715; found: 251.9726 (M<sup>+</sup>).

**7-Fluorothieno[3,2-*b*][1]benzothiophene (2d).** To a mixture of compound **2c** (4.05 g, 16.1 mmol) in quinoline (40 mL) at room temperature was added copper powder (1.02 g, 16.05 mmol) in one portion. The mixture was refluxed for 6 h at 230 °C. After cooled to RT, the reaction mixture was extracted with hexane (50 mL × 3), washed with brine, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography

affording the title product as a white solid (1.91 g, 57%). Mp: 122-123 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.76 (ddd, *J* = 8.9 Hz, *J* = 5.0 Hz, *J* = 0.24 Hz, 1H), 7.53-7.50 (m, 2H), 7.31 (d, *J* = 5.2 Hz, 1H), 7.10 (td, *J* = 8.8 Hz, *J* = 2.5 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 160.95 (d, *J* = 241 Hz), 140.03, 137.90 (d, *J* = 1.0 Hz), 134.26 (d, *J* = 4.0 Hz), 133.55 (d, *J* = 9.0 Hz), 128.77, 124.98 (d, *J* = 9.0 Hz), 120.42, 112.84 (d, *J* = 25 Hz), 107.12 (d, *J* = 23 Hz). EI-MS: *m/z* 208 (M<sup>+</sup>, 100%).

**2-Bromo-7-fluorothieno[3,2-*b*][1]benzothiophene (2e).** To a solution of compound **2d** (3.34 g, 16.02 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) at -35 °C was added a solution of bromine (2.56 g, 16.02 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) dropwise. The mixture was allowed to warm up to RT and stirred overnight. After quenched with 2M K<sub>2</sub>CO<sub>3</sub>, the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (30 mL × 3), washed with brine, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography affording the title product as a white solid (4.00 g, 87%). Mp: 140-141 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.75 (dd, *J* = 8.8 Hz, *J* = 4.8 Hz, 1H), 7.43 (dd, *J* = 9.0 Hz, *J* = 2.5 Hz, 1H), 7.31 (s, 1H), 7.10 (td, *J* = 8.8 Hz, *J* = 2.5 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 161.01 (d, *J* = 242 Hz), 138.81, 136.67, 134.26 (d, *J* = 5.0 Hz), 133.14 (d, *J* = 10.0 Hz), 124.92 (d, *J* = 10.0 Hz), 123.18, 115.27, 113.15 (d, *J* = 25 Hz), 106.97 (d, *J* = 24 Hz). EI-MS: *m/z* 286 (M<sup>+</sup>, 96%), 288 (M+2, 100%), 207 (M-Br, 23%).

**3-Bromo-7-fluorothieno[3,2-*b*][1]benzothiophene (2f).** To a solution of diisopropylamine (2.2 mL, 15.67 mmol) in dry THF (50 mL) at 0 °C was added 2.4 M *n*-BuLi (5.9 mL, 14.16 mmol) dropwise under N<sub>2</sub>. The mixture was stirred for 30 min at 0 °C, then cooled to -78 °C and added a solution of compound **2d** (3 g, 10.45 mmol) in dry THF (20 mL) dropwise. The mixture was stirred for 5 h at -78 °C, then allowed to warm up to RT slowly and stirred overnight at RT. After quenched with water (100 mL), the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (50 mL × 3), washed with brine, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography affording the title product as a white solid (1.49 g, 45%). Mp: 137-138 °C. <sup>1</sup>H NMR



(400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.78 (dd,  $J = 8.9$  Hz,  $J = 4.8$  Hz, 1H), 7.47 (dd,  $J = 8.9$  Hz,  $J = 2.5$  Hz, 1H), 7.41 (s, 1H), 7.13 (td,  $J = 8.8$  Hz,  $J = 2.5$  Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 160.94 (d,  $J = 242$  Hz), 141.41, 137.44, 133.97 (d,  $J = 9.0$  Hz), 133.56 (d,  $J = 4.0$  Hz), 125.31, 125.29 (d,  $J = 5.0$  Hz), 113.58 (d,  $J = 25$  Hz), 107.22 (d,  $J = 25$  Hz), 103.56. HRMS (MALDI-TOF): calcd for C<sub>10</sub>H<sub>4</sub>BrFS<sub>2</sub>: 287.8901; found: 287.8901 (M<sup>+</sup>).

**3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-7-fluorothieno[3,2-**

**b][1]benzothiophene (2g).** To a solution of **2f** (1.1 g, 3.83 mmol), bis(pinacolato)diboron (2.0 g, 7.66 mmol), KOAc (1.87 g, 19.15 mmol) in 1,4-dioxane (15 mL) was added Pd(dppf)Cl<sub>2</sub> (60 mg). The mixture was stirred overnight at 80 °C under N<sub>2</sub>. After cooled to RT, the reaction mixture was extracted with ethyl acetate (50 mL  $\times$  3), washed with brine, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography affording the title product as a white solid (0.91 g, 71%). Mp: 116-120 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.06 (s, 1H), 7.74 (dd,  $J = 9.0$  Hz,  $J = 4.9$  Hz, 1H), 7.46 (dd,  $J = 9.0$  Hz,  $J = 2.5$  Hz, 1H), 7.06 (td,  $J = 8.9$  Hz,  $J = 2.5$  Hz, 1H), 1.39 (s, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 160.64 (d,  $J = 241$  Hz), 145.54, 139.32, 138.49 (d,  $J = 2.0$  Hz), 133.81 (d,  $J = 4.0$  Hz), 133.13 (d,  $J = 10.0$  Hz), 124.74 (d,  $J = 9.0$  Hz), 112.45 (d,  $J = 24$  Hz), 106.81 (d,  $J = 24$  Hz), 84.12, 24.81. HRMS (MALDI-TOF): calcd for C<sub>16</sub>H<sub>16</sub>BFO<sub>2</sub>S<sub>2</sub>: 334.0669; found: 335.0763 (M+1).

**Compound 3a.** To a solution of 1,2-dibromo-4,5-dihexyloxybenzene (0.25 g, 0.57 mmol), compound **1g** (0.72 g, 2.28 mmol), K<sub>2</sub>CO<sub>3</sub> (0.32 g, 2.28 mmol) in THF/H<sub>2</sub>O (40 mL/4 mL) was added Pd(PPh<sub>3</sub>)<sub>4</sub> (35 mg). The mixture was refluxed overnight at 85 °C under N<sub>2</sub>. After cooled to RT, the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL  $\times$  3), washed with brine, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography affording the title product as translucent sticky liquid (0.34 g, 92%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.77 (d,  $J = 7.8$  Hz, 2H), 7.74 (d,  $J = 7.8$  Hz, 2H), 7.38-7.34 (m, 2H), 7.30-7.26 (m, 2H), 7.24 (s, 2H), 7.09 (s, 2H), 4.11 (t,  $J = 6.6$  Hz,

4H), 1.93-1.86 (m, 4H), 1.55-1.47 (m, 4H), 1.42-1.32 (m, 8H), 0.92 (t,  $J = 6.8$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 148.86, 142.53, 138.94, 134.50, 133.95, 132.96, 126.20, 125.20, 124.51, 124.26, 123.89, 120.69, 114.76, 69.36, 31.67, 29.26, 25.80, 22.71, 14.13. HRMS (MALDI-TOF): calcd for  $\text{C}_{38}\text{H}_{38}\text{O}_2\text{S}_4$ : 654.1755; found: 654.1769 ( $\text{M}^+$ ).

**Compound 3b.** To a solution of 1,2-dibromo-4,5-di(2'-ethylhexyloxy)benzene (0.28 g, 0.57 mmol), compound **1g** (0.72 g, 2.28 mmol),  $\text{K}_2\text{CO}_3$  (0.32 g, 2.28 mmol) in THF/ $\text{H}_2\text{O}$  (40 mL/4 mL) was added  $\text{Pd}(\text{PPh}_3)_4$  (35 mg). The mixture was refluxed overnight at 85 °C under  $\text{N}_2$ . After cooled to RT, the reaction mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (20 mL  $\times$  3), washed with brine, and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography affording the title product as translucent sticky liquid (0.39 g, 95%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.75-7.70 (m, 4H), 7.34-7.30 (m, 2H), 7.27-7.22 (m, 2H), 7.09 (s, 2H), 4.01-3.96 (m, 4H), 1.86-1.78 (m, 2H), 1.63-1.30 (m, 16H), 0.97 (t,  $J = 7.5$  Hz, 6H), 0.91 (t,  $J = 7.0$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 149.35, 142.61, 139.04, 134.69, 134.01, 133.02, 126.14, 125.22, 124.54, 124.29, 123.94, 120.72, 114.64, 71.68, 39.66, 30.73, 29.25, 24.08, 24.07, 23.20, 14.23, 11.36. HRMS (MALDI-TOF): calcd for  $\text{C}_{42}\text{H}_{46}\text{O}_2\text{S}_4$ : 710.2381; found: 710.2353 ( $\text{M}^+$ ).

**Compound 3c.** To a solution of 1,2-dibromo-4,5-di(octyloxy)benzene (0.27 g, 0.55 mmol), compound **1g** (0.70 g, 2.21 mmol),  $\text{K}_2\text{CO}_3$  (0.30 g, 2.21 mmol) in THF/ $\text{H}_2\text{O}$  (40 mL/4 mL) was added  $\text{Pd}(\text{PPh}_3)_4$  (35 mg). The mixture was refluxed overnight at 85 °C under  $\text{N}_2$ . After cooled to RT, the solution mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (20 mL  $\times$  3), washed with brine, and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography affording the title product as translucent sticky liquid (0.35 g, 90%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.77 (d,  $J = 7.6$  Hz, 2H), 7.74 (d,  $J = 7.8$  Hz, 2H), 7.38-7.34 (m, 2H), 7.30-7.26 (m, 2H), 7.24 (s, 2H), 7.09 (s, 2H), 4.11 (t,  $J = 6.5$  Hz, 4H), 1.93-1.86 (m, 4H), 1.54-1.47 (m, 4H), 1.42-1.26 (m, 16H), 0.89 (t,  $J = 6.5$  Hz, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 148.87, 142.52, 138.94, 134.50, 133.95, 132.96,

126.20, 125.19, 124.51, 124.26, 123.89, 120.69, 114.79, 69.37, 31.90, 29.46, 29.36, 29.29, 26.12, 22.74, 14.19. HRMS (MALDI-TOF): calcd for C<sub>42</sub>H<sub>46</sub>O<sub>2</sub>S<sub>4</sub>: 710.2375; found: 710.2382 (M<sup>+</sup>).

**Compound 3d.** To a solution of 1,2-dibromo-4,5-di(decyloxy)benzene (0.7 g, 1.28 mmol), compound **1g** (1.63 g, 5.15 mmol), K<sub>2</sub>CO<sub>3</sub> (0.7 g, 5.15 mmol) in THF/H<sub>2</sub>O (40 mL/4 mL) was added Pd(PPh<sub>3</sub>)<sub>4</sub> (40 mg). The mixture was refluxed overnight at 85 °C under N<sub>2</sub>. After cooled to RT, the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL × 3), washed with brine, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography affording the title product as translucent sticky liquid (0.86 g, 87.5%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.78 (d, *J* = 7.8 Hz, 2H), 7.76 (d, *J* = 7.8 Hz, 2H), 7.39-7.35 (m, 2H), 7.32-7.28 (m, 2H), 7.25 (s, 2H), 7.10 (s, 2H), 4.12 (t, *J* = 6.6 Hz, 4H), 1.94-1.86 (m, 4H), 1.55-1.48 (m, 4H), 1.42-1.24 (m, 24H), 0.89 (t, *J* = 6.6 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 148.83, 142.51, 138.92, 134.49, 133.94, 132.94, 126.16, 125.19, 124.50, 124.25, 123.89, 120.68, 114.74, 69.35, 31.97, 29.71, 29.66, 29.50, 29.42, 29.27, 26.11, 22.75, 14.19. HRMS (MALDI-TOF): calcd for C<sub>46</sub>H<sub>54</sub>O<sub>2</sub>S<sub>4</sub>: 766.3007; found: 766.2994 (M<sup>+</sup>).

**Compound 3e.** To a solution of 1,2-dibromo-4,5-di(dodecyloxy)benzene (0.33 g, 0.55 mmol), compound **1g** (0.7 g, 2.21 mmol), K<sub>2</sub>CO<sub>3</sub> (0.30 g, 2.21 mmol) in THF/H<sub>2</sub>O (40 mL/4 mL) was added Pd(PPh<sub>3</sub>)<sub>4</sub> (30 mg). The mixture was refluxed overnight at 85 °C under N<sub>2</sub>. After cooled to RT, the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL × 3), washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography affording the title product as translucent sticky liquid (0.40 g, 88%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.79 (d, *J* = 7.8 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.40-7.36 (m, 2H), 7.32-7.28 (m, 2H), 7.26 (s, 2H), 7.11 (s, 2H), 4.13 (t, *J* = 6.4 Hz, 4H), 1.95-1.88 (m, 4H), 1.56-1.50 (m, 4H), 1.43-1.26 (m, 32H), 0.90 (t, *J* = 6.5 Hz, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 148.87, 142.53, 138.94, 134.51, 133.96, 132.96, 126.20, 125.20, 124.51, 124.26, 123.89, 120.69, 114.80, 69.38, 31.99, 29.79,

29.74, 29.53, 29.44, 29.30, 26.14, 22.77, 14.20. HRMS (MALDI-TOF): calcd for  $C_{50}H_{62}O_2S_4$ : 822.3633; found: 822.3585 ( $M^+$ ).

**Compound 3f.** To a solution of 1,2-dibromo-4,5-di(decyloxy)benzene (0.25 g, 0.45 mmol), compound **2g** (0.6 g, 1.8 mmol),  $K_2CO_3$  (0.3 g, 1.8 mmol) in THF/ $H_2O$  (40 mL/4 mL) was added  $Pd(PPh_3)_4$  (30 mg). The mixture was refluxed overnight at 85 °C under  $N_2$ . After cooled to RT, the reaction mixture was extracted with  $CH_2Cl_2$  (30 mL  $\times$  3), washed with brine, and dried over anhydrous  $Na_2SO_4$ . The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography affording the title product as translucent sticky liquid (0.33 g, 91%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$ : 7.60 (dd,  $J = 8.8$  Hz,  $J = 4.8$  Hz, 2H), 7.39 (dd,  $J = 8.8$  Hz,  $J = 2.5$  Hz, 2H), 7.20 (s, 2H), 7.09 (s, 2H), 6.99 (td,  $J = 8.8$  Hz,  $J = 2.5$  Hz, 2H), 4.09 (t,  $J = 6.5$  Hz, 4H), 1.92-1.84 (m, 4H), 1.54-1.46 (m, 4H), 1.41-1.25 (m, 24H), 0.88 (t,  $J = 6.5$  Hz, 6H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$ : 160.88 (d,  $J = 241$  Hz), 149.09, 140.94, 137.69 (d,  $J = 1.0$  Hz), 134.64, 133.85 (d,  $J = 9.0$  Hz), 133.40 (d,  $J = 4.0$  Hz), 126.0, 125.97, 124.94 (d,  $J = 9.0$  Hz), 114.84, 112.72 (d,  $J = 25$  Hz), 106.84 (d,  $J = 24$  Hz), 69.41, 32.00, 29.74, 29.69, 29.53, 29.45, 29.34, 26.16, 22.77, 14.19. HRMS (MALDI-TOF): calcd for  $C_{46}H_{52}F_2O_2S_4$ : 802.2818; found: 802.2802 ( $M^+$ ).

**Compound NBTBT-6.** To a solution of **3a** (0.3 g, 0.46 mmol) in dry DCM (100 mL) at room temperature was added a solution of  $FeCl_3$  (0.16 g, 0.96 mmol) in nitromethane (10 mL) dropwise. After stirred at room temperature for 1 hour, methanol (100 mL) was added and the solid was collected by filtration, washed with methanol (30 mL), recrystallized from  $CHCl_3$ , and dried in vacuum at 60 °C affording the title product as a light yellow solid (0.22 g, 73%). Mp: 250.0 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$ : 7.97-7.92 (m, 4H), 7.82 (s, 2H), 7.52-7.48 (m, 2H), 7.44-7.40 (m, 2H), 4.36 (t,  $J = 6.5$  Hz, 4H), 2.08-2.01 (m, 4H), 1.70-1.63 (m, 4H), 1.51-1.41 (m, 8H), 0.98 (t,  $J = 6.5$  Hz, 6H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$ : 149.12, 142.26, 133.40, 133.15, 132.54, 131.67, 127.50, 125.18, 124.77, 123.68, 121.99, 121.12, 106.69, 69.18, 31.76, 29.18, 25.92, 22.71, 14.11. HRMS (MALDI-TOF): calcd for  $C_{38}H_{36}O_2S_4$ : 652.1598; found: 652.1607 ( $M^+$ ). calcd for  $C_{38}H_{36}O_2S_4$ : C 69.90, H 5.56;

found: C 69.94, H 5.55.

**Compound NBTBT-2,6.** To a solution of **3b** (0.36 g, 0.51 mmol) in dry DCM (100 mL) at room temperature was added a solution of FeCl<sub>3</sub> (0.17 g, 1.06 mmol) in nitromethane (10 mL) dropwise. After stirred at room temperature for 1 hour, methanol (100 mL) was added and the solid was collected by filtration, washed with methanol (30 mL), recrystallized from CHCl<sub>3</sub>, and dried in vacuum at 60 °C affording the title product as a light yellow solid (0.25 g, 70%). Mp: 144.6 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.80 (d, *J* = 7.8 Hz, 2H), 7.76 (d, *J* = 7.8 Hz, 2H), 7.53 (s, 2H), 7.42-7.38 (m, 2H), 7.34-7.30 (m, 2H), 4.19-4.13 (m, 4H), 2.00-1.94 (m, 2H), 1.77-1.56 (m, 8H), 1.53-1.39 (m, 8H), 1.09 (t, *J* = 7.4 Hz, 6H), 1.00 (t, *J* = 7.0 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 149.20, 142.19, 133.20, 132.68, 132.33, 131.30, 127.10, 124.87, 124.39, 123.45, 121.58, 120.82, 106.16, 71.32, 39.49, 30.79, 29.34, 24.11, 23.24, 14.24, 11.41. HRMS (MALDI-TOF): calcd for C<sub>42</sub>H<sub>44</sub>O<sub>2</sub>S<sub>4</sub>: 708.2224; found: 708.2263 (M<sup>+</sup>). calc. for C<sub>42</sub>H<sub>44</sub>O<sub>2</sub>S<sub>4</sub>: C 71.14, H 6.25; found: C 70.96, H 6.21.

**Compound NBTBT-8.** To a solution of **3c** (0.34 g, 0.48 mmol) in dry DCM (100 mL) at room temperature was added a solution of FeCl<sub>3</sub> (0.16 g, 0.96 mmol) in nitromethane (10 mL) dropwise. After stirred at room temperature for 1 hour, methanol (100 mL) was added and the solid was collected by filtration, washed with methanol (30 mL), recrystallized from CHCl<sub>3</sub>, and dried in vacuum at 60 °C affording the title product as a light yellow solid (0.26 g, 78%). Mp: 246.1 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.98-7.93 (m, 4H), 7.83 (s, 2H), 7.52-7.48 (m, 2H), 7.44-7.41 (m, 2H), 4.36 (t, *J* = 6.5 Hz, 4H), 2.08-2.01 (m, 4H), 1.70-1.62 (m, 4H), 1.50-1.34 (m, 16H), 0.92 (t, *J* = 6.8 Hz, 6H). <sup>13</sup>C NMR was not obtained because of the very poor solubility. HRMS (MALDI-TOF): calcd for C<sub>42</sub>H<sub>44</sub>O<sub>2</sub>S<sub>4</sub>: 708.2224; found: 708.2210 (M<sup>+</sup>). calc. for C<sub>42</sub>H<sub>44</sub>O<sub>2</sub>S<sub>4</sub>: C 71.14, H 6.25; found: C 70.79, H 6.27.

**Compound NBTBT-10.** To a solution of **3d** (0.4 g, 0.52 mmol) in dry DCM (100 mL) at room temperature was added a solution of FeCl<sub>3</sub> (0.18 g, 1.09 mmol) in nitromethane (10 mL) dropwise. After stirred at room temperature for 1 hour, methanol (100 mL) was added and the solid was collected by filtration, washed with

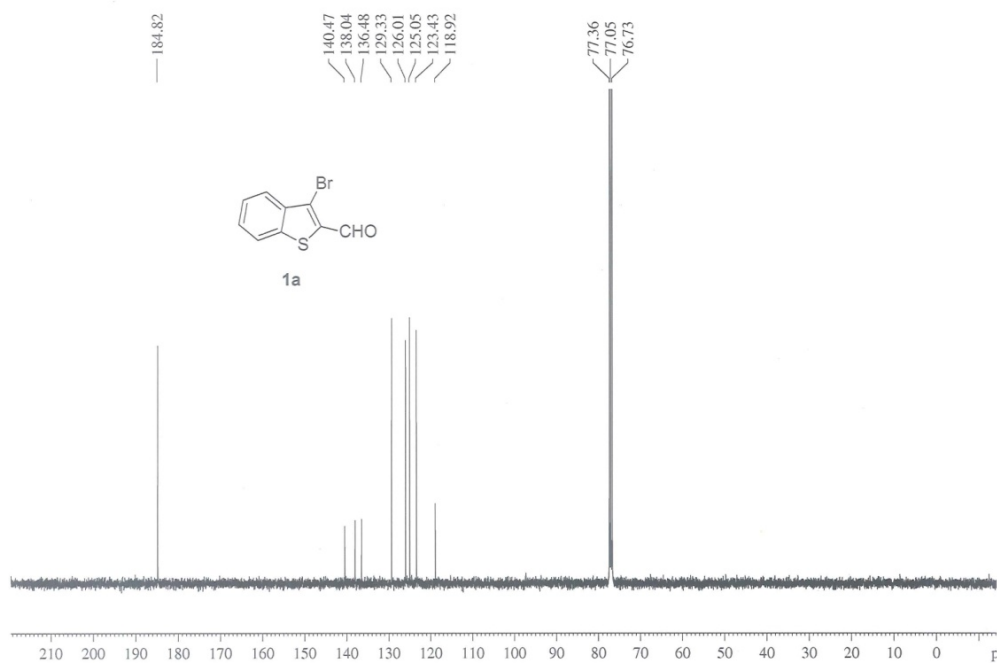
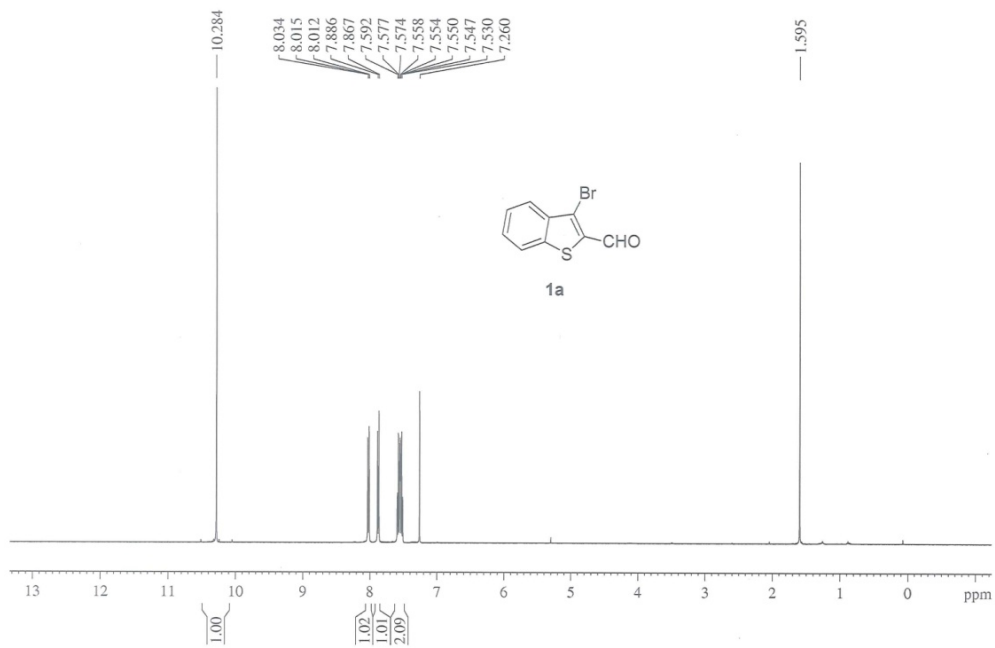
methanol (30 mL), recrystallized from CHCl<sub>3</sub>, and dried in vacuum at 60 °C affording the title product as a light yellow solid (0.30 g, 75%). Mp: 226.3 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.99-7.95 (m, 4H), 7.87 (s, 2H), 7.53-7.50 (m, 2H), 7.46-7.42 (m, 2H), 4.40-4.36 (m, 4H), 2.10-1.99 (m, 4H), 1.70-1.61 (m, 4H), 1.51-1.22 (m, 24H), 0.92-0.86 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 148.95, 142.18, 133.27, 132.99, 132.43, 131.54, 127.33, 125.06, 124.62, 123.57, 121.81, 121.01, 106.52, 69.08, 31.96, 29.76, 29.67, 29.61, 29.43, 29.22, 26.25, 22.72, 14.14. HRMS (MALDI-TOF): calcd for C<sub>46</sub>H<sub>52</sub>O<sub>2</sub>S<sub>4</sub>: 764.2850; found: 764.2827 (M<sup>+</sup>). calcd for C<sub>46</sub>H<sub>52</sub>O<sub>2</sub>S<sub>4</sub>: C 72.21, H 6.85; found: C 71.89, H 6.55.

**Compound NBTBT-12.** To a solution of **3e** (0.38 g, 0.46 mmol) in dry DCM (100 mL) at room temperature was added a solution of FeCl<sub>3</sub> (0.16 g, 0.97 mmol) in nitromethane (10 mL) dropwise. After stirred at room temperature for 1 hour, methanol (30 mL) was added and the solid was collected by filtration, washed with methanol (30 mL), recrystallized from CHCl<sub>3</sub>, and dried in vacuum at 60 °C affording the title product as a light yellow solid (0.28 g, 74%). Mp: 215.8 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.01-7.97 (m, 4H), 7.91 (s, 2H), 7.55-7.51 (m, 2H), 7.47-7.43 (m, 2H), 4.42-4.35 (m, 4H), 2.09-2.00 (m, 4H), 1.69-1.64 (m, 4H), 1.50-1.22 (m, 28H), 0.89-0.85 (m, 6H). <sup>13</sup>C NMR was not obtained because of the very poor solubility. HRMS (MALDI-TOF): calcd for C<sub>50</sub>H<sub>60</sub>O<sub>2</sub>S<sub>4</sub>: 820.3476; found: 820.3458 (M<sup>+</sup>). calcd for C<sub>50</sub>H<sub>60</sub>O<sub>2</sub>S<sub>4</sub>: C 73.12, H 7.36; found: C 72.78, H 7.44.

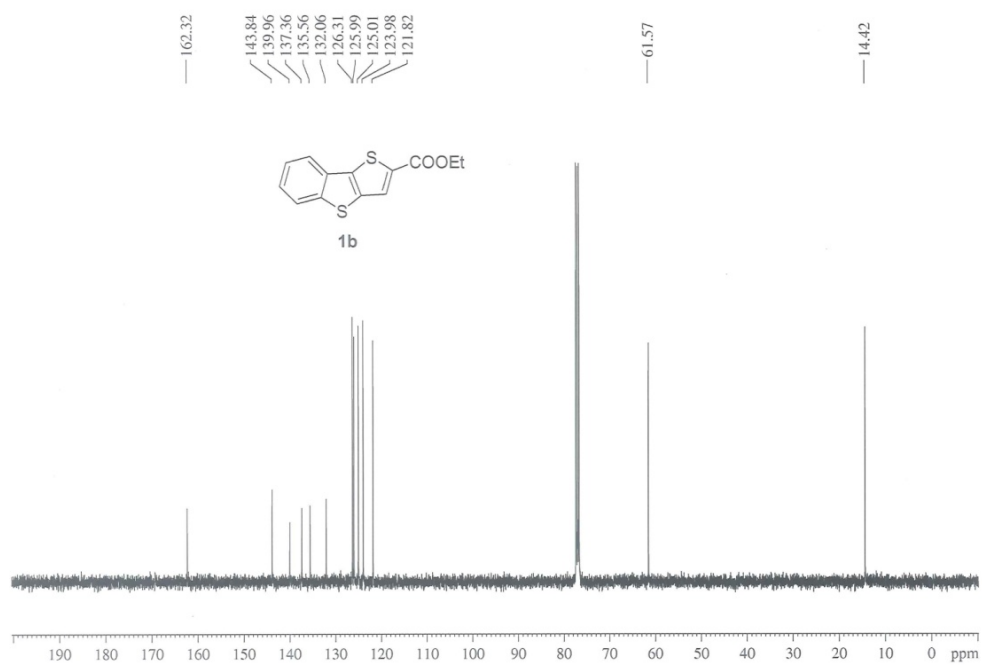
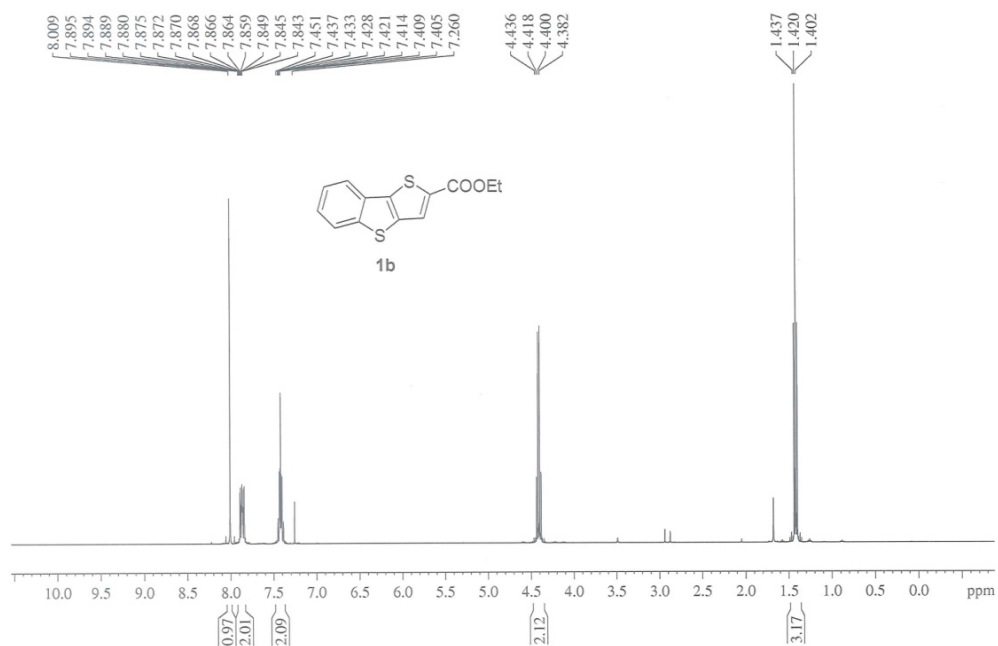
**Compound NBTBTF-10.** To a solution of **3f** (0.3 g, 0.37 mmol) in dry DCM (100 mL) at room temperature was added a solution of FeCl<sub>3</sub> (0.13 g, 0.79 mmol) in nitromethane (10 mL) dropwise. After stirred at room temperature for 1 hour, methanol (30 mL) was added and the solid was collected by filtration, washed with methanol (30 mL), recrystallized from CHCl<sub>3</sub>, and dried in vacuum at 60 °C affording the title product as a light yellow solid (0.23 g, 78%). Mp: 200.0 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.75 (dd, *J* = 8.8 Hz, *J* = 4.8 Hz, 2H), 7.51 (s, 2H), 7.43 (dd, *J* = 8.8 Hz, *J* = 2.4 Hz, 2H), 7.08 (td, *J* = 8.8 Hz, *J* = 2.4 Hz, 2H), 4.25 (t, *J* = 6.5 Hz, 4H), 2.06-1.98 (m, 4H), 1.68-1.60 (m, 4H), 1.50-1.28 (m, 24H), 0.90 (t, *J* = 6.5 Hz, 6H).

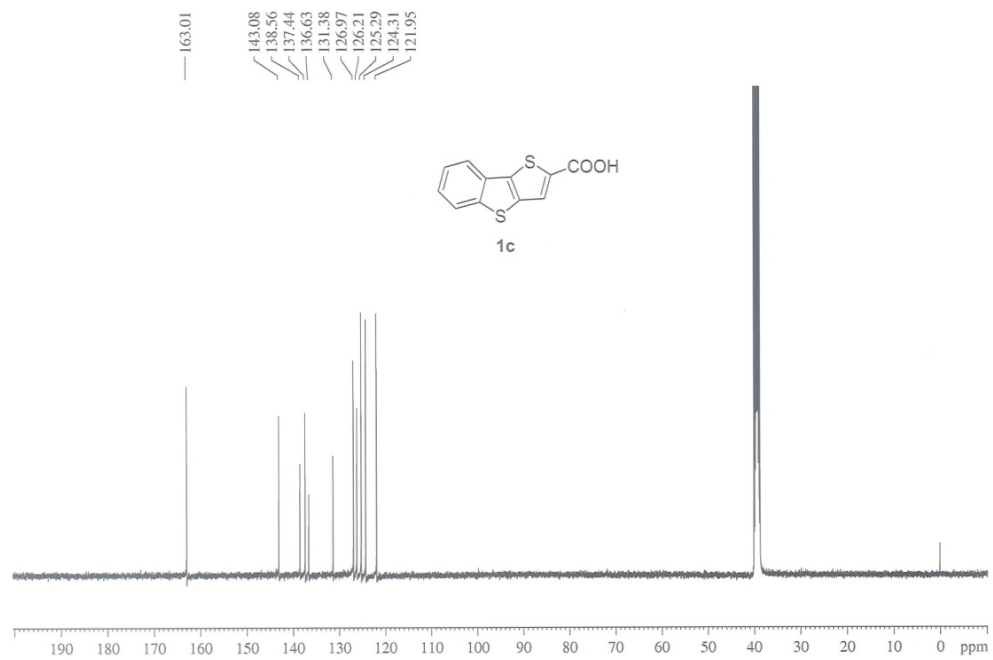
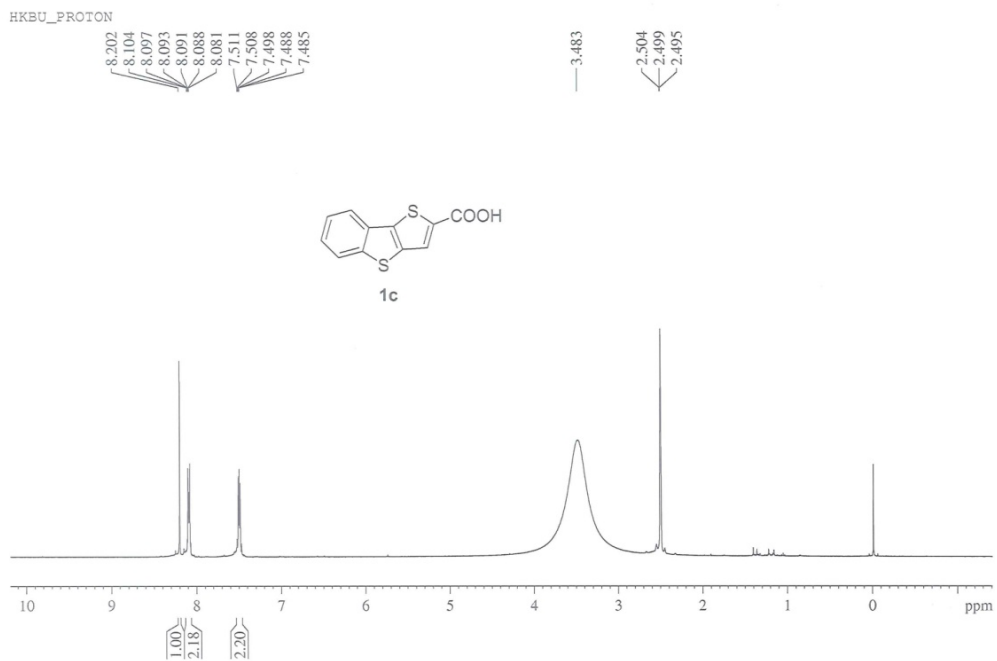
$^{13}\text{C}$  NMR was not obtained because of the very poor solubility. HRMS (MALDI-TOF): calcd for  $\text{C}_{46}\text{H}_{50}\text{F}_2\text{O}_2\text{S}_4$ : 800.2662; found: 800.2679 ( $\text{M}^+$ ). calcd for  $\text{C}_{46}\text{H}_{50}\text{F}_2\text{O}_2\text{S}_4$ : C 68.96, H 6.29; found: C 68.65, H 6.32.

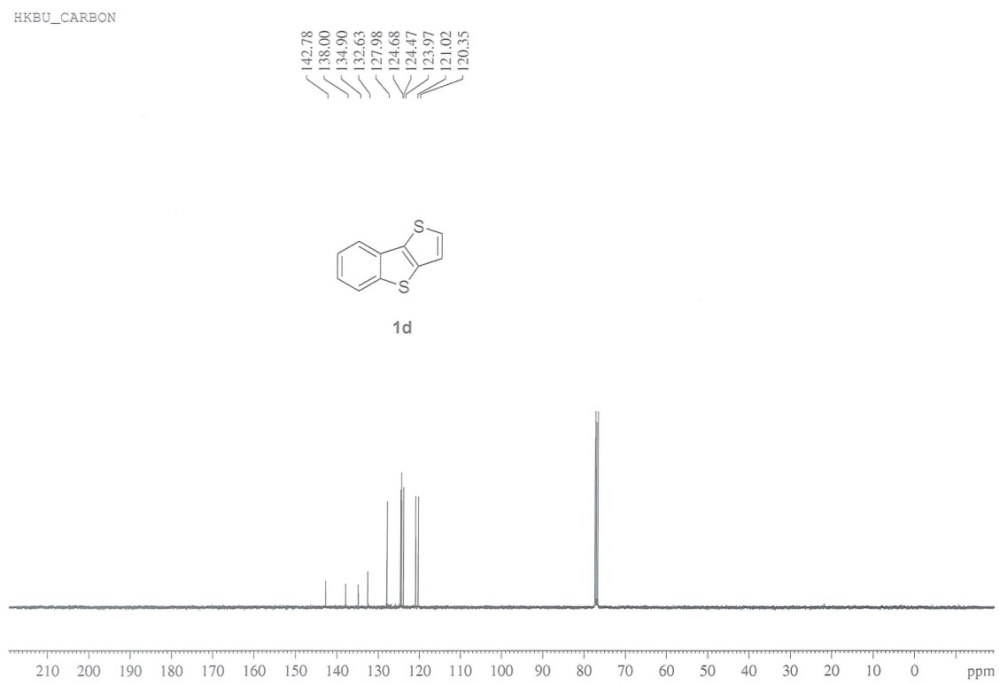
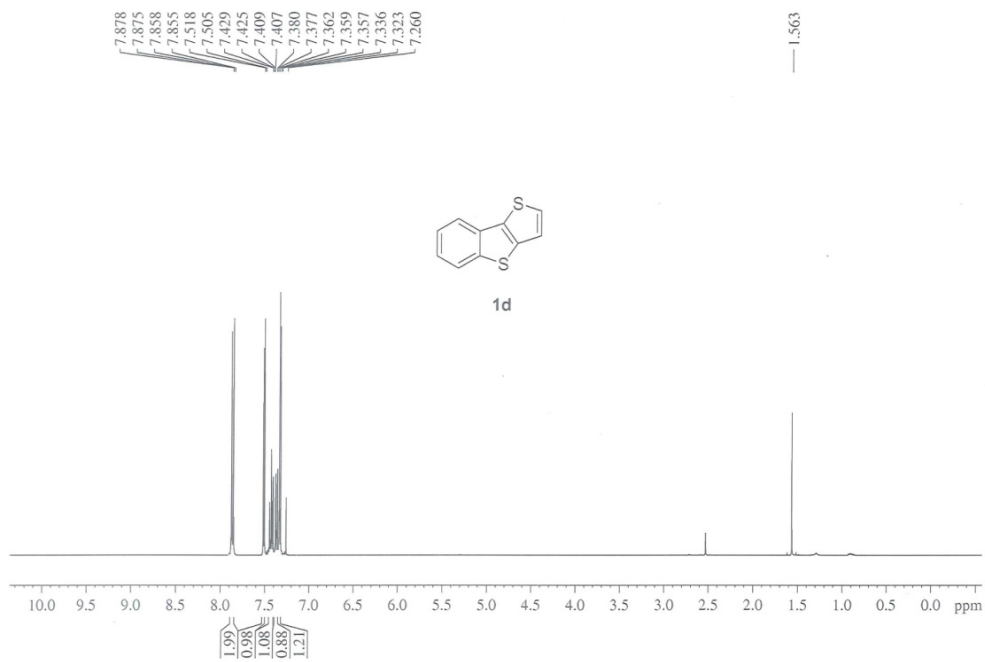
### **3. $^1\text{H}$ NMR, $^{13}\text{C}$ NMR, and HR-MS Spectra of all compounds.**

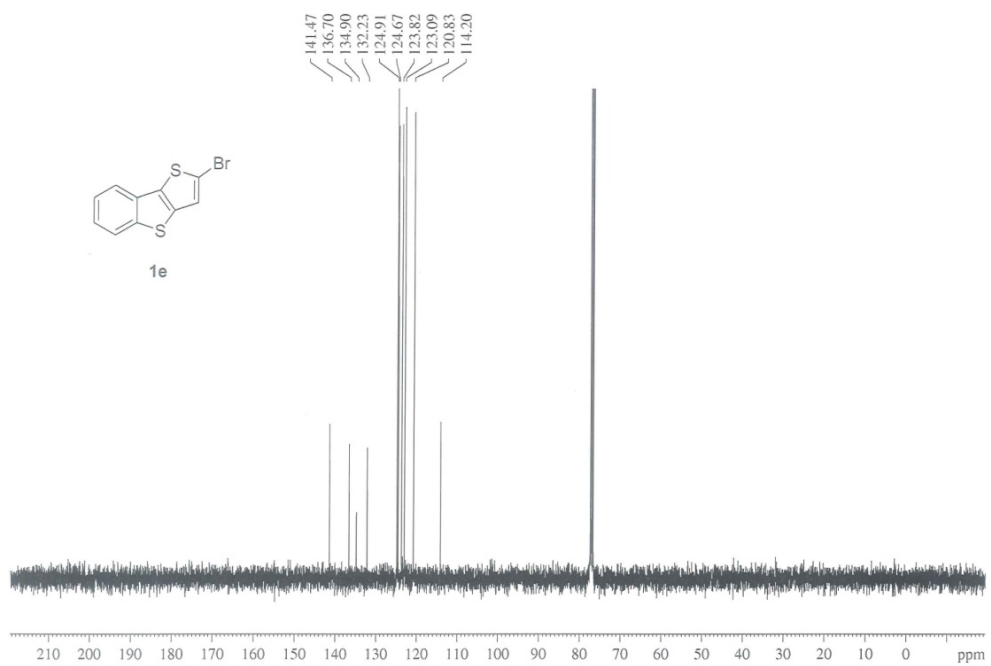
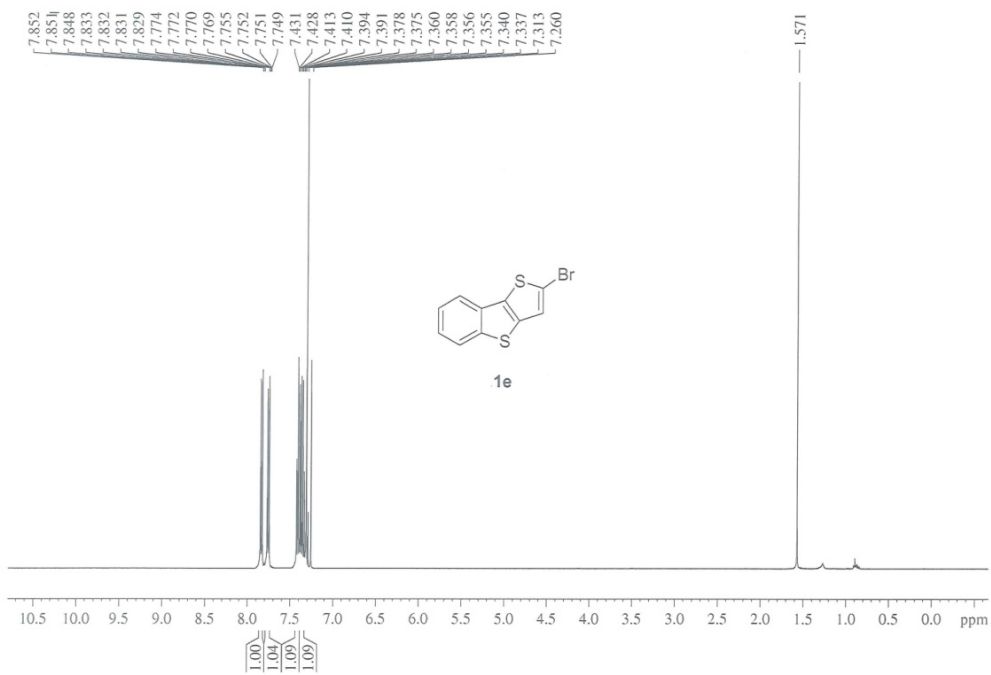


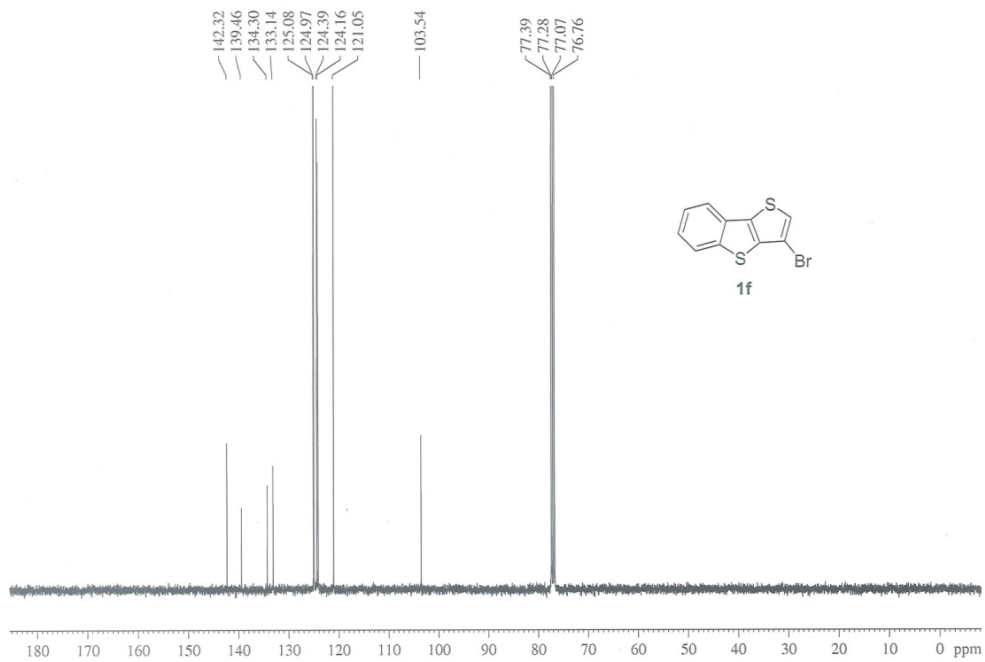
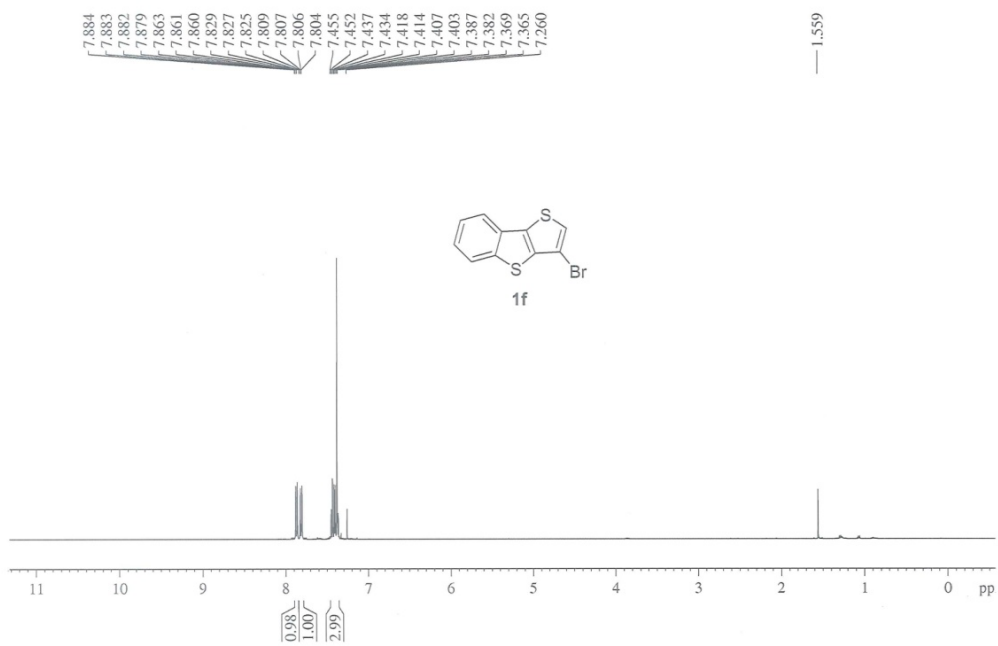


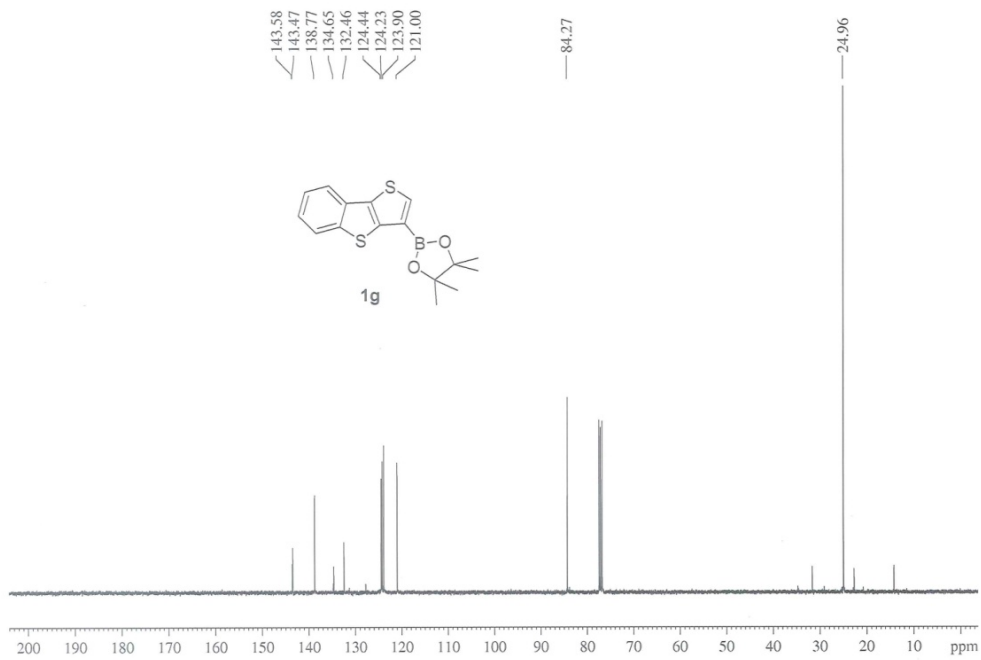
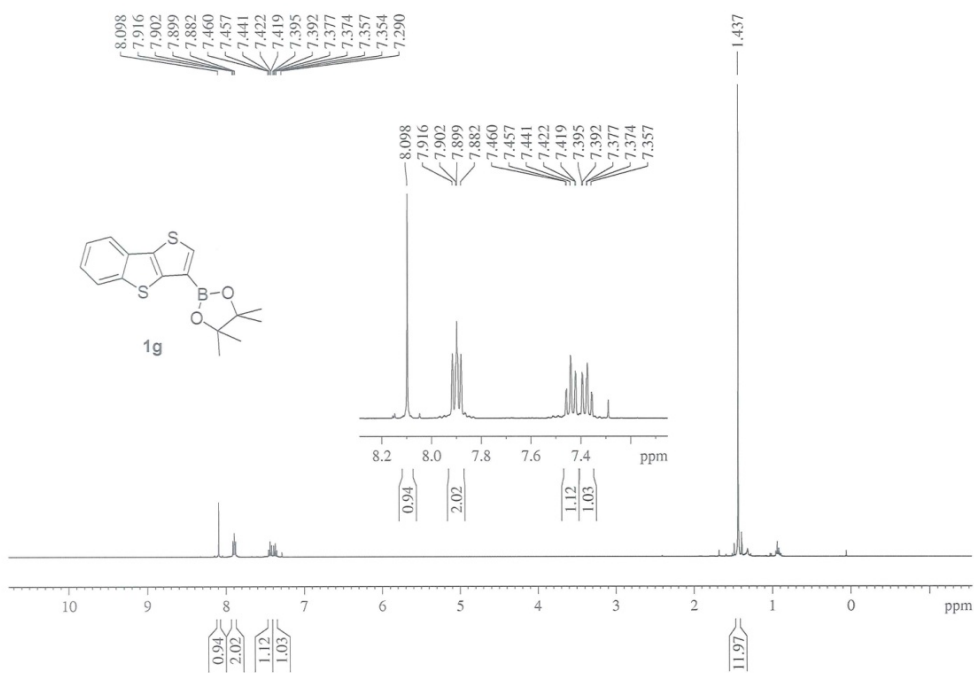


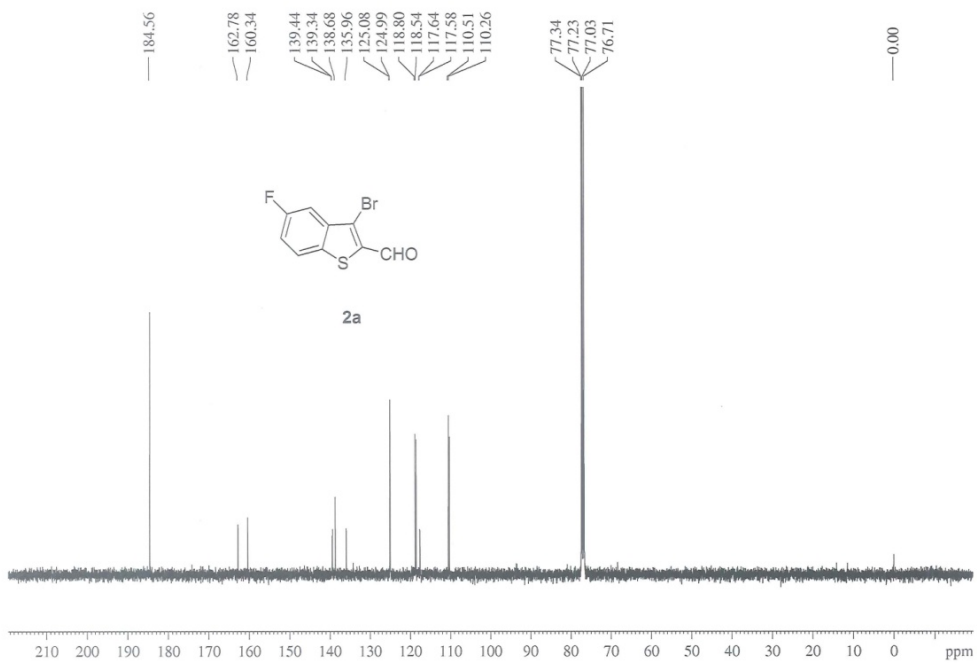
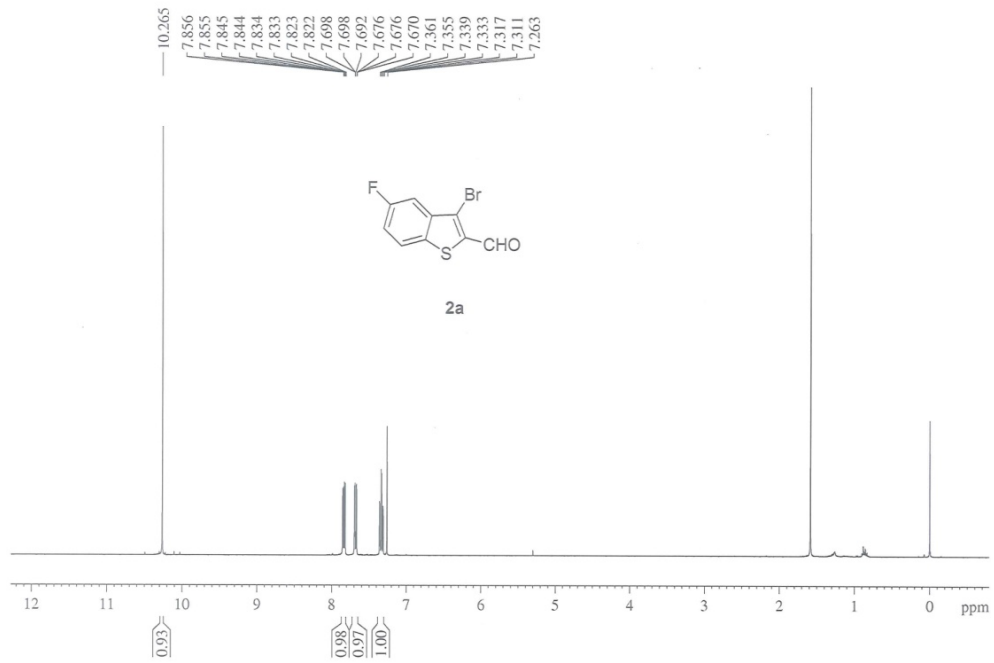


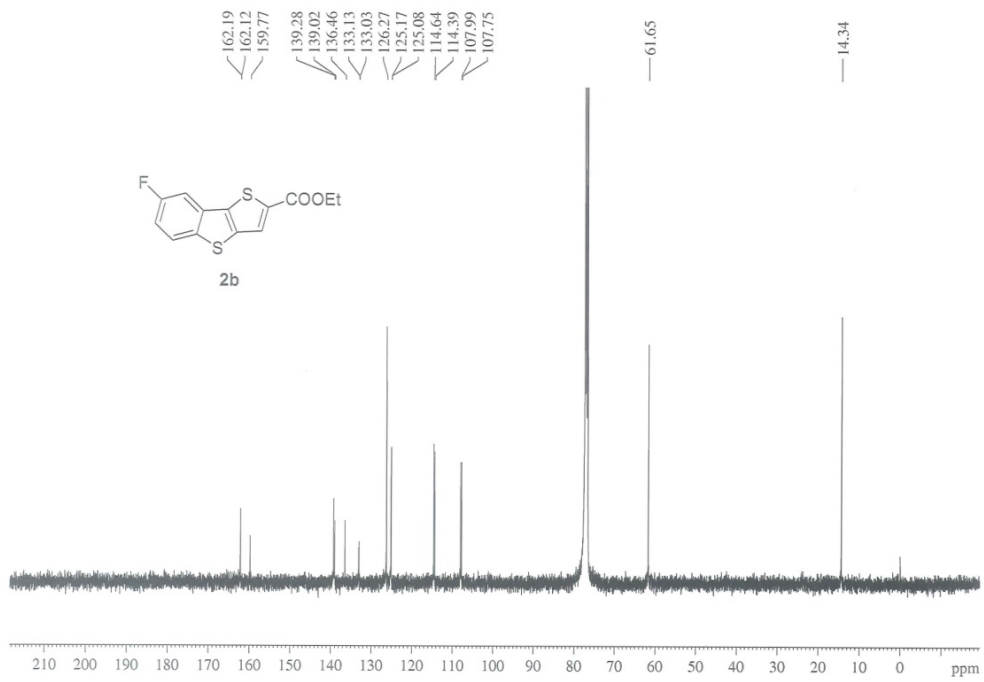
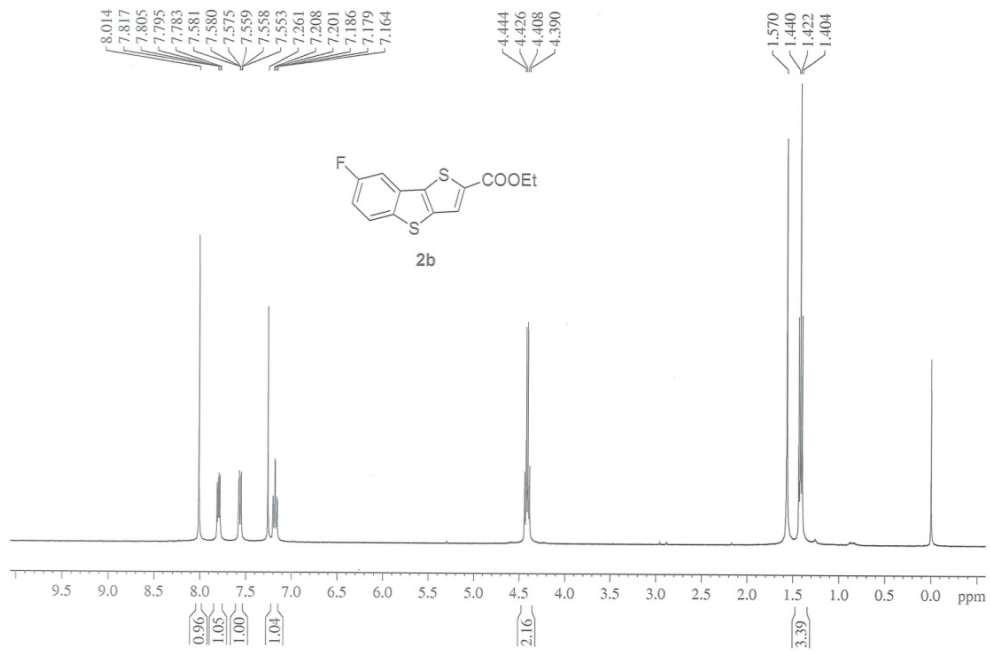




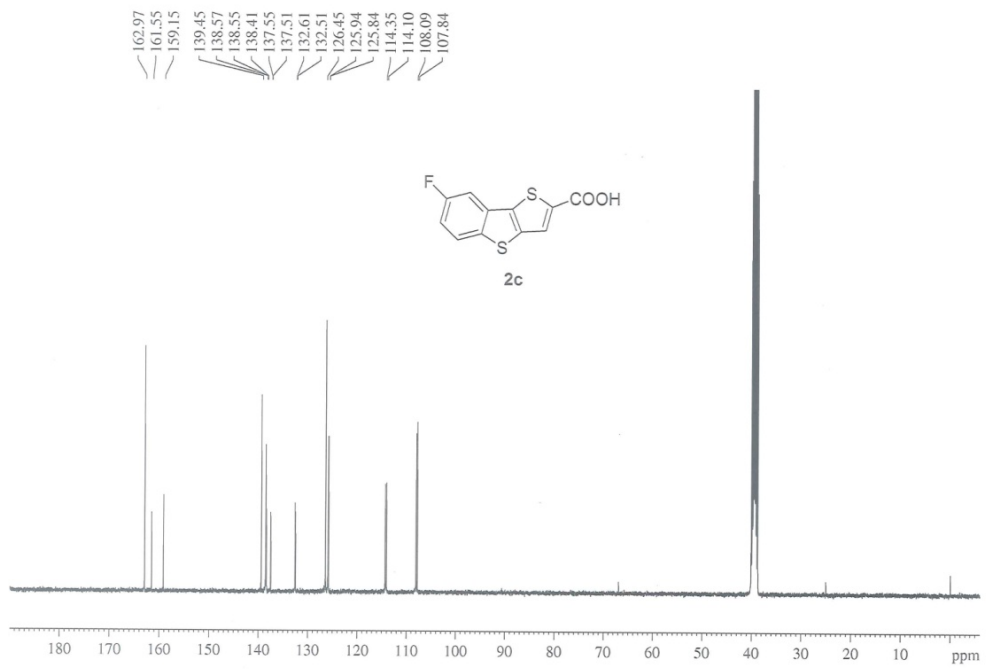
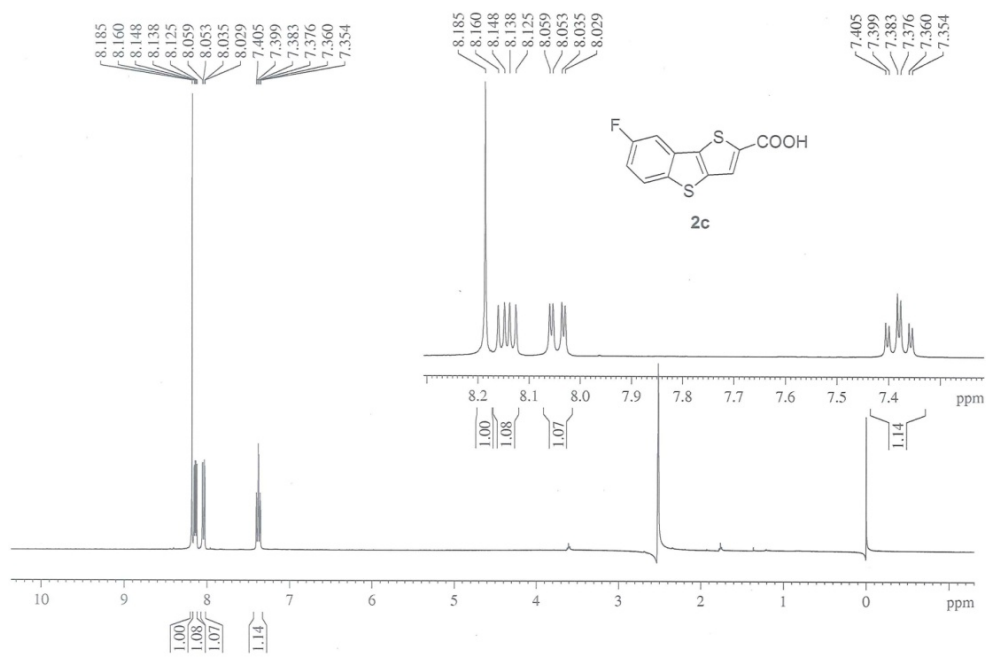


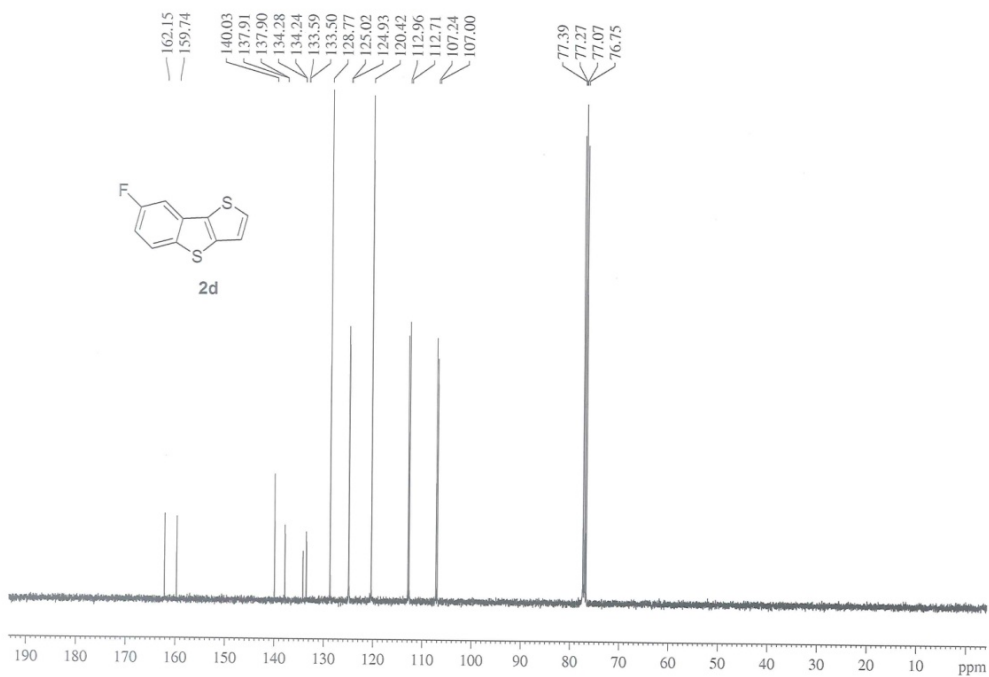
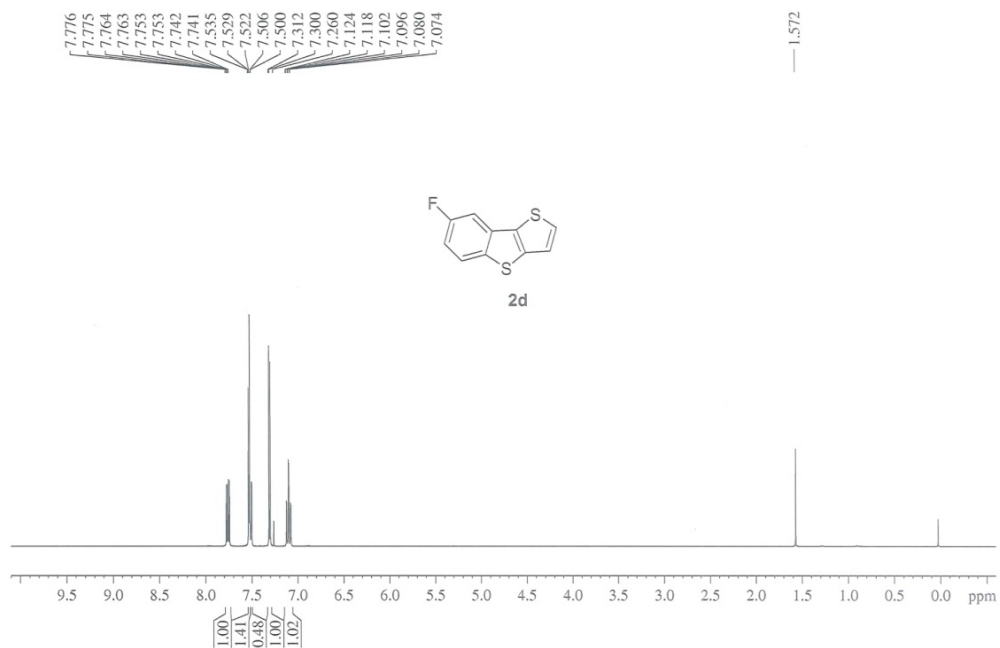


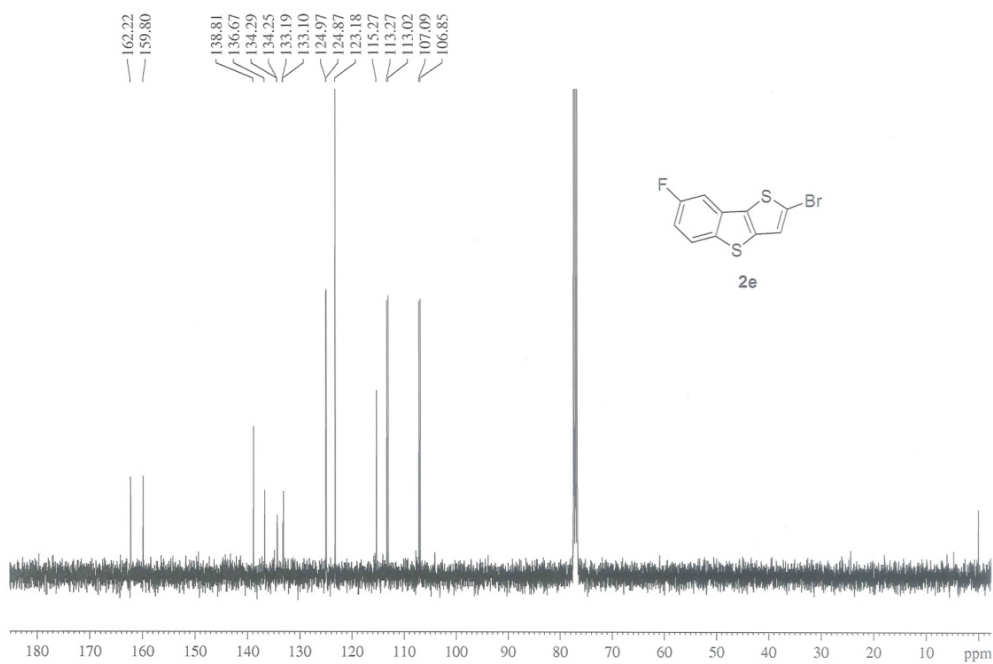
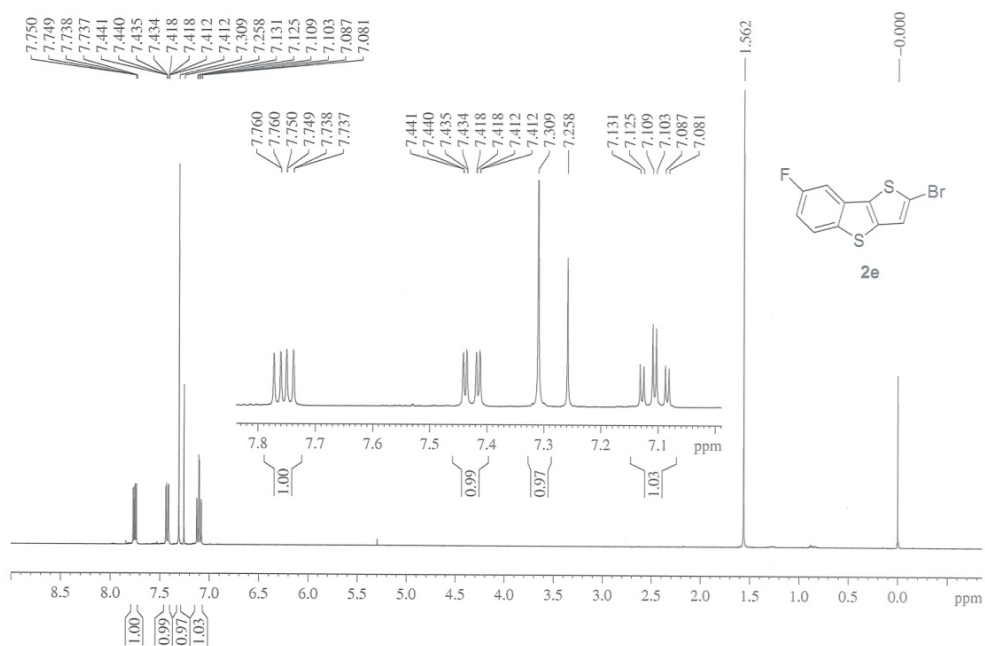


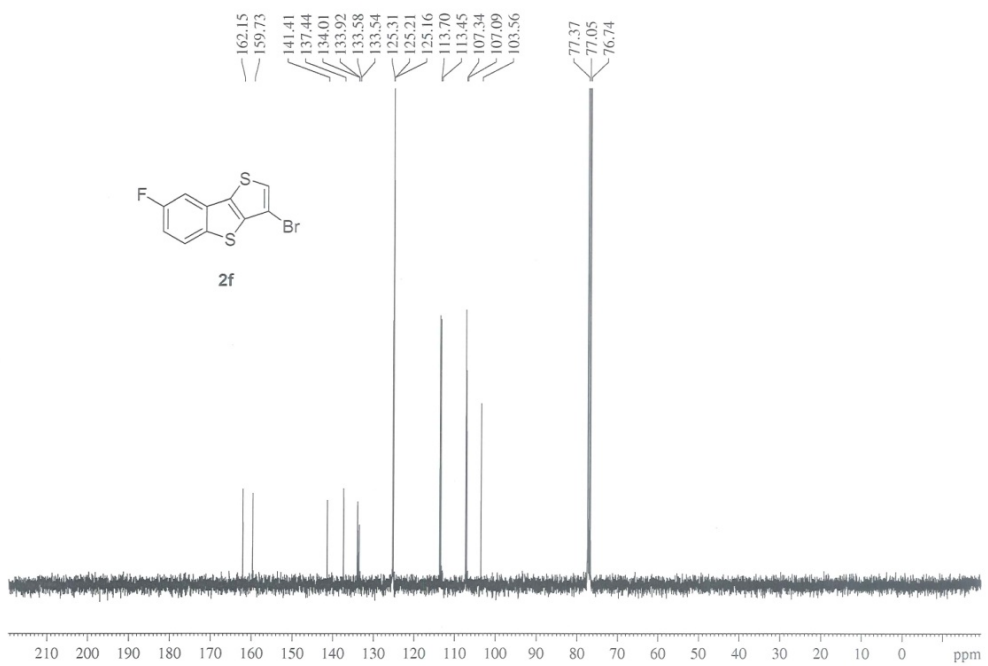
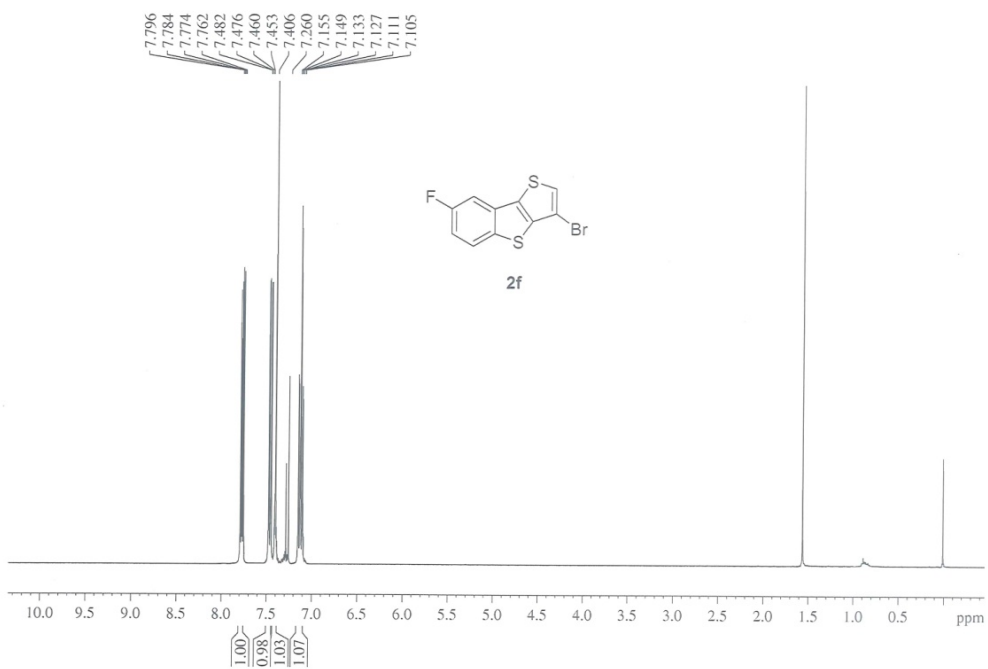


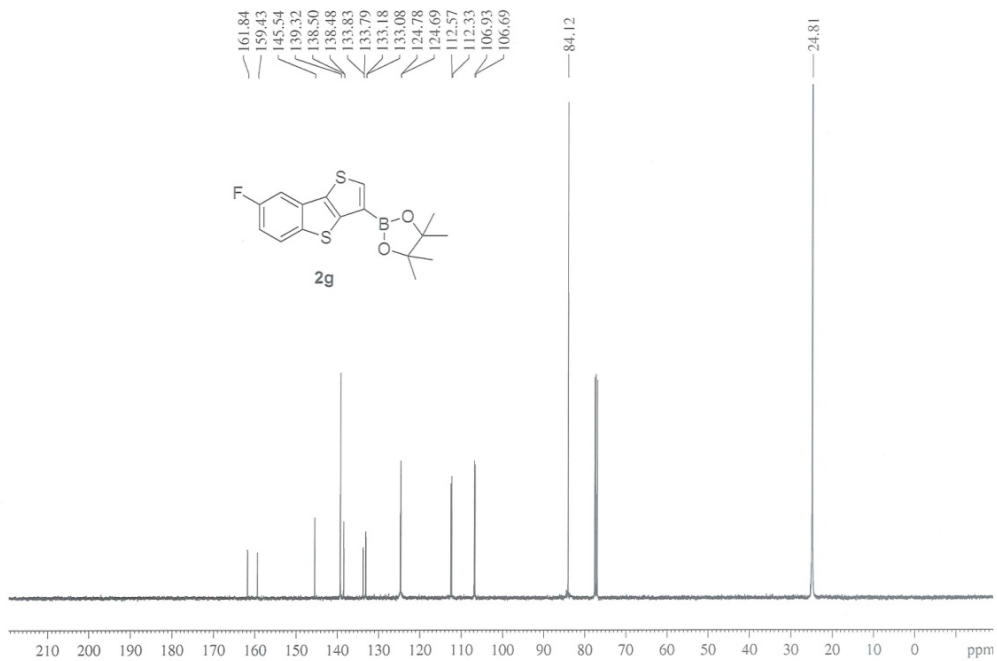
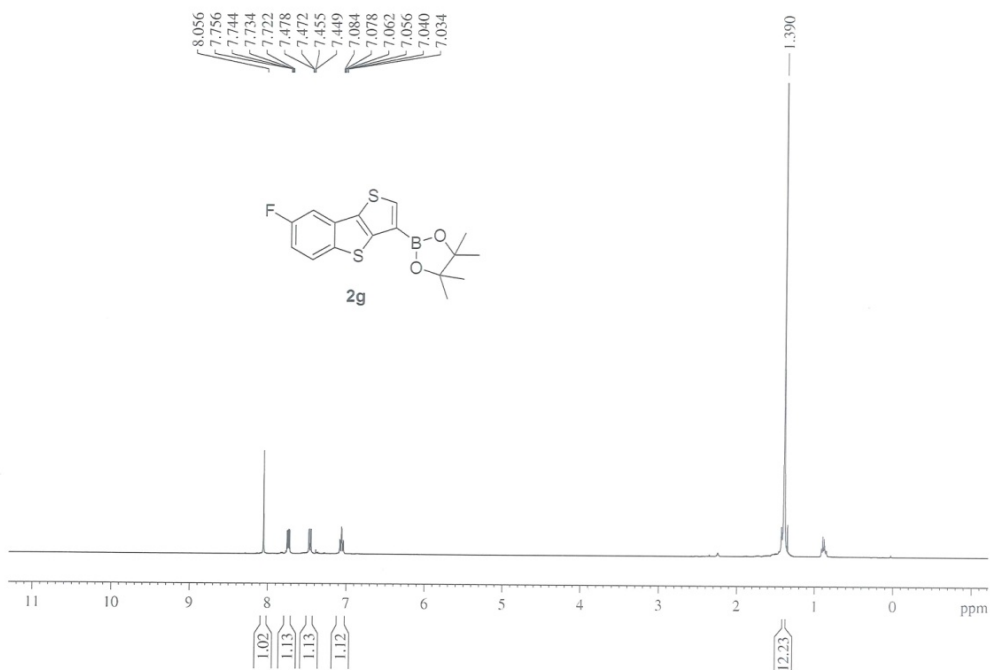


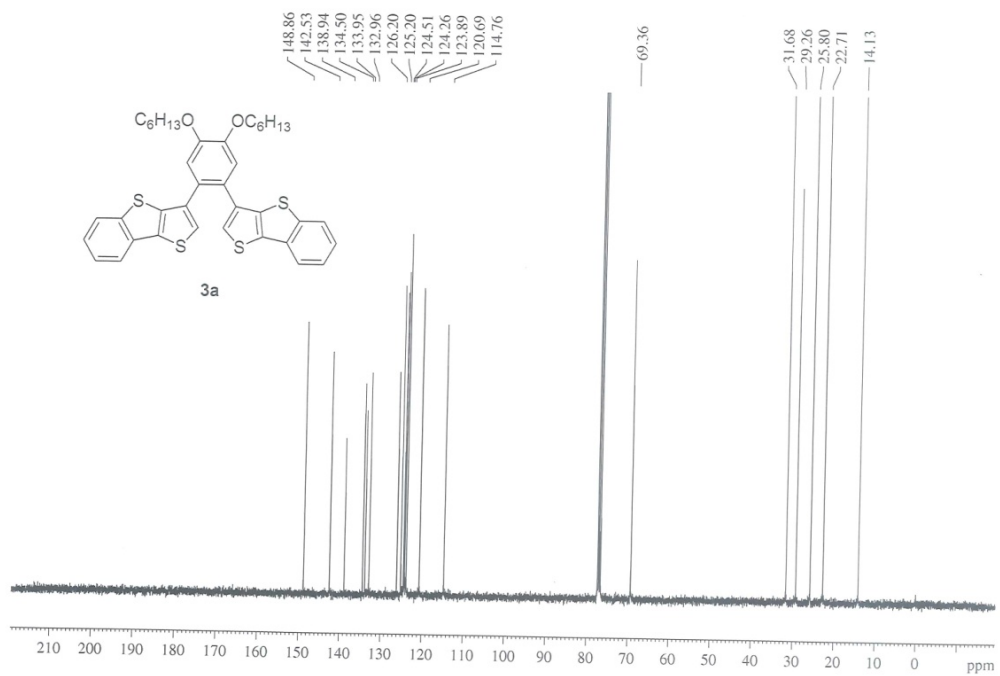
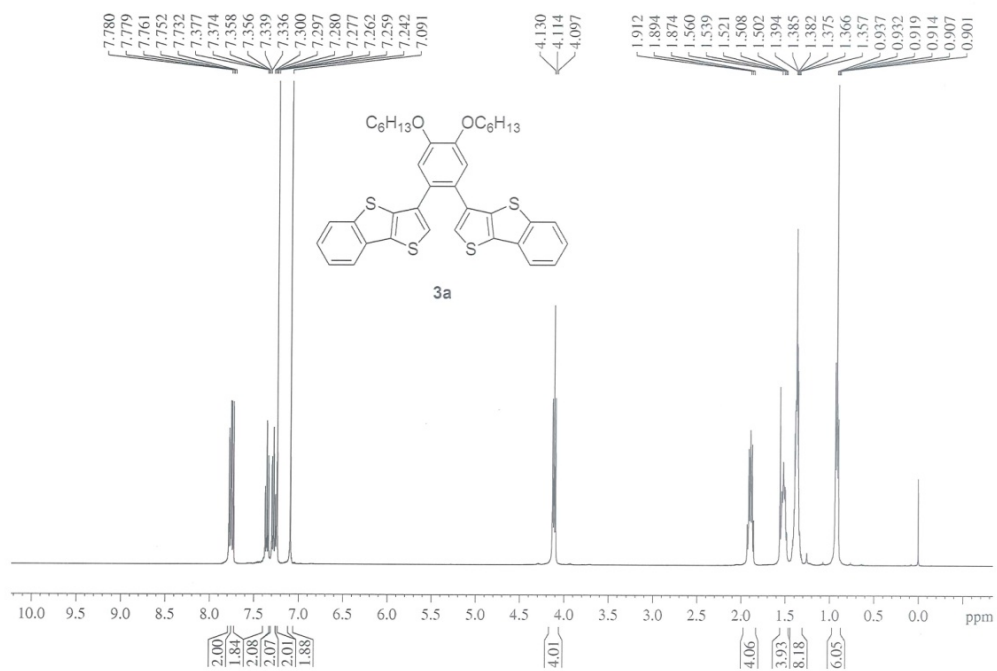


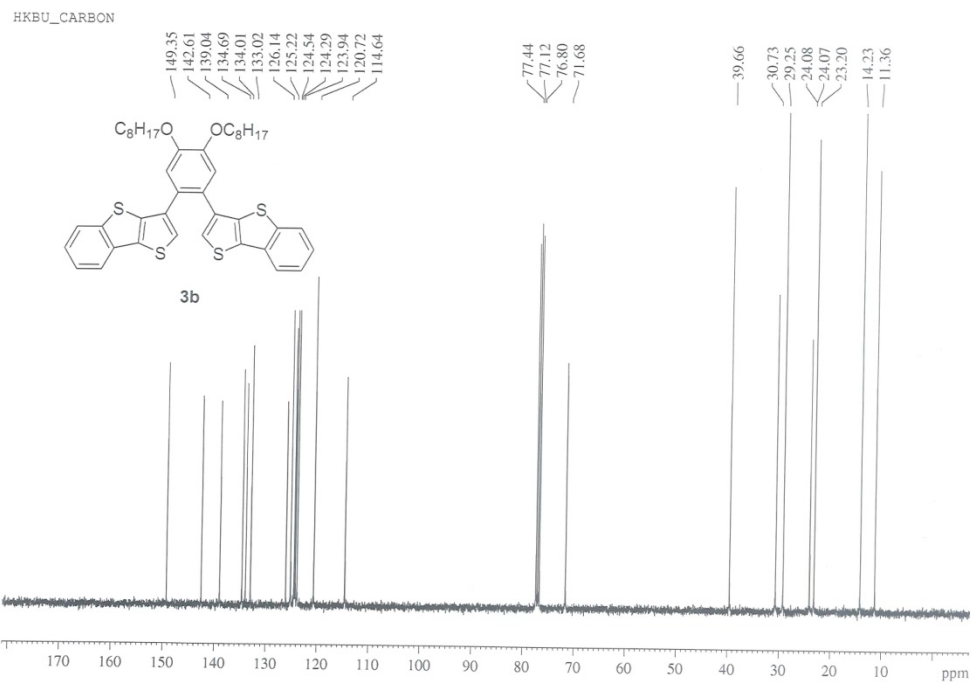
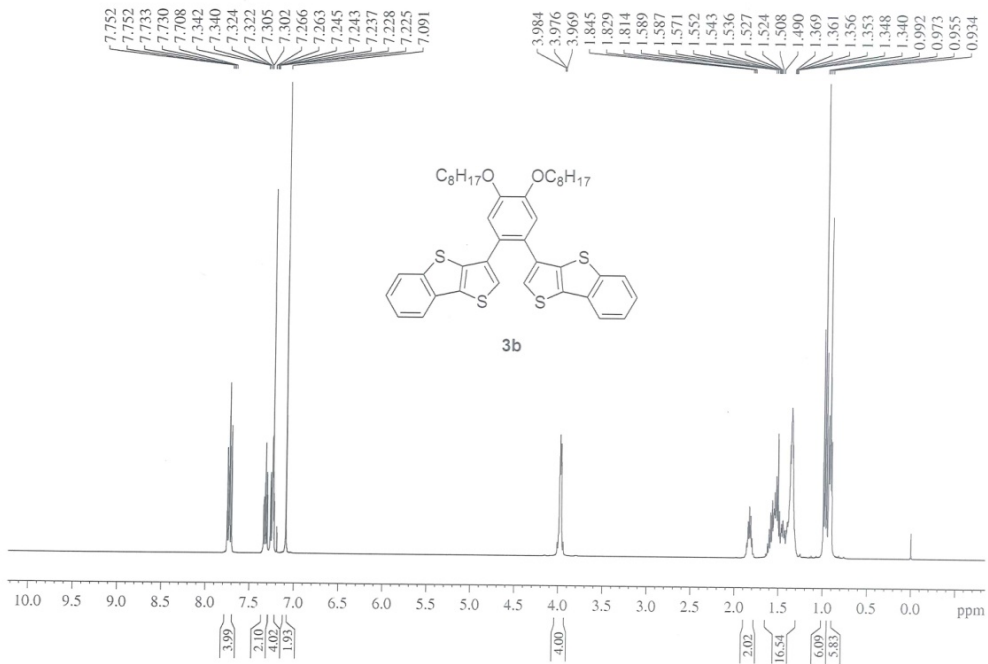


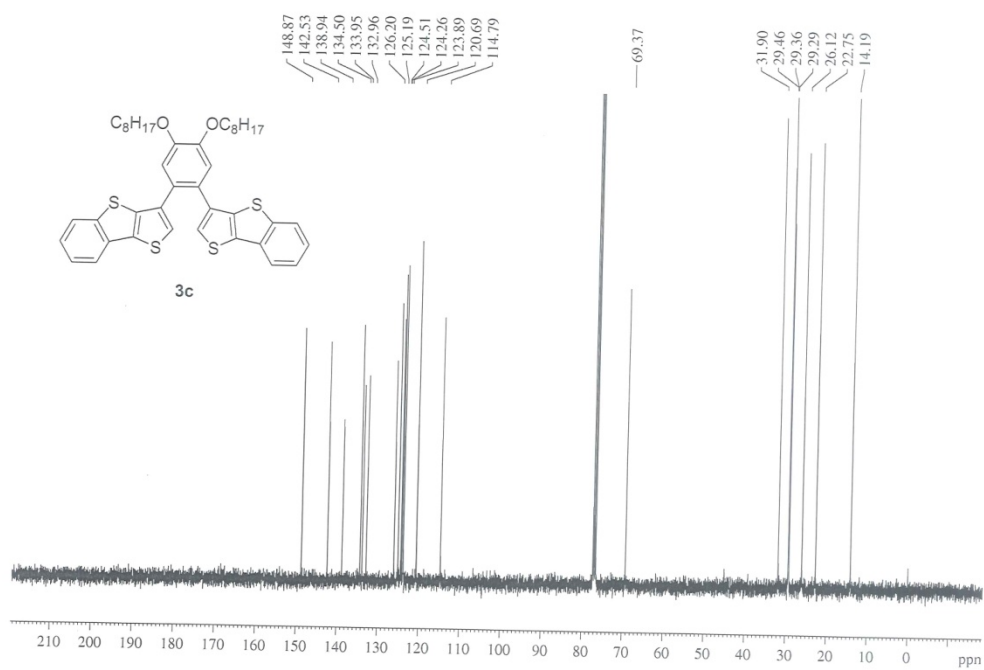
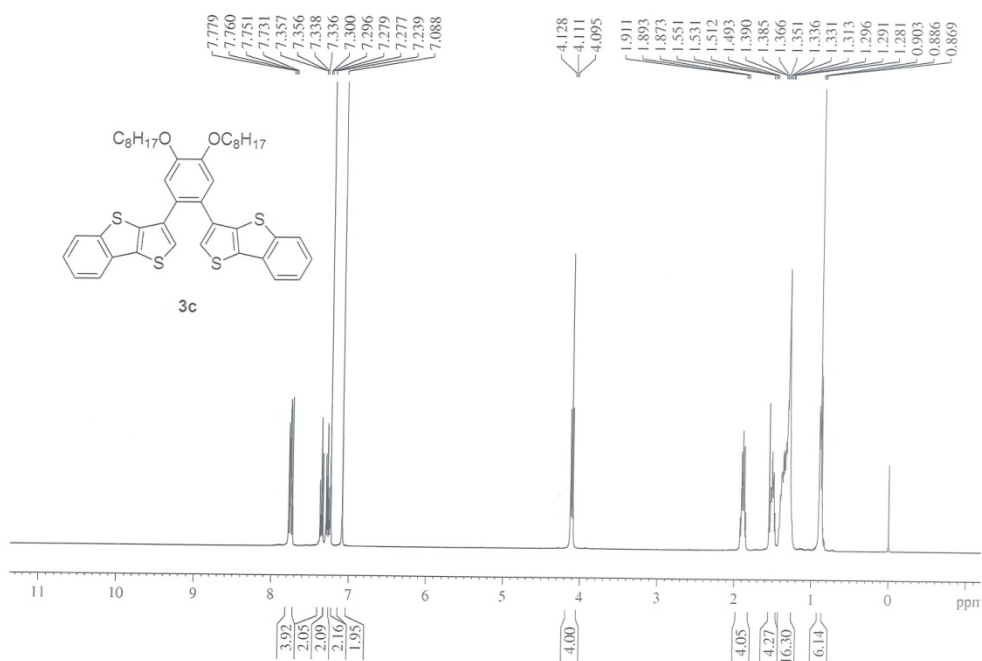




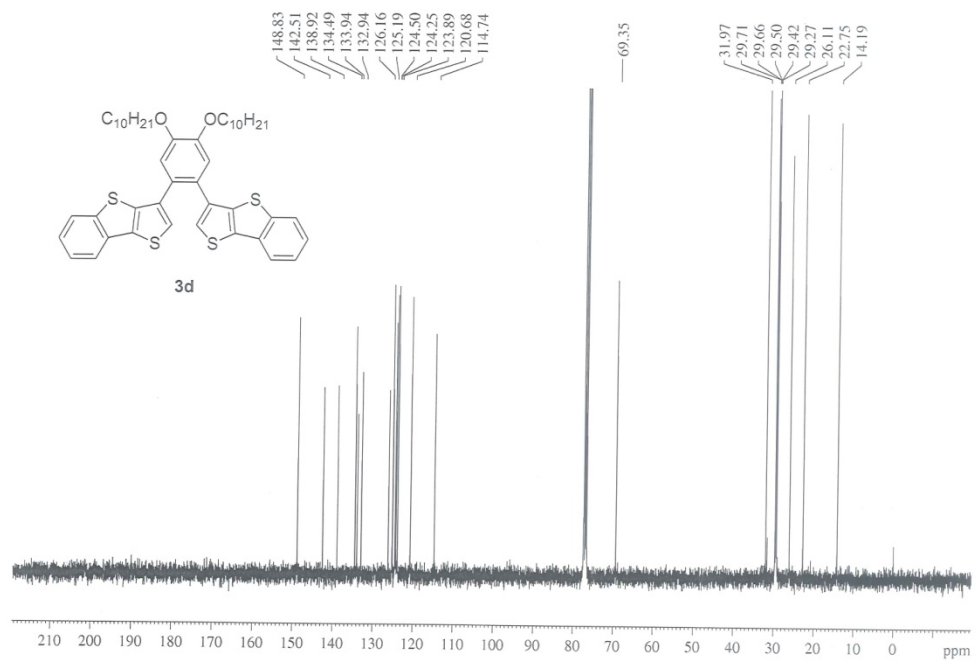
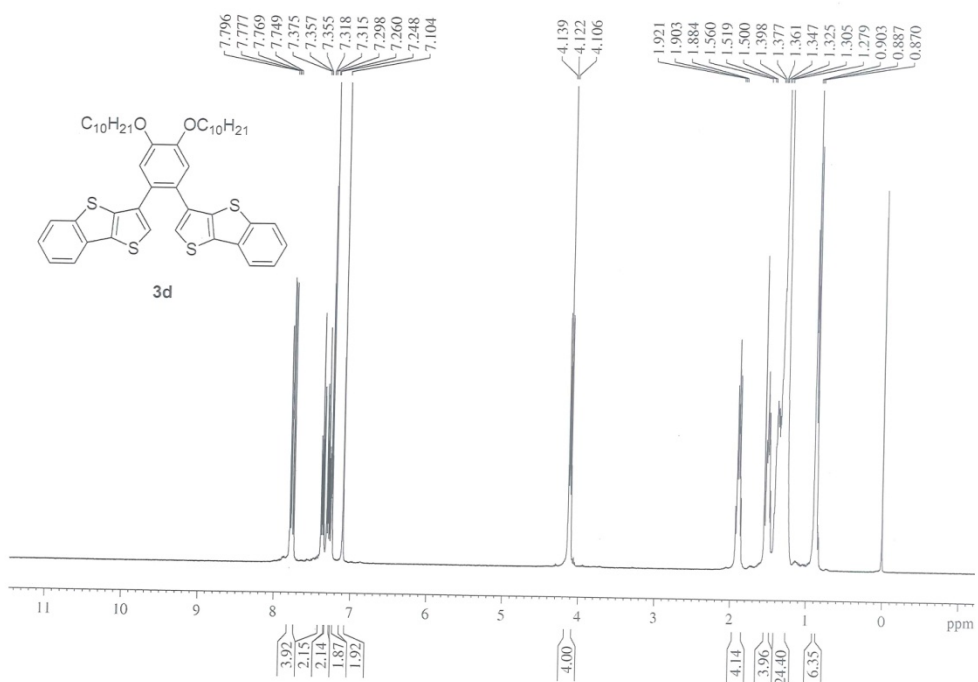


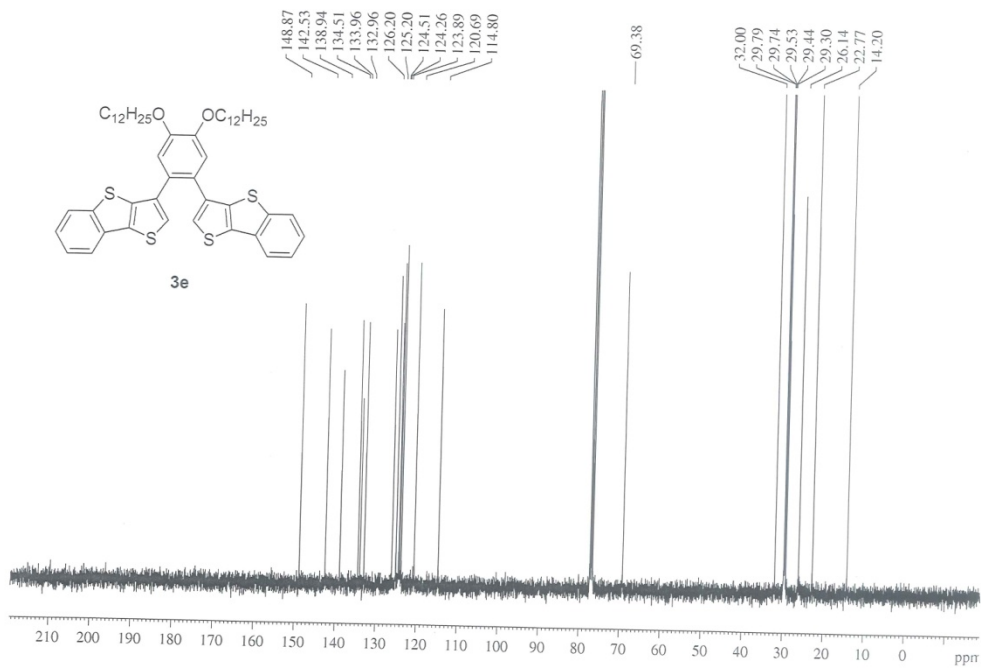
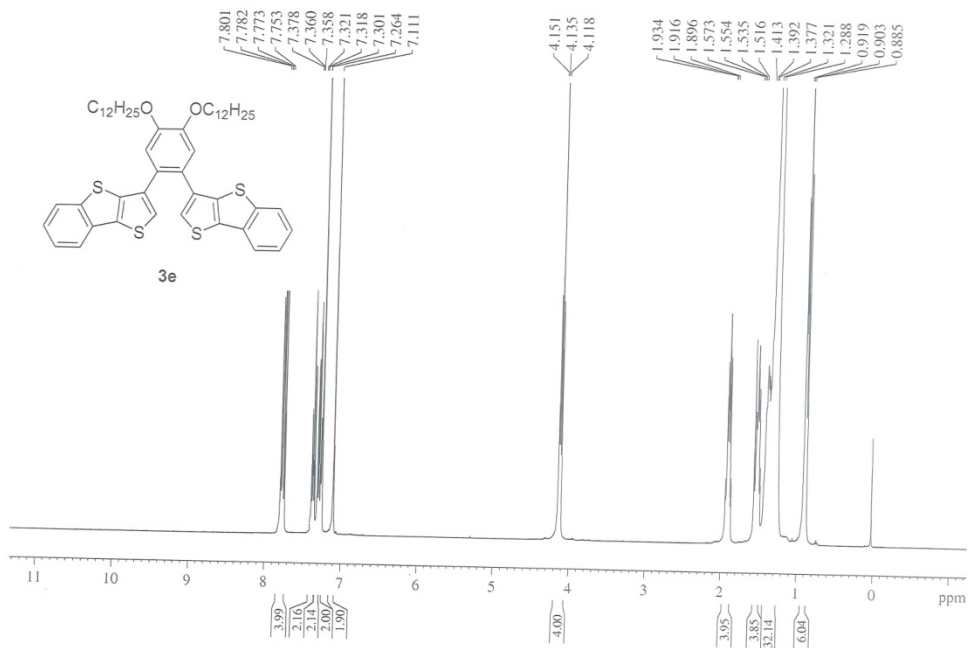


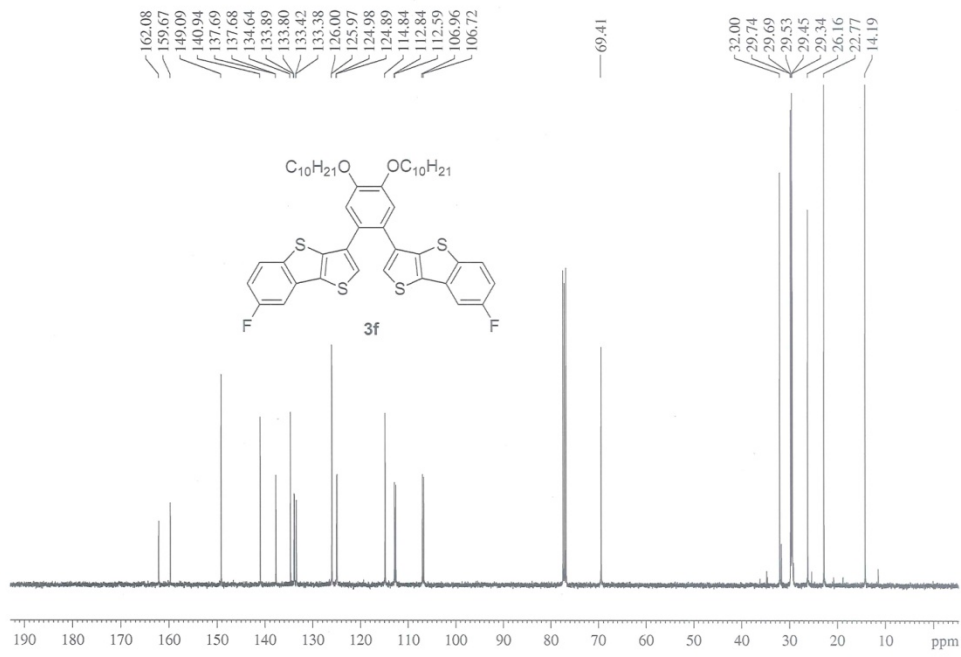
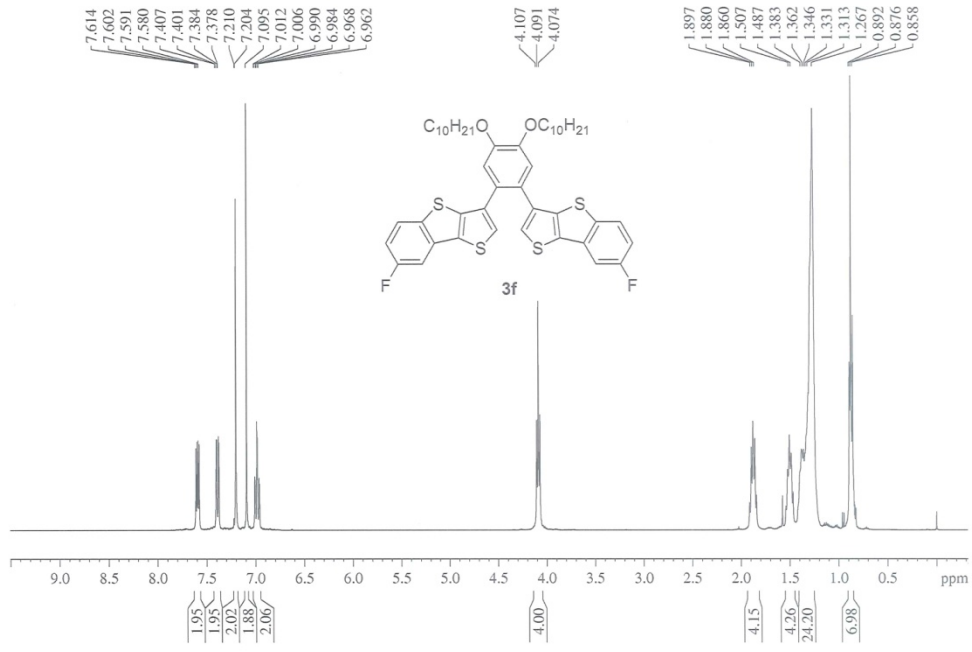




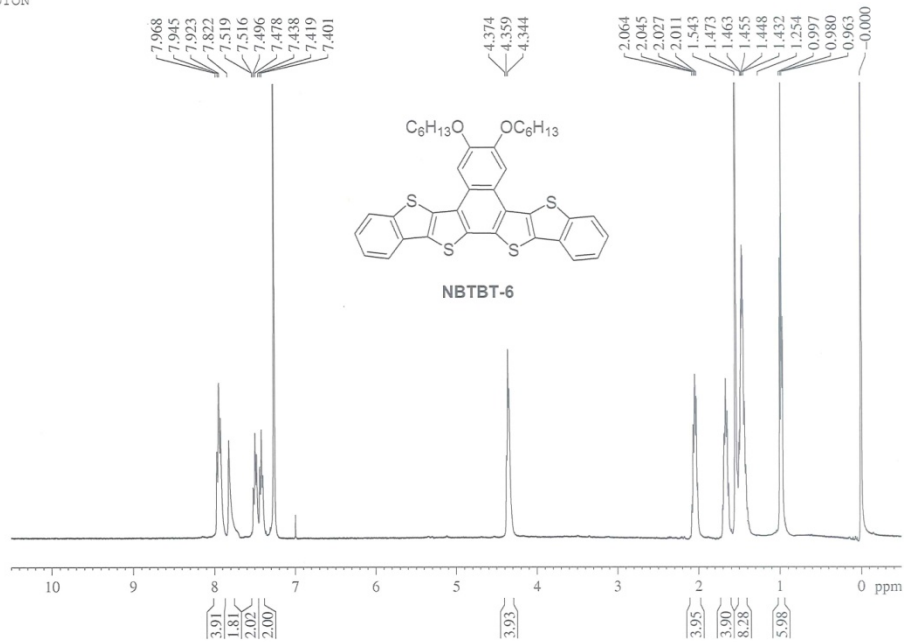




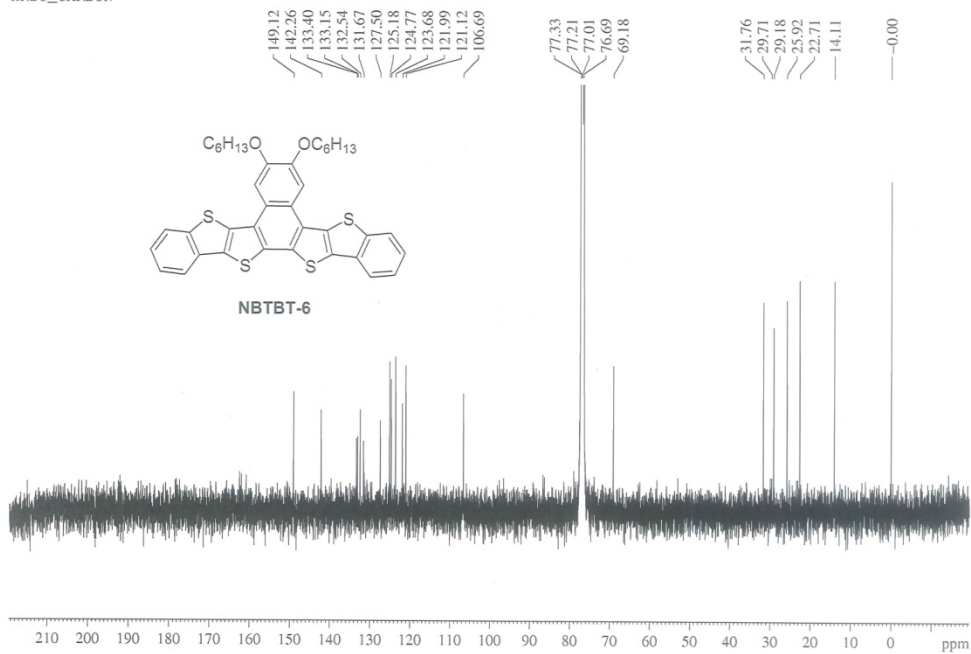




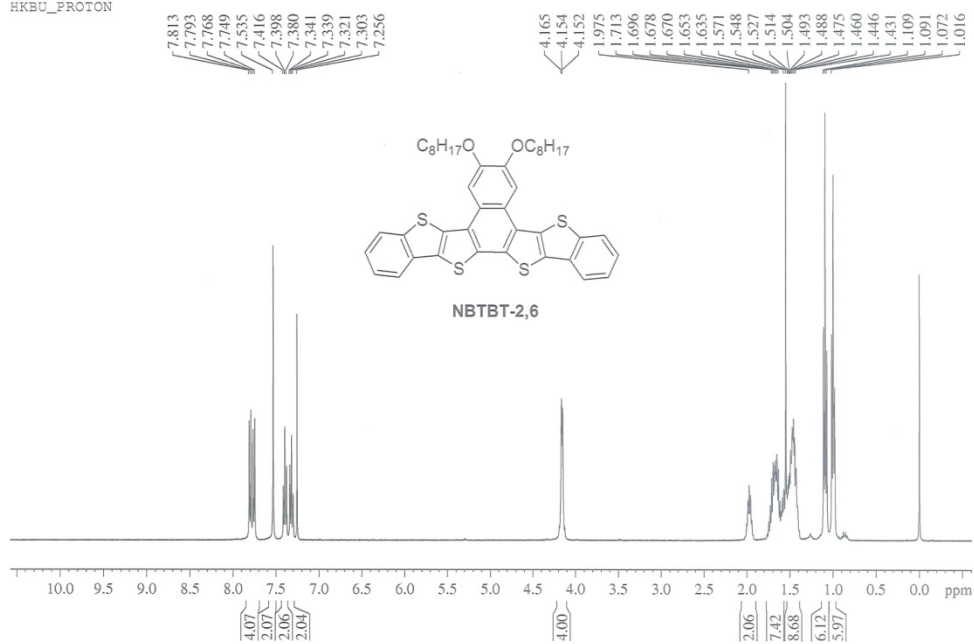
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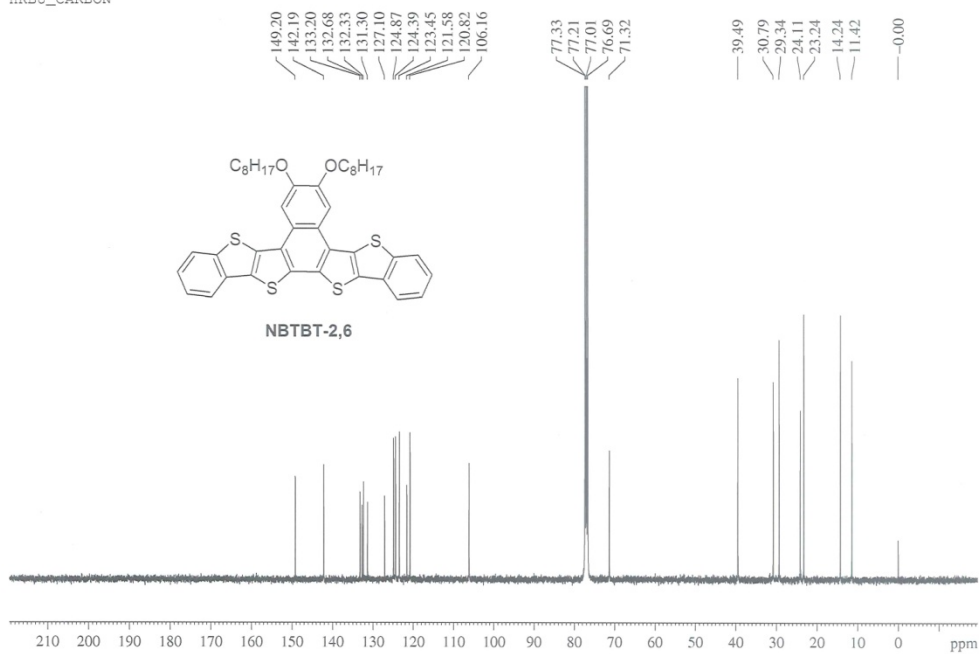
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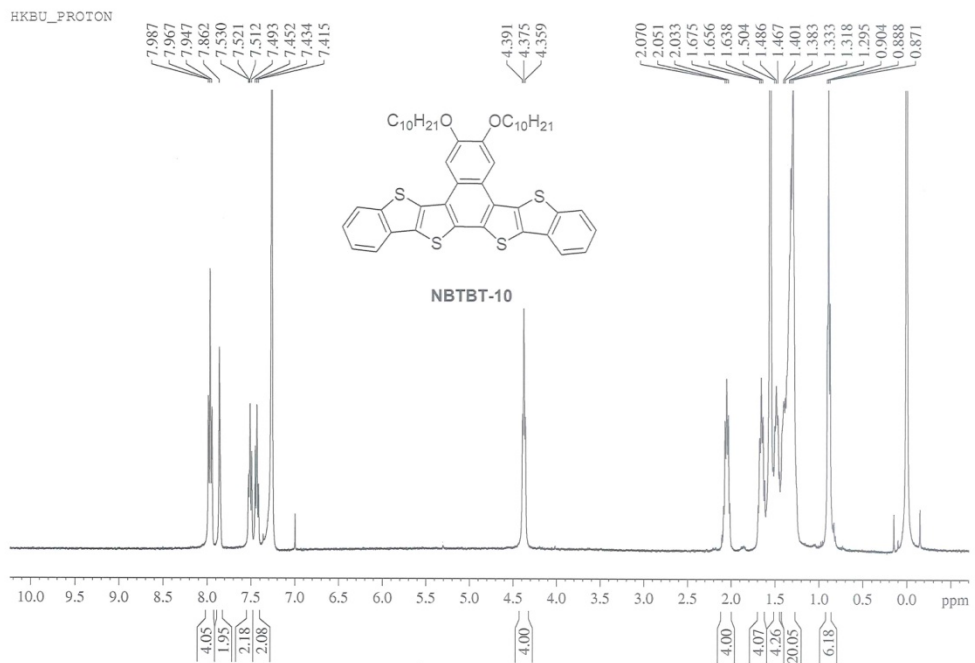
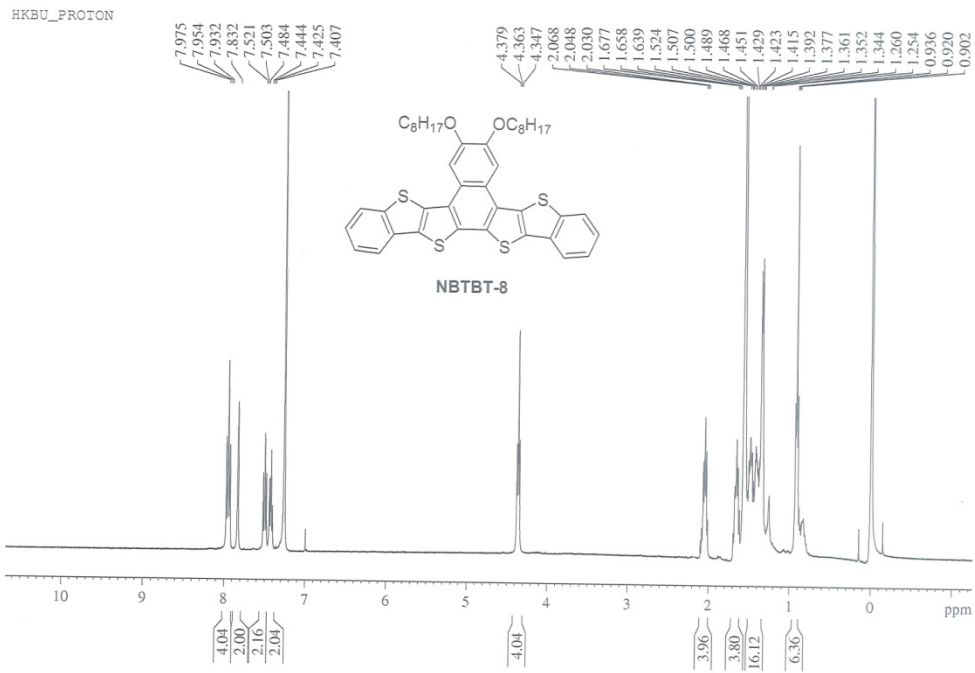


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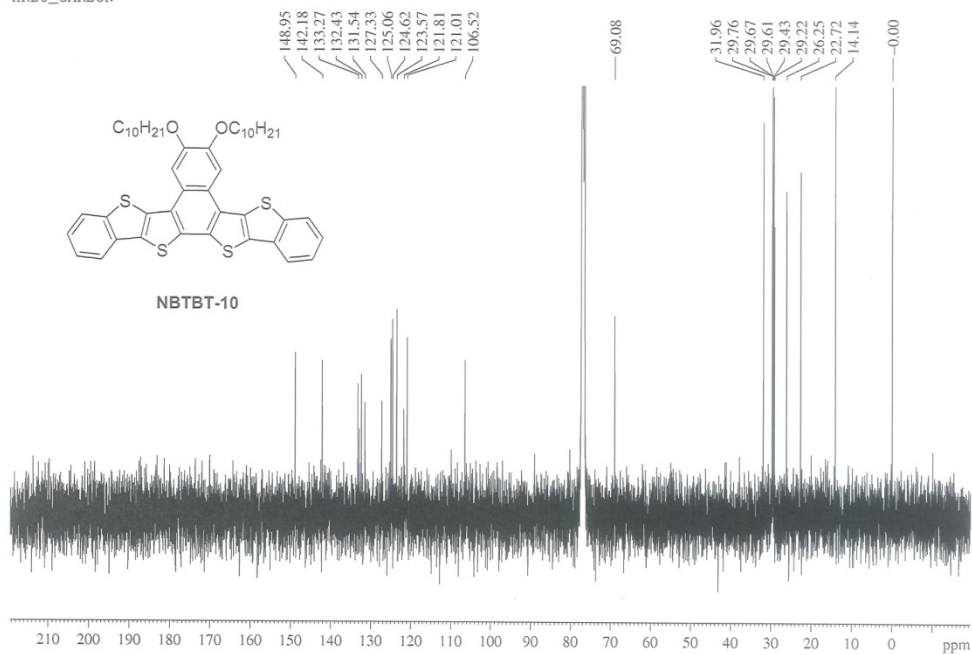


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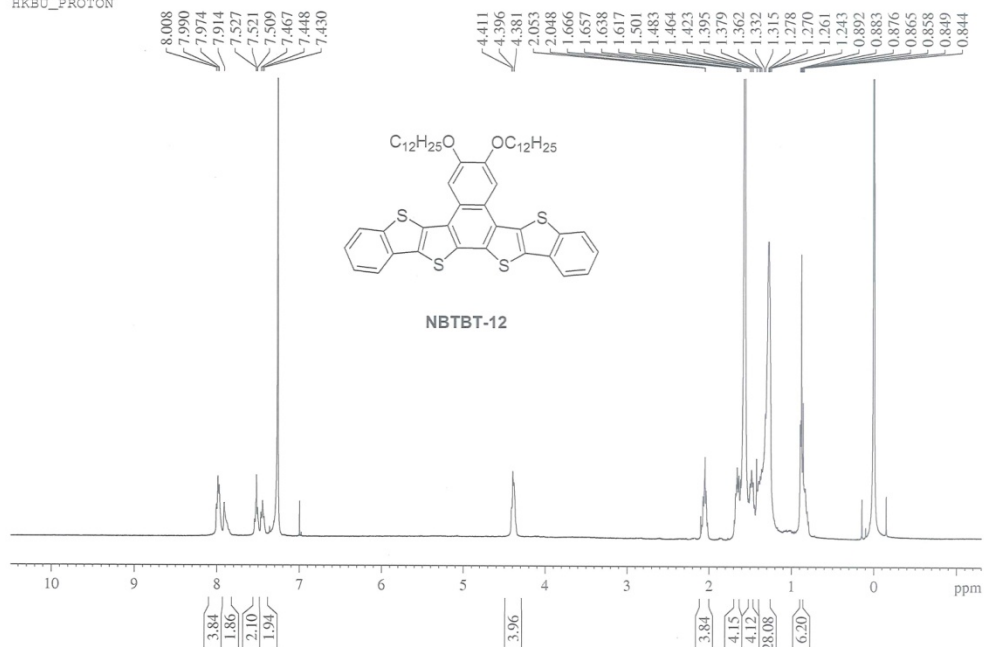




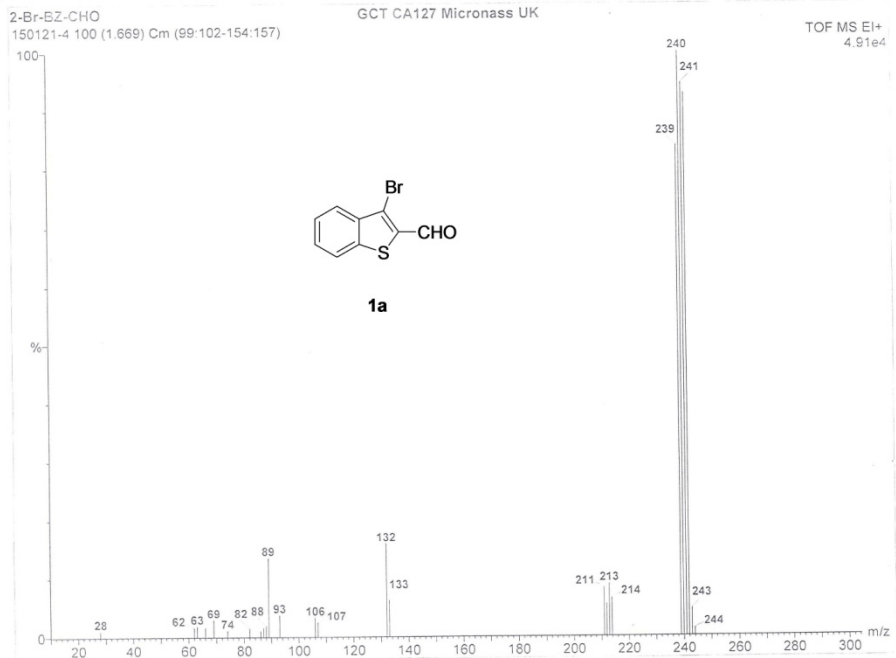
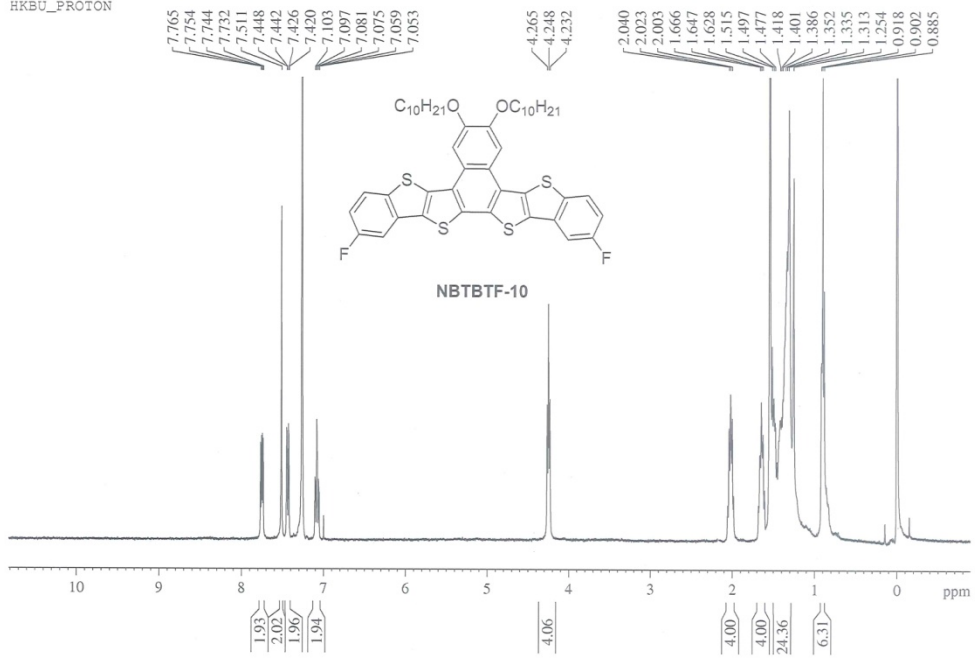
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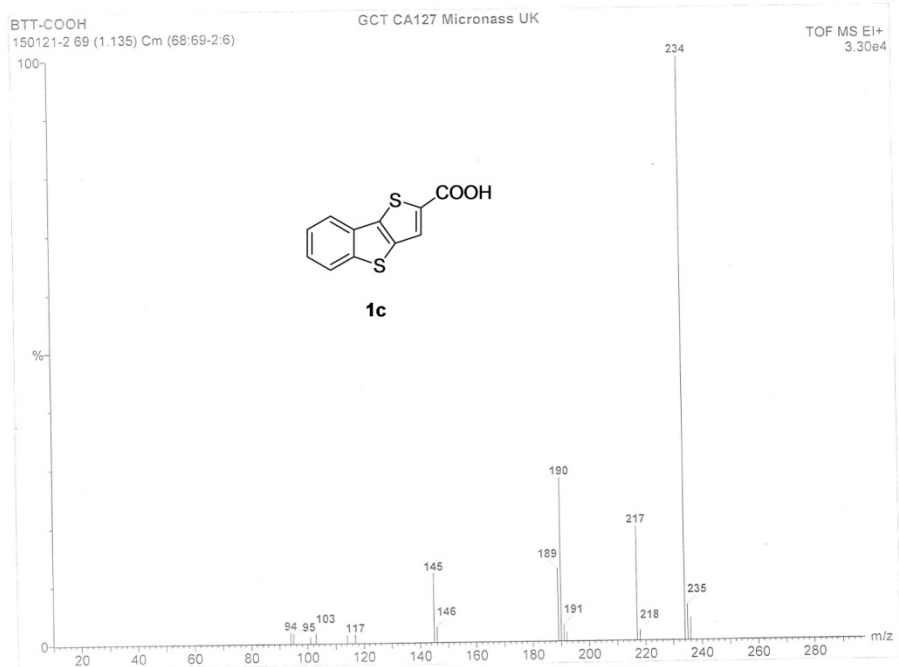
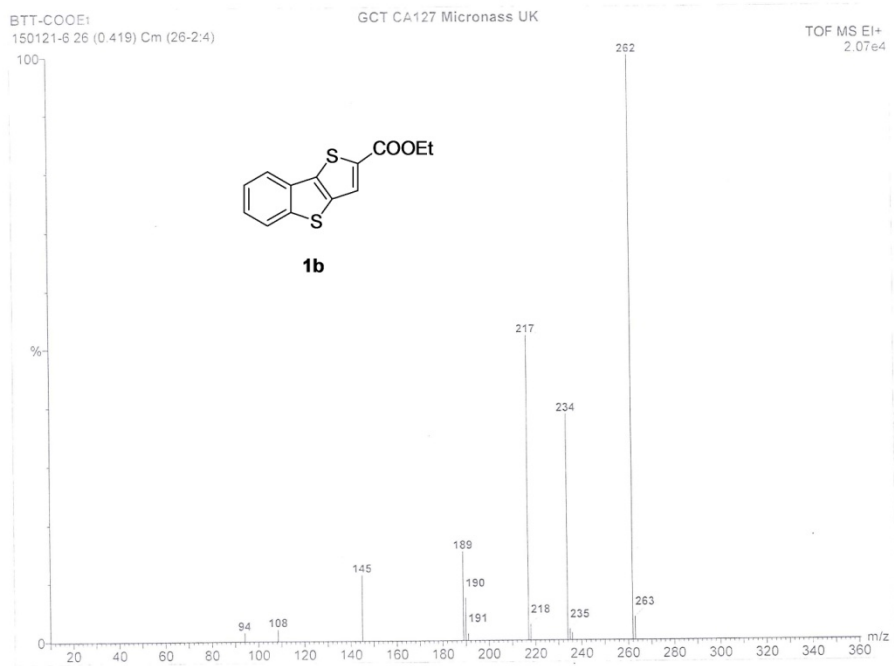
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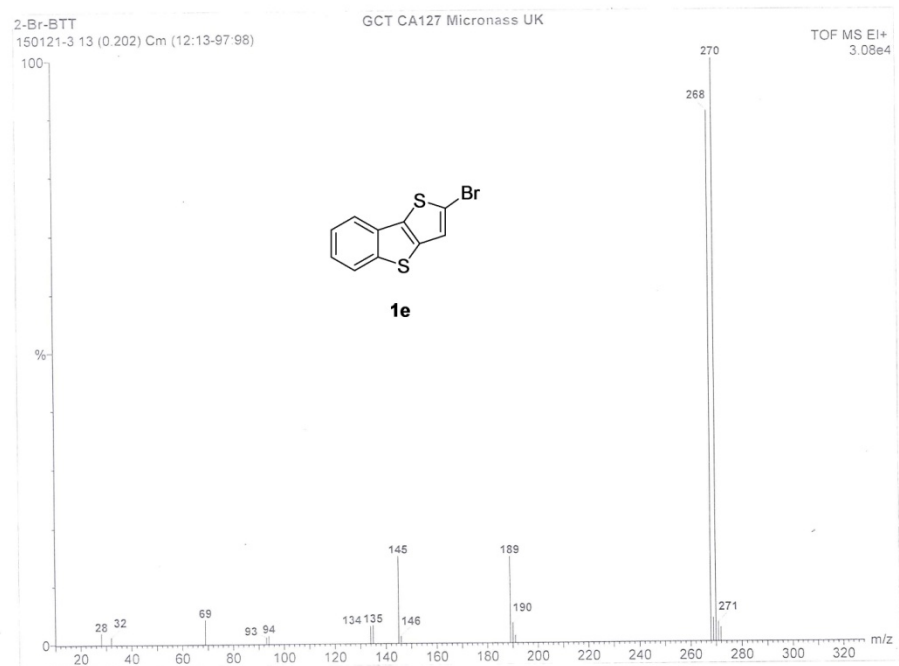
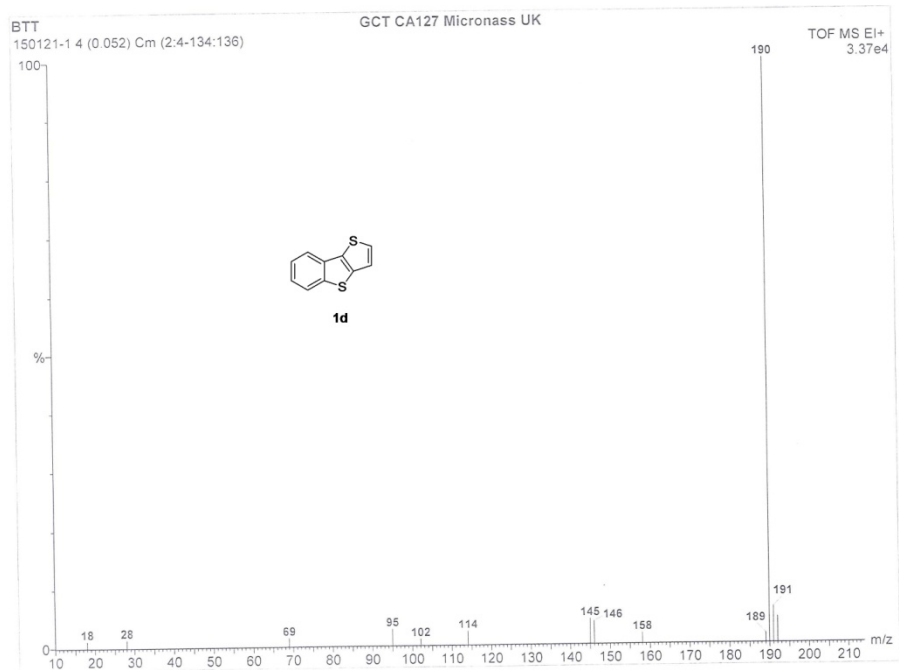


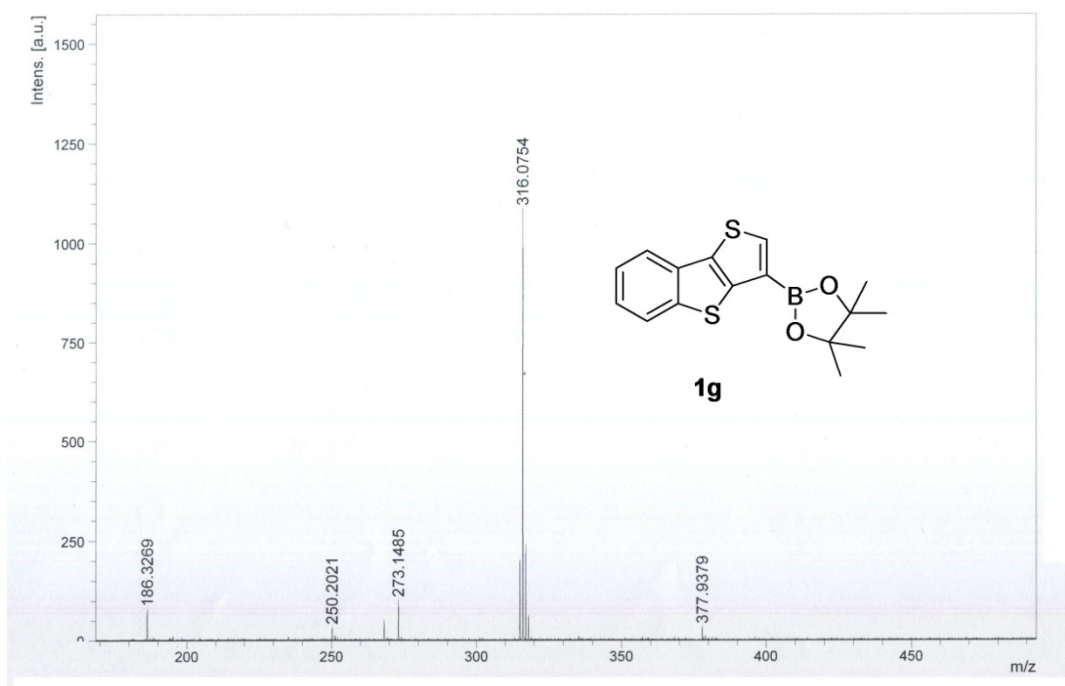
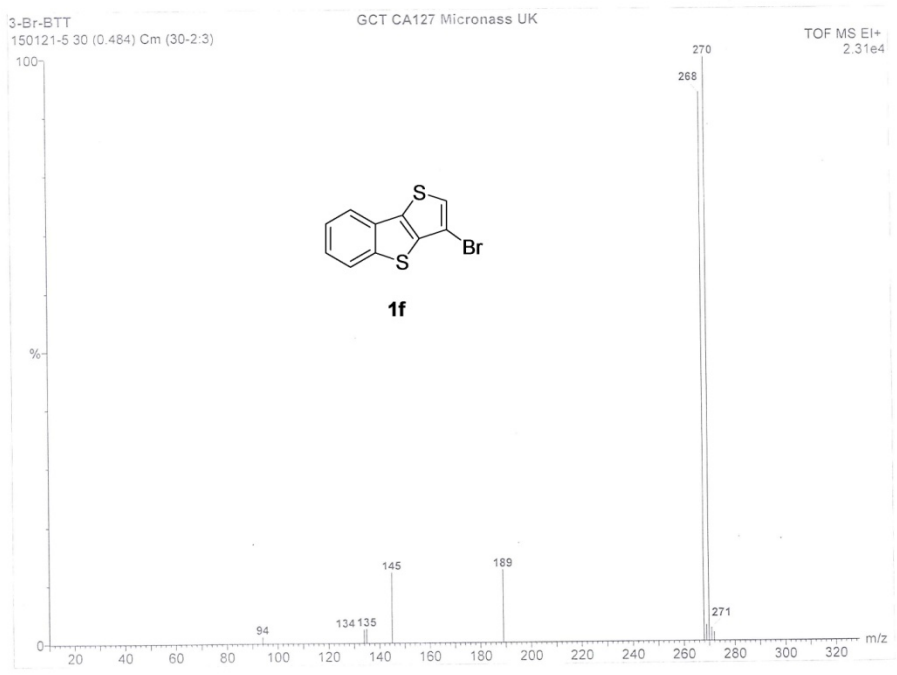
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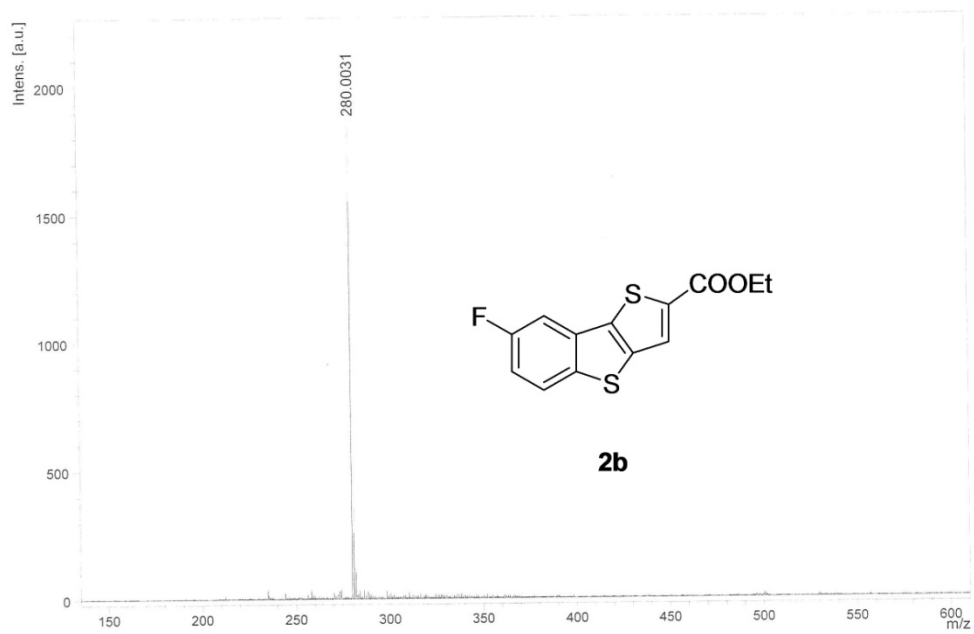
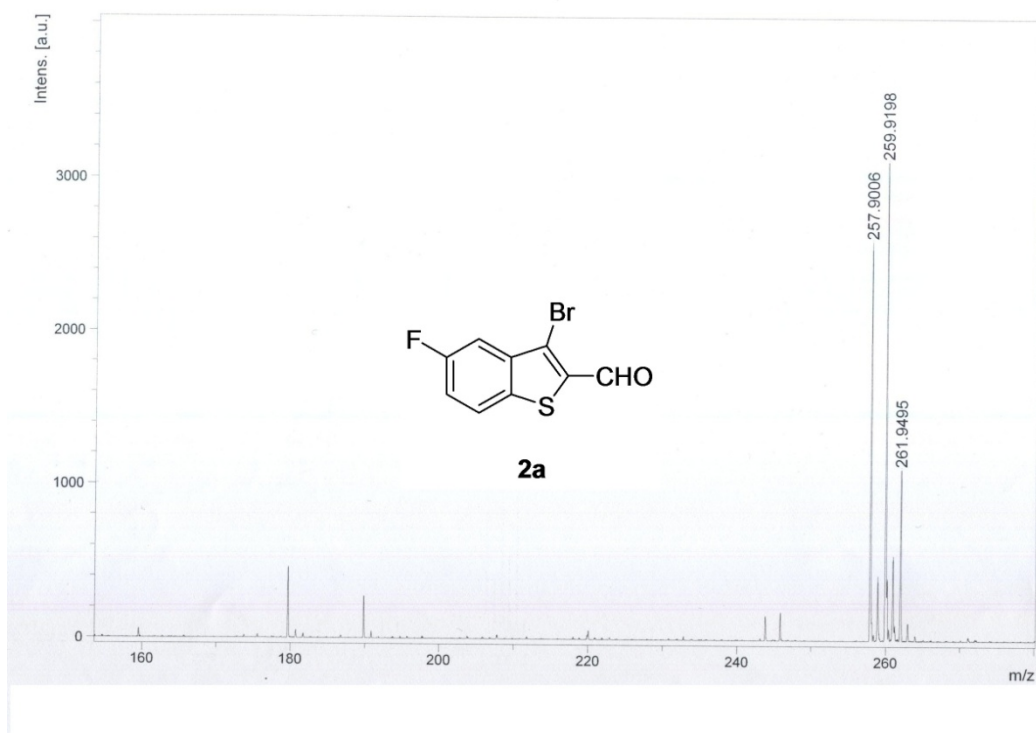


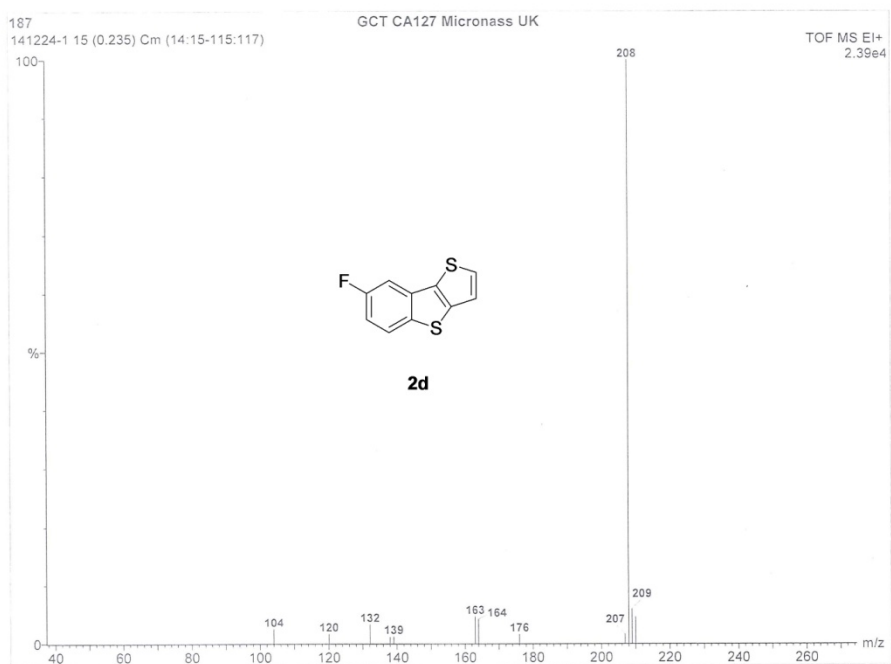
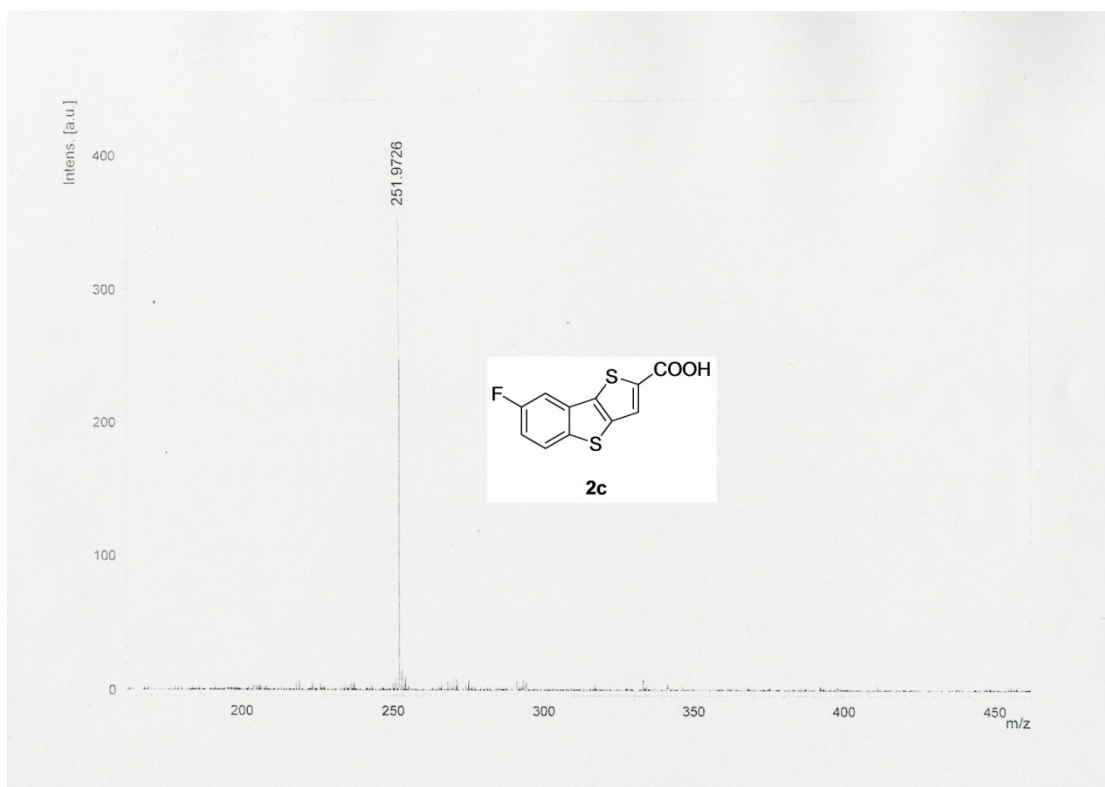


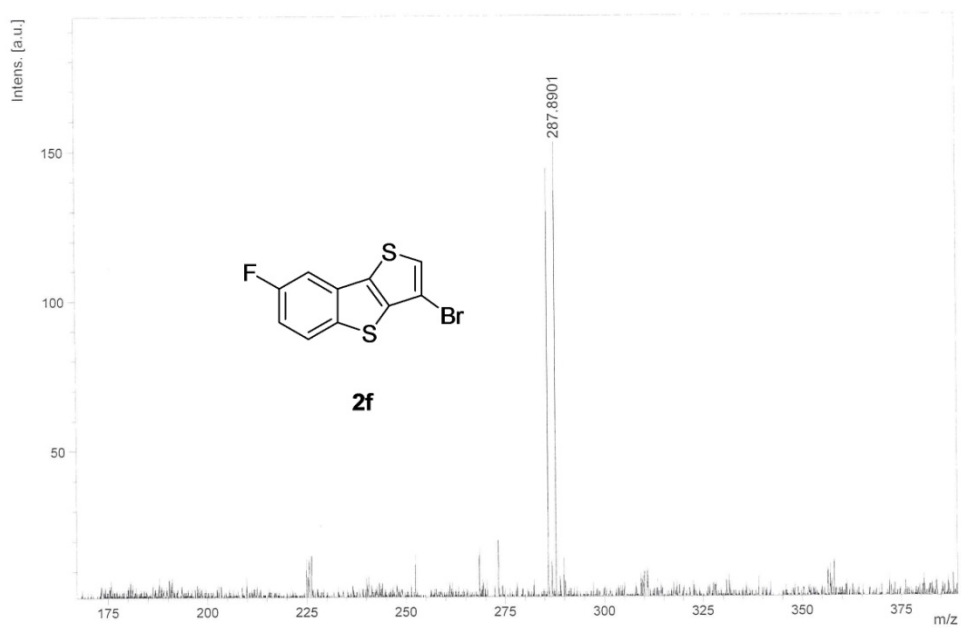
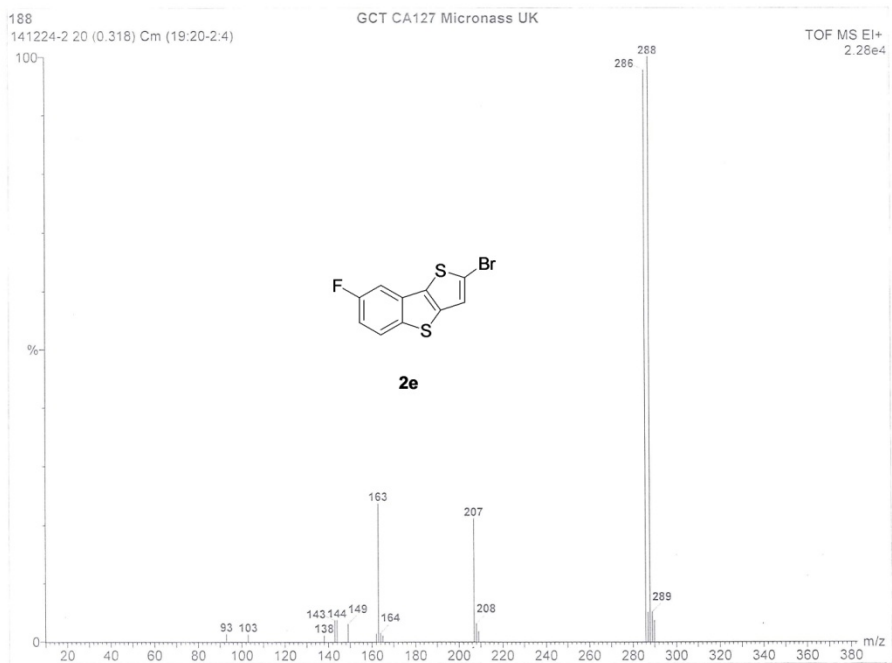


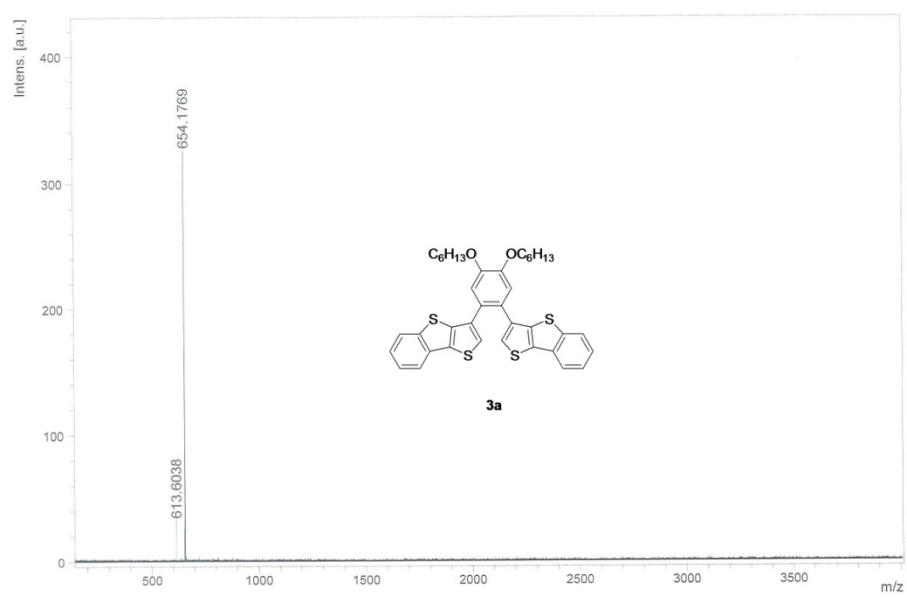
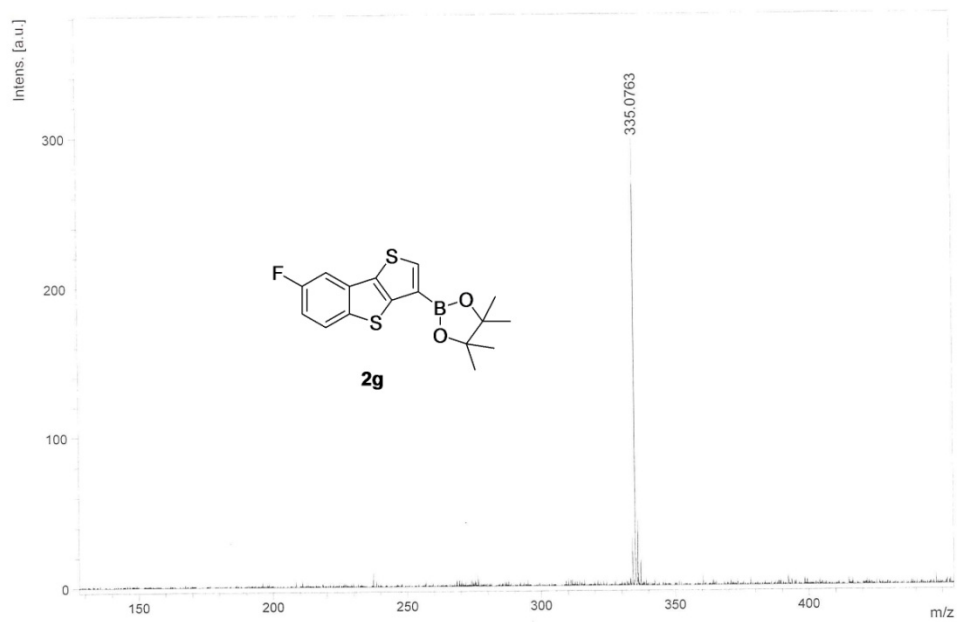


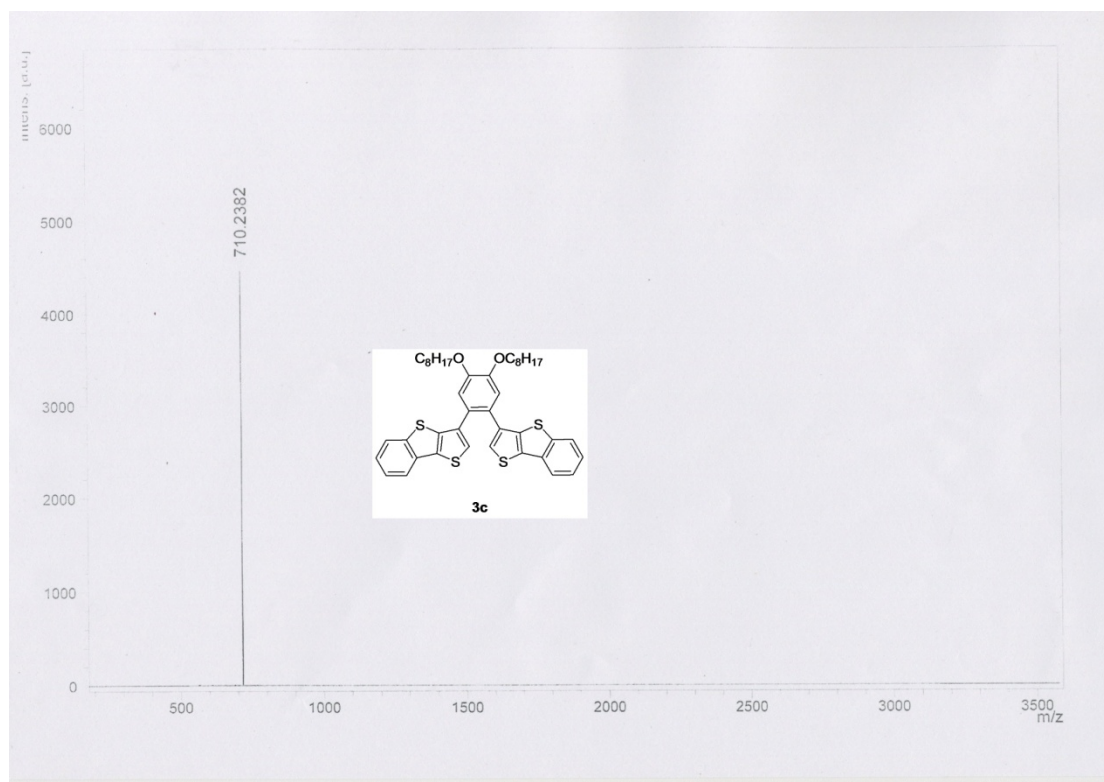
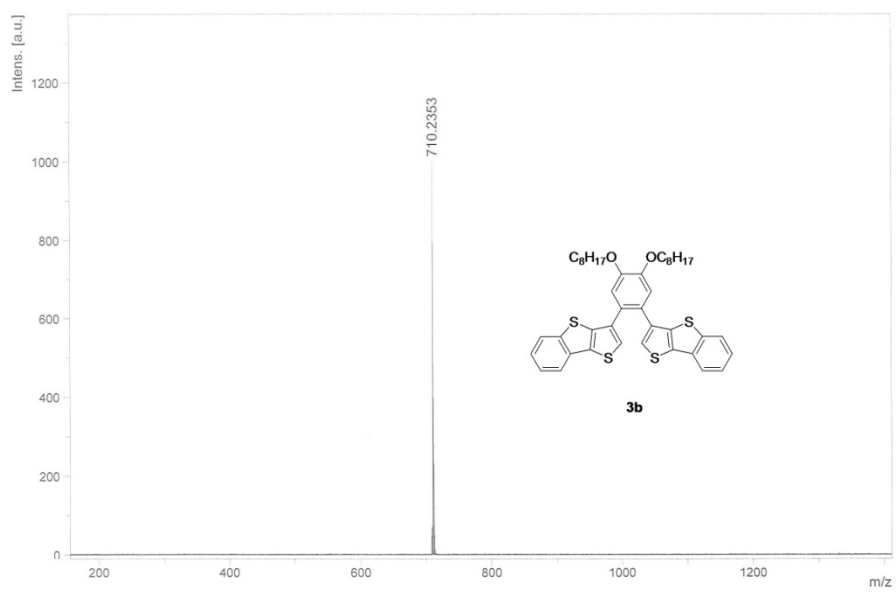




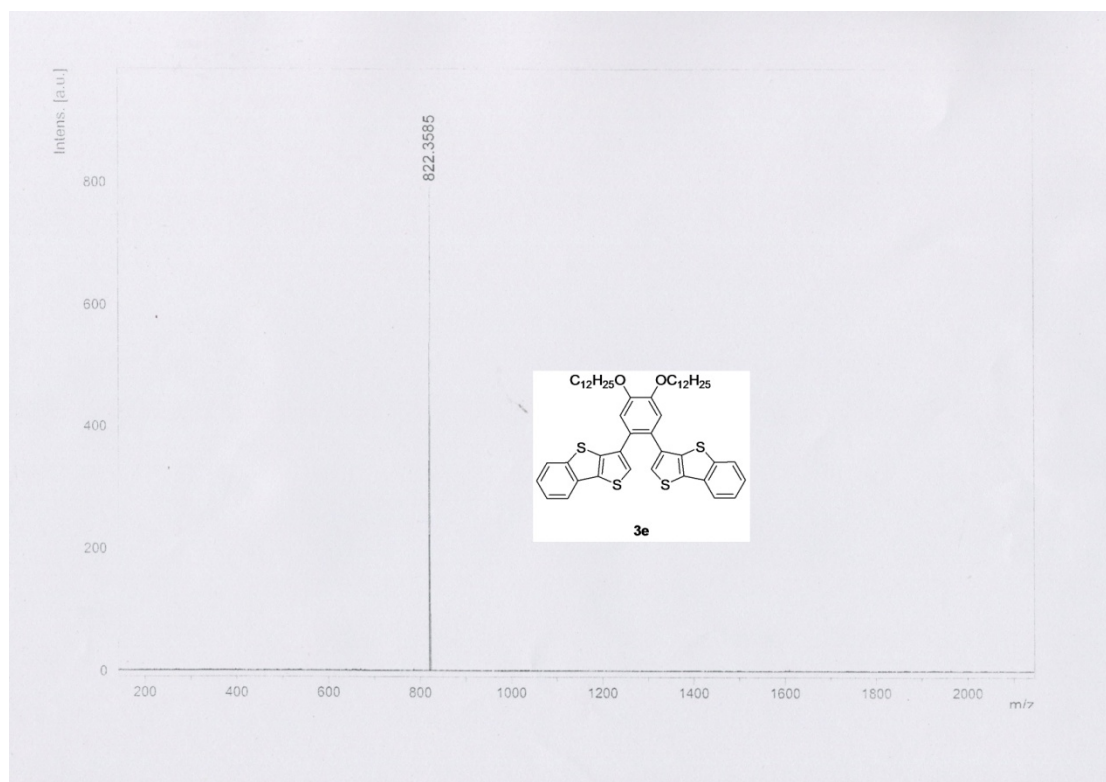
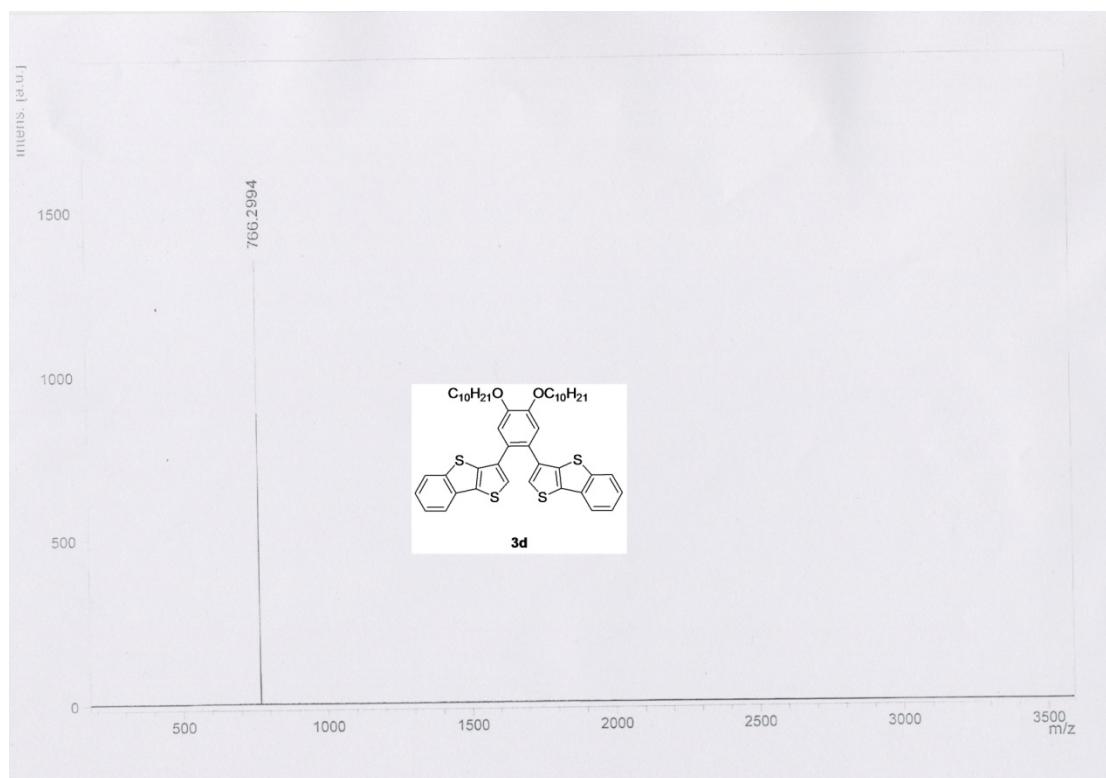


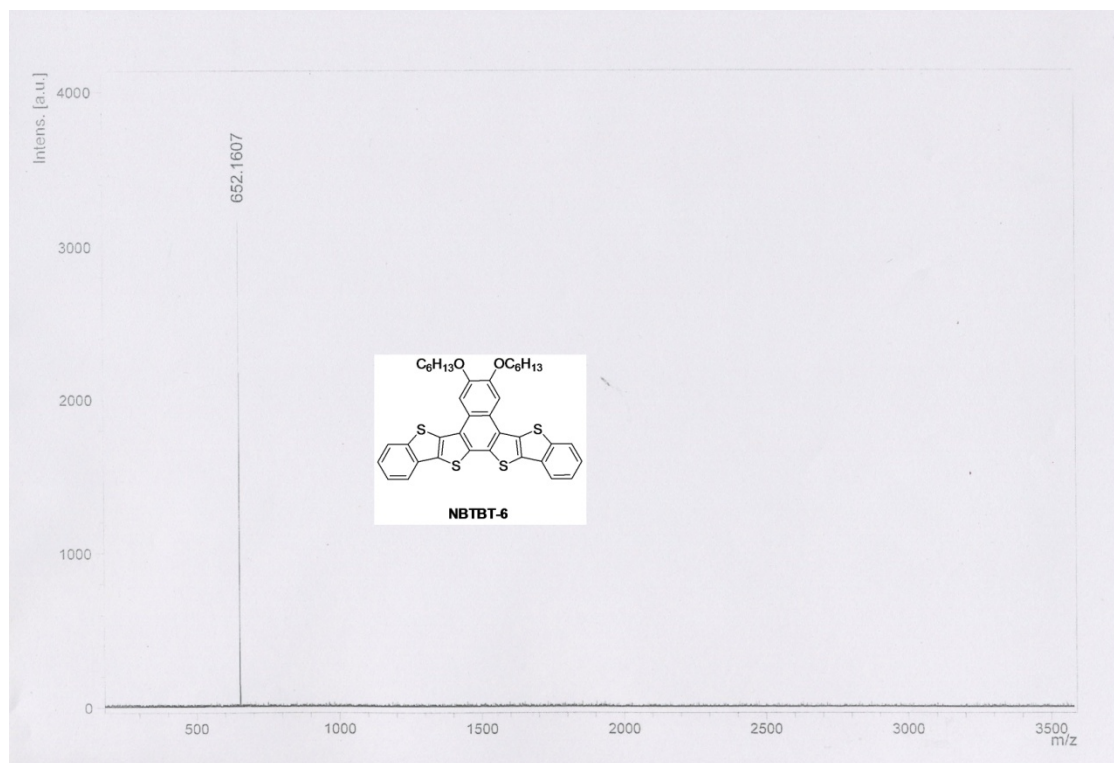
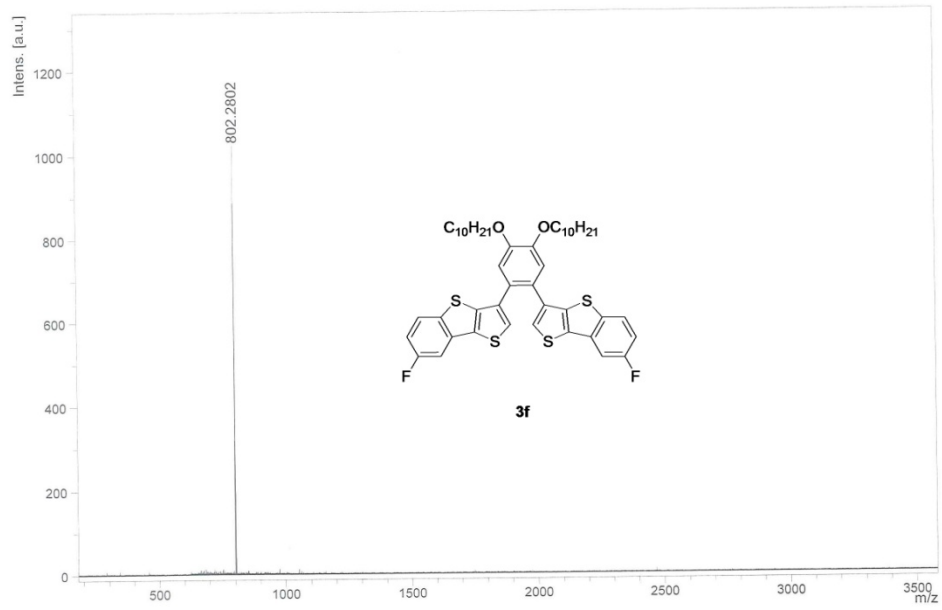


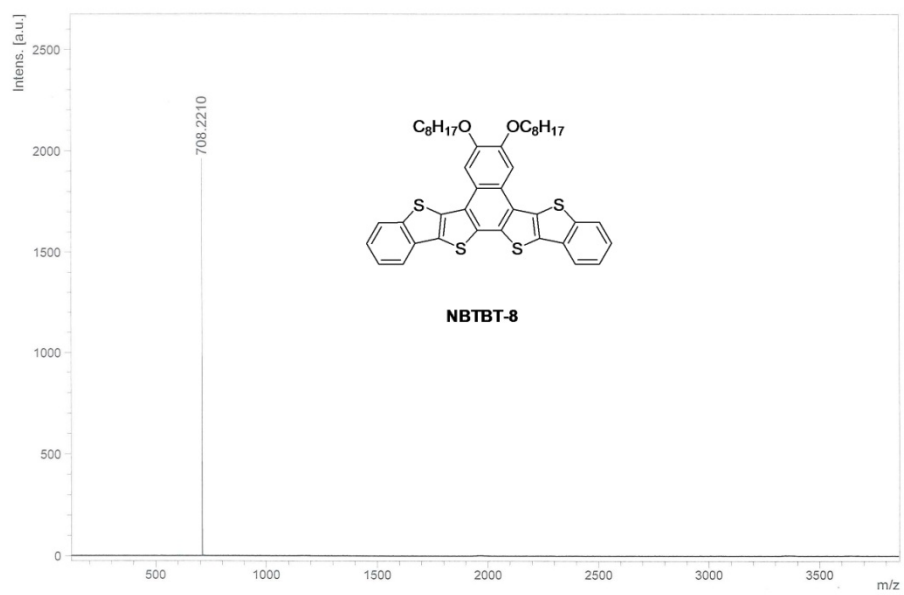
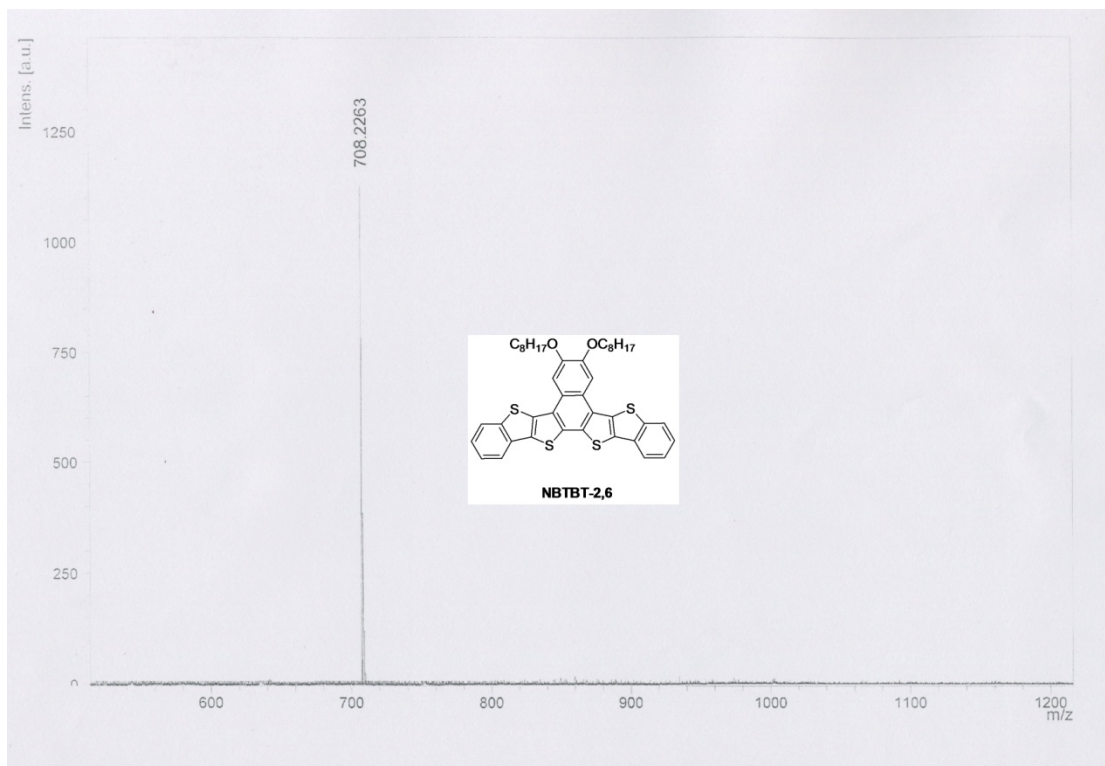


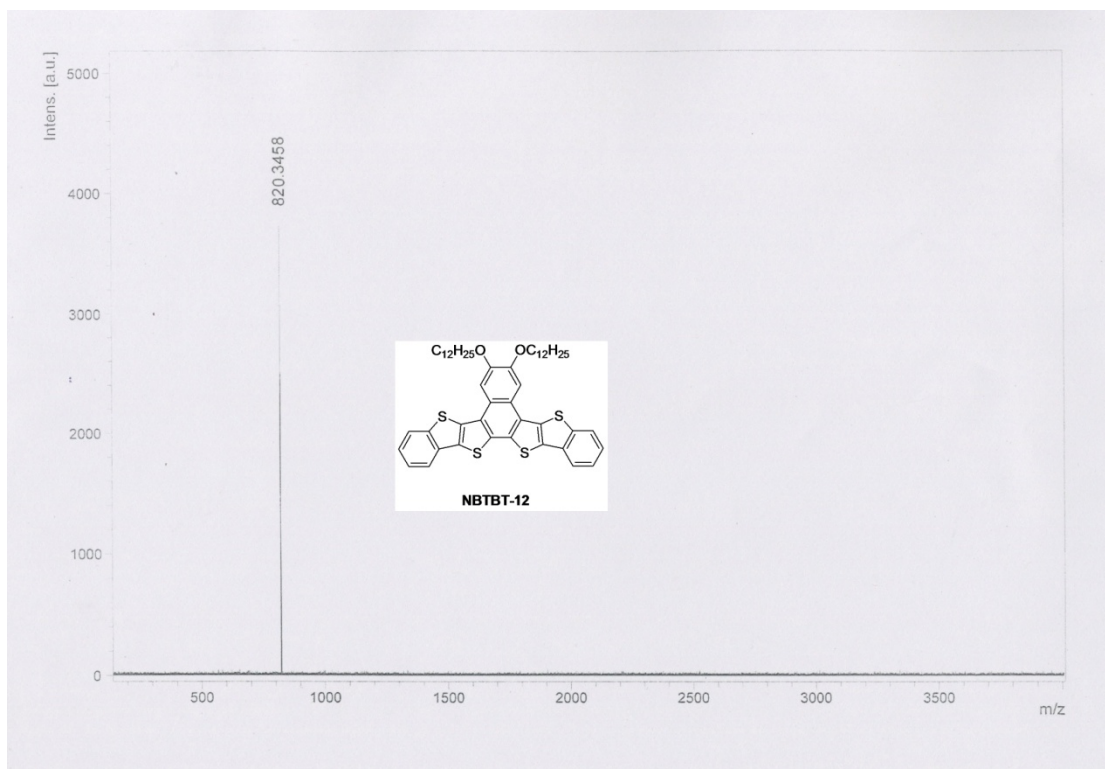
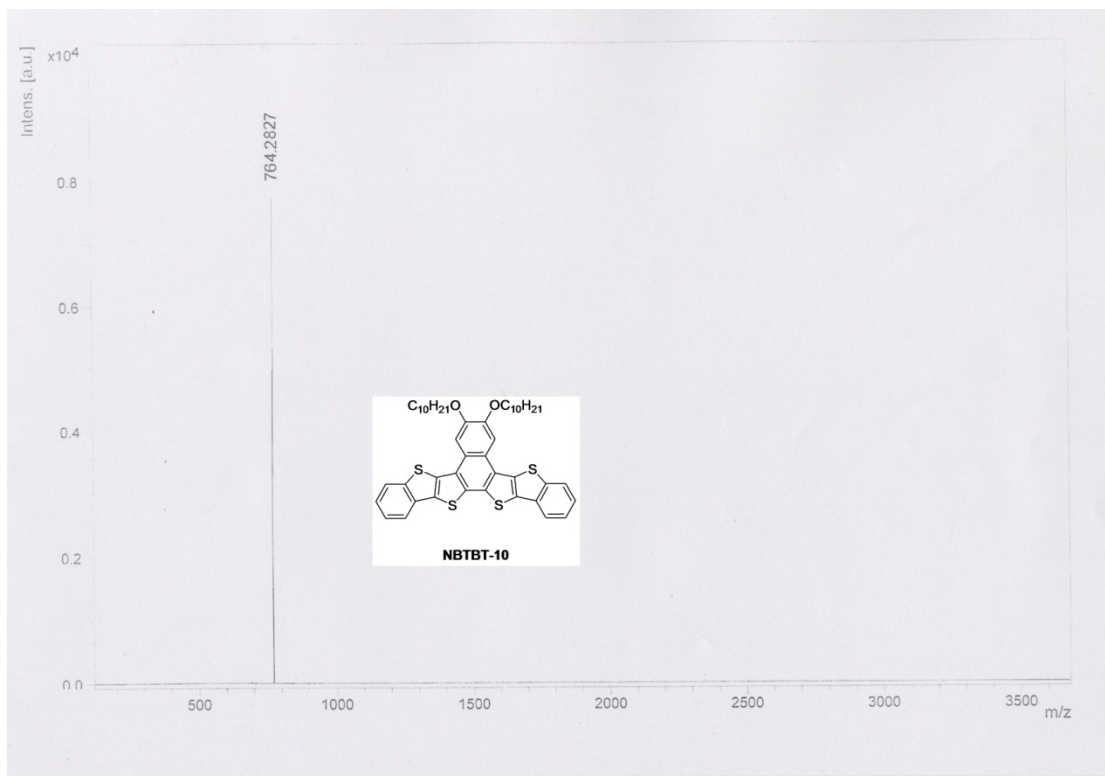




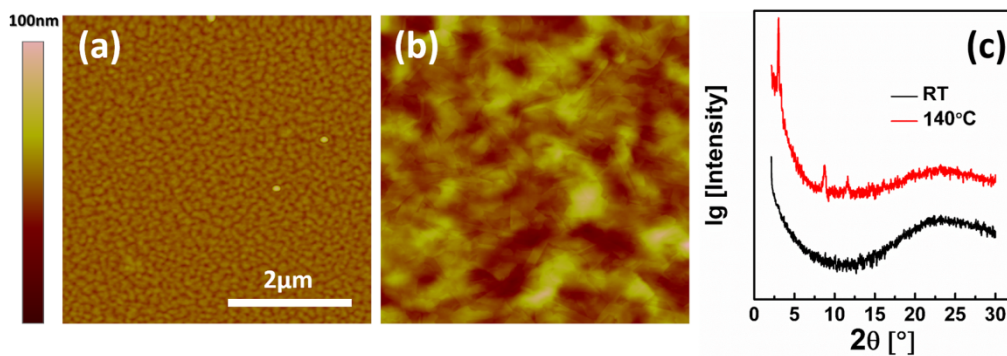
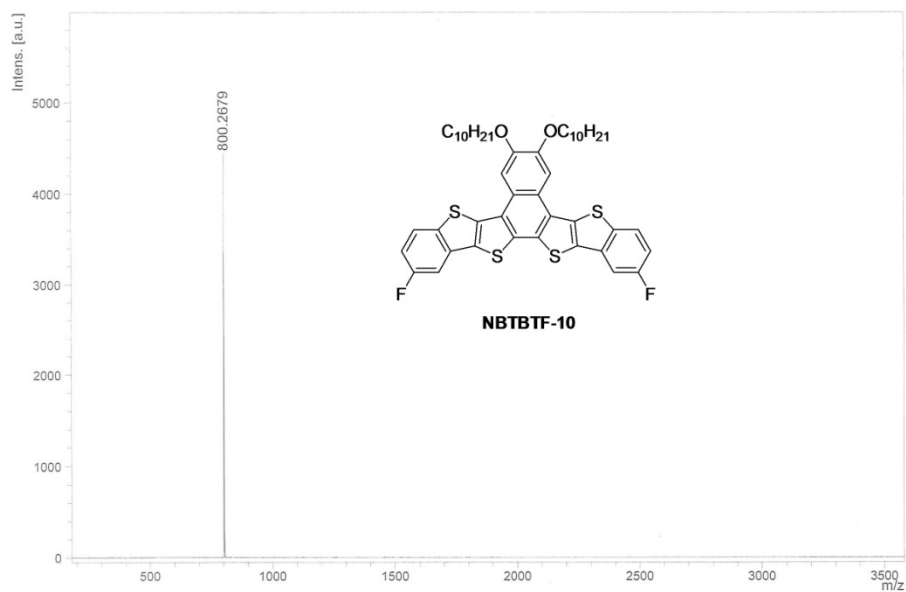




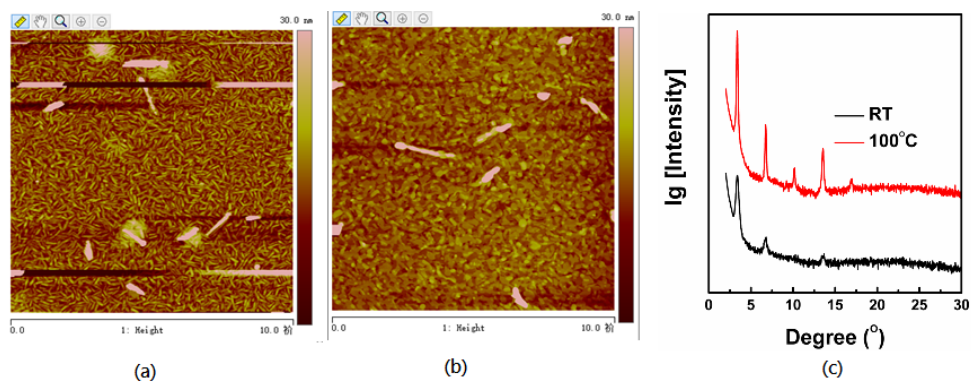








**Fig. S1** AFM images of thin-film of **NBTBTF-10** with annealing temperature at (a) RT; and (b) 140 °C; and (c) x-ray diffraction patterns of thin films of **NBTBTF-10** at RT and 140 °C.



**Fig. S2** AFM images of thin-film of **NBTBT-2,6** with annealing temperature at (a) RT; and (b) 100 °C; and (c) x-ray diffraction patterns of thin films of **NBTBT-2,6** at RT and 100 °C.

RT; and (b) 100 °C; and (c) x-ray diffraction patterns of thin films of **NBTBT-2,6** at RT and 100 °C.

**Table S1** The device performances of **NBTBT** series at different annealing temperatures by vacuum deposition.

		$T_{\text{annealing}} [^{\circ}\text{C}]$								
		RT	80	120	160	200	220	240	260	
<b>NBTBT-6</b>	$\mu_{\text{max}}$ ( $\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ )	$6.6 \times 10^{-5}$	$1.6 \times 10^{-4}$	$9.3 \times 10^{-3}$	$1.1 \times 10^{-2}$	$2.3 \times 10^{-2}$	$2.7 \times 10^{-2}$	0.10	—	
	$I_{\text{on}}/I_{\text{off}}$	$10^3 - 10^4$	$10^4$	$10^6 - 10^7$	$10^6 - 10^7$	$10^7 - 10^8$	$10^6 - 10^7$	$10^6 - 10^7$	—	
	$V_{\text{threshold}} [\text{V}]$	10	1	-15	-20	-20	-14	-8	—	
		RT	80	100	120	140				
<b>NBTBT-2.6</b>	$\mu_{\text{max}}$ ( $\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ )	$8.1 \times 10^{-4}$	$1.4 \times 10^{-2}$	$1.7 \times 10^{-2}$	$3.6 \times 10^{-3}$	—				
	$I_{\text{on}}/I_{\text{off}}$	$10^4 - 10^5$	$10^6$	$10^6$	$10^5 - 10^6$	—				
	$V_{\text{threshold}} [\text{V}]$	-13	-10	-15	-15	—				
		RT	80	120	160	200	220	240	260	
<b>NBTBT-8</b>	$\mu_{\text{max}}$ ( $\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ )	$6.7 \times 10^{-5}$	$7.2 \times 10^{-5}$	$1.2 \times 10^{-2}$	$1.6 \times 10^{-2}$	$3.2 \times 10^{-2}$	$2.8 \times 10^{-2}$	0.10	—	
	$I_{\text{on}}/I_{\text{off}}$	$10^2 - 10^3$	$10^4$	$10^7 - 10^8$	$10^7$	$10^7 - 10^8$	$10^7 - 10^8$	$10^7 - 10^8$	—	
	$V_{\text{threshold}} [\text{V}]$	16	4	-16	-14	-18	-10	-19	—	
		RT	80	120	160	180	200	220	240	
<b>NBTBT-10</b>	$\mu_{\text{max}}$ ( $\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ )	$1.8 \times 10^{-4}$	$7.8 \times 10^{-4}$	$1.3 \times 10^{-2}$	$2.2 \times 10^{-2}$	$4.0 \times 10^{-2}$	$5.8 \times 10^{-2}$	0.25	—	
	$I_{\text{on}}/I_{\text{off}}$	$10^4$	$10^6 - 10^7$	$10^7$	$10^7$	$10^8$	$10^8 - 10^9$	$10^5 - 10^6$	—	
	$V_{\text{threshold}} [\text{V}]$	-4	-14	-25	-10	-9	-4	-6	—	
		RT	80	120	160	180	200	220		
<b>NBTBT-12</b>	$\mu_{\text{max}}$ ( $\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ )	$3.9 \times 10^{-5}$	$3.1 \times 10^{-4}$	$2.6 \times 10^{-3}$	$4.7 \times 10^{-3}$	$5.7 \times 10^{-3}$	$3.8 \times 10^{-3}$	—		
	$I_{\text{on}}/I_{\text{off}}$	$10^1 - 10^2$	$10^2 - 10^3$	$10^6$	$10^6 - 10^7$	$10^6 - 10^7$	$10^6 - 10^7$	—		
	$V_{\text{threshold}} [\text{V}]$	6	-13	-12	-21	-20	-12	—		
		RT	80	120	140	180	200	220		
<b>NBTBTF-10</b>	$\mu_{\text{max}}$ ( $\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ )	—	$2.3 \times 10^{-2}$	0.154	0.24	$8.0 \times 10^{-2}$	$6.6 \times 10^{-2}$	$1.7 \times 10^{-2}$		
	$I_{\text{on}}/I_{\text{off}}$	—	$10^5 - 10^6$	$10^7 - 10^8$	$10^6 - 10^7$	$10^6 - 10^7$	$10^6 - 10^7$	$10^5$		
	$V_{\text{threshold}} [\text{V}]$	—	-19	-22	-24	-12	-9	-9		