

# Supporting Information

## Step-Saving Synthesis of Star-Shaped Hole-Transporting Materials with Carbazole or Phenothiazine Cores via Optimized C-H/C-Br Coupling Reactions

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## 1. General information:

Unless otherwise noted, all reactions were carried out with magnetic stirring and in flame-dried glassware under nitrogen. Required chemicals such as Pd(OAc)<sub>2</sub>, phosphine ligands, PivOH and K<sub>2</sub>CO<sub>3</sub> are commercially available. Anhydrous or reagent-grade solvents such as dichloromethane, chloroform, and *N,N*-dimethylformamide (DMF) purchased from Sigma-Aldrich, Acros or Alfa Aesar were used directly without further purifications. Syringes used to transfer reagents and solvents were purged with nitrogen prior to use. Reactions were monitored by thin layer chromatography (TLC, aluminum plates coated with silica gel, Merck 60, F-254). The spots were visualized by UV light. Flash column chromatography was performed using silica gel (spherical, 63-210 μm or 40-75 μm). Melting points were measured on a Fargo MP-2D apparatus. NMR spectra were recorded on a Bruker Magnet System 300 or 500 MHz instrument. Chemical shifts were given relative to CDCl<sub>3</sub> (7.26 ppm for <sup>1</sup>H NMR, 77.0 ppm for <sup>13</sup>C NMR). For the characterization of the observed signal multiplicities, the following abbreviations were applied: s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet), quint (quintet), m (multiplet), comp (complex), app (apparent) and br (broad). The mass spectra was recorded by Matrix-Assisted Laser Desorption/Ionization (MALDI) techniques operating with a Bruker autoflex speed. Absorption spectra (UV-Vis) were measured on a Hitachi U-4100 UV-Vis spectrophotometer. Photoluminescence spectra (PL) were measured on a Hitachi F-7000 fluorescence spectrophotometer. The optical band gap ( $E_g^{opt}$ ) of the synthesized hole-transporting materials was calculated from the intersection of absorption and PL spectra. The experiments of cyclic voltammetry were carried out with an Autolab electrochemical analyzer using a Pt working electrode, a Pt wire counter electrode and a Ag/AgCl reference electrode. The measurements were conducted in dry CH<sub>2</sub>Cl<sub>2</sub> solution containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate as a supporting electrolyte under a scan rate of 100 mVs<sup>-1</sup>. The half-wave potential,  $E_{1/2}$ , was calculated by  $(E_{pa}+E_{pc})/2$ , where  $E_{pa}$  and  $E_{pc}$  are the potential energy of anodic and cathodic peaks, respectively. The HOMO energy level,  $E_{HOMO}$ , was calculated by  $-[E_{1/2} (vs. Ag/AgCl_{sat'd}) + 0.197 (vs. NHE) + 4.500]$  eV;  $E_{LUMO} = E_{HOMO} + E_g^{opt}$ . Thermogravimetric analysis (TGA) was run on a TA Instrument Q500. Differential scanning calorimetry (DSC) was run on a Netzsch Instrument LT-DSC (Netzsch 204 F1).

## 2. Device fabrication of the perovskite solar cells (PSCs):

A TiO<sub>2</sub> compact layer (~30 nm in thickness) was deposited onto the FTO substrate surface by spin-coating a solution of titanium diisopropoxide bis(acetylacetonate) (75 wt.% of Ti(acac)<sub>2</sub>O*i*Pr<sub>2</sub> in isopropanol). A 150 nm-thick mesoporous TiO<sub>2</sub> film (TiO<sub>2</sub> particle size: ~20 nm, crystalline phase: anatase) was spin-coated onto the compact-TiO<sub>2</sub>/FTO substrate surface using home-made pastes and heated to 500 °C for 30 min. After sintering the TiO<sub>2</sub> layer, the films were cooled to room temperature and immersed in TiCl<sub>4</sub> solution (0.04 M in water) at 70 °C for 30 min. The films were then rinsed by deionized water and then annealed at 500 °C for 30 min again. After cooling to room temperature, the substrate/films were transferred to a nitrogen-filled glove box. A solution consisting of PbI<sub>2</sub> (1.80 M) and CH<sub>3</sub>NH<sub>3</sub>I (1.80 M) in  $\gamma$ -butyrolactone (GBL) and DMSO (5/5, v/v) was coated onto the TiO<sub>2</sub> substrate by a two-step spin-coating process at 1000 and 5000 rpm for 10 and 20 sec, respectively. At the second spin-coating step, the substrate/films were treated with 75 μL toluene by drop-casting. The substrate/films were then left on standing for over 60 mins before heated on a hot plate at 100 °C for 10 min. **6~13** and **spiro-OMeTAD** (as reference cell) was each dissolved in chlorobenzene (50 mg/mL). Each solution was stirred while heating to 80~90 °C for 30 min. Next, 17.5 μL of a solution of lithium bis(trifluoromethane)sulfonimide (Li-TFSI, 520 mg) in acetonitrile (1 mL) and 28.5 μL 4-*tert*-butylpyridine (TBP) were added directly to the corresponding hole-transporting material (HTM) solutions prepared from previous step. This as-prepared HTM solution was spin-coated onto the substrate/films at 2000 rpm for 30 sec. Finally, the Ag cathode layer was

deposited by thermal evaporation (~100 nm). The active area of each cell was fixed at 0.16 cm<sup>2</sup> by a metal mask.

In order to evaluate the hole-mobility of **6~13**, hole-only devices were fabricated using the space-charge-limited current (SCLC) method based on the device structure of FTO/PEDOT:PSS/HTM/Ag. The hole-mobility data was obtained according to the Mott–Gurney law by fitting the equation (S1) to experimental data in the voltage range where the obtained slope in the double log plot is equal to 2.

$$J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu_h \frac{V^2}{d^3} \quad (\text{S1})$$

In equation (S1),  $J$  is the current density,  $\varepsilon_0$  is the permittivity of free space ( $8.85 \times 10^{-12} \text{ Fm}^{-1}$ ),  $\varepsilon_r$  is the relative permittivity of the material (approaching 3 for organic semiconductors),  $\mu_h$  is the hole mobility,  $V$  is the applied voltage and  $d$  is the thickness of the active layer. The hole-only devices were fabricated by spin-coating PEDOT:PSS (Clevios P, VP Al4083) onto pre-cleaned, patterned indium tin oxide (ITO) substrates ( $8 \text{ } \Omega/\text{square}$ ). The HTM film was spin-coated on top from a chloroform solution with the concentration of 8 mg/mL. The film thickness was varied by using different spin-coating speeds. Ag was deposited on top as a counter electrode by vacuum evaporation. The current density–voltage curves of the devices were recorded with a Keithley 2400 source.

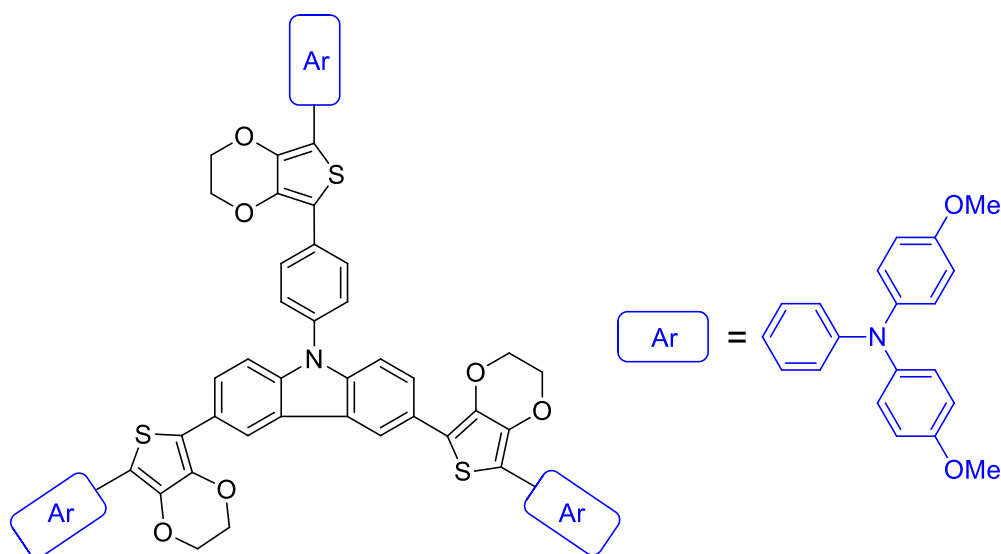
### 3. PCE evaluation of the perovskite solar cells (PSCs):

An IPCE spectrometer (EQE-R-3011, ENLI Technology Co. Ltd., Taiwan) calibrated with a single-crystal silicon reference cell was used for the incident monochromatic photon-to-current conversion efficiency (IPCE) measurements. An AM 1.5G solar simulator (Yamashita Denso Corporation, YSS-50A) was used as the irradiation light source for the characteristic current density-voltage (J-V) measurements. The intensity of the simulated sunlight was calibrated to  $100 \text{ mW}/\text{cm}^2$ . The J-V characteristics of the cell under an illumination of AM 1.5G simulated sunlight were obtained by applying the external potential bias to the cell and measuring the photocurrent output with a Keithley model 2400 digital source meter (Keithley, USA).

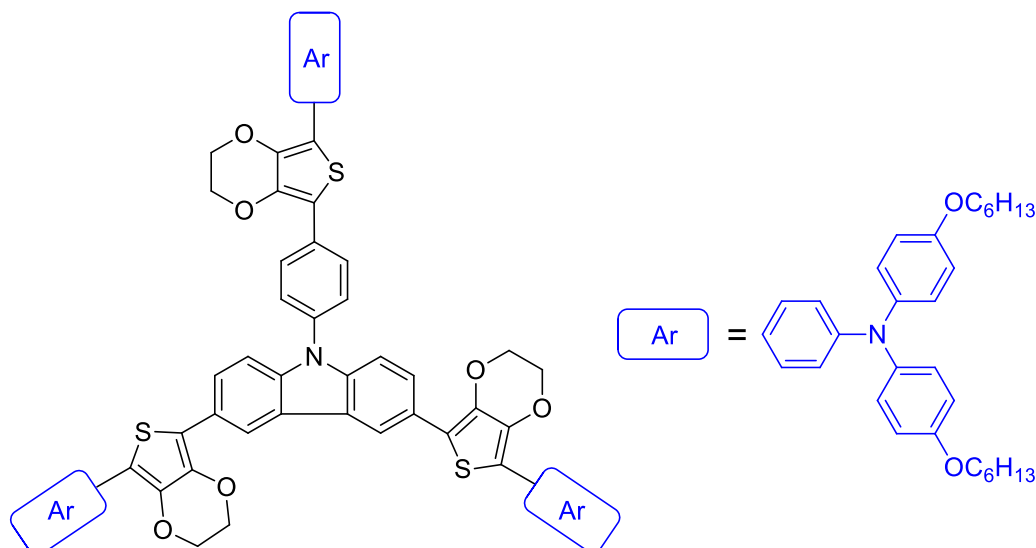
### General Procedure for the synthesis of 6~13:

To a solution of Pd(OAc)<sub>2</sub> (15 mol%), P(*o*-tolyl)<sub>3</sub> (30 mol%), PivOH (60 mol%) and K<sub>2</sub>CO<sub>3</sub> (3.60 equiv.) in DMF (3 mL) in a flame-dried Schlenk flask were added 3,6-dibromo-9-(4-bromophenyl)-9*H*-carbazole (**1**) or 3,7-dibromo-10-(4-bromophenyl)-10*H*-phenothiazine (**2**) (0.30 mmol) and the corresponding end-groups (**3a-d**) (0.96 mmol) under N<sub>2</sub>. The reaction mixture was then heated at 125 °C under N<sub>2</sub> for 30 h. After the reaction mixture had cooled to room temperature, water (10 mL) was added. The mixture was extracted with dichloromethane (2 × 20 mL), and the combined organic layers were washed with brine (50 mL), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated in *vacuo*. Purification by flash chromatography afforded the desired products **6~13**.

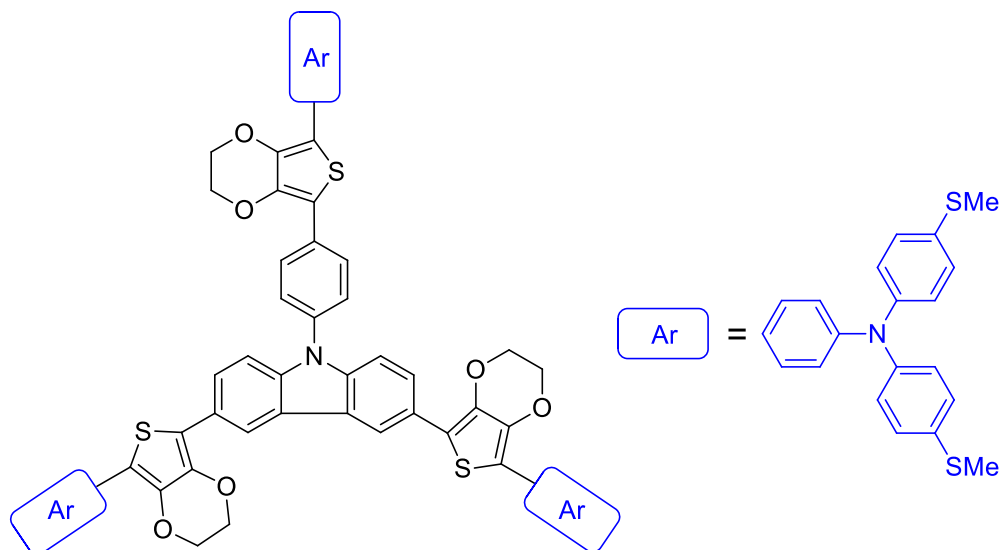
### Synthesis and characterization of carbazole core-based HTMs: 6~9



**6** was prepared from **1** (144 mg, 0.30 mmol), **3a** (427 mg, 0.96 mmol), Pd(OAc)<sub>2</sub> (10 mg, 0.045 mmol), P(*o*-tolyl)<sub>3</sub> (27 mg, 0.09 mmol), PivOH (18 mg, 0.18 mmol), K<sub>2</sub>CO<sub>3</sub> (149 mg, 1.08 mmol), and DMF (3 mL) according to the **General Procedure** and giving after column chromatography (dichloromethane : ethyl acetate : hexanes = 60 : 2 : 38) the pure product **6** (330 mg, 70 %). Yellow solid; m.p.: 232-235 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, ppm): δ 8.50 (s, 2 H), 7.96 (d, *J* = 8.6 Hz, 2 H), 7.82 (dd, *J* = 8.6, 1.7 Hz, 2 H), 7.66-7.56 (comp, 6 H), 7.53 (d, *J* = 8.6 Hz, 2 H), 7.43 (d, *J* = 8.6 Hz, 2 H), 7.14-7.02 (comp, 12 H), 7.00-6.90 (comp, 6 H), 6.88-6.76 (comp, 12 H), 4.46-4.30 (comp, 12 H), 3.80 (app s, 18 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, ppm): δ 155.9, 155.7, 147.5, 147.0, 140.9, 140.7, 139.9, 139.1, 137.7, 137.6, 137.5, 135.1, 132.4, 127.0, 126.8, 126.7, 126.5, 126.4, 125.6, 125.4, 124.9, 123.8, 120.9, 120.5, 118.1, 116.5, 115.2, 114.7, 114.6, 113.0, 110.1, 64.6, 64.5, 55.5; HRMS (MALDI): calcd. for C<sub>96</sub>H<sub>76</sub>N<sub>4</sub>O<sub>12</sub>S<sub>3</sub>: 1573.4695, found: 1573.4682 ([M+H]<sup>+</sup>).

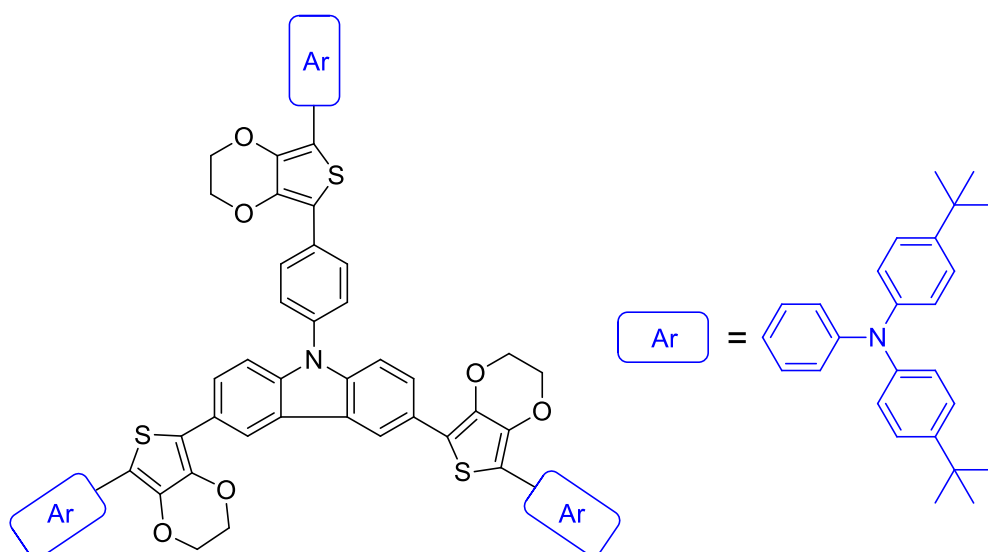


(**7**) was prepared from **1** (144 mg, 0.30 mmol), **3b** (563 mg, 0.96 mmol), Pd(OAc)<sub>2</sub> (10 mg, 0.045 mmol), P(*o*-tolyl)<sub>3</sub> (27 mg, 0.09 mmol), PivOH (18 mg, 0.18 mmol), K<sub>2</sub>CO<sub>3</sub> (149 mg, 1.08 mmol), and DMF (3 mL) according to the **General Procedure** and giving after column chromatography (dichloromethane : hexanes = 50 : 50) the pure product **7** (371 mg, 62%). Yellow solid; m.p.: 135-137 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, ppm): δ 8.51 (s, 2 H), 7.96 (d, *J* = 8.5 Hz, 2 H), 7.82 (app s, 2 H), 7.70-7.55 (comp, 6 H), 7.53 (d, *J* = 8.5 Hz, 2 H), 7.43 (d, *J* = 8.6 Hz, 2 H), 7.12-7.00 (comp, 12 H), 6.99-6.90 (comp, 6 H), 6.87-6.75 (comp, 12 H), 4.46-4.30 (comp, 12 H), 3.94 (app t, 12 H), 1.84-1.75 (comp, 12 H), 1.53-1.45 (comp, 12 H), 1.40-1.32 (comp, 24 H), 0.94 (app t, 18 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, ppm): δ 155.5, 155.3, 147.6, 147.1, 140.5, 139.9, 139.1, 137.6, 137.5, 135.1, 132.4, 127.0, 126.8, 126.6, 126.5, 126.4, 125.4, 124.9, 124.8, 123.8, 120.8, 120.4, 118.1, 116.6, 115.2, 112.9, 110.0, 68.2, 64.6, 64.5, 31.6, 29.3, 25.7, 22.6, 14.0; HRMS (MALDI): calcd. for C<sub>126</sub>H<sub>136</sub>N<sub>4</sub>O<sub>12</sub>S<sub>3</sub>: 1993.9390, found: 1993.9398 ([M+H]<sup>+</sup>).



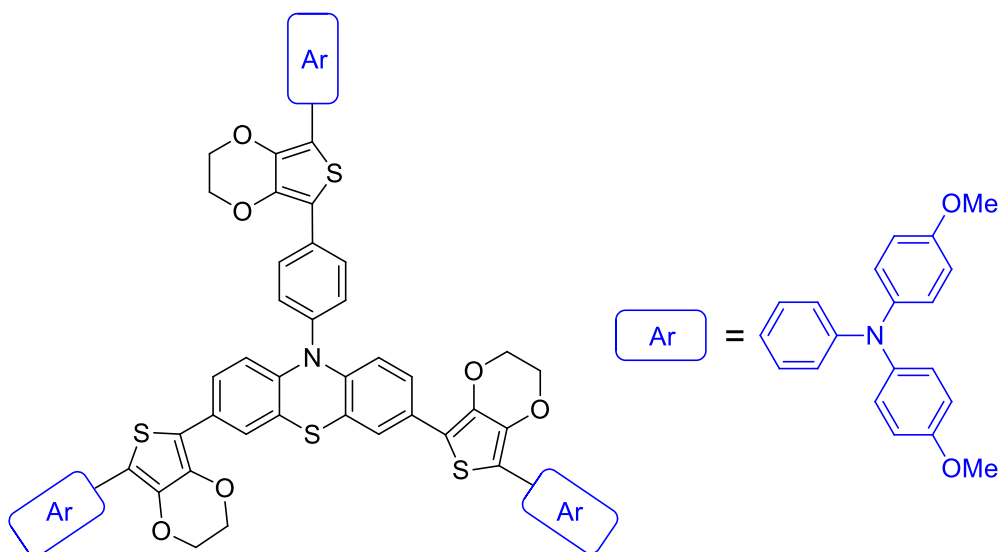
(**8**) was prepared from **1** (144 mg, 0.30 mmol), **3c** (458 mg, 0.96 mmol), Pd(OAc)<sub>2</sub> (10 mg, 0.045 mmol), P(*o*-tolyl)<sub>3</sub> (27 mg, 0.09 mmol), PivOH (18 mg, 0.18 mmol), K<sub>2</sub>CO<sub>3</sub> (149 mg, 1.08 mmol), and DMF (3 mL) according to the **General Procedure** and giving after column chromatography (dichloromethane : hexanes = 60 : 40) the pure product **8** (225 mg, 45 %). Yellow solid; m.p.: 239-240 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, ppm): δ 8.50 (s, 2 H), 7.95 (d, *J* = 8.5 Hz, 2 H), 7.82 (d, *J* = 8.6 Hz, 2 H), 7.70-7.61 (comp, 6 H), 7.53 (d, *J* = 8.5 Hz, 2 H), 7.42 (d, *J* = 8.6 Hz, 2 H), 7.22-7.12 (comp, 12 H), 7.10-6.98 (comp, 18 H), 4.45-4.30 (comp, 12 H), 2.47 (app s, 18 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>,

125 MHz, ppm):  $\delta$  146.0, 145.5, 145.1, 145.0, 139.9, 139.1, 138.1, 138.0, 137.6, 135.2, 132.2, 132.0, 131.7, 128.5, 128.4, 127.7, 127.1, 127.0, 126.8, 125.3, 125.0, 124.8, 124.7, 123.7, 123.6, 123.4, 118.2, 116.0, 115.8, 114.1, 113.6, 110.1, 64.6, 64.5, 16.8, 16.7; HRMS (MALDI): calcd. for  $C_{96}H_{76}N_4O_6S_9$ : 1669.3324, found: 1669.3352 ( $[M+H]^+$ ).

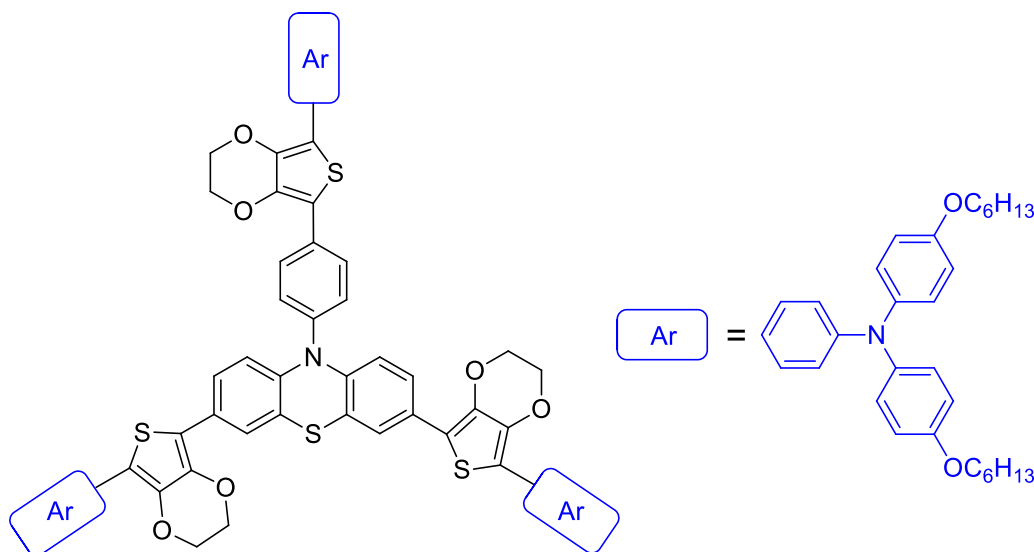


(**9**) was prepared from **1** (144 mg, 0.30 mmol), **3d** (477 mg, 0.96 mmol),  $Pd(OAc)_2$  (10 mg, 0.045 mmol),  $P(o\text{-tolyl})_3$  (27 mg, 0.09 mmol), PivOH (18 mg, 0.18 mmol),  $K_2CO_3$  (149 mg, 1.08 mmol), and DMF (3 mL) according to the **General Procedure** and giving after column chromatography (dichloromethane : hexanes = 50 : 50) the pure product **9** (389 mg, 75 %). Yellow solid; m.p.: 268-270 °C.  $^1H$  NMR ( $CDCl_3$ , 500 MHz, ppm):  $\delta$  8.52 (s, 2 H), 7.97 (d,  $J = 8.5$  Hz, 2 H), 7.84 (d,  $J = 8.5$  Hz, 2 H), 7.70-7.62 (comp, 6 H), 7.54 (d,  $J = 8.5$  Hz, 2 H), 7.44 (d,  $J = 8.5$  Hz, 2 H), 7.35-7.27 (comp, 12 H), 7.14-7.03 (comp, 18 H), 4.46-4.32 (comp, 12 H), 1.35 (app s, 54 H);  $^{13}C$  NMR ( $CDCl_3$ , 125 MHz, ppm):  $\delta$  146.9, 146.4, 145.8, 145.6, 144.9, 144.8, 139.9, 139.1, 137.9, 137.8, 137.6, 135.2, 132.3, 127.1, 126.8, 126.7, 126.6, 126.0, 125.9, 125.4, 125.0, 124.1, 123.9, 123.8, 123.2, 122.8, 118.2, 116.4, 115.5, 114.6, 113.2, 110.1, 64.6, 64.5, 34.3, 31.4; HRMS (MALDI): calcd. for  $C_{114}H_{112}N_4O_6S_3$ : 1729.7817, found: 1729.7824 ( $[M+H]^+$ ).

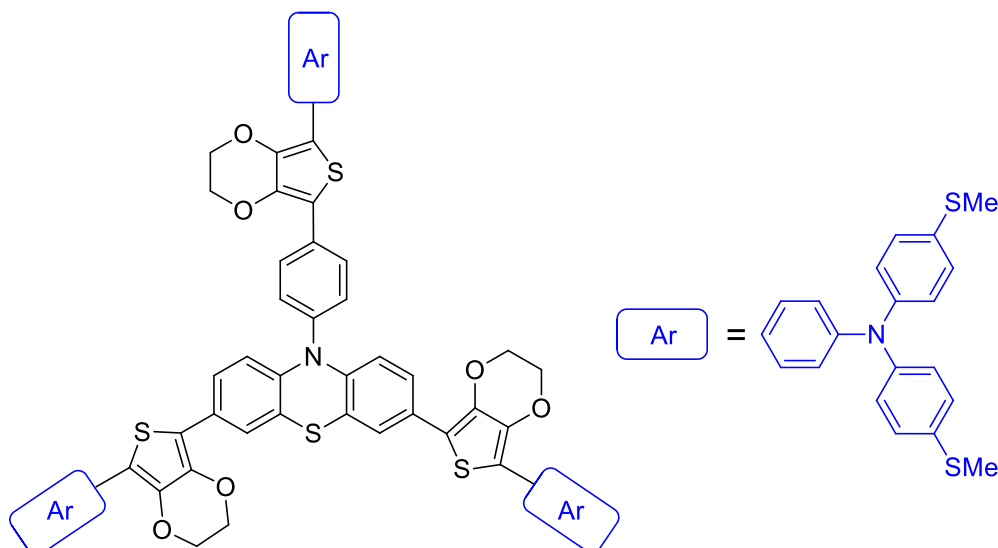
### Synthesis and characterization of phenothiazine core-based HTMs: 10~13



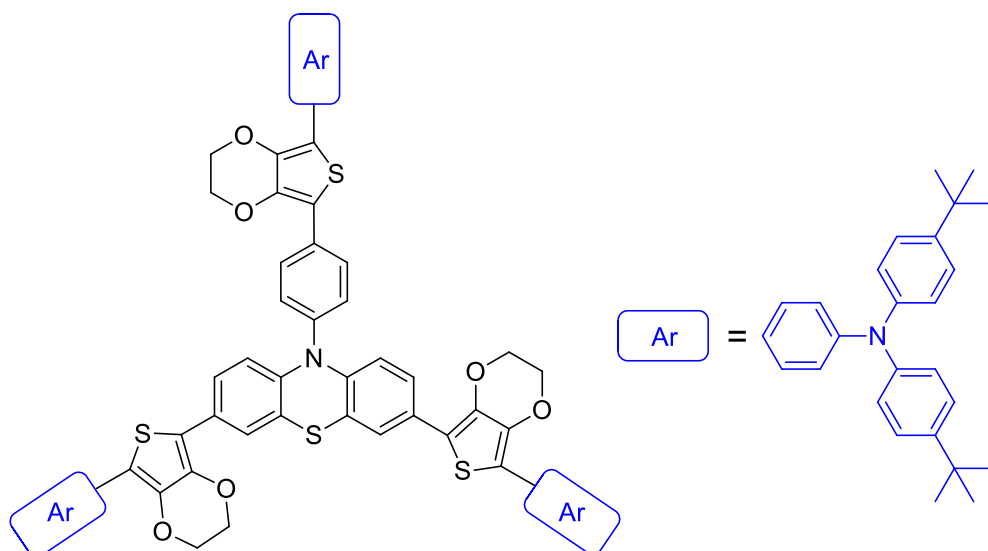
(**10**) was prepared from **2** (154 mg, 0.30 mmol), **3a** (427 mg, 0.96 mmol), Pd(OAc)<sub>2</sub> (10 mg, 0.045 mmol), P(*o*-tolyl)<sub>3</sub> (27 mg, 0.09 mmol), PivOH (18 mg, 0.18 mmol), K<sub>2</sub>CO<sub>3</sub> (149 mg, 1.08 mmol), and DMF (3 mL) according to the **General Procedure** and giving after column chromatography (dichloromethane : ethyl acetate : hexanes = 55 : 1 : 44) the pure product **10** (304 mg, 63 %). Yellow solid; m.p.: 212-213 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, ppm): δ 7.96 (d, *J* = 8.6 Hz, 2 H), 7.60 (d, *J* = 8.9 Hz, 2 H), 7.53 (d, *J* = 8.9 Hz, 4 H), 7.44 (d, *J* = 2.2 Hz, 2 H), 7.35 (d, *J* = 8.6 Hz, 2 H), 7.17 (dd, *J* = 8.7, 2.2 Hz, 2 H), 7.12-7.03 (comp, 12 H), 6.99-6.90 (comp, 6 H), 6.88-6.79 (comp, 12 H), 6.23 (d, *J* = 8.7 Hz, 2 H), 4.40-4.20 (comp, 12 H), 3.85-3.75 (comp, 18 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, ppm): δ 155.9, 155.7, 147.5, 147.1, 141.9, 140.8, 140.7, 139.2, 138.3, 138.0, 137.5, 137.4, 133.2, 130.8, 127.9, 127.6, 126.8, 126.6, 126.5, 126.4, 125.2, 124.8, 124.3, 123.8, 120.7, 120.5, 119.7, 116.7, 115.9, 114.8, 114.7, 114.6, 113.0, 112.8, 64.6, 64.5, 55.4; HRMS (MALDI): calcd. for C<sub>96</sub>H<sub>76</sub>N<sub>4</sub>O<sub>12</sub>S<sub>4</sub>: 1605.4415, found: 1605.4477 ([M+H]<sup>+</sup>).



(**11**) was prepared from **2** (154 mg, 0.30 mmol), **3b** (563 mg, 0.96 mmol), Pd(OAc)<sub>2</sub> (10 mg, 0.045 mmol), P(*o*-tolyl)<sub>3</sub> (27 mg, 0.09 mmol), PivOH (18 mg, 0.18 mmol), K<sub>2</sub>CO<sub>3</sub> (149 mg, 1.08 mmol), and DMF (3 mL) according to the **General Procedure** and giving after column chromatography (dichloromethane : hexanes = 45 : 55) the pure product **11** (395 mg, 65 %). Yellow solid; m.p.: 145-146 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, ppm): δ 7.97 (d, *J* = 8.0 Hz, 2 H), 7.60 (d, *J* = 8.5 Hz, 2 H), 7.52 (d, *J* = 8.1 Hz, 4 H), 7.43 (s, 2 H), 7.35 (d, *J* = 8.0 Hz, 2 H), 7.17 (app s, 2 H), 7.08-7.01 (comp, 12 H), 6.99-6.90 (comp, 6 H), 6.88-6.75 (comp, 12 H), 6.22 (app s, 2 H), 4.43-4.23 (comp, 12 H), 4.01-3.85 (comp, 12 H), 1.85-1.70 (comp, 12 H), 1.53-1.47 (comp, 12 H), 1.42-1.33 (comp, 24 H), 1.01-0.87 (comp, 18 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, ppm): δ 155.5, 155.4, 147.6, 147.2, 140.6, 140.5, 139.3, 138.1, 138.0, 137.4, 137.5, 133.3, 130.8, 127.9, 126.8, 126.6, 126.5, 126.4, 124.7, 124.3, 120.6, 120.4, 116.8, 115.9, 115.24, 115.20, 113.0, 112.7, 68.2, 64.7, 64.5, 31.6, 29.3, 25.7, 22.6, 14.0; HRMS (MALDI): calcd. for C<sub>126</sub>H<sub>136</sub>N<sub>4</sub>O<sub>12</sub>S<sub>4</sub>: 2024.9032, found: 2024.9016 (M<sup>+</sup>).



**(12)** was prepared from **2** (154 mg, 0.30 mmol), **3c** (458 mg, 0.96 mmol), Pd(OAc)<sub>2</sub> (10 mg, 0.045 mmol), P(*o*-tolyl)<sub>3</sub> (27 mg, 0.09 mmol), PivOH (18 mg, 0.18 mmol), K<sub>2</sub>CO<sub>3</sub> (149 mg, 1.08 mmol), and DMF (3 mL) according to the **General Procedure** and giving after column chromatography (dichloromethane : hexanes = 50 : 50) the pure product **12** (286 mg, 56 %). Orange solid; m.p.: 229-230 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, ppm): δ 7.96 (d, *J* = 8.4 Hz, 2 H), 7.65 (d, *J* = 8.6 Hz, 2 H), 7.58 (d, *J* = 8.6 Hz, 4 H), 7.43 (s, 2 H), 7.35 (d, *J* = 8.4 Hz, 2 H), 7.22 -7.13 (comp, 14 H), 7.08-7.00 (comp, 18 H), 6.22 (d, *J* = 8.6 Hz, 2 H), 4.40-4.25 (comp, 12 H), 2.50-2.41 (comp, 18 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, ppm): δ 146.0, 145.6, 145.0, 144.9, 142.0, 139.2, 138.0, 133.1, 132.0, 131.8, 130.9, 128.5, 128.0, 127.5, 127.4, 127.0, 126.8, 124.8, 124.7, 124.4, 123.9, 123.5, 123.4, 119.7, 116.2, 115.9, 114.3, 113.7, 113.4, 64.7, 64.5, 16.8, 16.7; HRMS (MALDI): calcd. for C<sub>96</sub>H<sub>76</sub>N<sub>4</sub>O<sub>6</sub>S<sub>10</sub>: 1701.3045, found: 1701.3046 ([M+H]<sup>+</sup>).

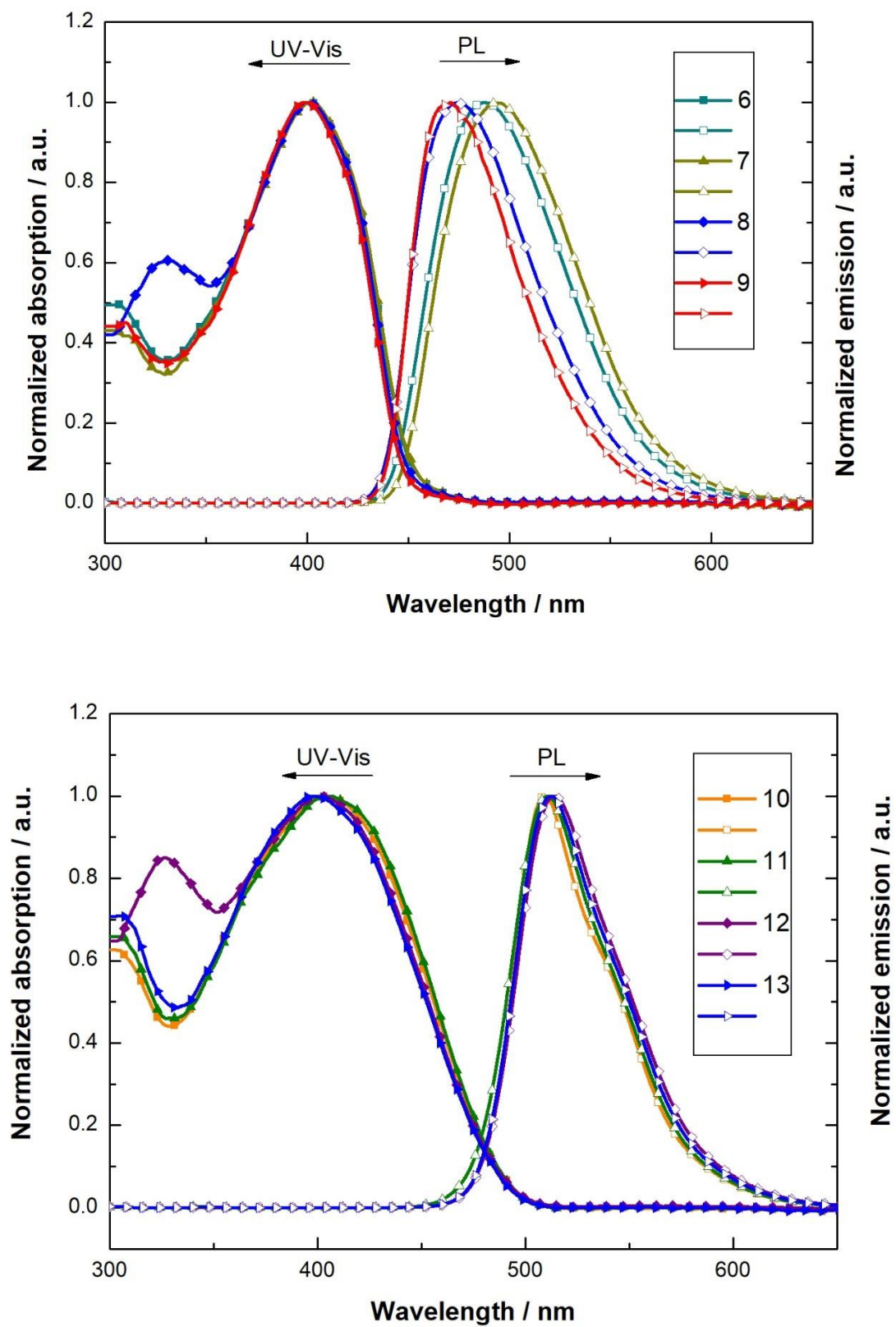


**(13)** was prepared from **2** (154 mg, 0.30 mmol), **3d** (477 mg, 0.96 mmol), Pd(OAc)<sub>2</sub> (10 mg, 0.045 mmol), P(*o*-tolyl)<sub>3</sub> (27 mg, 0.09 mmol), PivOH (18 mg, 0.18 mmol), K<sub>2</sub>CO<sub>3</sub> (149 mg, 1.08 mmol), and DMF (3 mL) according to the **General Procedure** and giving after column chromatography (dichloromethane : hexanes = 35 : 65) the pure product **13** (354 mg, 67 %). Yellow solid; m.p.: 269-271 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, ppm): δ 7.99 (app s, 2 H), 7.64 (d, *J* = 8.8 Hz, 2 H), 7.63- 7.57 (app s, 4 H), 7.45 (app s, 2 H), 7.37 (app s, 2 H), 7.33-7.26 (comp, 12 H), 7.19-6.94 (comp, 20 H), 6.26 (app s, 2 H), 4.50-4.22 (comp, 12 H), 1.40-1.30 (comp, 54 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, ppm): δ 146.9, 146.5, 145.8, 145.6, 144.8, 139.3, 138.1, 137.7, 133.3, 128.0, 126.9, 126.7, 126.0,

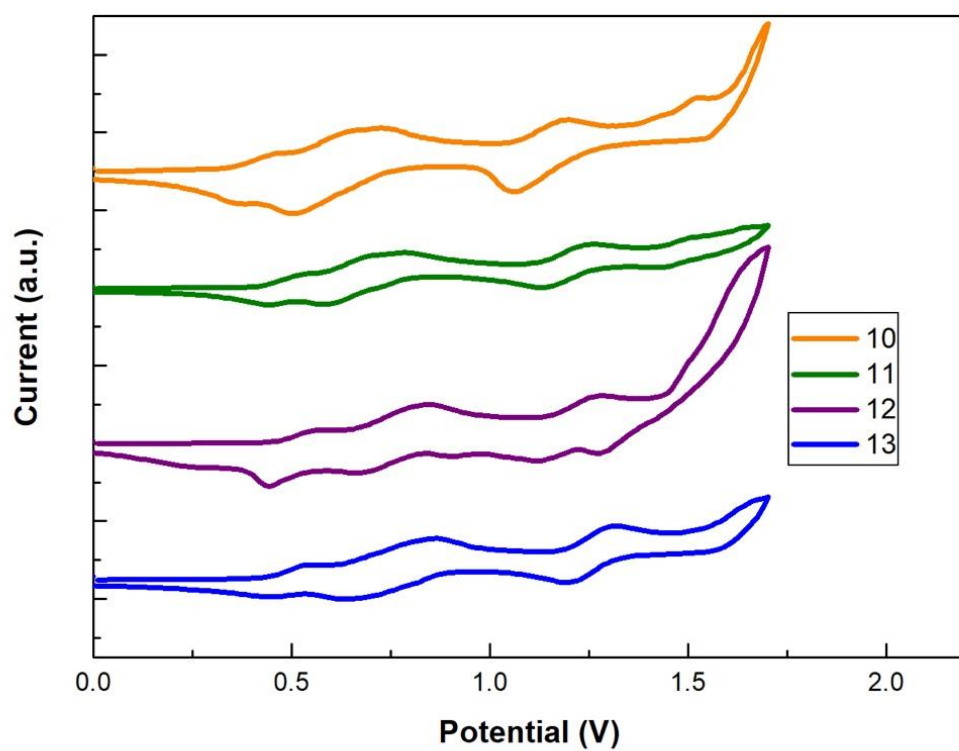
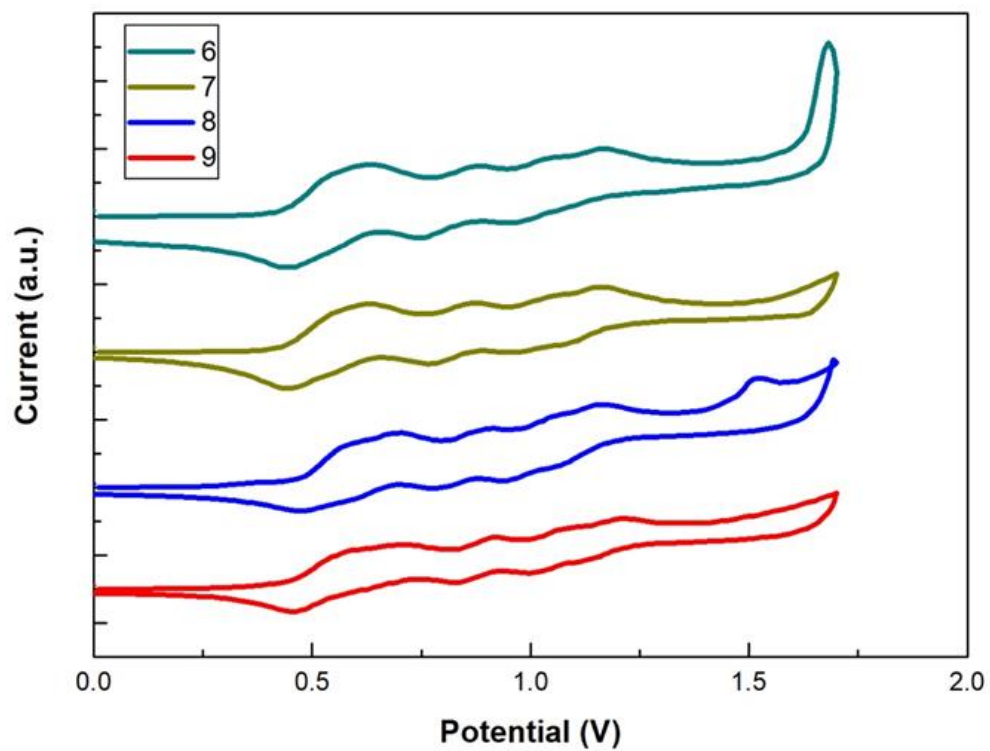


125.9, 124.4, 124.1, 123.9, 123.0, 122.8, 116.6, 115.9, 113.3, 113.1, 64.7, 64.5, 34.3, 31.4; HRMS (MALDI): calcd. for  $C_{114}H_{112}N_4O_6S_4$ : 1761.7537, found: 1761.7543 ( $[M+H]^+$ ).

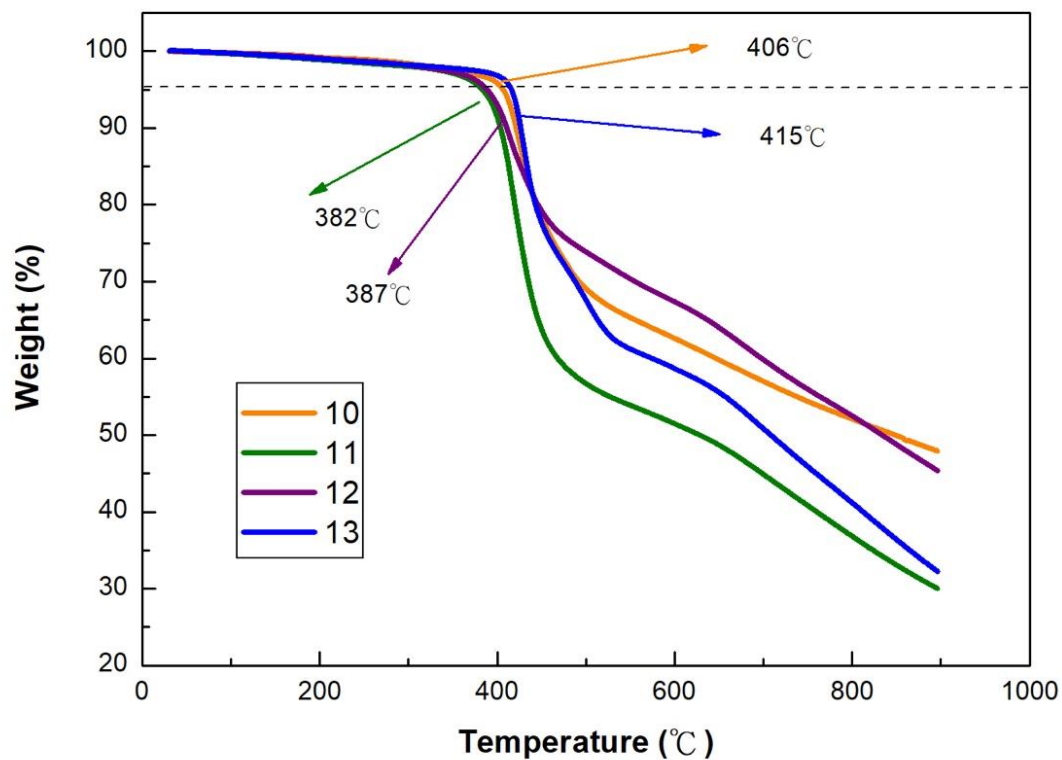
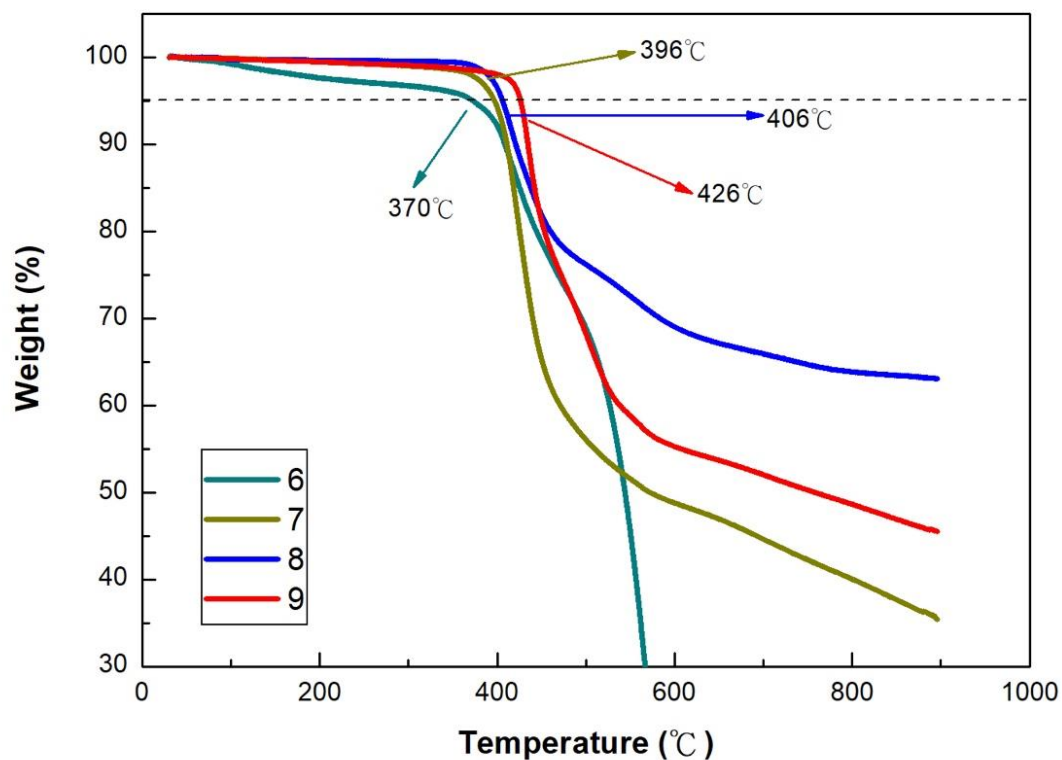
**Figure S1.** The UV-Vis absorption and photoluminescence spectra of **6~13** in  $\text{CH}_2\text{Cl}_2$  solution.



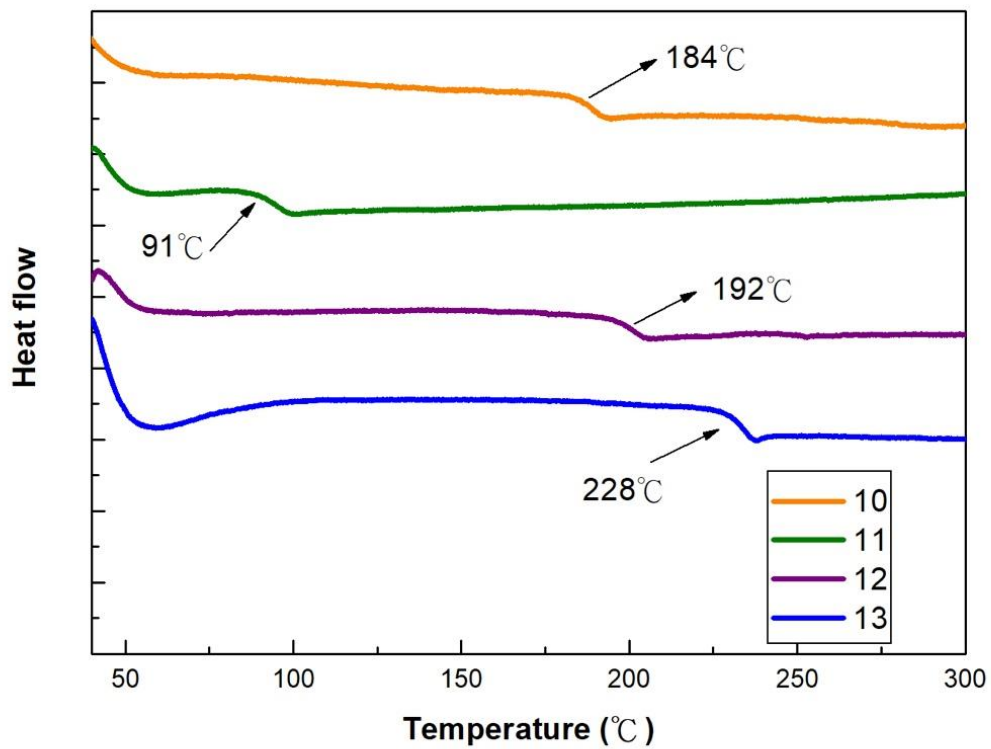
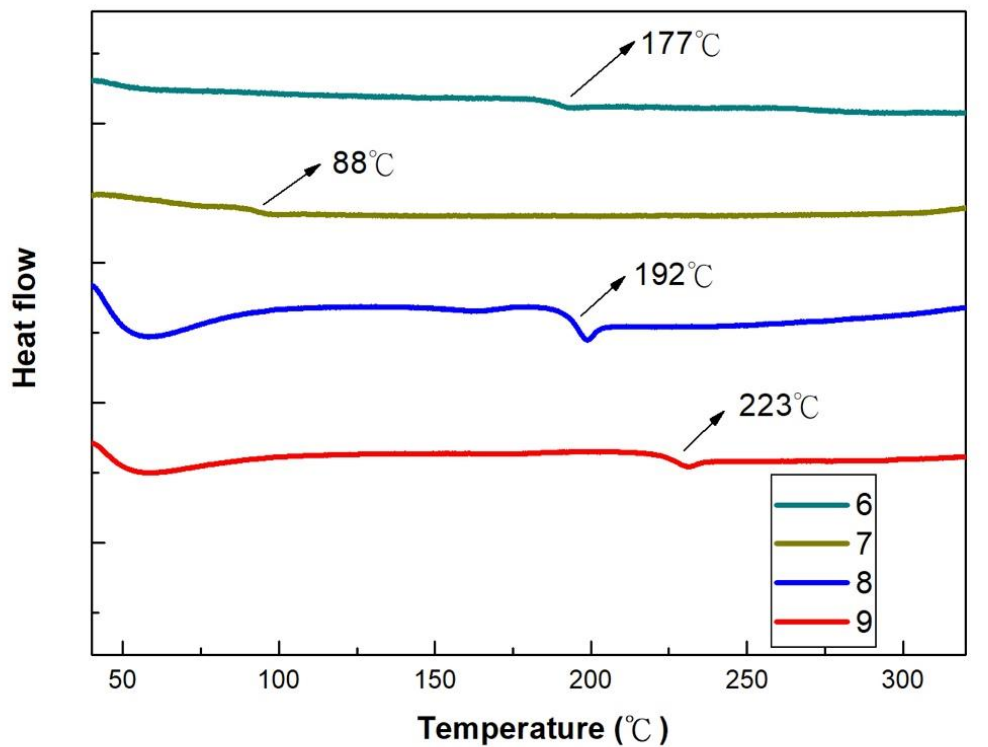
**Figure S2.** Cyclic voltammetry spectra of **6~13** in CH<sub>2</sub>Cl<sub>2</sub> solution.



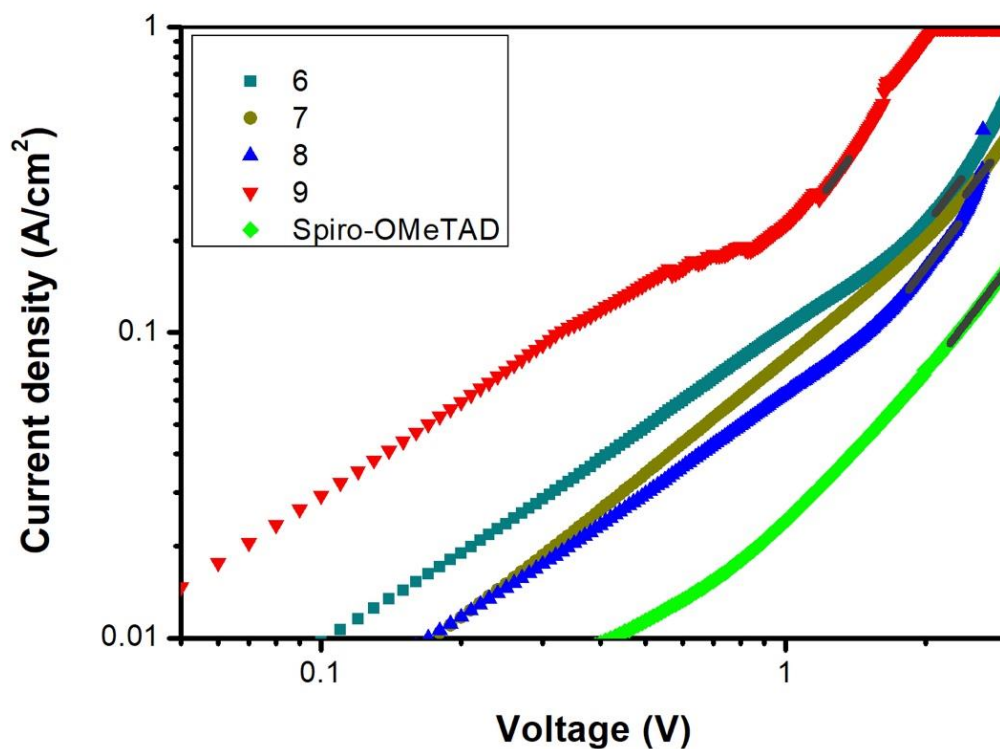
**Figure S3.** Thermogravimetric analysis (TGA) curves of **6~13**.



**Figure S4.** Differential scanning calorimetry (DSC) curves of **6~13**.

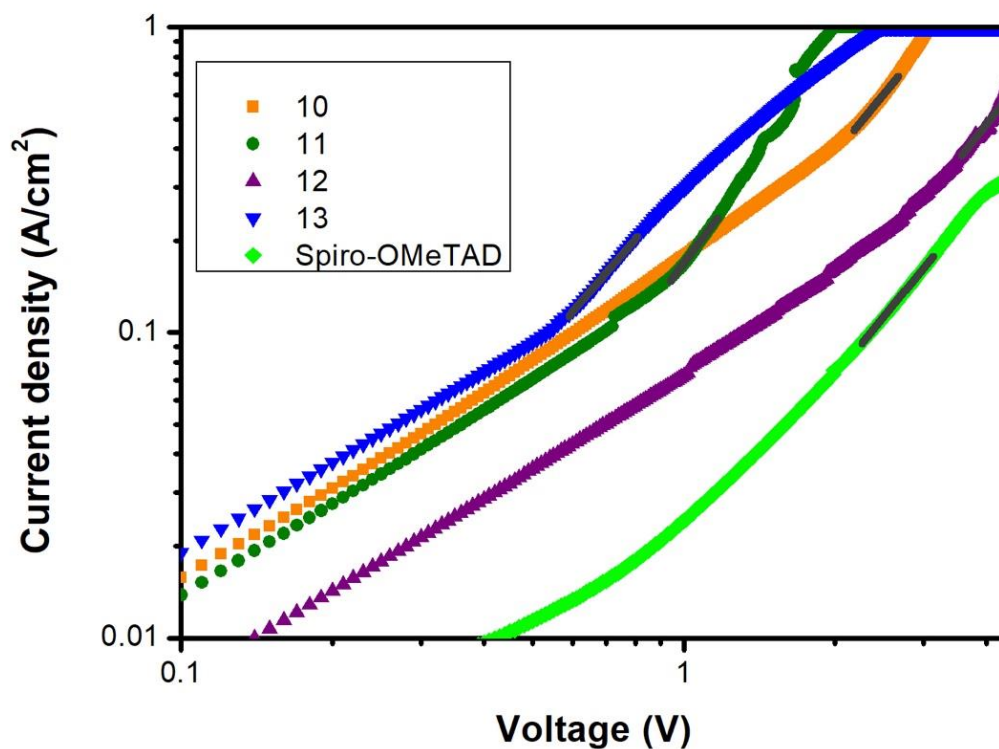


**Figure S5.** J-V curves for the determination of the hole mobility of HTMs in the space-charge limited current (SCLC) region (6~9).



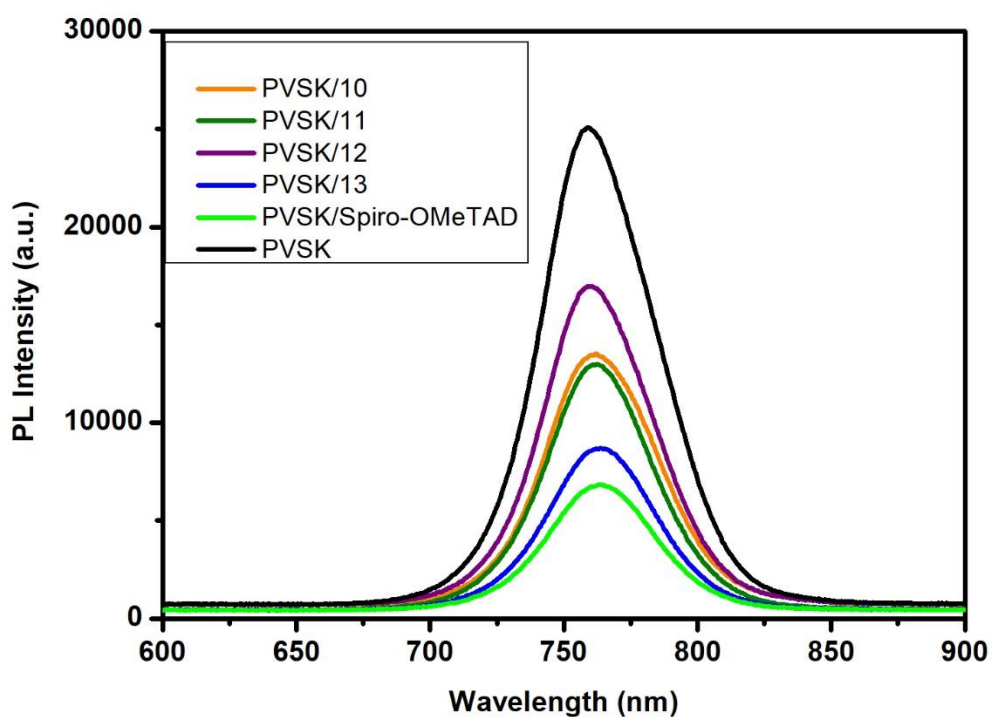
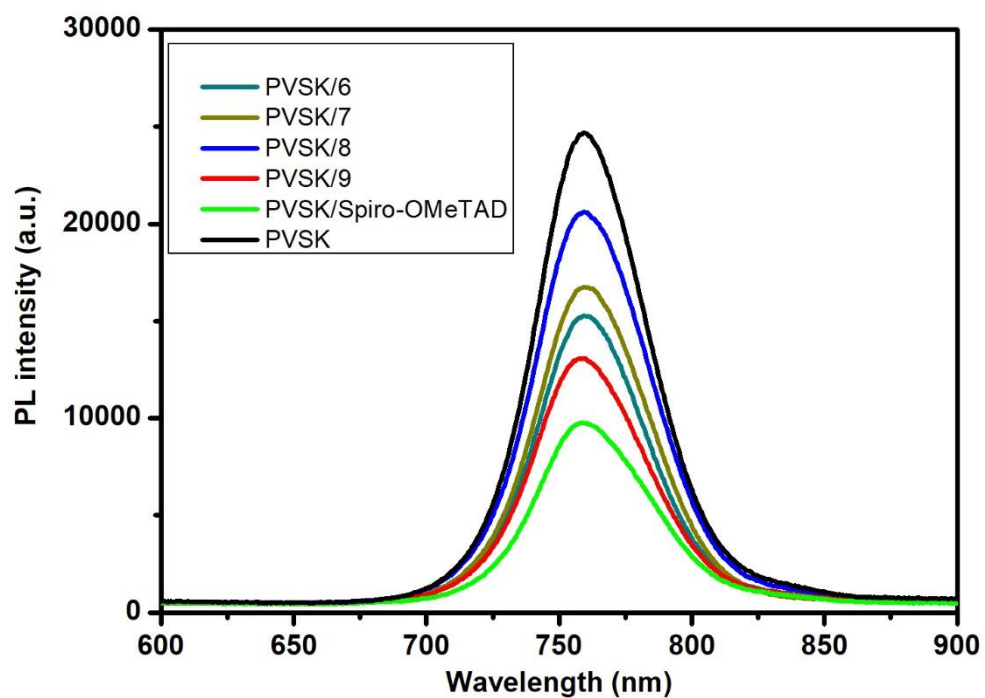
HTMs	hole mobility, $\mu$ ( $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ )
<b>6</b>	$1.71 \times 10^{-4}$
<b>7</b>	$1.59 \times 10^{-4}$
<b>8</b>	$1.35 \times 10^{-4}$
<b>9</b>	$6.46 \times 10^{-4}$
<b>spiro-OMeTAD</b>	$8.38 \times 10^{-4}$

**Figure S6.** J-V curves for the determination of the hole mobility of HTMs in the space-charge limited current (SCLC) region (**10~13**).



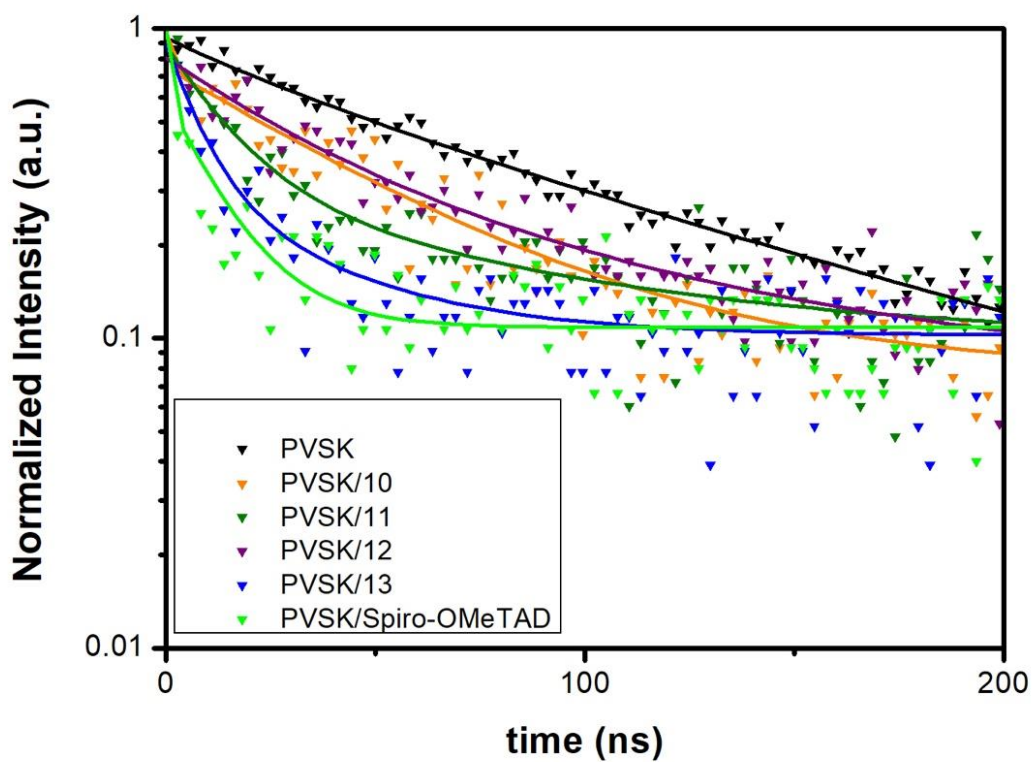
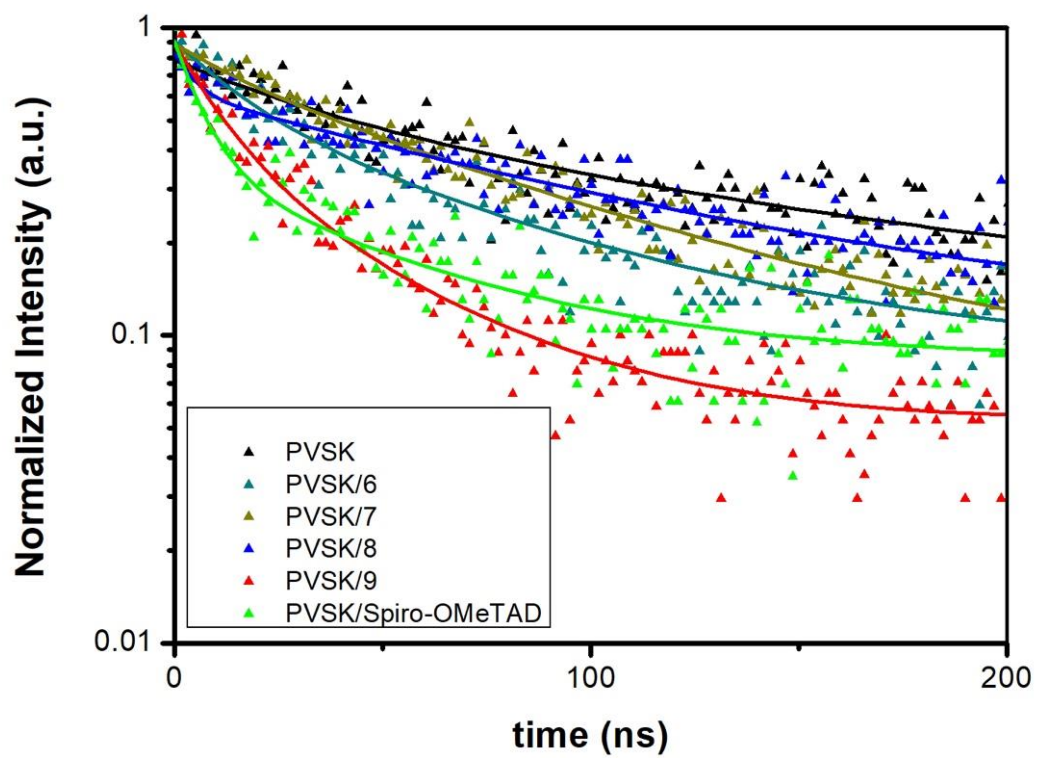
HTMs	hole mobility, $\mu$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )
<b>10</b>	$2.34 \times 10^{-4}$
<b>11</b>	$4.10 \times 10^{-4}$
<b>12</b>	$6.68 \times 10^{-5}$
<b>13</b>	$7.53 \times 10^{-4}$
<b>spiro-OMeTAD</b>	$8.38 \times 10^{-4}$

**Figure S7.** Steady-state PL spectra of the devices fabricated as glass/perovskite/HTMs.

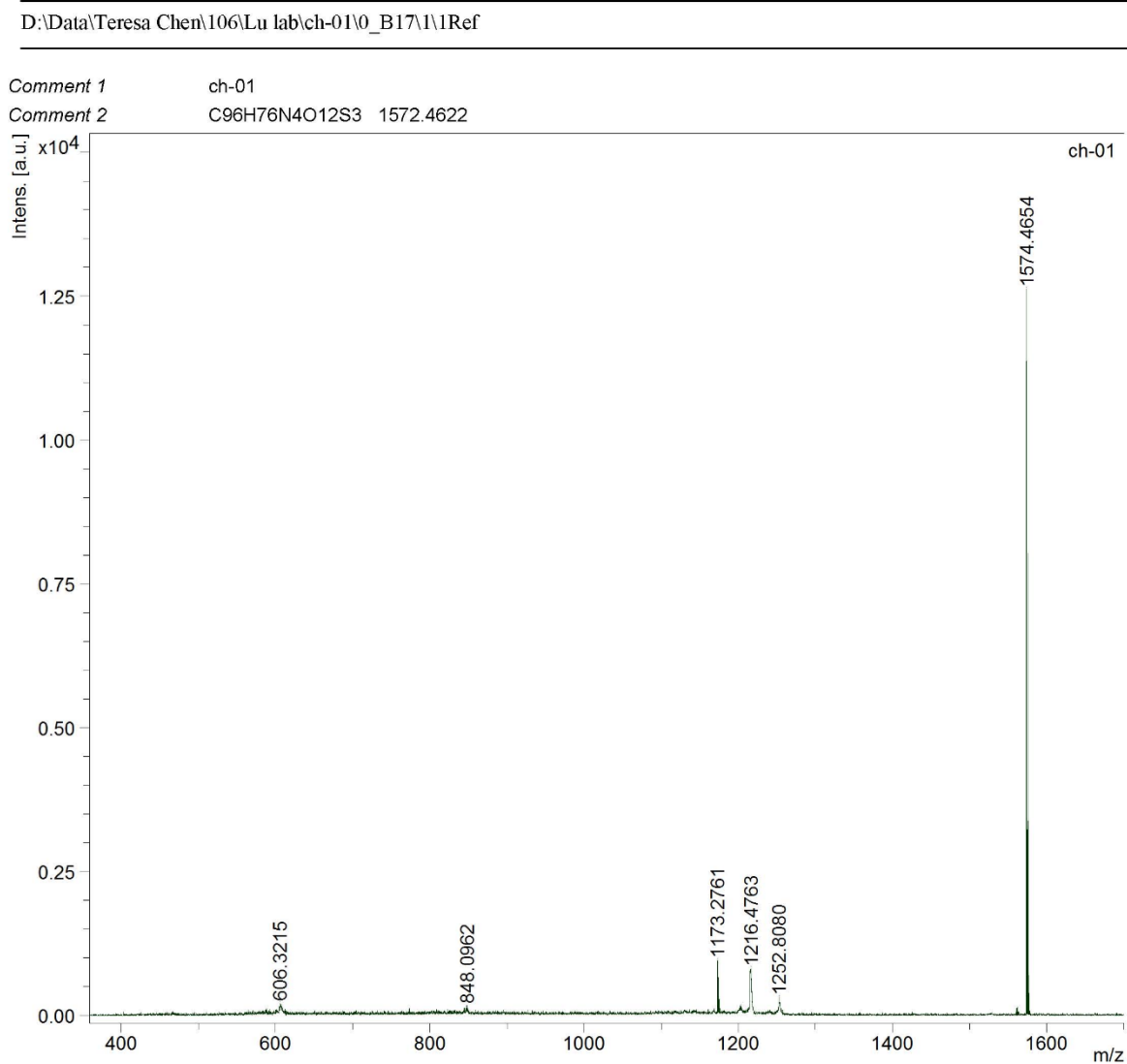




**Figure S8.** Time-resolved PL spectra of the devices fabricated as glass/perovskite/HTMs.



**Figure S9.** Mass Spectrum of **6** (MALDI).



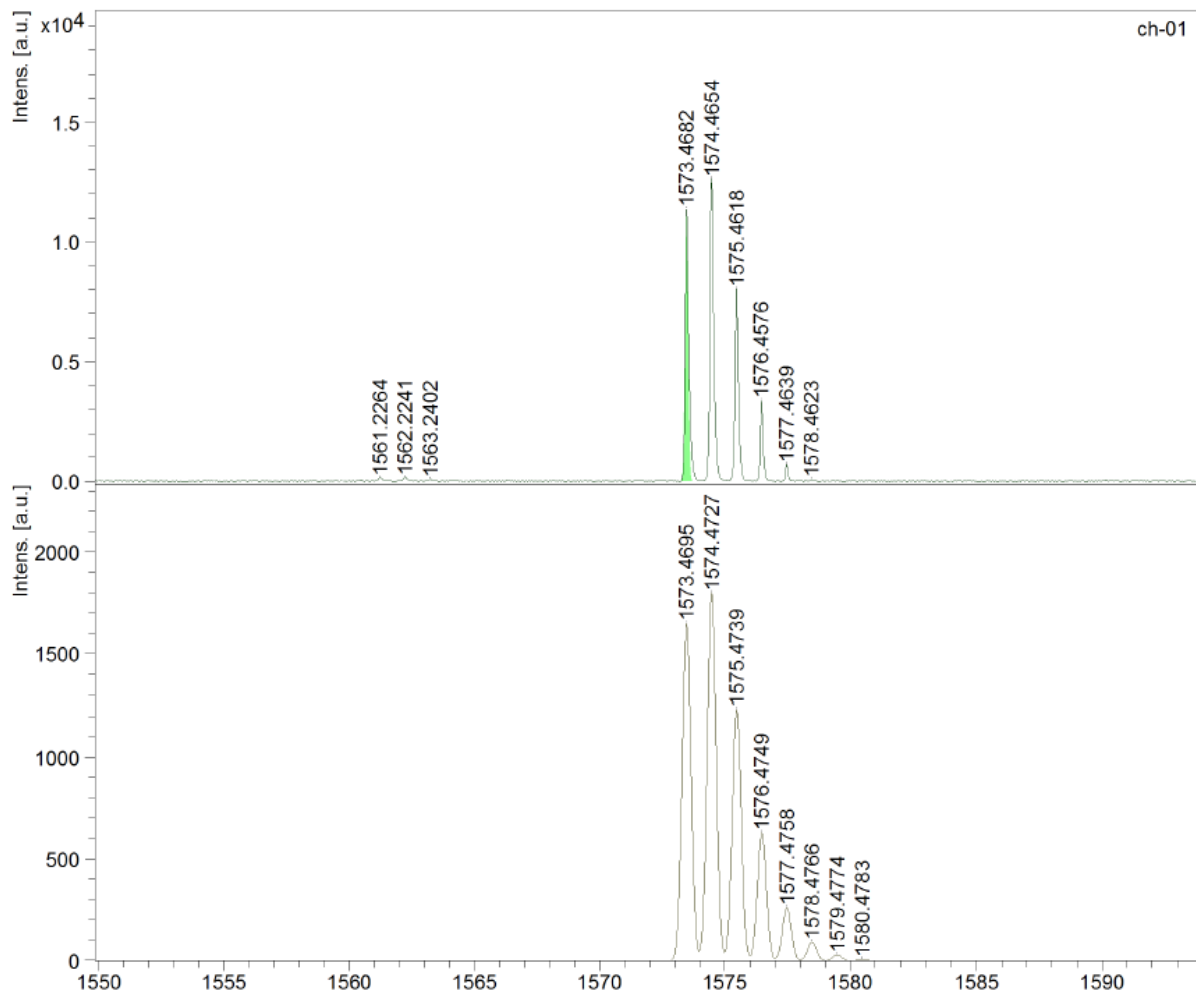
**Acquisition Parameter**

Date of acquisition 2017-08-29T17:20:57.915+08:00  
Acquisition method name D:\Methods\flexControl\Methods\Teresac\RP\_UltraMark 1000-1500\_Da.par  
Acquisition operation mode Reflector  
Voltage polarity POS  
Number of shots 2000  
Name of spectrum used for calibration  
Calibration reference list used Ultramark1621

**Instrument Info**

User NCU  
Instrument ATS-00670  
Instrument type autoflex

Comment 1 ch-01  
 Comment 2 C96H76N4O12S3 1572.4622



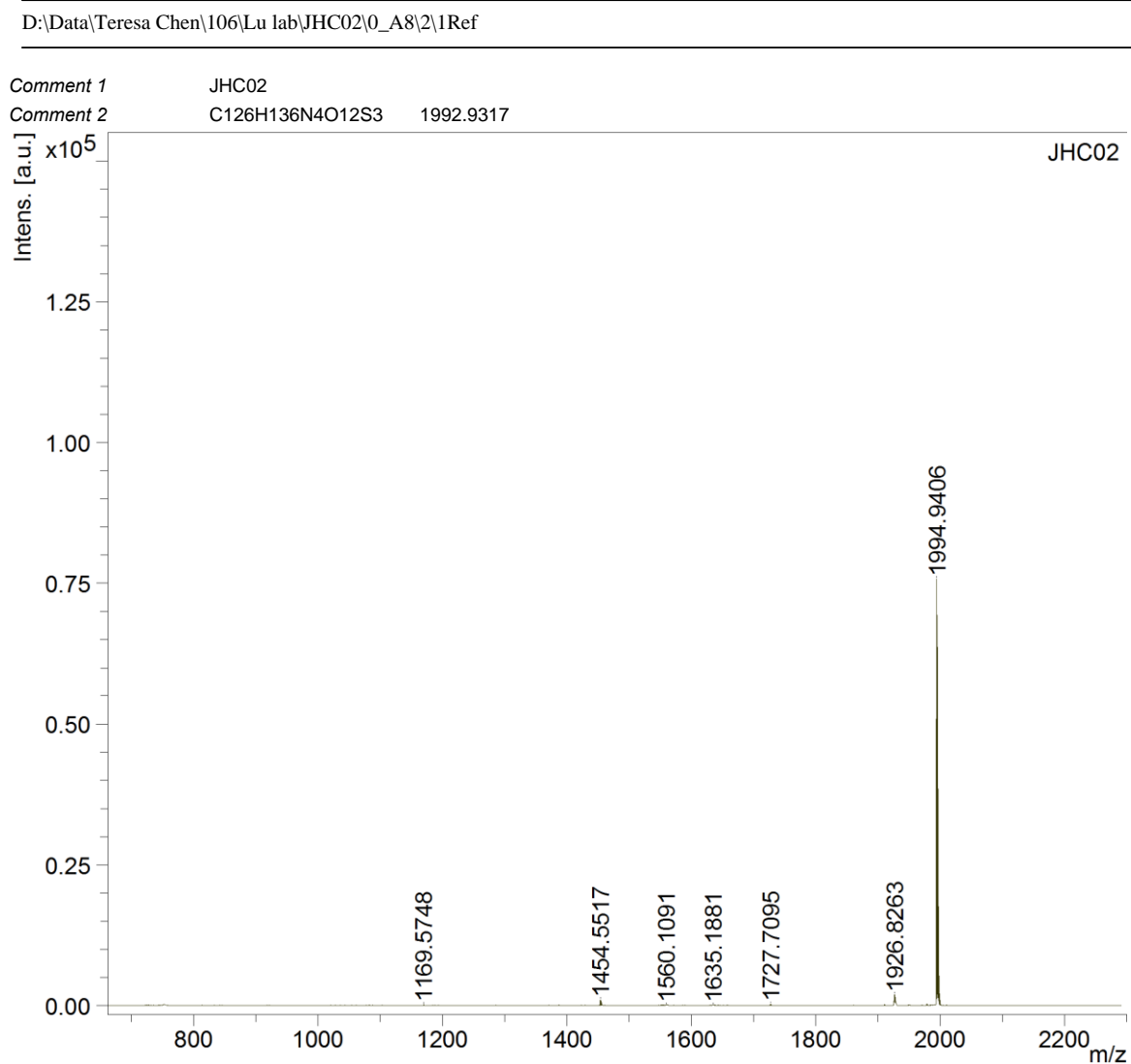
**Acquisition Parameter**

Date of acquisition 2017-08-29T17:20:57.915+08:00  
 Acquisition method name D:\Methods\flexControlMethods\Teresac\RP\_UltraMark 1000-1500\_Da.par  
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 Voltage polarity POS  
 Number of shots 2000  
 Name of spectrum used for calibration  
 Calibration reference list used Ultramark1621

**Instrument Info**

User NCU  
 Instrument ATS-00670  
 Instrument type autoflex

**Figure S10.** Mass Spectrum of **7** (MALDI).



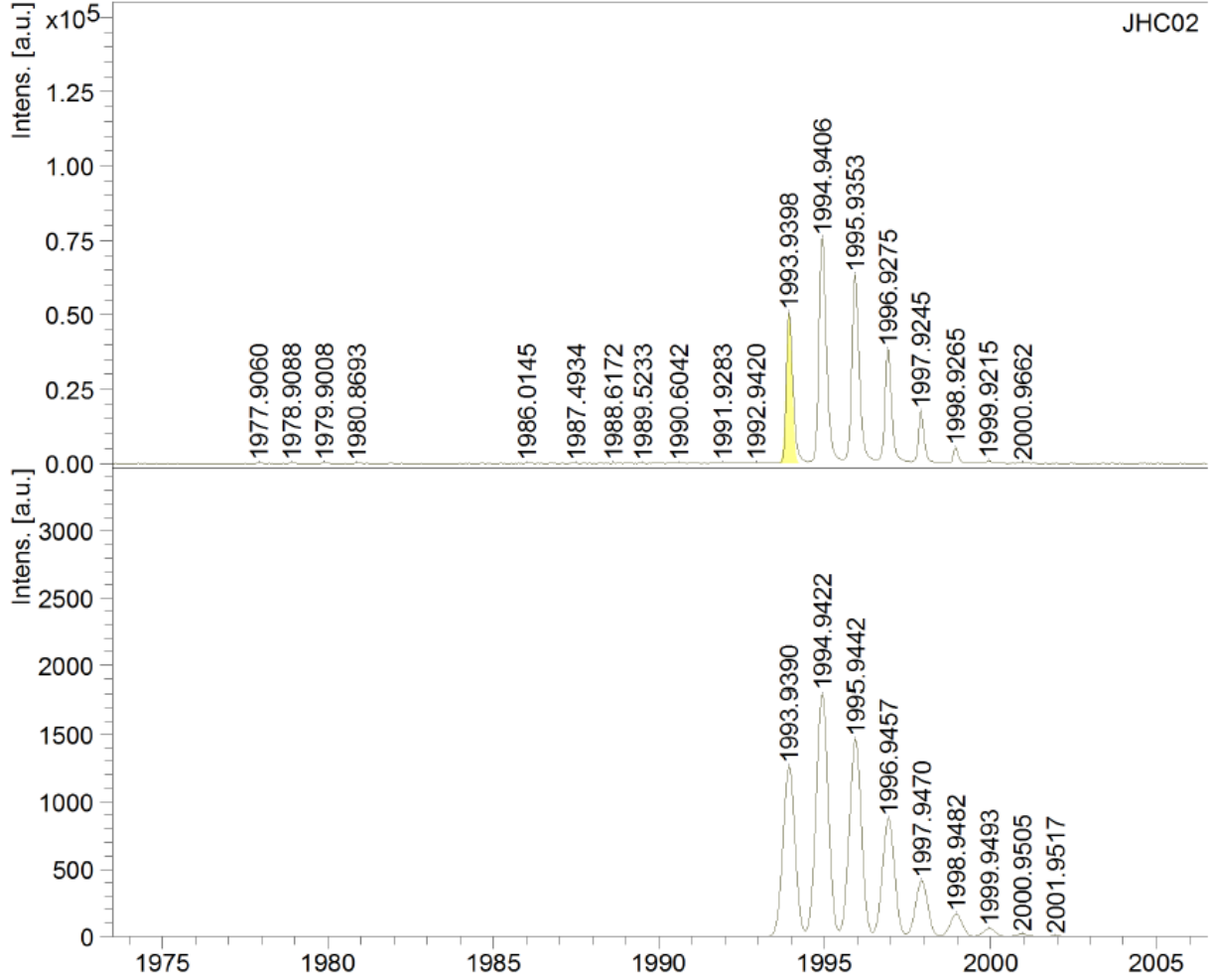
**Acquisition Parameter**

Date of acquisition 2017-11-09T16:01:35.870+08:00  
Acquisition method name D:\Methods\flexControlMethods\Teresac\RP\_UltraMark 1500-2000Da.par  
Acquisition operation mode Reflector  
Voltage polarity POS  
Number of shots 2000  
Name of spectrum used for calibration  
Calibration reference list used Ultramark1500-2000 Da

**Instrument Info**

User NCU  
Instrument ATS-00670  
Instrument type autoflex

Comment 1 JHC02  
Comment 2 C126H136N4O12S3 1992.9317



**Acquisition Parameter**

Date of acquisition 2017-11-09T16:01:35.870+08:00  
Acquisition method name D:\Methods\flexControlMethods\Teresac\RP\_UltraMark\_1500-2000Da.par  
Acquisition operation mode Reflector  
Voltage polarity POS  
Number of shots 2000  
Name of spectrum used for calibration  
Calibration reference list used Ultramark1500-2000 Da

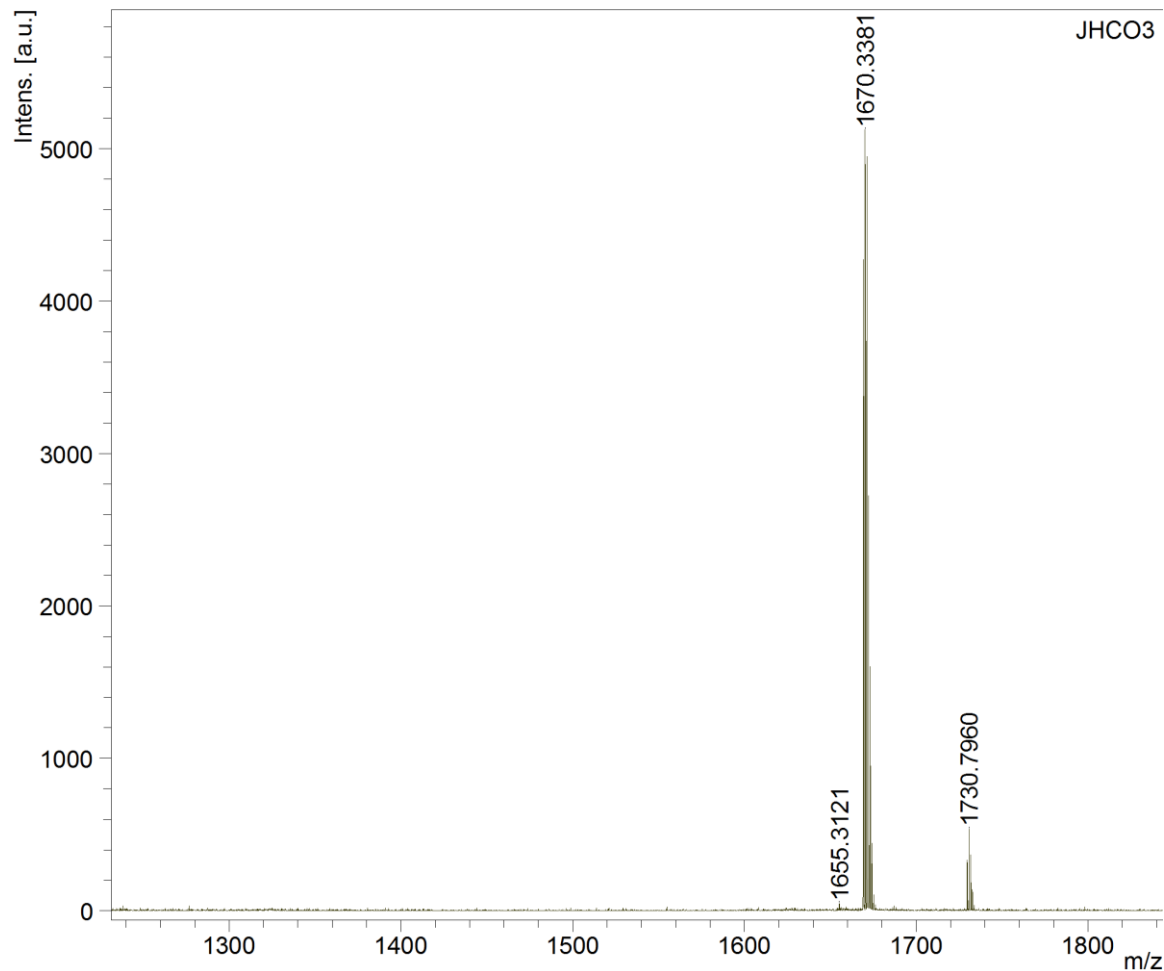
**Instrument Info**

User NCU  
Instrument ATS-00670  
Instrument type autoflex

**Figure S11.** Mass Spectrum of **8** (MALDI).

D:\Data\Teresa Chen\106\Lu lab\JHCO3\0\_A7\1\1Ref

Comment 1 JHCO3  
Comment 2 1668.3251



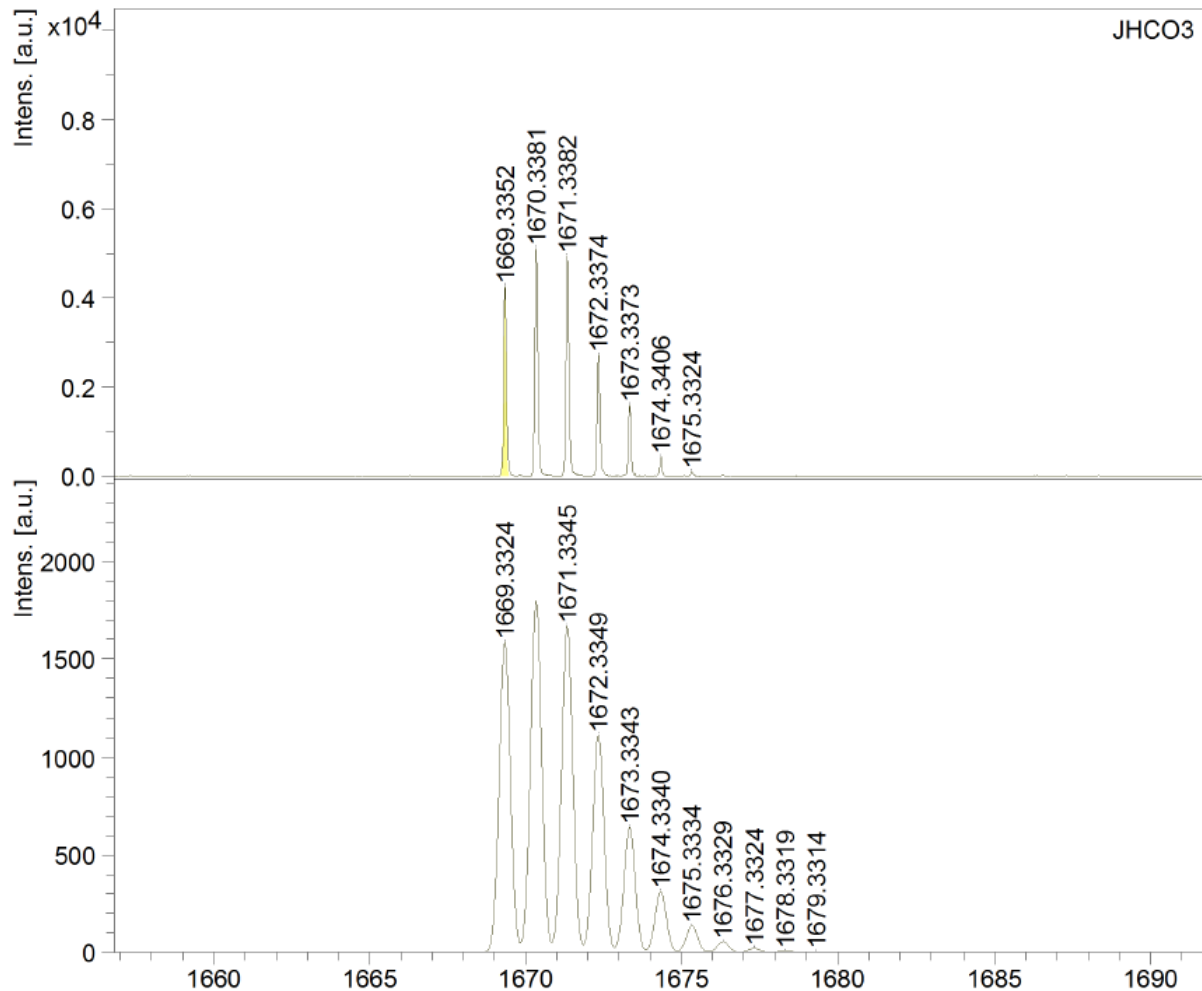
**Acquisition Parameter**

Date of acquisition 2017-11-09T15:21:46.188+08:00  
Acquisition method name D:\Methods\flexControl\Methods\Teresac\RP\_UltraMark 1000-1500\_Da.par  
Acquisition operation mode Reflector  
Voltage polarity POS  
Number of shots 2000  
Name of spectrum used for calibration  
Calibration reference list used Ultramark1621

**Instrument Info**

User NCU  
Instrument ATS-00670  
Instrument type autoflex

Comment 1 JHCO3  
 Comment 2 1668.3251



**Acquisition Parameter**

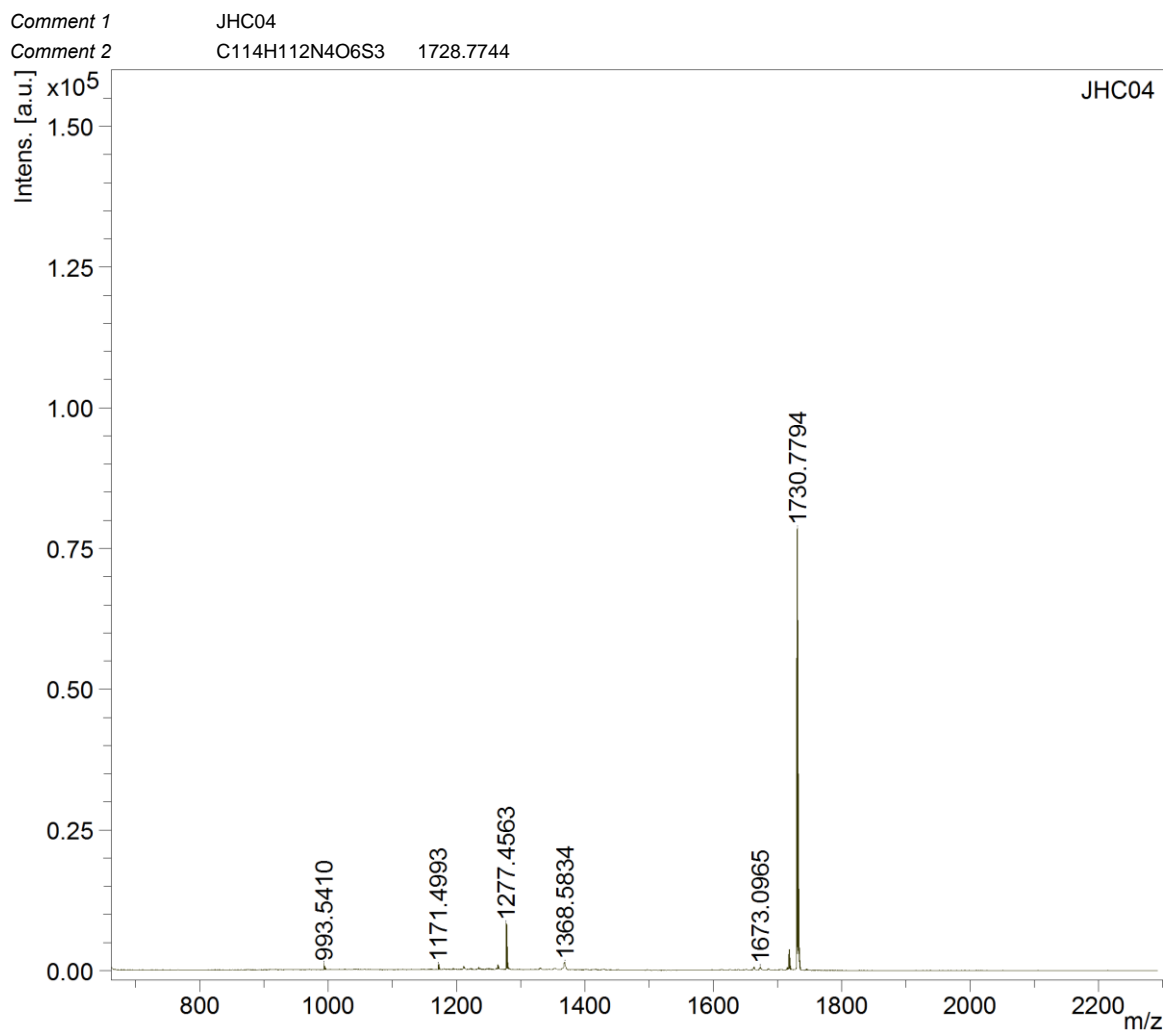
Date of acquisition 2017-11-09T15:21:46.188+08:00  
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 Acquisition operation mode Reflector  
 Voltage polarity POS  
 Number of shots 2000  
 Name of spectrum used for calibration  
 Calibration reference list used Ultramark1621

**Instrument Info**

User NCU  
 Instrument ATS-00670  
 Instrument type autoflex

**Figure S12.** Mass Spectrum of **9** (MALDI).

D:\Data\Teresa Chen\106\Lu lab\JHC04\0\_A6\1\1Ref



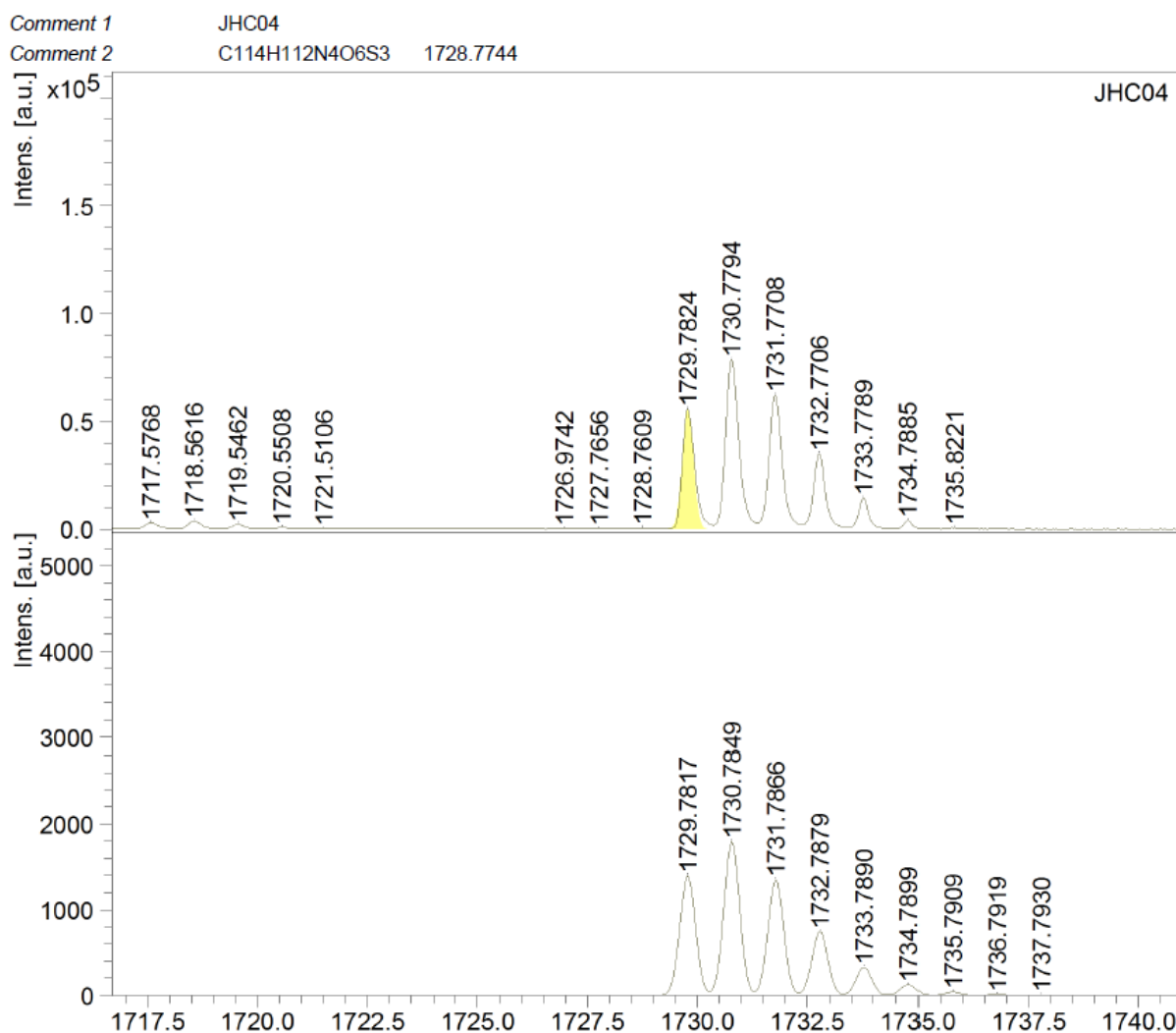
**Acquisition Parameter**

Date of acquisition 2017-11-09T16:19:32.790+08:00  
Acquisition method name D:\Methods\flexControl\Methods\Teresac\RP\_UltraMark 1500-2000Da.par  
Acquisition operation mode Reflector  
Voltage polarity POS  
Number of shots 2000  
Name of spectrum used for calibration  
Calibration reference list used Ultramark1500-2000 Da

**Instrument Info**

User NCU  
Instrument ATS-00670  
Instrument type autoflex





**Acquisition Parameter**

Date of acquisition 2017-11-09T16:19:32.790+08:00  
 Acquisition method name D:\Methods\flexControl\Methods\Teresa\IRP\_UltraMark 1500-2000Da.par  
 Acquisition operation mode Reflector  
 Voltage polarity POS  
 Number of shots 2000  
 Name of spectrum used for calibration  
 Calibration reference list used Ultramark1500-2000 Da

**Instrument Info**

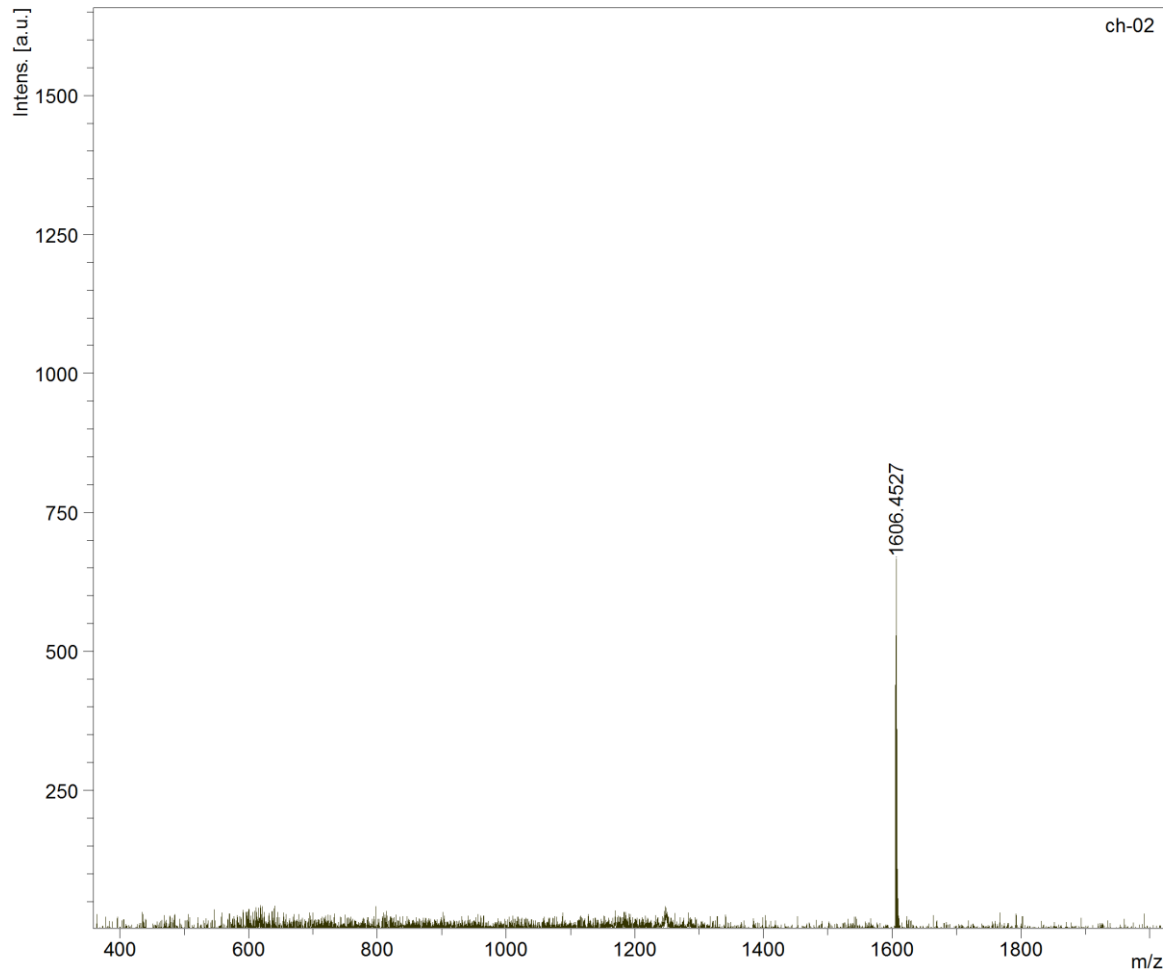
User NCU  
 Instrument ATS-00670  
 Instrument type autoflex

**Figure S13.** Mass Spectrum of **10** (MALDI).

D:\Data\Teresa Chen\106\Lu lab\ch-02\0\_B20\2\1Ref

Comment 1 ch-02

Comment 2 C96H76N4O12S4 1604.4343



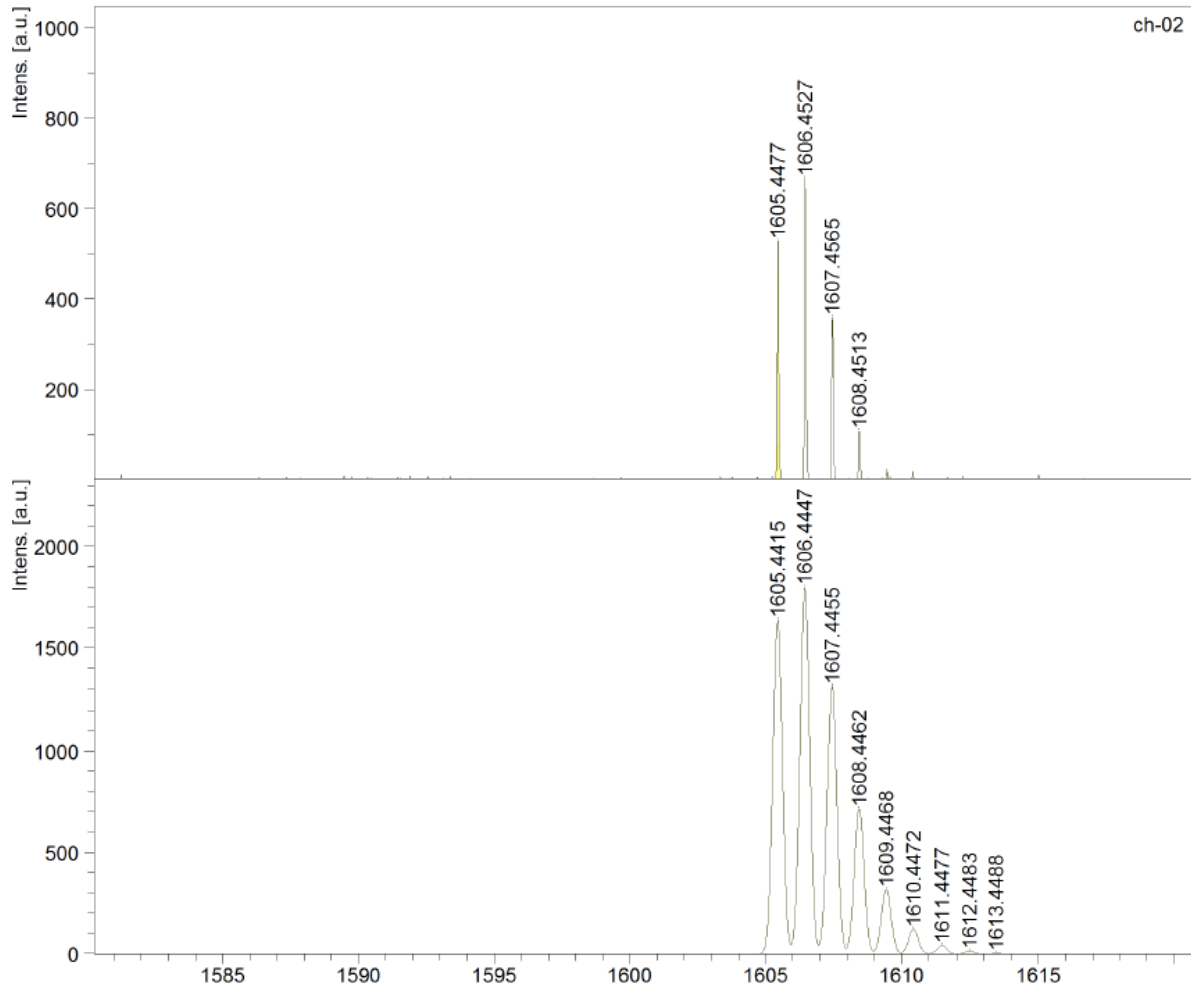
**Acquisition Parameter**

Date of acquisition 2017-08-29T17:36:54.525+08:00  
Acquisition method name D:\Methods\flexControlMethods\Teresa\RP\_UltraMark 1000-1500\_Da.par  
Acquisition operation mode Reflector  
Voltage polarity POS  
Number of shots 2000  
Name of spectrum used for calibration  
Calibration reference list used Ultramark1621

**Instrument Info**

User NCU  
Instrument ATS-00670  
Instrument type autoflex

Comment 1 ch-02  
 Comment 2 C96H76N4O12S4 1604.4343



**Acquisition Parameter**

Date of acquisition 2017-08-29T17:36:54.525+08:00  
 Acquisition method name D:\Methods\flexControlMethods\Teresac\RP\_UltraMark 1000-1500\_Da.par  
 Acquisition operation mode Reflector  
 Voltage polarity POS  
 Number of shots 2000  
 Name of spectrum used for calibration  
 Calibration reference list used Ultramark1621

**Instrument Info**

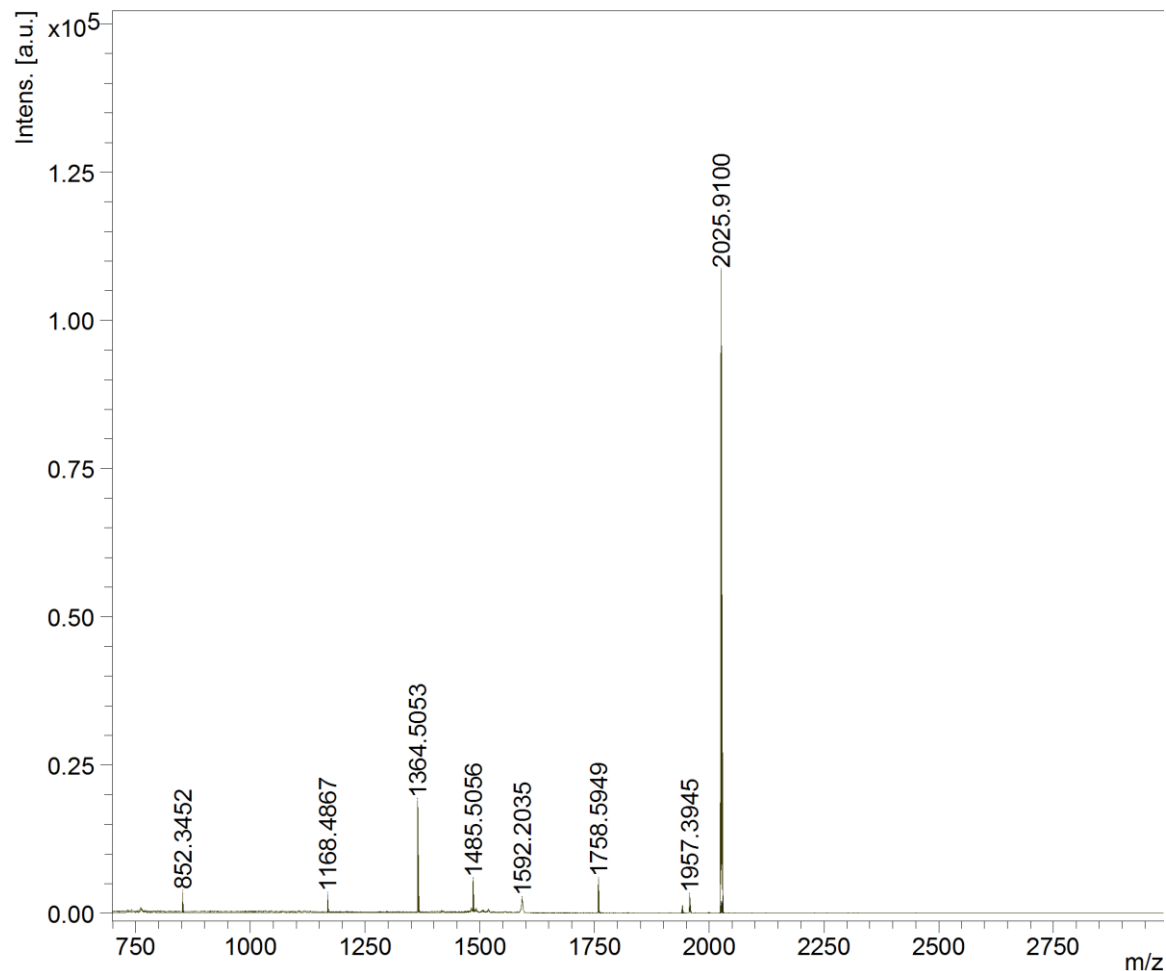
User NCU  
 Instrument ATS-00670  
 Instrument type autoflex

**Figure S14.** Mass Spectrum of **11** (MALDI).

D:\Data\Teresa Chen\106\Lu lab\JHC06\0\_J1\2\1Ref

Comment 1 JHC06

Comment 2 C126H136N4O12S4 2024.9038

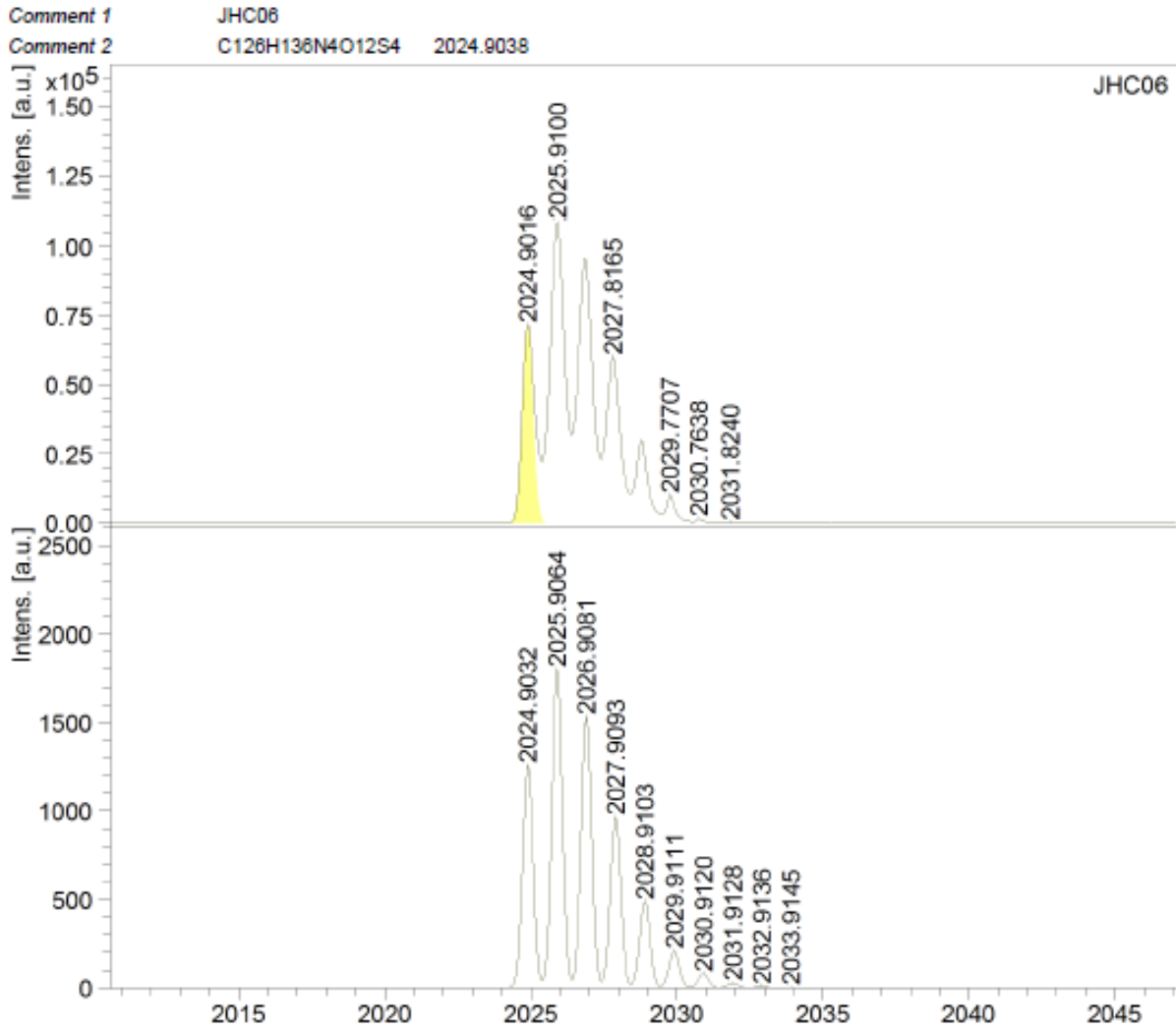


**Acquisition Parameter**

Date of acquisition 2017-12-05T15:19:08.201+08:00  
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Acquisition operation mode Reflector  
Voltage polarity POS  
Number of shots 2000  
Name of spectrum used for calibration  
Calibration reference list used PeptideCalibStandard mono

**Instrument Info**

User NCU  
Instrument ATS-00670  
Instrument type autoflex



**Acquisition Parameter**

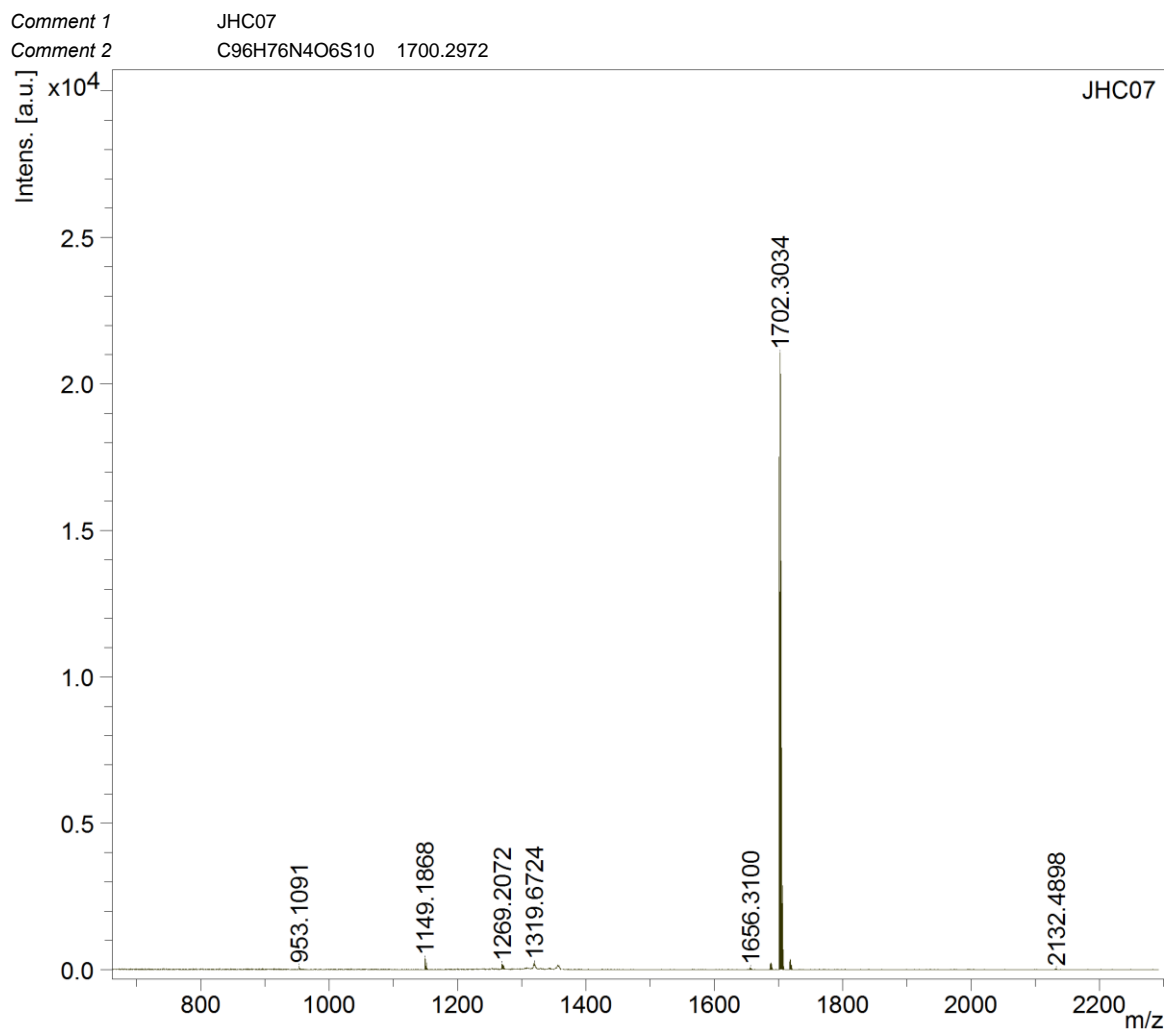
Date of acquisition 2017-12-05T15:19:08.201+08:00  
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 Acquisition operation mode Reflector  
 Voltage polarity POS  
 Number of shots 2000  
 Name of spectrum used for calibration  
 Calibration reference list used PeptideCalbStandard mono

**Instrument Info**

User NCU  
 Instrument ATS-00670  
 Instrument type autoflex

**Figure S15.** Mass Spectrum of **12** (MALDI).

D:\Data\Teresa Chen\106\Lu lab\JHC07\0\_F22\1\1Ref



**Acquisition Parameter**

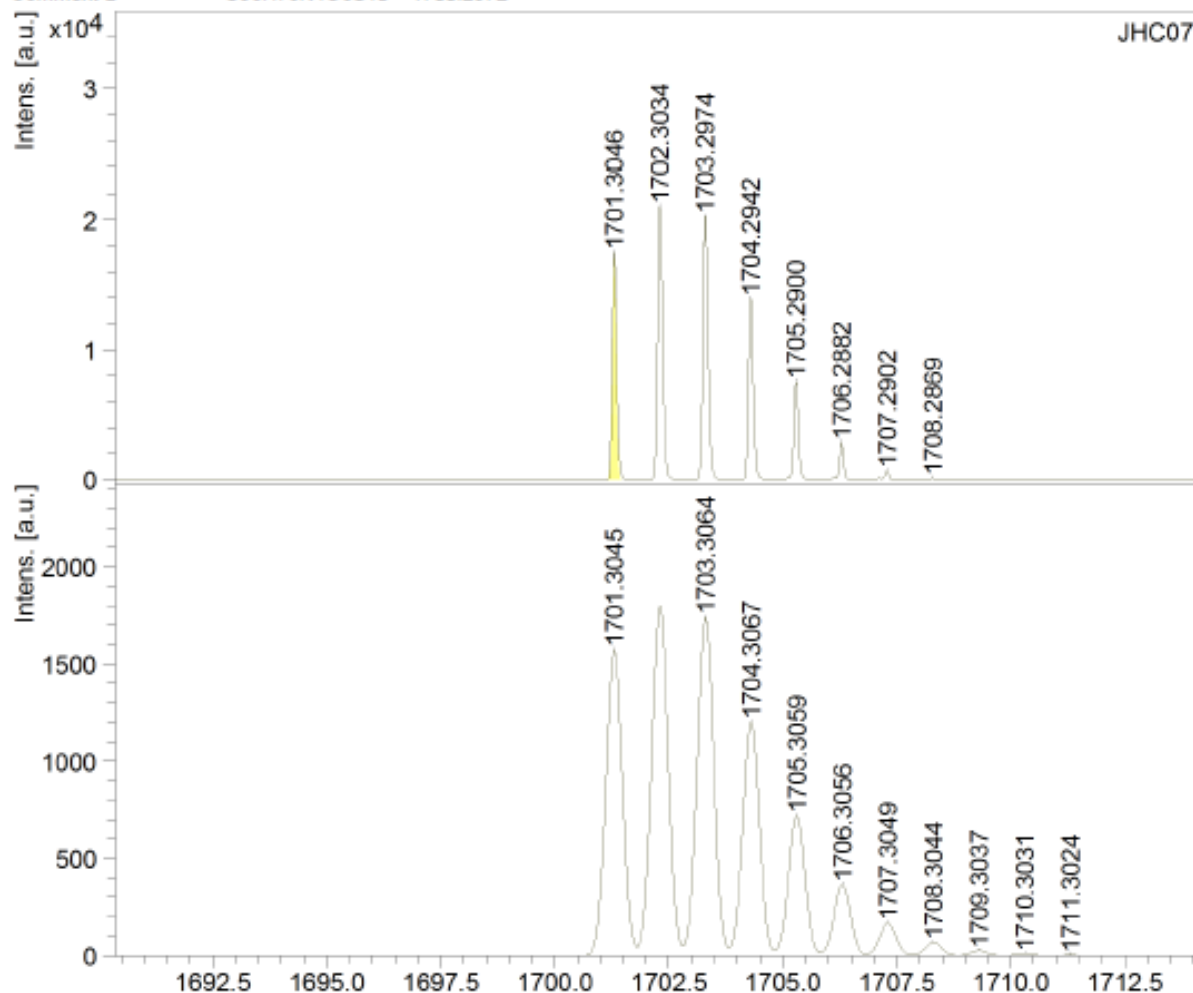
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Acquisition method name D:\Methods\flexControlMethods\Teresac\RP\_UltraMark 1500-2000Da.par  
Acquisition operation mode Reflector  
Voltage polarity POS  
Number of shots 2000  
Name of spectrum used for calibration  
Calibration reference list used Uitrarnark1621

**Instrument Info**

User NCU  
Instrument ATS-00670  
Instrument type autoflex

Comment 1 JHC07

Comment 2 C96H76N4O6S10 1700.2972



**Acquisition Parameter**

Date of acquisition 2017-12-04T15:36:04.968+08:00  
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 Voltage polarity POS  
 Number of shots 2000  
 Name of spectrum used for calibration  
 Calibration reference list used Ultramark1621

**Instrument Info**

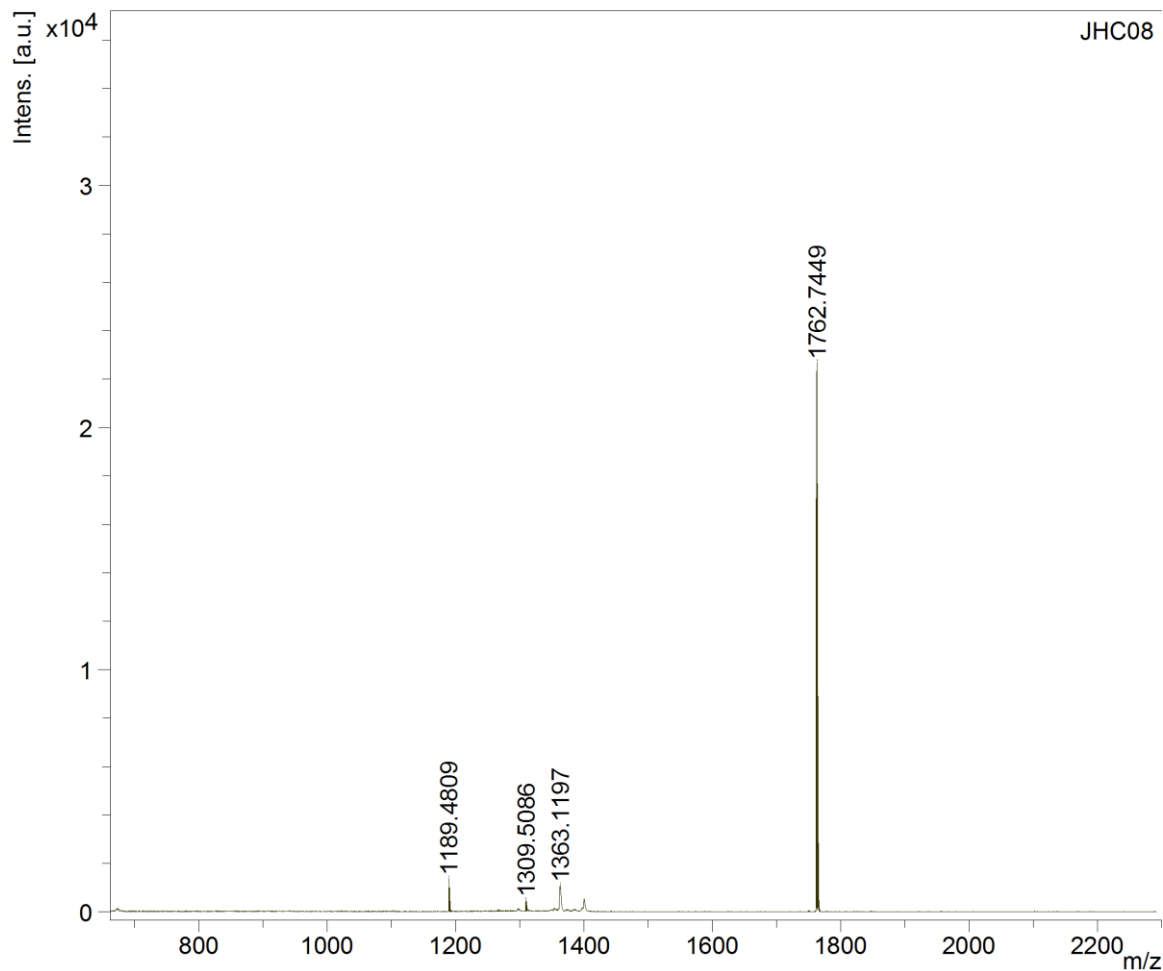
User NCU  
 Instrument ATS-00670  
 Instrument type autoflex

**Figure S16.** Mass Spectrum of **13** (MALDI).

D:\Data\Teresa Chen\106\Lu lab\JHC08\0\_E23\1\1Ref

Comment 1 JHC08

Comment 2 C114H112N4O6S4 1760.7465



**Acquisition Parameter**

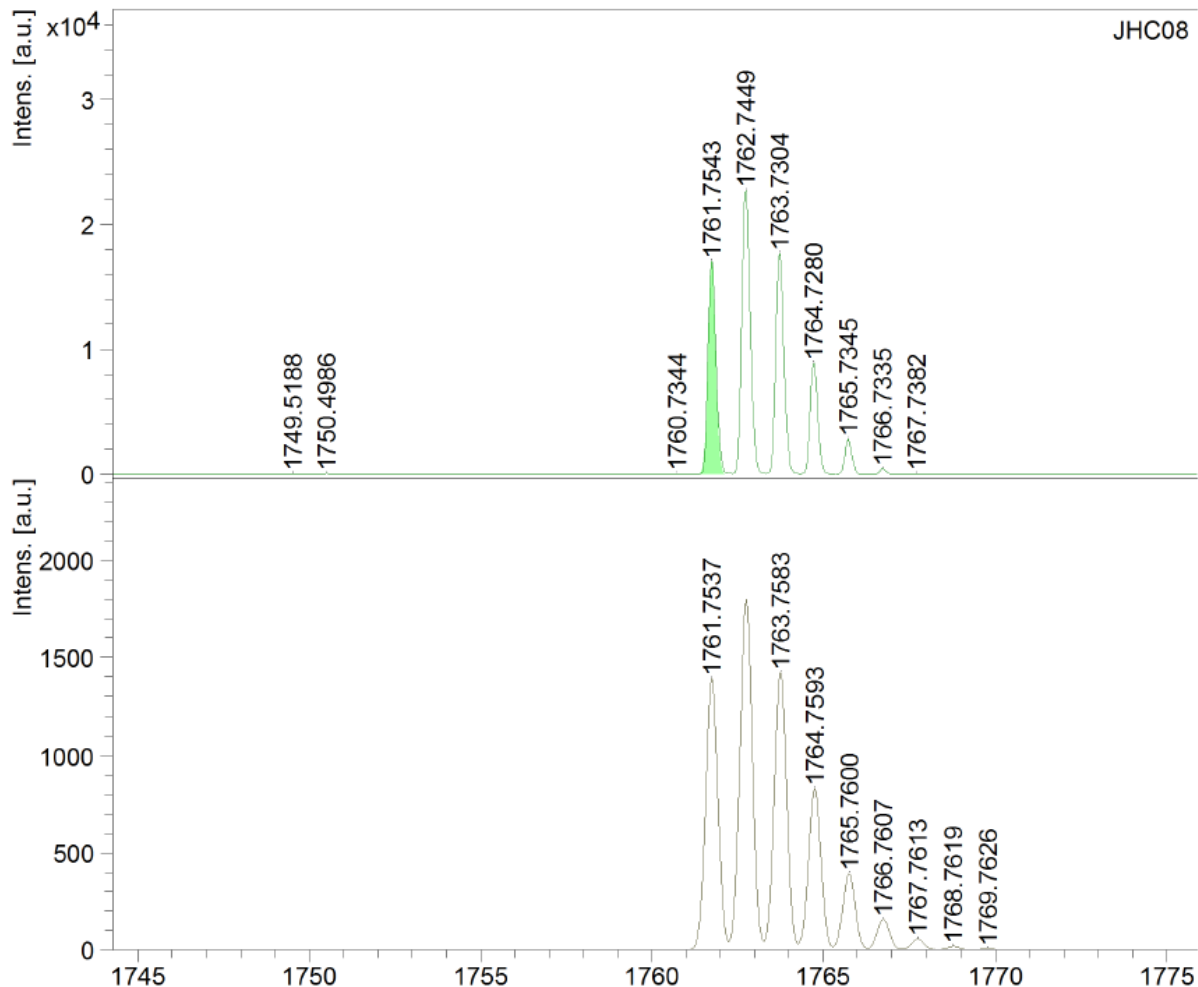
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Acquisition operation mode Reflector  
Voltage polarity POS  
Number of shots 2000  
Name of spectrum used for calibration  
Calibration reference list used Ultramark1621

**Instrument Info**

User NCU  
Instrument ATS-00670  
Instrument type autoflex



Comment 1 JHC08  
 Comment 2 C114H112N4O6S4 1760.7465



**Acquisition Parameter**

Date of acquisition 2017-12-04T15:45:51.952+08:00  
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 Voltage polarity POS  
 Number of shots 2000  
 Name of spectrum used for calibration  
 Calibration reference list used Ultramark1621

**Instrument Info**

User NCU  
 Instrument ATS-00670  
 Instrument type autoflex

Figure S17.  $^1\text{H}$  NMR Spectrum of **6** (500 MHz,  $\text{CDCl}_3$ )

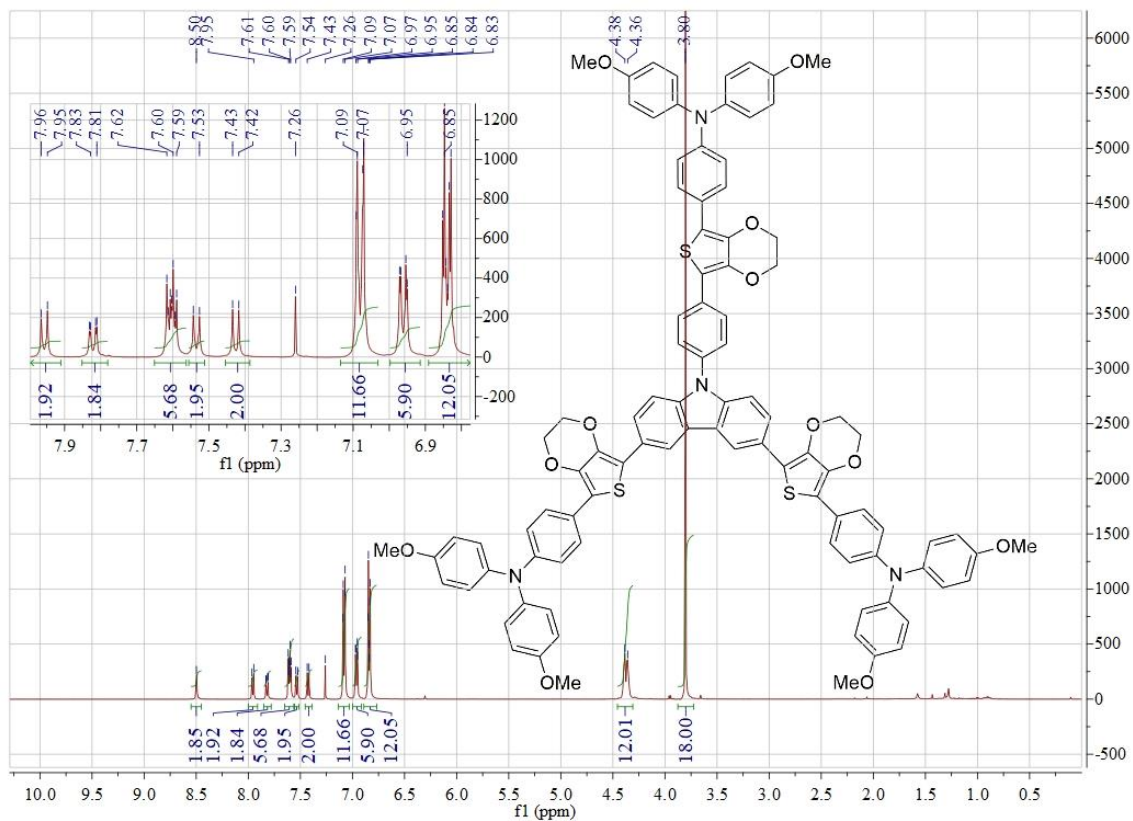
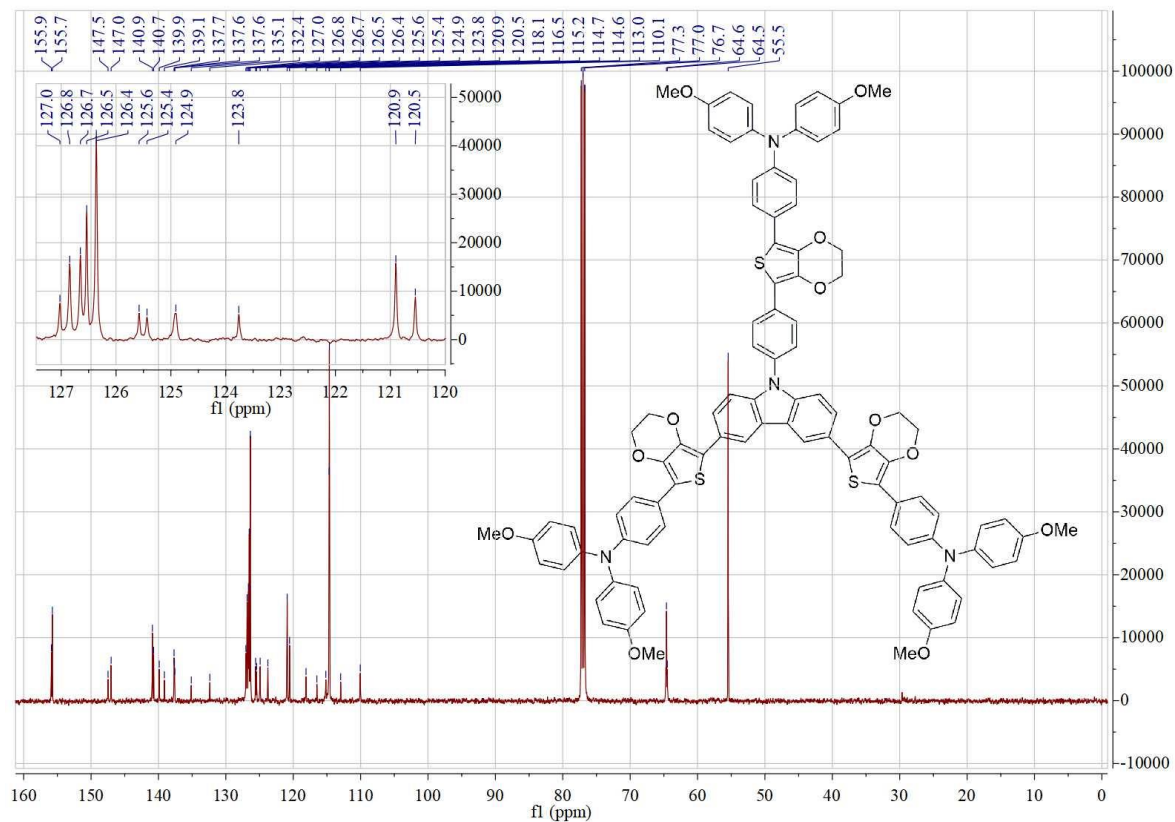
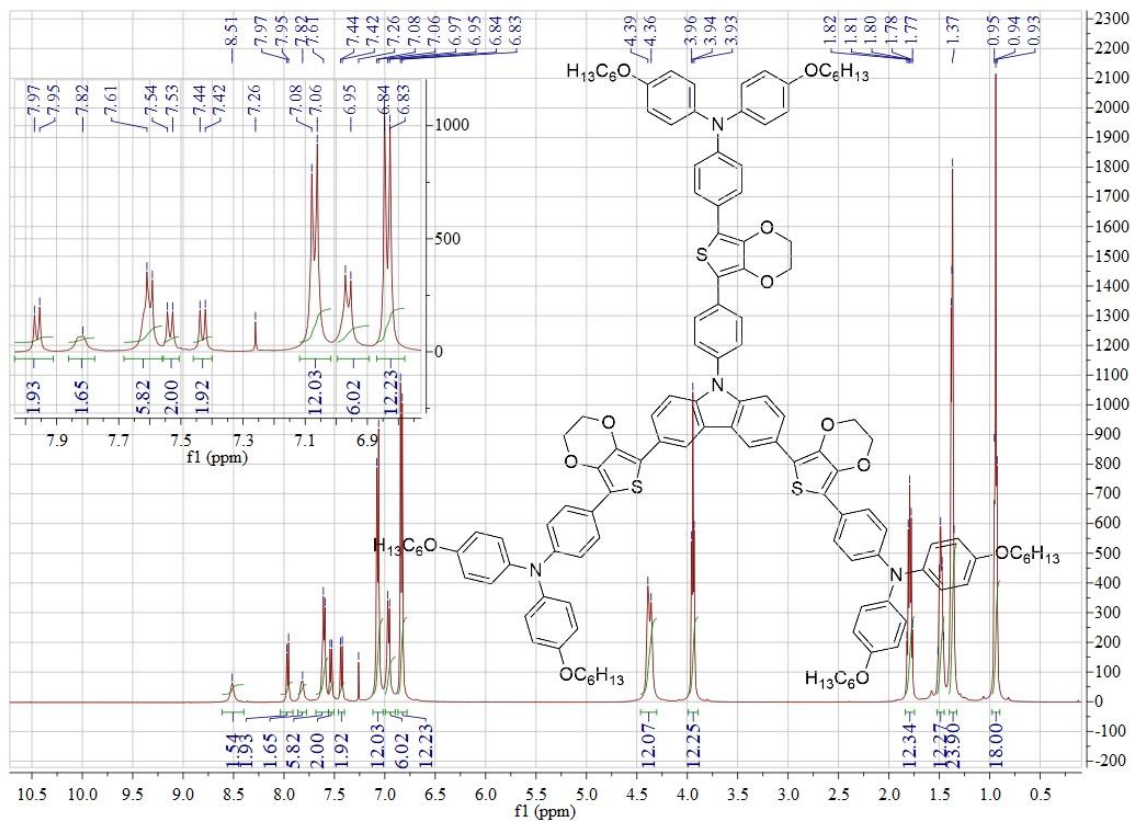


Figure S18.  $^{13}\text{C}$  NMR Spectrum of **6** (125 MHz,  $\text{CDCl}_3$ )



**Figure S19.**  $^1\text{H}$  NMR Spectrum of **7** (500 MHz,  $\text{CDCl}_3$ )



**Figure S20.**  $^{13}\text{C}$  NMR Spectrum of **7** (125 MHz,  $\text{CDCl}_3$ )

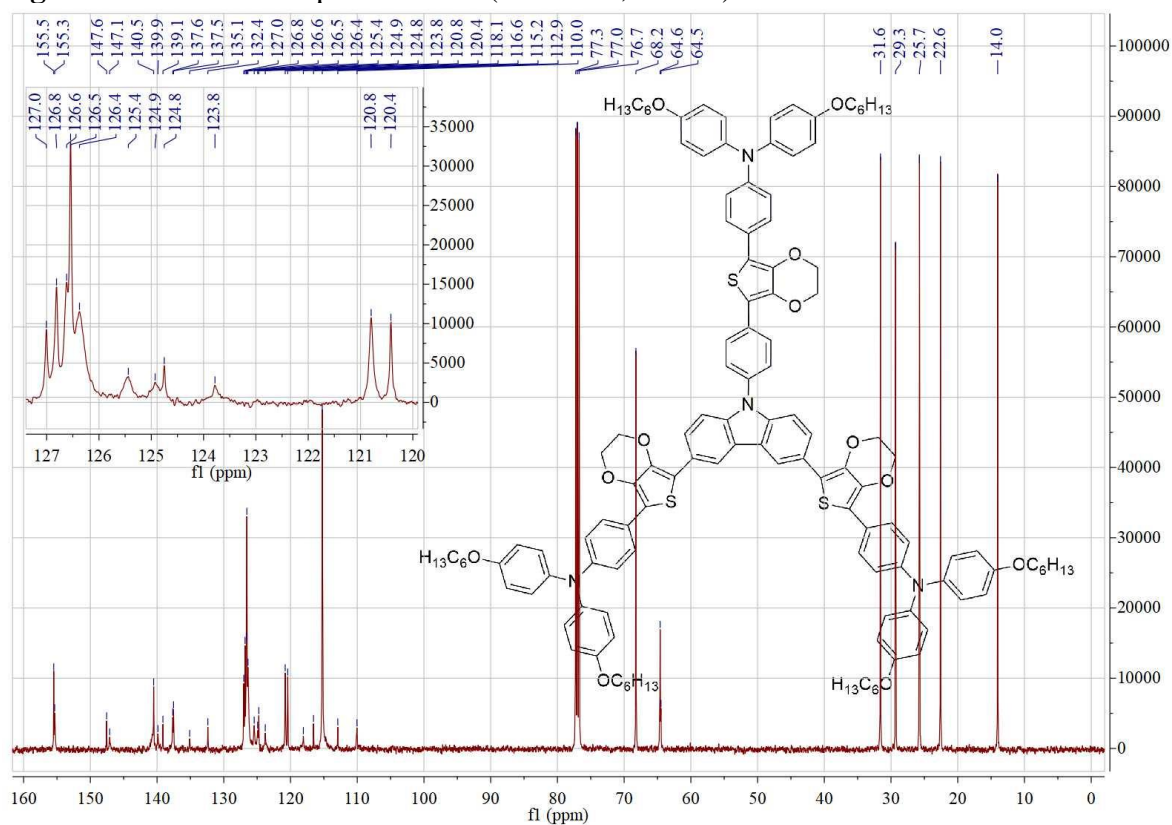


Figure S21.  $^1\text{H}$  NMR Spectrum of **8** (500 MHz,  $\text{CDCl}_3$ )

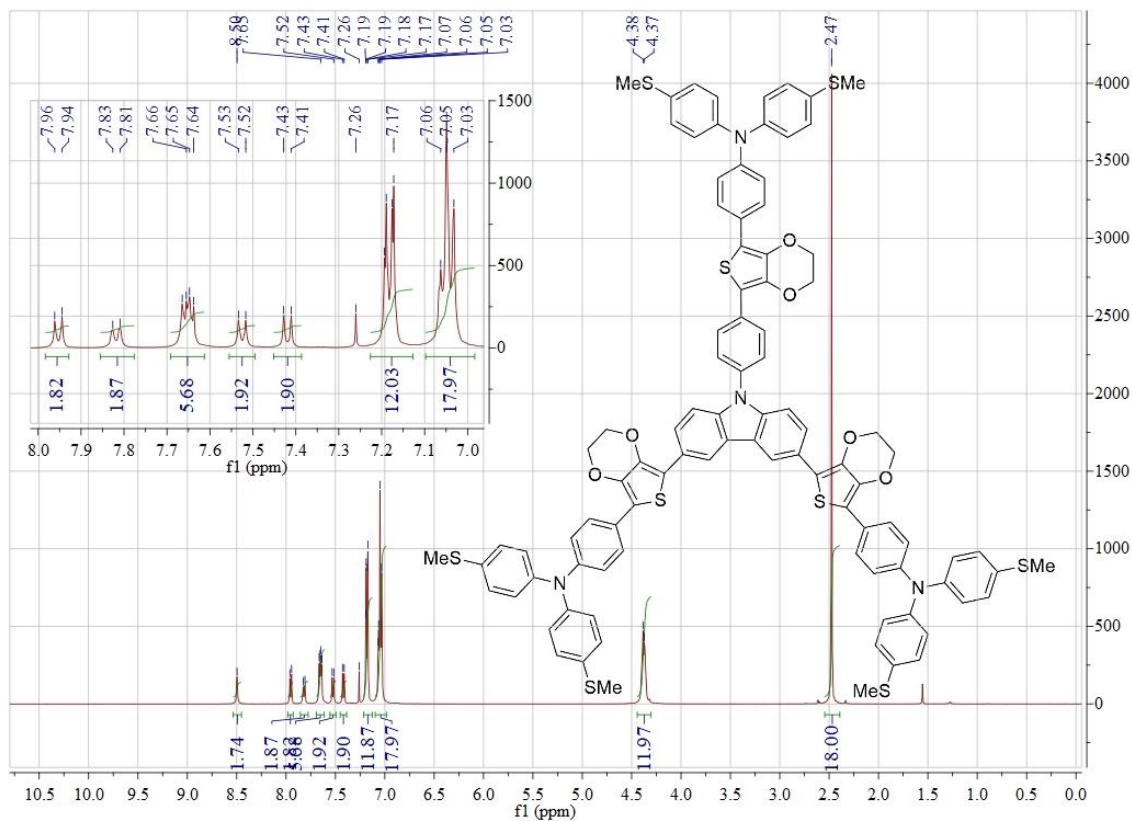
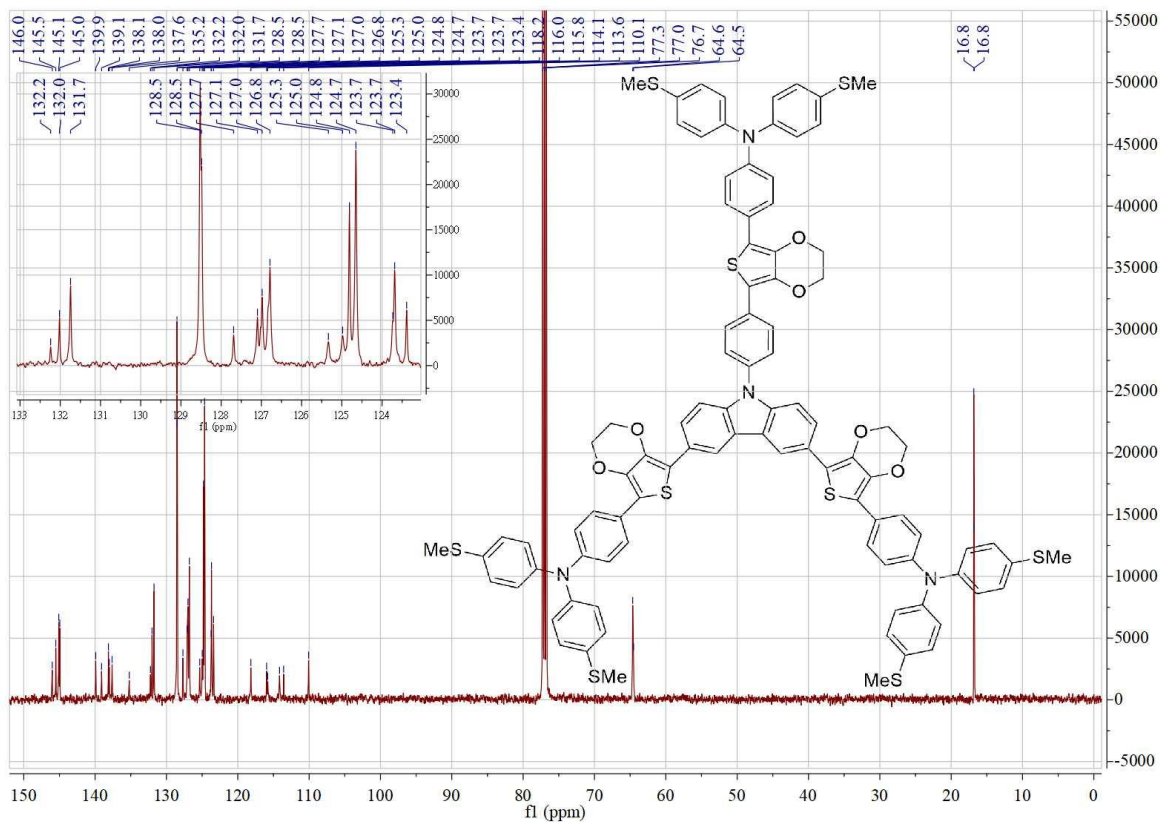
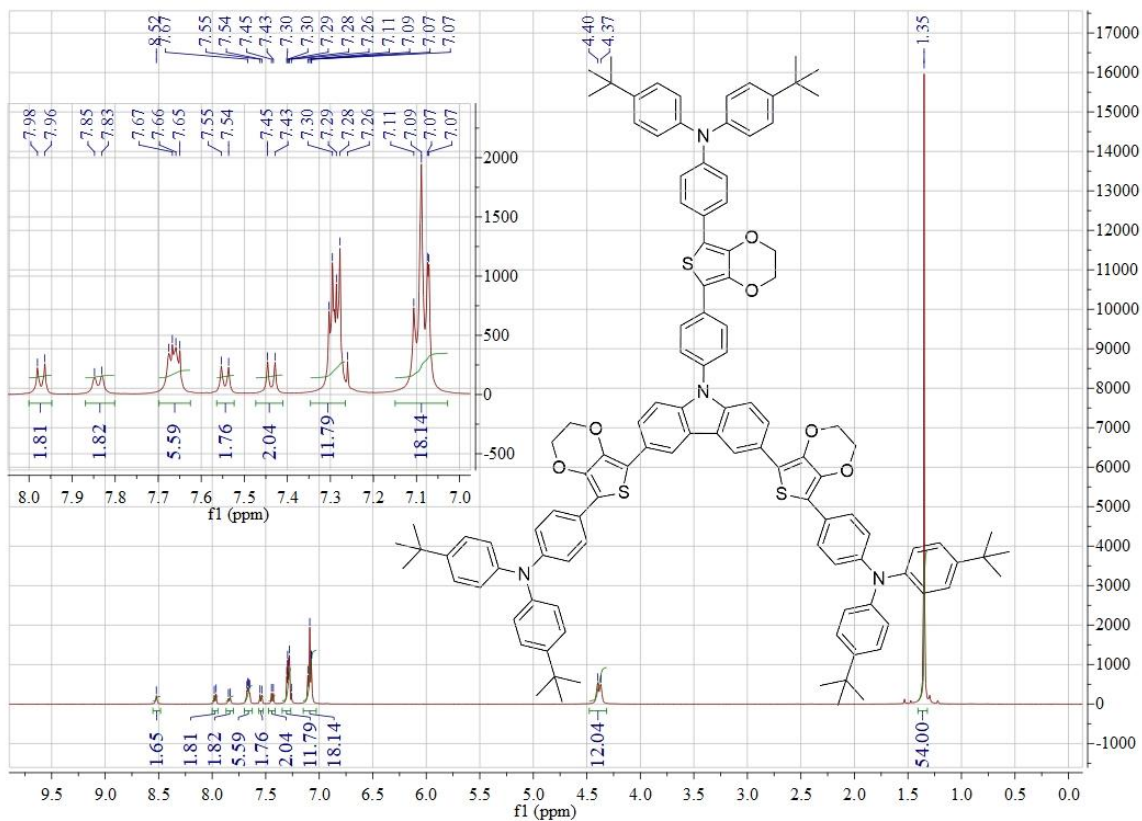


Figure S22.  $^{13}\text{C}$  NMR Spectrum of **8** (125 MHz,  $\text{CDCl}_3$ )





**Figure S23.**  $^1\text{H}$  NMR Spectrum of **9** (500 MHz,  $\text{CDCl}_3$ )



**Figure S24.**  $^{13}\text{C}$  NMR Spectrum of **9** (125 MHz,  $\text{CDCl}_3$ )

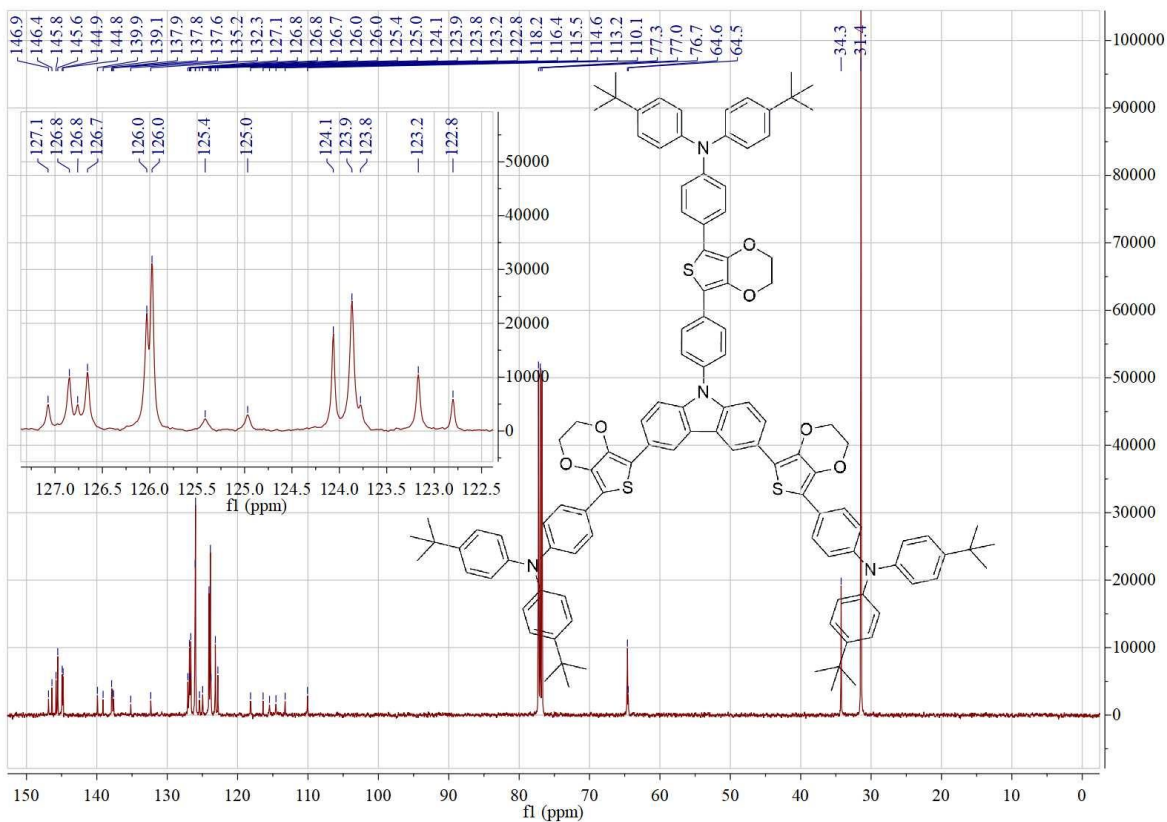


Figure S25.  $^1\text{H}$  NMR Spectrum of **10** (300 MHz,  $\text{CDCl}_3$ )

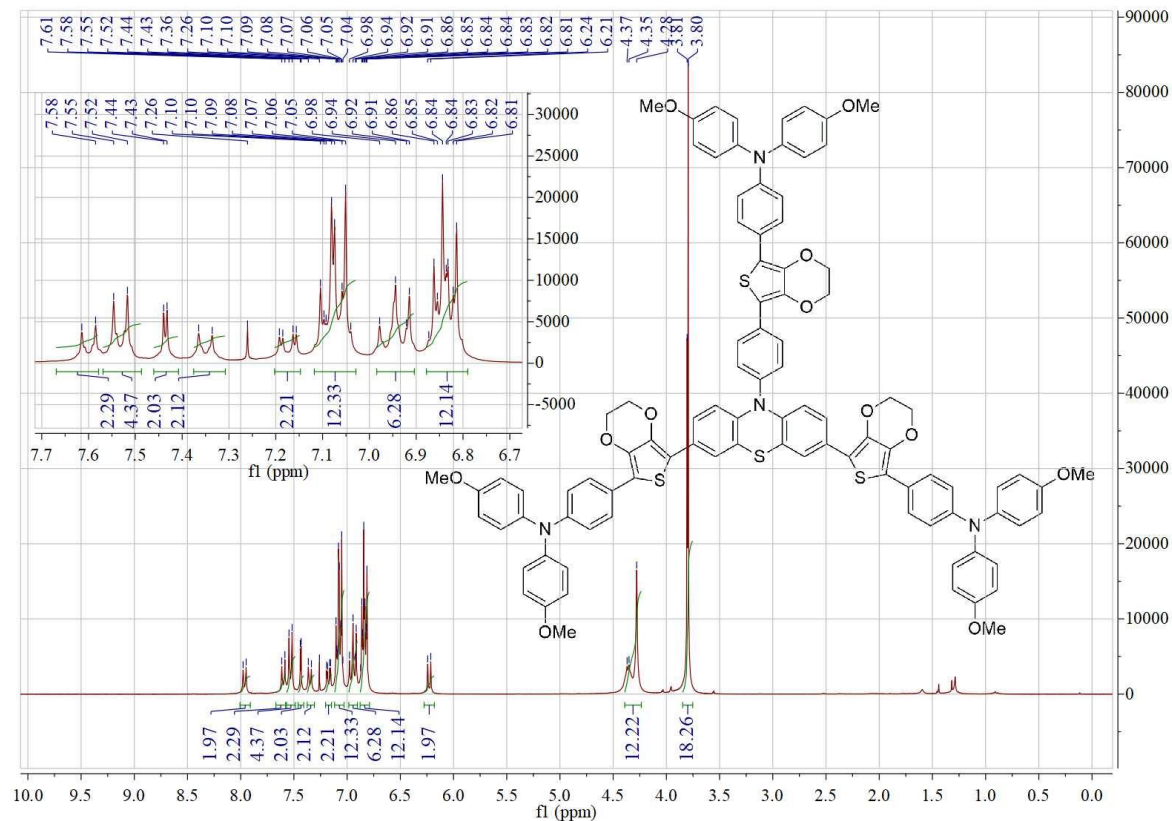


Figure S26.  $^{13}\text{C}$  NMR Spectrum of **10** (75 MHz,  $\text{CDCl}_3$ )

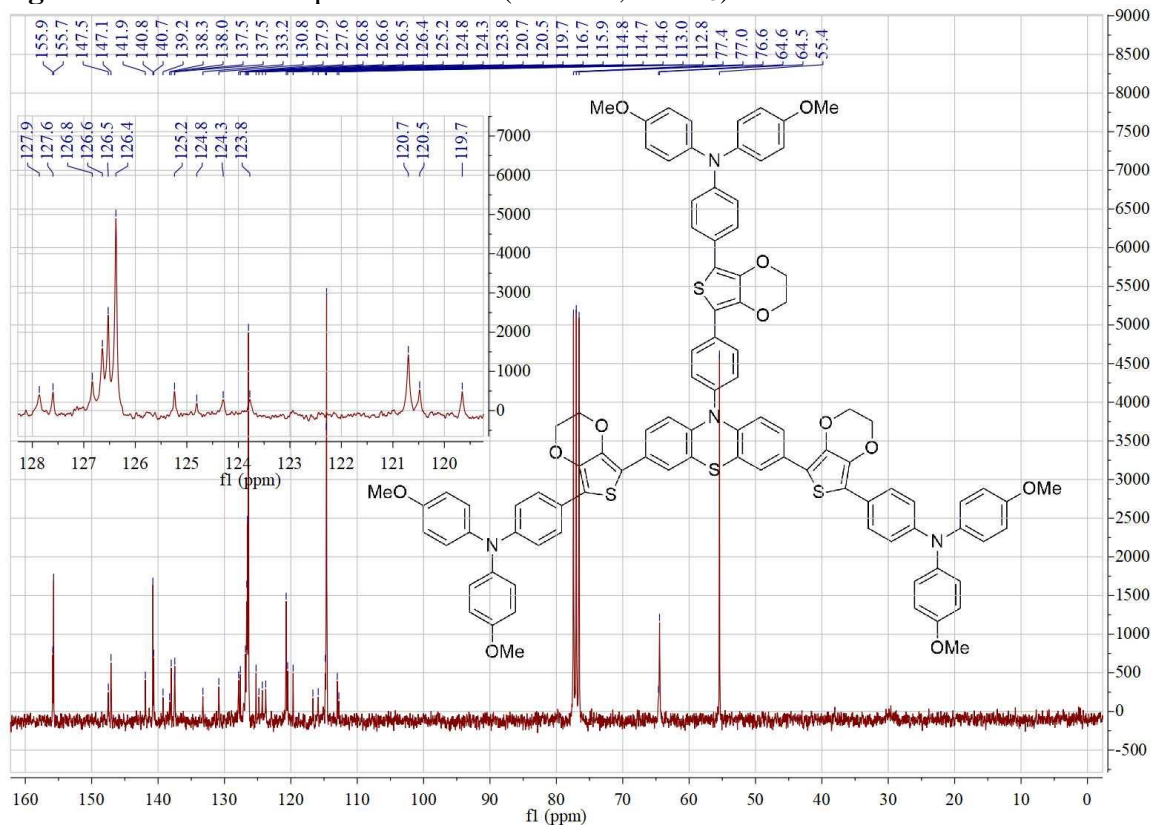


Figure S27.  $^1\text{H}$  NMR Spectrum of **11** (500 MHz,  $\text{CDCl}_3$ )

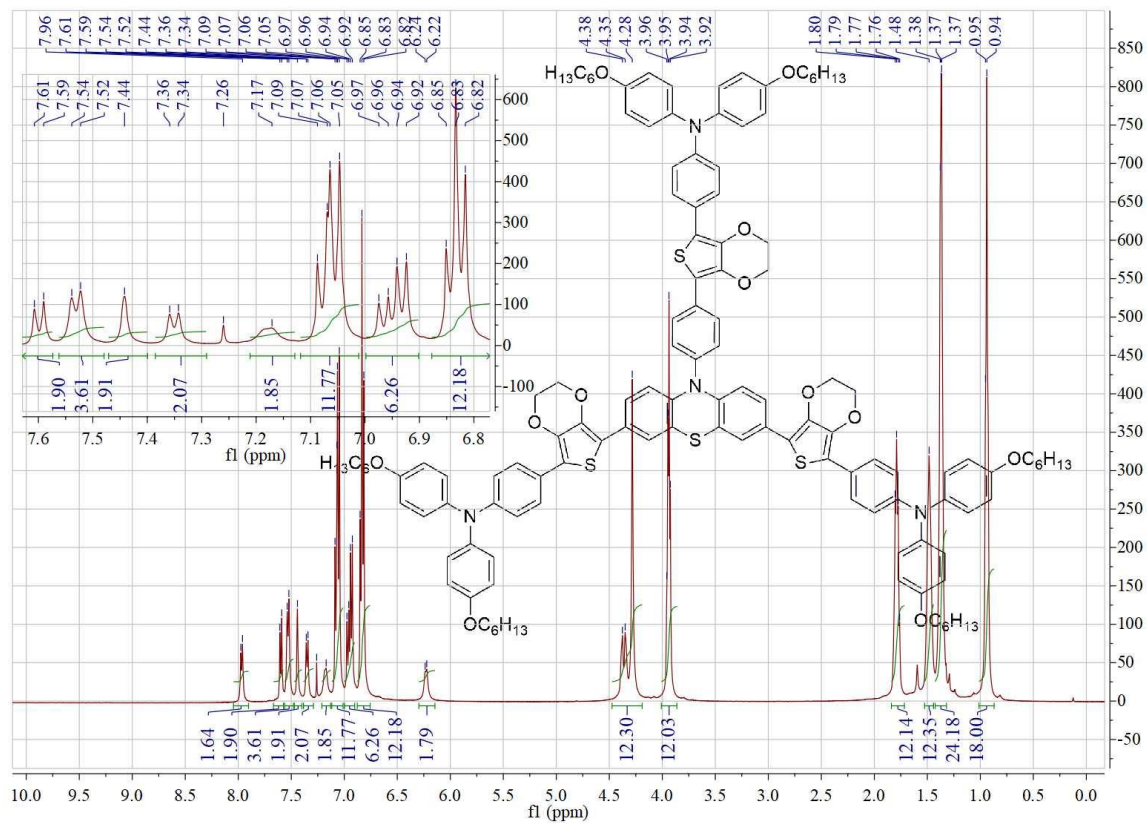
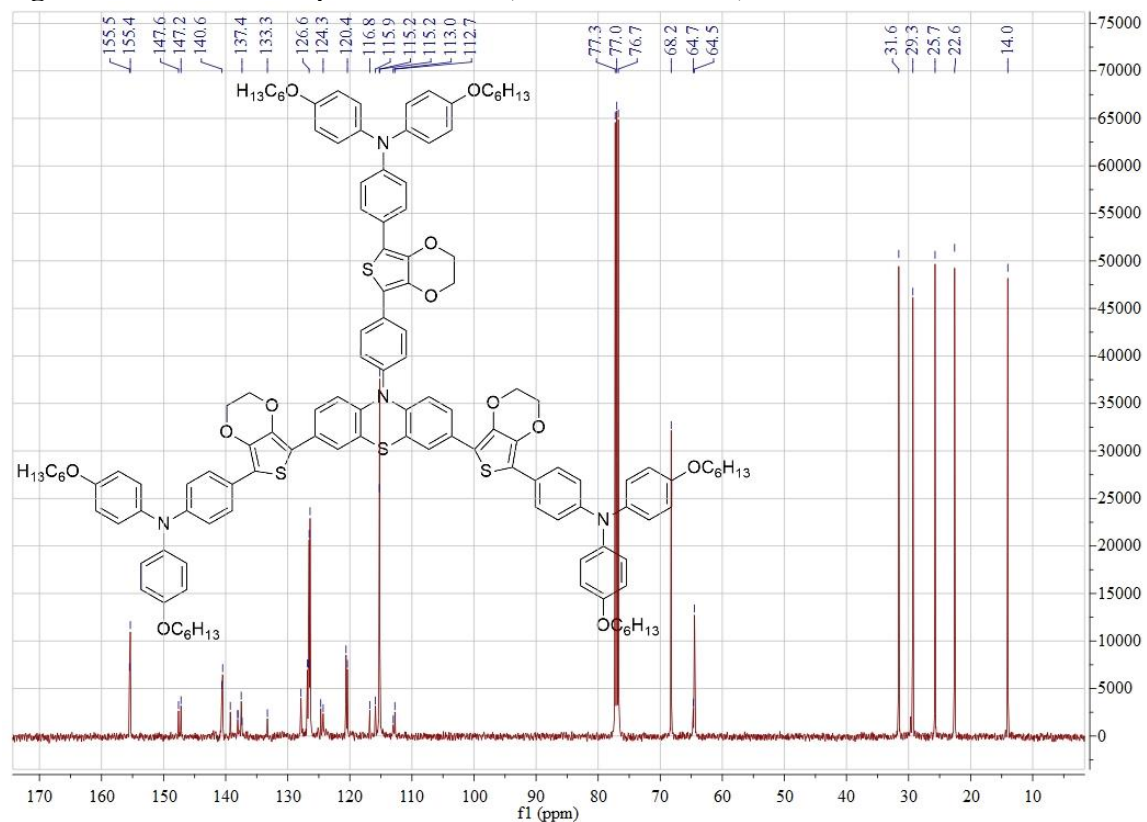
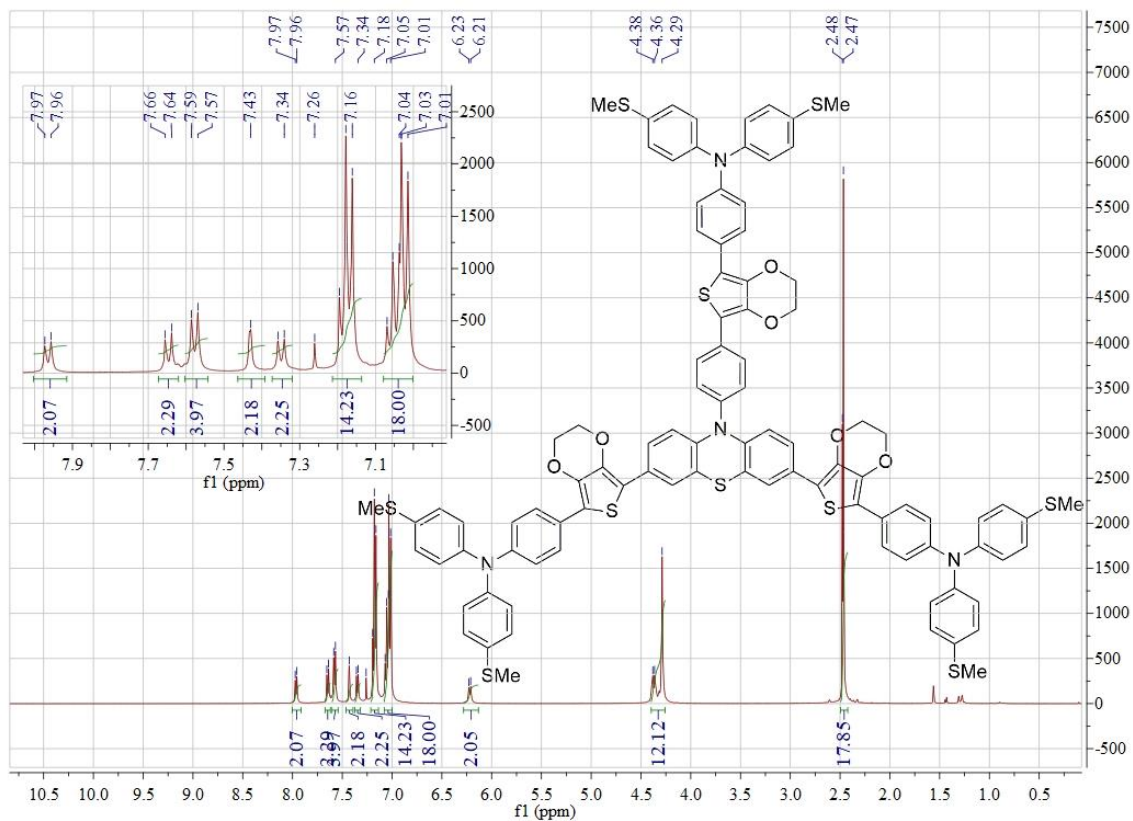


Figure S28.  $^{13}\text{C}$  NMR Spectrum of **11** (125 MHz,  $\text{CDCl}_3$ )



**Figure S29.**  $^1\text{H}$  NMR Spectrum of **12** (500 MHz,  $\text{CDCl}_3$ )



**Figure S30.**  $^{13}\text{C}$  NMR Spectrum of **12** (125 MHz,  $\text{CDCl}_3$ )

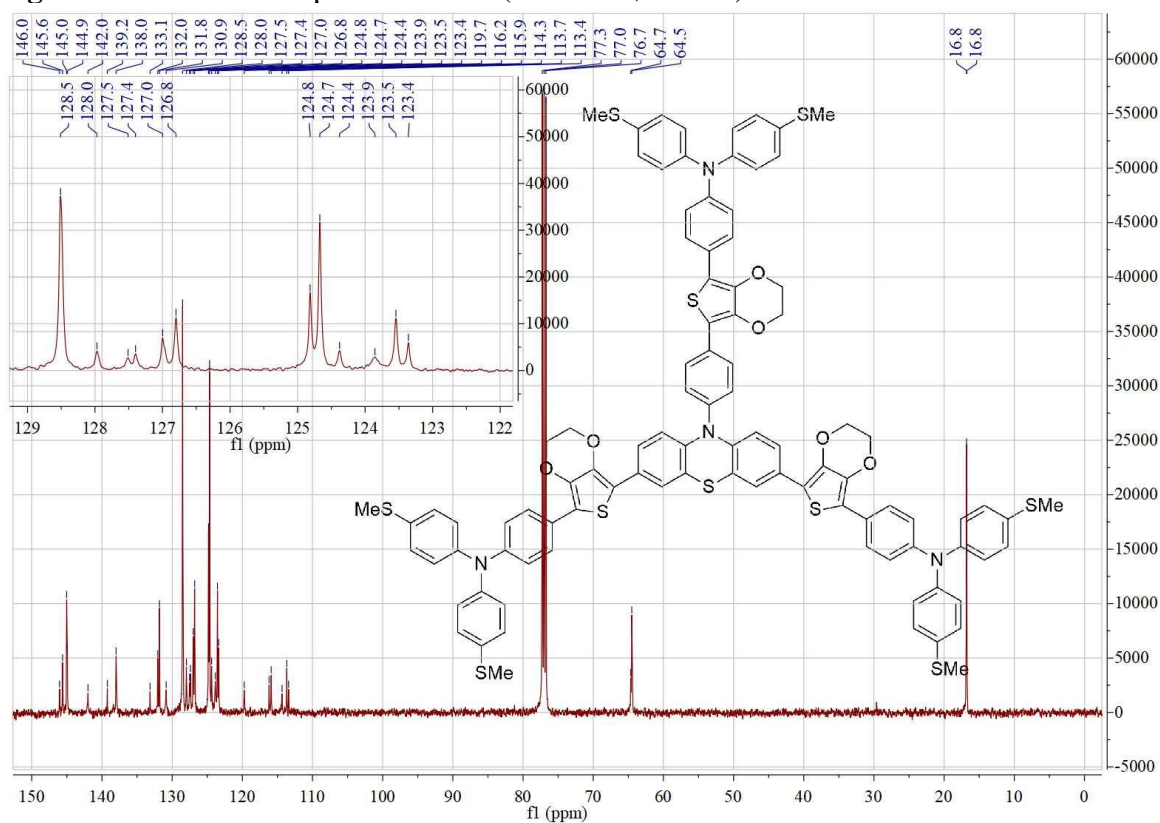




Figure S31. <sup>1</sup>H NMR Spectrum of **13** (500 MHz, CDCl<sub>3</sub>)

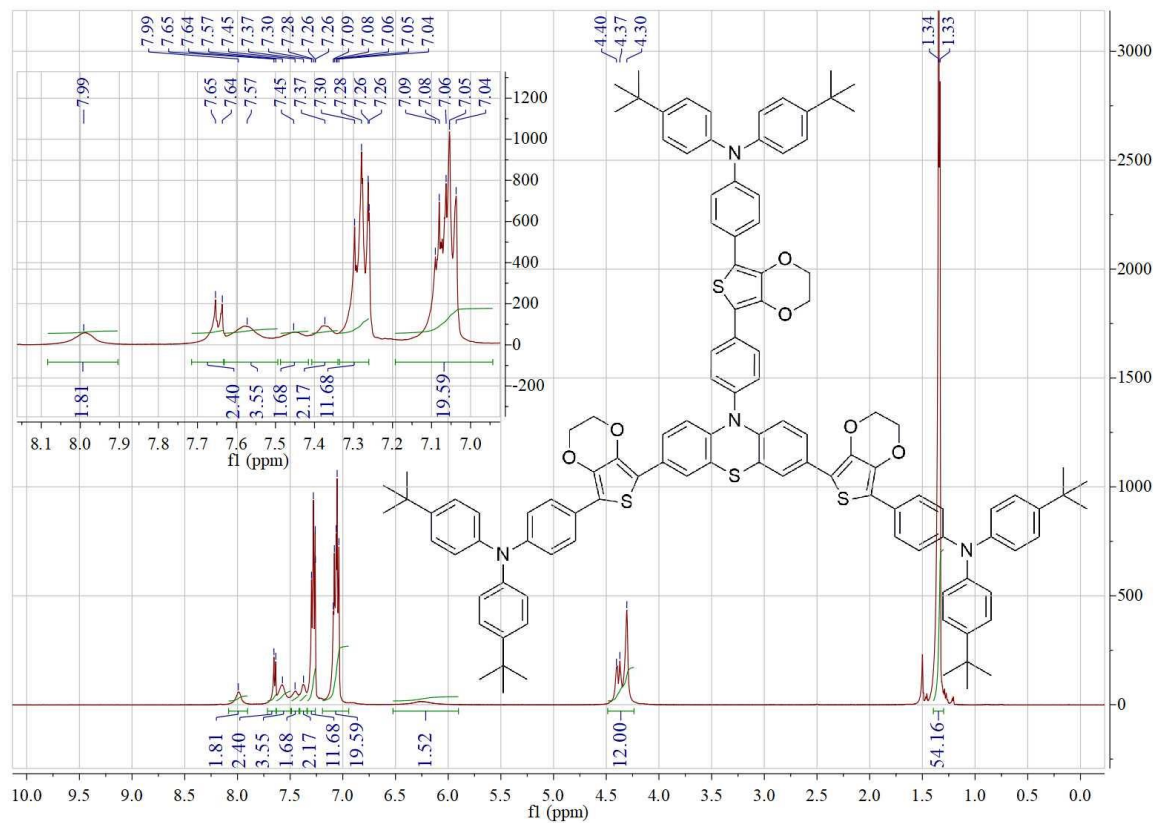


Figure S32. <sup>13</sup>C NMR Spectrum of **13** (125 MHz, CDCl<sub>3</sub>)

