Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Step-Efficient Access to New Starburst Hole-Transport Materials with Carbazole End-Groups for Perovskite Solar Cells via Direct 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 $Pd(OAc)_2$, $P(adamantyl)_2(n\mathrm{Bu})$, $P(Cy)_3$, PivOH, and K_2CO_3 are commercially available. Anhydrous or reagent-grade solvents such as dichloromethane, chloroform, and *N*,*N*-dimethylformamide (DMF) were purchased from Sigma-Aldrich, Acros, or Alfa Aesar and 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 $CDCl_3$ (7.26 ppm for ^1H NMR, 77.0 ppm for ^{13}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). Mass spectra were recorded on a JEOL JMS-700 for electron impact ionization (EI) and high resolution mass spectra (HRMS) on a JEOL JMS-700 spectrometers. Fast atom bombardment (FAB) samples were recorded in a 3-nitrobenzyl alcohol- or glycerine-matrix. Some of the mass spectra were also 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 material 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 THF solution containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate as a supporting electrolyte under a scan rate of 100 mVs^{-1}. 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 $-(E_{1/2} + 0.197 + 4.500 - 0.177)$ eV (*vs.* Ag/AgCl and NHE); $E_{LUMO} = E_{HOMO} + E_g^{opt}$. 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):

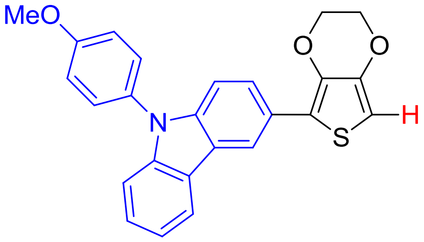
A TiO_2 compact layer (~30 nm in thickness) was deposited onto the FTO substrate surface by spin-coating a solution of titanium diisopropoxide bis(acetylacetonate) (75 wt.% of $Ti(acac)_2O\mathit{i}Pr_2$ in isopropanol). A 150 nm-thick mesoporous TiO_2 film (TiO_2 particle size: ~20 nm, crystalline phase: anatase) was spin-coated onto the compact-TiO_2/FTO substrate surface using home-made pastes and heated to 500 ℃ for 30 min. After sintering the TiO_2 layer, the films were cooled to room temperature and immersed in $TiCl_4$ solution (0.04 M in water) at 70 ℃ for 30 min. The films were then rinsed by deionized water and then annealed at 500 ℃ 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_2 (1.80 M) and CH_3NH_3I (1.80 M) in γ-butyrolactone (GBL) and DMSO (5/5, v/v) was coated onto the TiO_2 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 50 μL toluene by drop-casting. The substrate/films were dried on a hot plate at 100 ^{o}C for 10 min. **YC05-08** or **spiro-OMeTAD** (as reference cell) was each dissolved in chlorobenzene (50 mg/mL). Each solution was heated to 80~90 ^{o}C for 20 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^2 by a metal mask.

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

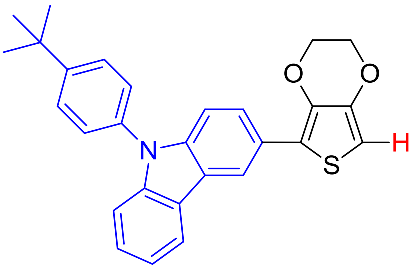
An IPCE spectrometer (EQE-R-3011, ENLI Technology Co. Ltd., Taiwan) calibrated with a single-crystal silicon reference cell was used for the incident monochromatic photon-to-current conversion efficiency (IPCE) measurements. An AM 1.5G solar simulator (Yamashita Denso Corporation, YSS-50A) was used as the irradiation light source for the characteristic current density-voltage (J-V) measurements. The intensity of the simulated sunlight was calibrated to 100 mW/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 A for the Synthesis of EDOT–Cbz (end-group molecules):

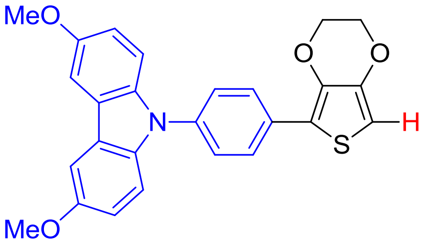
To a solution of $Pd(OAc)_2$ (0.05 mmol), ligand (0.10 mmol), PivOH (0.30 mmol), and K_2CO_3 (1.50 mmol) in DMF (3 mL) in a flame-dried Schlenk tube were added the corresponding aryl bromide (**1a-d**) (1.00 mmol) and ethylenedioxythiophene (EDOT) (**2**) (3.00 mmol) under N_2. The reaction mixture was then heated at 100 °C under N_2 for 6 h. After the reaction mixture had cooled to room temperature, water (10 mL) was added. The mixture was extracted with ethyl acetate (2 × 20 mL), and the combined organic layers were washed with brine (50 mL), dried (Na_2SO_4) and concentrated in *vacuo*. Purification by flash chromatography yielded the desired products **3a-d**.



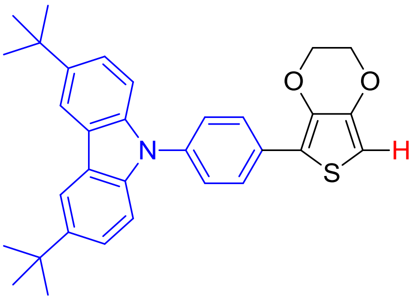
3-(2,3-Dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-9-(4-methoxyphenyl)-9*H*-carbazole (3a) was prepared from **1a** (352 mg, 1.00 mmol), **2** (426 mg, 3.00 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), $P(adamantyl)_2(nBu)$ (36 mg, 0.10 mmol), PivOH (31 mg, 0.30 mmol), K_2CO_3 (207 mg, 1.50 mmol), and DMF (3 mL) according to the general procedure **A** and yielding after column chromatography (ethyl acetate : hexanes = 30 : 70) the pure product **3a** (248 mg, 60 %). White solid; m.p.: 185.1-186.0 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.47 (d, J = 1.2 Hz, 1 H), 8.20 (d, J = 7.7 Hz, 1 H), 7.76 (dd, J = 8.6, 1.6 Hz, 1 H), 7.46 (d, J = 8.9 Hz, 2 H), 7.40 (dd, J = 7.0, 1.1 Hz, 1 H), 7.27-7.36 (comp, 3 H), 7.12 (d, J = 8.9 Hz, 2 H), 6.30 (s, 1H), 4.33-4.40 (comp, 2 H), 4.25-4.31 (comp, 2 H), 3.92 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 158.8, 142.3, 141.7, 140.2, 137.0, 130.1, 128.4, 126.0, 125.0, 124.7, 123.3, 123.1, 120.5, 119.7, 118.6, 118.1, 115.0, 114.9, 109.8, 96.4, 64.8, 64.5, 55.6; MS (FAB): 413 (M^+, 45 %), 107 (69 %), 69 (100 %); HRMS (FAB): calcd. for $C_{25}H_{19}NO_3S$: 413.1086, found: 413.1091.



9-(4-(*tert*-Butyl)phenyl)-3-(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-9*H*-carbazole (3b) was prepared from **1b** (378 mg, 1.00 mmol), **2** (426 mg, 3.00 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), $P(adamantyl)_2(n\mathrm{Bu})$ (36 mg, 0.10 mmol), PivOH (31 mg, 0.30 mmol), K_2CO_3 (207 mg, 1.50 mmol), and DMF (3 mL) according to the general procedure **A** and yielding after column chromatography (ethyl acetate : hexanes = 5 : 95) the pure product **3b** (233 mg, 53 %). Pale red solid; m.p.: 177.5-178.5 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.50 (d, J = 1.2 Hz, 1 H), 8.22 (d, J = 7.7 Hz, 1 H), 7.78 (dd, J = 8.6, 1.8 Hz, 1 H), 7.63 (d, J = 8.7 Hz, 2 H), 7.50 (d, J = 8.7 Hz, 2 H), 7.39-7.48 (comp, 3 H), 7.31 (ddd, J = 8.0, 6.1, 2.1 Hz, 1 H), 6.31 (s, 1 H), 4.33-4.38 (comp, 2 H), 4.27-4.32 (comp, 2 H), 1.46 (s, 9 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 150.4, 142.2, 141.3, 139.8, 137.0, 134.8, 126.7, 126.4, 126.0, 125.1, 124.7, 123.5, 123.3, 120.4, 119.8, 118.6, 118.1, 110.0, 96.4, 64.7, 64.5, 34.7, 31.4; MS (EI): 439 (M^+, 0.39 %), 119 (16 %), 84 (100 %); HRMS (EI): calcd. for $C_{28}H_{25}NO_2S$: 439.1606, found: 439.1600.



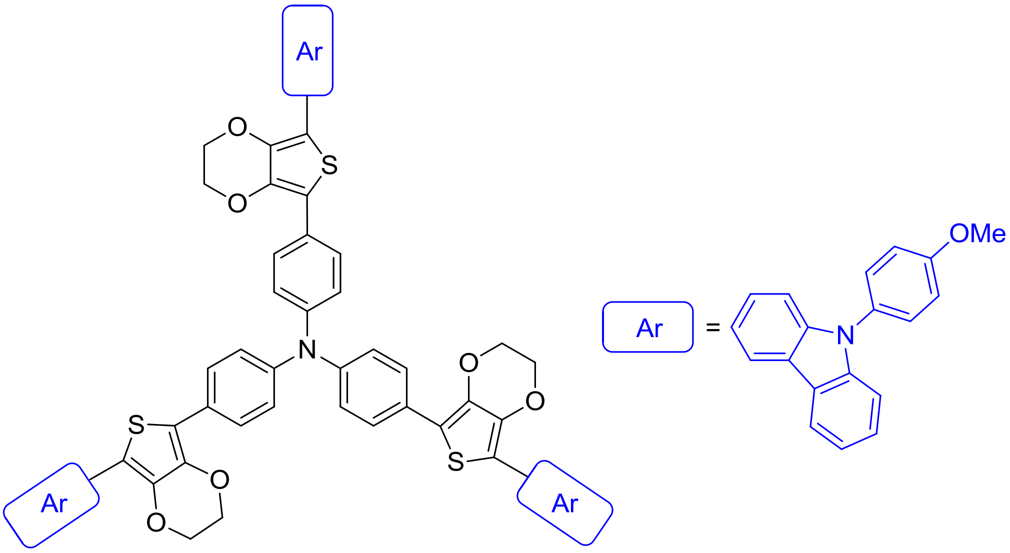
9-(4-(2,3-Dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)phenyl)-3,6-dimethoxy-9*H*-carbazole (3c) was prepared from **1c** (382 mg, 1.00 mmol), **2** (426 mg, 3.00 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), $P(Cy)_3$ (28 mg, 0.10 mmol), PivOH (31 mg, 0.30 mmol), K_2CO_3 (207 mg, 1.50 mmol), and DMF (3 mL) according to the general procedure **A** and yielding after column chromatography (dichloromethane : ethyl acetate : hexanes = 10 : 20 : 70) the pure product **3c** (270 mg, 61 %). White solid; m.p.: 179.0-179.9 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.91 (d, J = 8.6 Hz, 2 H), 7.56 (d, J = 2.5 Hz, 2 H), 7.53 (d, J = 8.6 Hz, 2 H), 7.37 (d, J = 8.9 Hz, 2 H), 7.05 (dd, J = 8.9, 2.5 Hz, 2 H), 6.36 (s, 1 H), 4.33-4.38 (comp, 2 H), 4.26-4.31 (comp, 2 H), 3.96 (s, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 154.0, 142.3, 138.4, 136.23, 136.16, 131.8, 127.2, 126.6, 123.6, 116.6, 115.1, 110.8, 102.9, 98.0, 64.8, 64.4, 56.1; MS (EI): 443 (M^+, 45 %), 304 (50 %), 139 (100 %); HRMS (EI): calcd. for $C_{26}H_{21}NO_4S$: 443.1191, found: 443.1185.



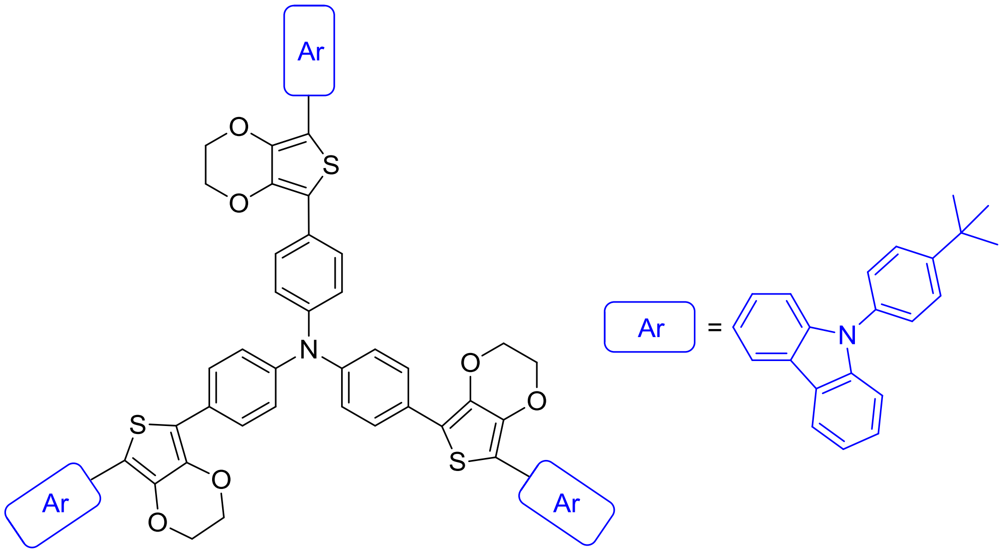
3,6-Di-*tert*-butyl-9-(4-(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)phenyl)-9*H*-carbazole[1] **(3d)** was prepared from **1d** (434 mg, 1.00 mmol), **2** (426 mg, 3.00 mmol), Pd(OAc)$_2$ (12 mg, 0.05 mmol), P(Cy)$_3$ (28 mg, 0.10 mmol), PivOH (31 mg, 0.30 mmol), K_2CO_3 (207 mg, 1.50 mmol), and DMF (3 mL) according to the general procedure **A** and yielding after column chromatography (dichloromethane : hexanes = 30 : 70) the pure product **3d** (322 mg, 65 %). White solid; m.p.: 244.0-244.4 ^oC. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.16 (d, J = 1.8 Hz, 2 H), 7.93 (d, J = 8.6 Hz, 2 H), 7.56 (d, J = 8.6 Hz, 2 H), 7.48 (dd, J = 8.6, 1.8 Hz, 2 H), 7.40 (d, J = 8.6 Hz, 2 H), 6.37 (s, 1H), 4.35-4.40 (comp, 2 H), 4.27-4.31 (comp, 2 H), 1.48 (s, 18 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 142.8, 142.3, 139.1, 138.4, 136.2, 131.8, 127.1, 126.7, 123.6, 123.3, 116.7, 116.2, 109.2, 98.0, 64.8, 64.4, 34.7, 32.0.

General Procedure B for the Synthesis of YC05-08:

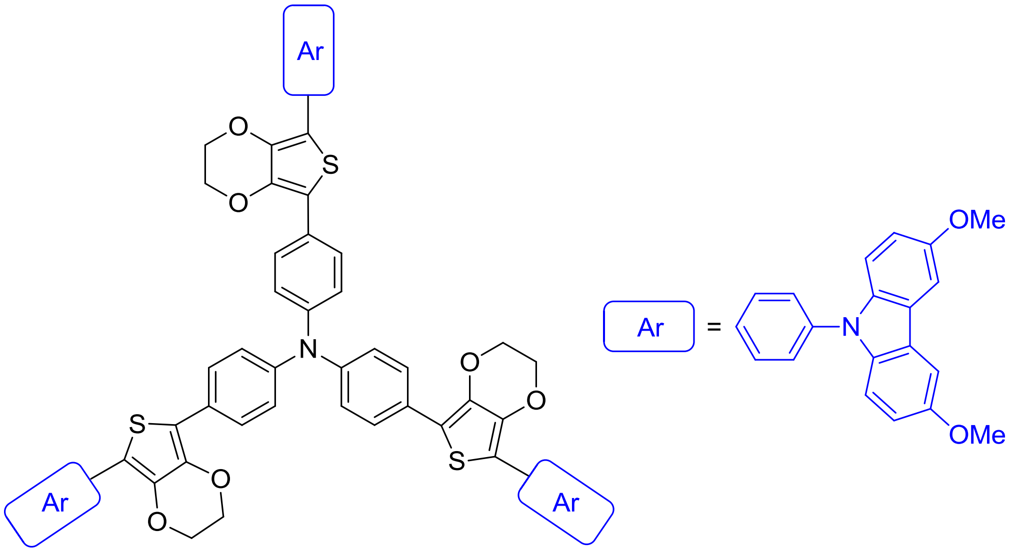
To a solution of Pd(OAc)$_2$ (0.15 mmol), P(adamantyl)$_2$(*n*Bu) (0.30 mmol), PivOH (0.60 mmol), and K_2CO_3 (3.60 mmol) in DMF (10 mL) in a flame-dried Schlenk flask were added tris(4-bromophenyl)amine (1.00 mmol) and the corresponding end groups (**3a-d**) (3.50 mmol) under N_2. The reaction mixture was then heated at 125 °C under N_2 for 30 h. After the reaction mixture had cooled to room temperature, water (15 mL) was added. The mixture was extracted with dichloromethane (2 × 30 mL), and the combined organic layers were washed with brine (60 mL), dried (Na_2SO_4) and concentrated in *vacuo*. Purification by flash chromatography yielded the desired hole-transporting materials **YC05-08**.



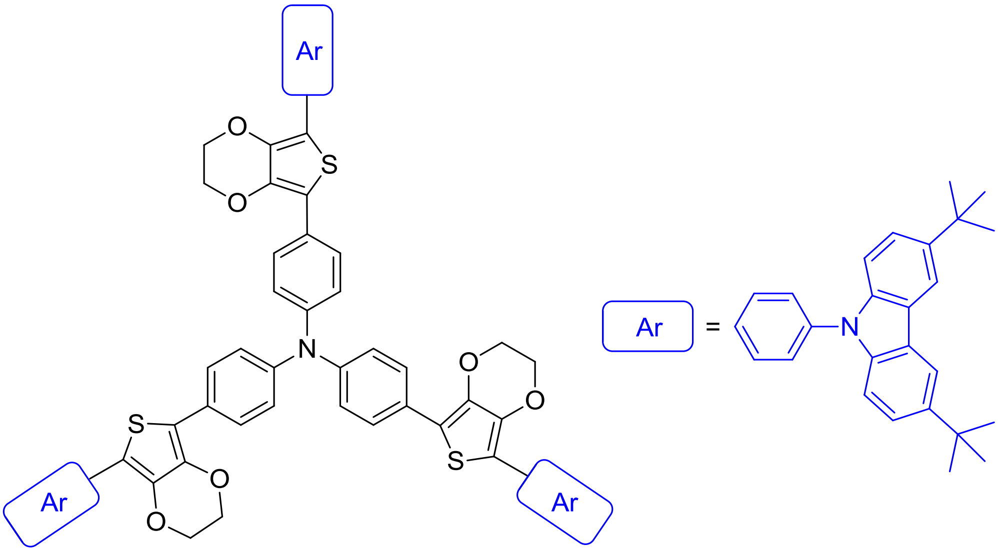
(**YC05**) was prepared from tris(4-bromophenyl)amine (482 mg, 1.00 mmol), **3a** (1446 mg, 3.50 mmol), $Pd(OAc)_2$ (36 mg, 0.15 mmol), P(adamantyl)$_2$(*n*Bu) (108 mg, 0.30 mmol), PivOH (62 mg, 0.60 mmol), K_2CO_3 (497 mg, 3.60 mmol), and DMF (10 mL) according to the general procedure **B** and yielding after column chromatography (dichloromethane : hexanes = 60 : 40) the pure product **YC05** (1243 mg, 84 %). Yellow/Green solid; m.p.: 243.8-245.0 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.49 (app s, 3 H), 8.18 (d, J = 7.7 Hz, 3 H), 7.78 (dd, J = 8.8, 1.7 Hz, 3 H), 7.67 (d, J = 8.8 Hz, 6 H), 7.43 (d, J = 8.9 Hz, 6 H), 7.37 (d, J = 7.1 Hz, 3 H), 7.30 (d, J = 9.0 Hz, 6 H), 7.24 (dd, J = 9.0, 1.8 Hz, 3 H), 7.05-7.18 (comp, 12 H), 4.37 (app s, 12 H), 3.89 (s, 9 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 158.8, 145.5, 141.7, 140.2, 138.2, 137.6, 130.1, 128.4, 127.8, 126.8, 126.0, 124.9, 124.7, 124.2, 123.4, 123.2, 120.5, 119.8, 118.0, 115.9, 115.04, 114.97, 114.2, 109.8, 64.7, 64.6, 55.6; MS (FAB): 1479 (M^{+}, 1 %), 664 (7 %), 69 (69 %), 57 (100 %); HRMS (FAB): calcd. for $C_{93}H_{66}N_4O_9S_3$: 1478.3992, found: 1478.3988.



(**YC06**) was prepared from tris(4-bromophenyl)amine (482 mg, 1.00 mmol), **3b** (1537 mg, 3.50 mmol), $Pd(OAc)_2$ (36 mg, 0.15 mmol), P(adamantyl)$_2$(*n*Bu) (108 mg, 0.30 mmol), PivOH (62 mg, 0.60 mmol), K_2CO_3 (497 mg, 3.60 mmol), and DMF (10 mL) according to the general procedure **B** and yielding after column chromatography (dichloromethane : hexanes = 45 : 55) the pure product **YC06** (1091 mg, 70 %). Yellow/Green solid; m.p.: 245.0-246.5 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 8.42-8.60 (comp, 3 H), 8.22 (d, J = 7.7 Hz, 3 H), 7.67-7.88 (comp, 9 H), 7.62 (d, J = 8.5 Hz, 6 H), 7.50 (d, J = 8.4 Hz, 6 H), 7.27-7.48 (comp, 15 H), 7.03-7.23 (comp, 3 H), 4.41 (app s, 12 H), 1.45 (s, 27 H); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ 150.4, 141.4, 139.8, 138.3, 138.24, 138.20, 134.8, 126.7, 126.4, 126.0, 124.72, 124.69, 123.6, 123.4, 120.5, 119.9, 118.15, 118.12, 118.08, 118.03, 114.27, 114.23, 114.18, 110.0, 64.64, 64.59, 34.7, 31.4; MS (FAB): 1558 ($[M+1]^+$, 11 %), 77 (100 %); HRMS (FAB): calcd. for $C_{102}H_{84}N_4O_6S_3$: 1556.5553, found: 1556.5546.



(**YC07**) was prepared from tris(4-bromophenyl)amine (482 mg, 1.00 mmol), **3c** (1551 mg, 3.50 mmol), $Pd(OAc)_2$ (36 mg, 0.15 mmol), P(adamantyl)$_2$(*n*Bu) (108 mg, 0.30 mmol), PivOH (62 mg, 0.60 mmol), K_2CO_3 (497 mg, 3.60 mmol), and DMF (10 mL) according to the general procedure **B** and yielding after column chromatography (dichloromethane : ethyl acetate : hexanes = 55 : 5 : 40) the pure product **YC07** (1256 mg, 80 %). Yellow solid; m.p.: 231.7-233.2 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.95 (d, *J* = 8.6 Hz, 6 H), 7.70 (d, *J* = 8.8 Hz, 6 H), 7.56 (d, *J* = 2.5 Hz, 6 H), 7.54 (d, *J* = 8.6 Hz, 6 H), 7.38 (d, *J* = 8.9 Hz, 6 H), 7.18 (d, *J* = 8.8 Hz, 6 H), 7.05 (dd, *J* = 8.9, 2.5 Hz, 6 H), 4.36-4.43 (comp, 12 H), 3.95 (s, 18 H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 154.0, 145.7, 139.0, 138.1, 136.2, 136.1, 131.7, 127.6, 127.1, 127.0, 126.6, 124.2, 123.6, 115.7, 115.1, 113.9, 110.8, 102.9, 64.7, 64.6, 56.1; MS (MALDI): 1570 ([M+1]$^{+}$, 58 %), 1159 (100 %), 847 (69 %); HRMS (MALDI): calcd. for $C_{96}H_{72}N_4O_{12}S_3$: 1568.4309, found: 1569.4382 ([M+1]$^{+}$).



(**YC08**) was prepared from tris(4-bromophenyl)amine (482 mg, 1.00 mmol), **3d** (1733 mg, 3.50 mmol), $Pd(OAc)_2$ (36 mg, 0.15 mmol), P(adamantyl)$_2$(*n*Bu) (108 mg, 0.30 mmol), PivOH (62 mg, 0.60 mmol), K_2CO_3 (497 mg, 3.60 mmol), and DMF (10 mL) according to the general procedure **B** and yielding after column chromatography (dichloromethane : hexanes = from 40 : 60 to 80 : 20) the pure product **YC08** (1312 mg, 76 %). Yellow solid; m.p.: 278.0-279.1 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 8.17 (d, *J* = 1.7 Hz, 6 H), 7.98 (d, *J* = 8.5 Hz, 6 H), 7.73 (d, *J* = 8.7 Hz, 6 H), 7.58 (d, *J* = 8.6 Hz, 6 H), 7.49 (dd, *J* = 8.7, 1.7 Hz, 6 H), 7.42 (d, *J* = 8.6 Hz, 6 H), 7.21 (d, *J* = 8.5 Hz, 6 H), 4.37-4.46 (comp, 12 H), 1.49 (s, 54 H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 145.7, 142.8, 139.2, 139.0, 138.1, 136.1, 131.7, 127.6, 127.1, 126.8, 124.2, 123.6, 123.4, 116.2, 115.7, 113.9, 109.3, 64.7, 64.6, 34.7, 32.0; MS (MALDI): 1726 (M^{+}, 100 %), 495 (12 %), 396 (21 %); HRMS (MALDI): calcd. for $C_{114}H_{108}N_4O_6S_3$:

1724.7431, found: 1725.7504 ([M+1]$^+$).

References:

1. Lu, T.-J.; Lin, P.-H.; Lee, K.-M.; Liu, C.-Y. *Eur. J. Org. Chem.* **2017**, 111-123.

Figure S1. The UV-Vis absorption and photoluminescence spectra of **YC05-08**.

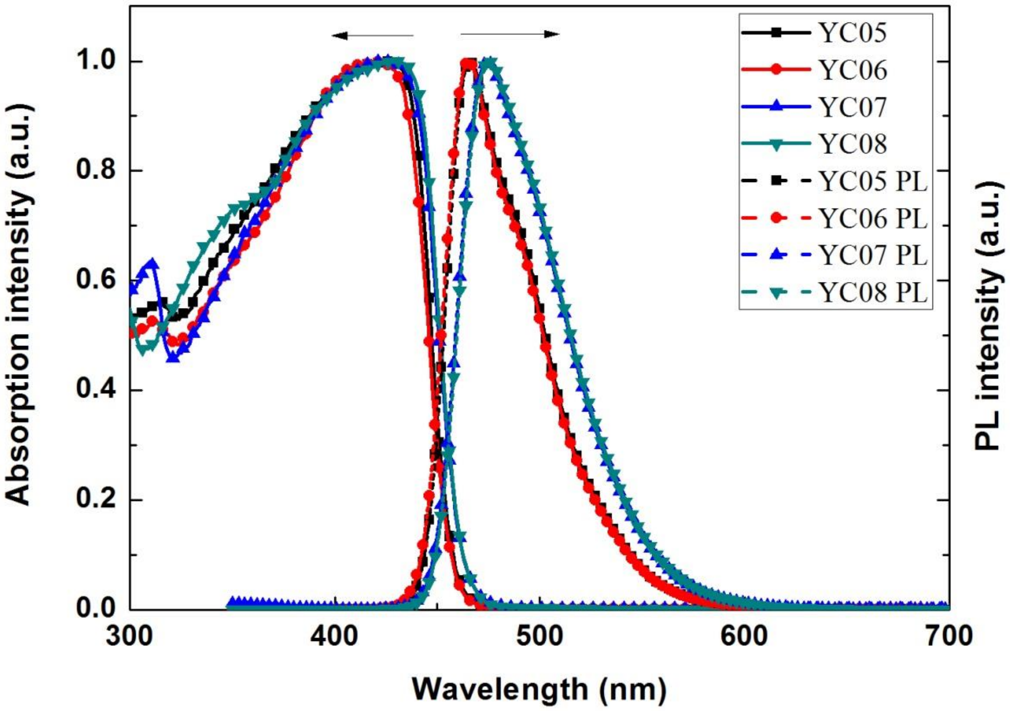


Figure S2. Cyclic voltammetry spectra of **YC05-08** and **spiro-OMeTAD**.

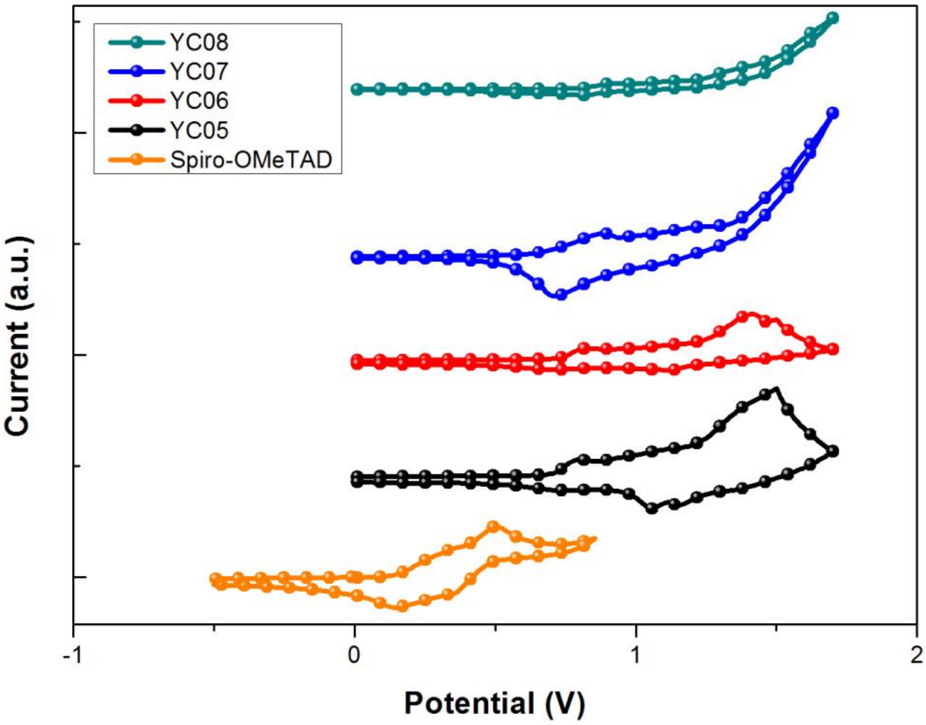
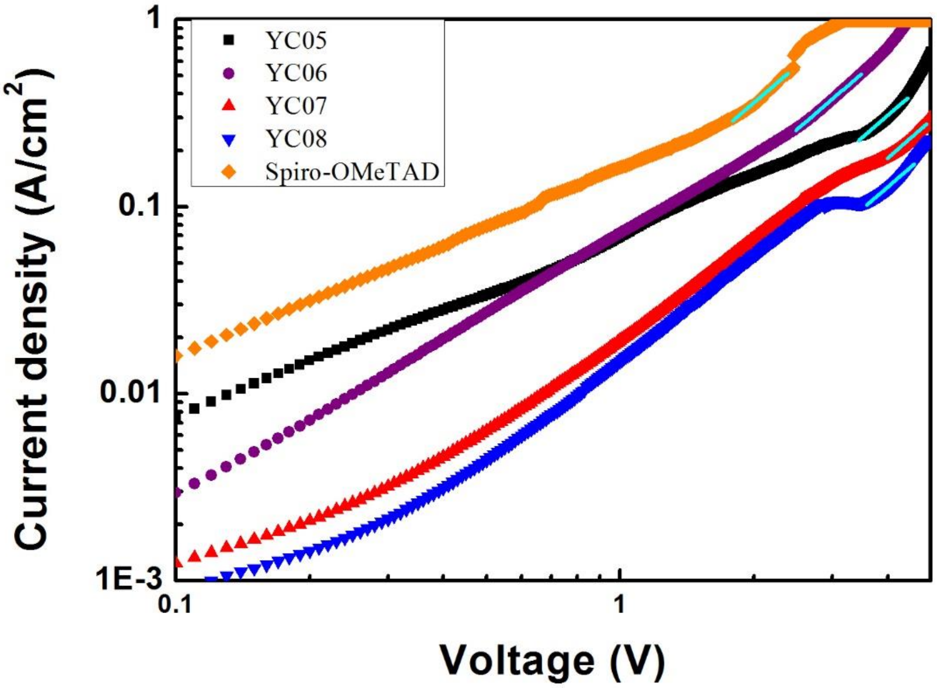


Figure S3. J-V curves for the determination of the hole mobility of **YC05-08** in the space-charge limited current (SCLC) region.



HTMs	hole mobility (cm^{2}V^{-1}s^{-1})
YC05	5.97x10^{-5}
YC06	1.32x10^{-4}
YC07	3.42x10^{-5}
YC08	2.40x10^{-5}
spiro-OMeTAD	2.93x10^{-4}

Figure S4. Thermogravimetric analysis curves of **YC05-08**.

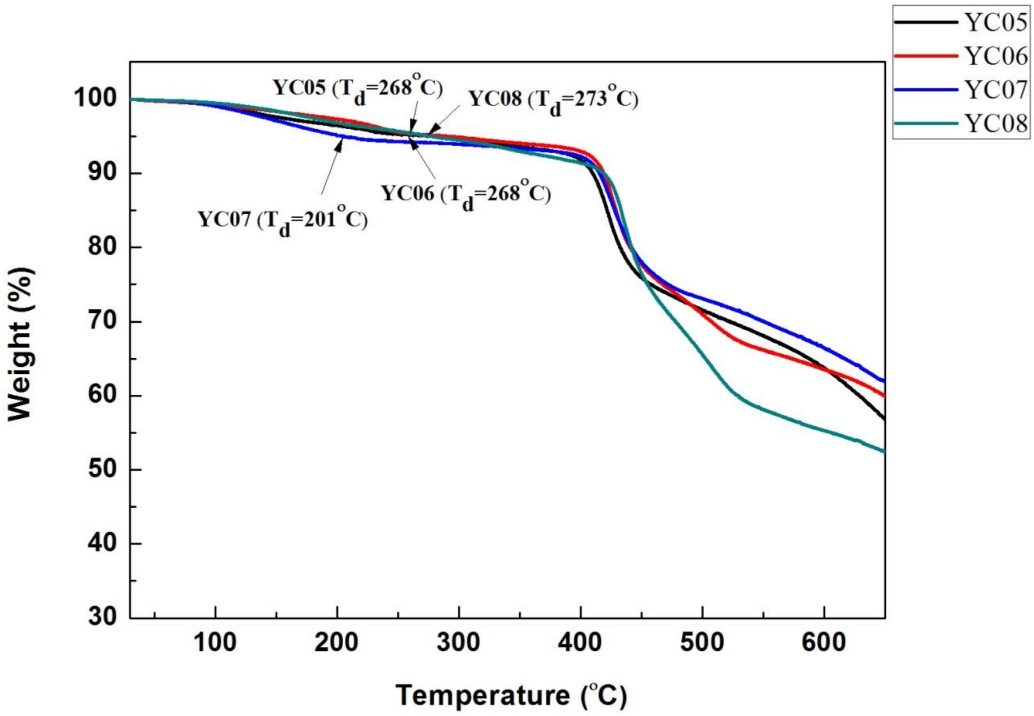


Figure S5. Differential scanning calorimetry curves of **YC05-08**.

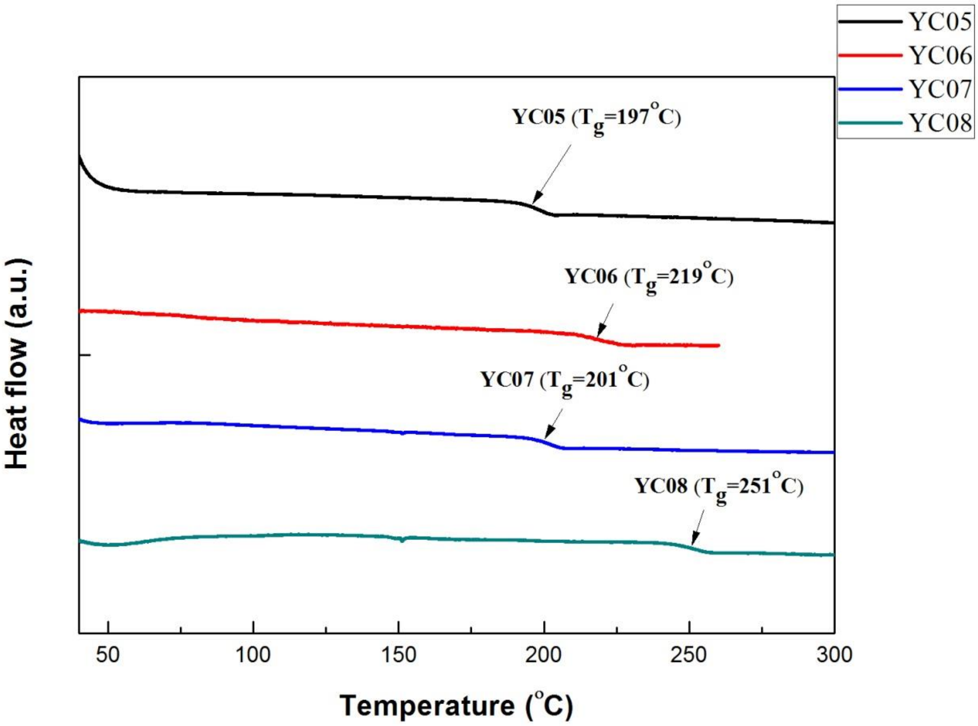


Figure S6. ^{1}H NMR Spectrum of **3a** (300 MHz, CDCl$_3$)

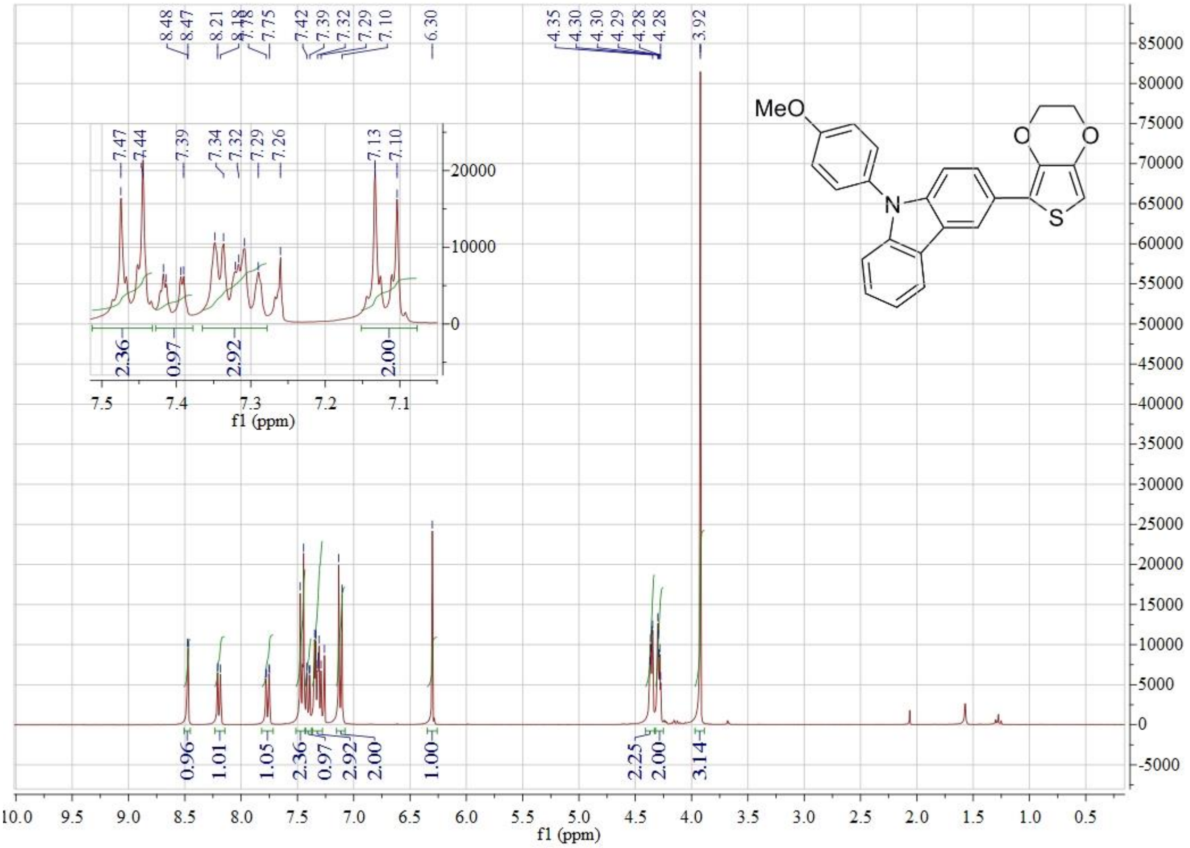


Figure S7. ^{13}C NMR Spectrum of **3a** (75 MHz, CDCl$_3$)

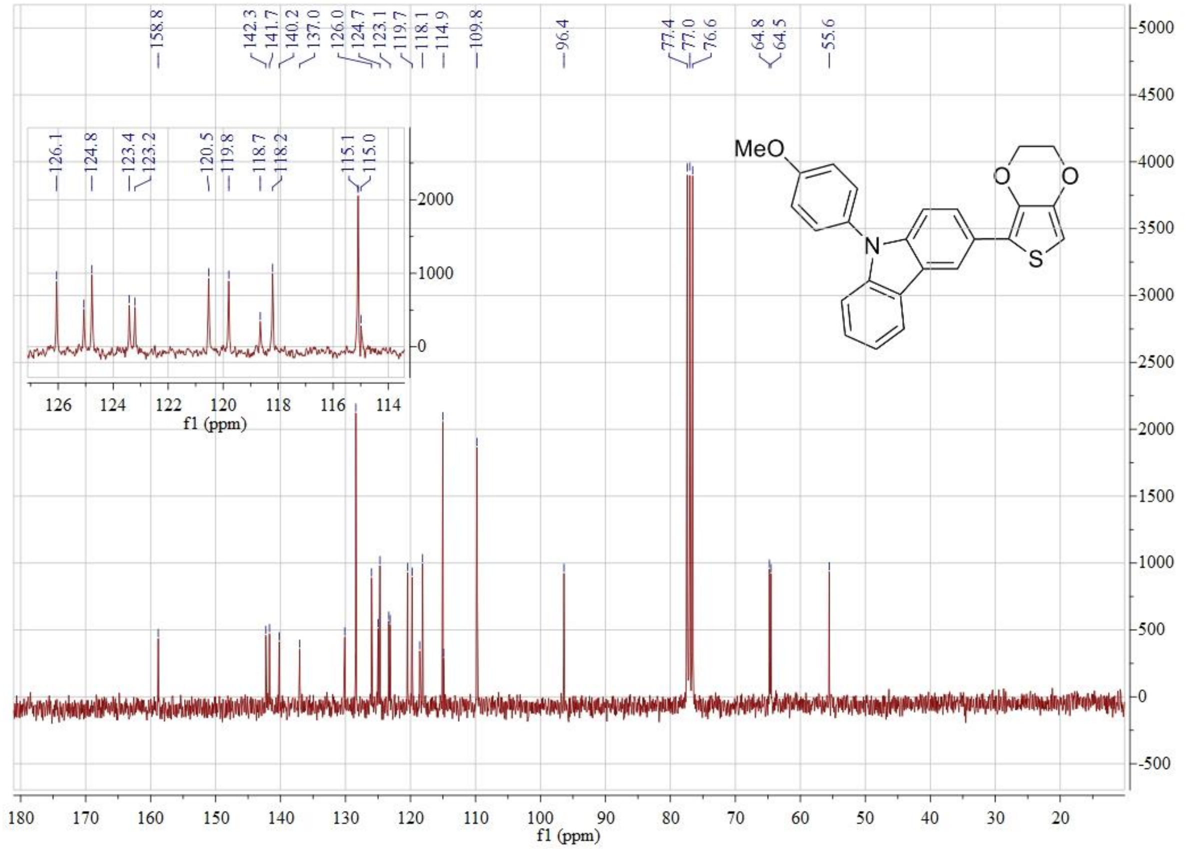


Figure S8. ^{1}H NMR Spectrum of **3b** (300 MHz, $CDCl_3$)

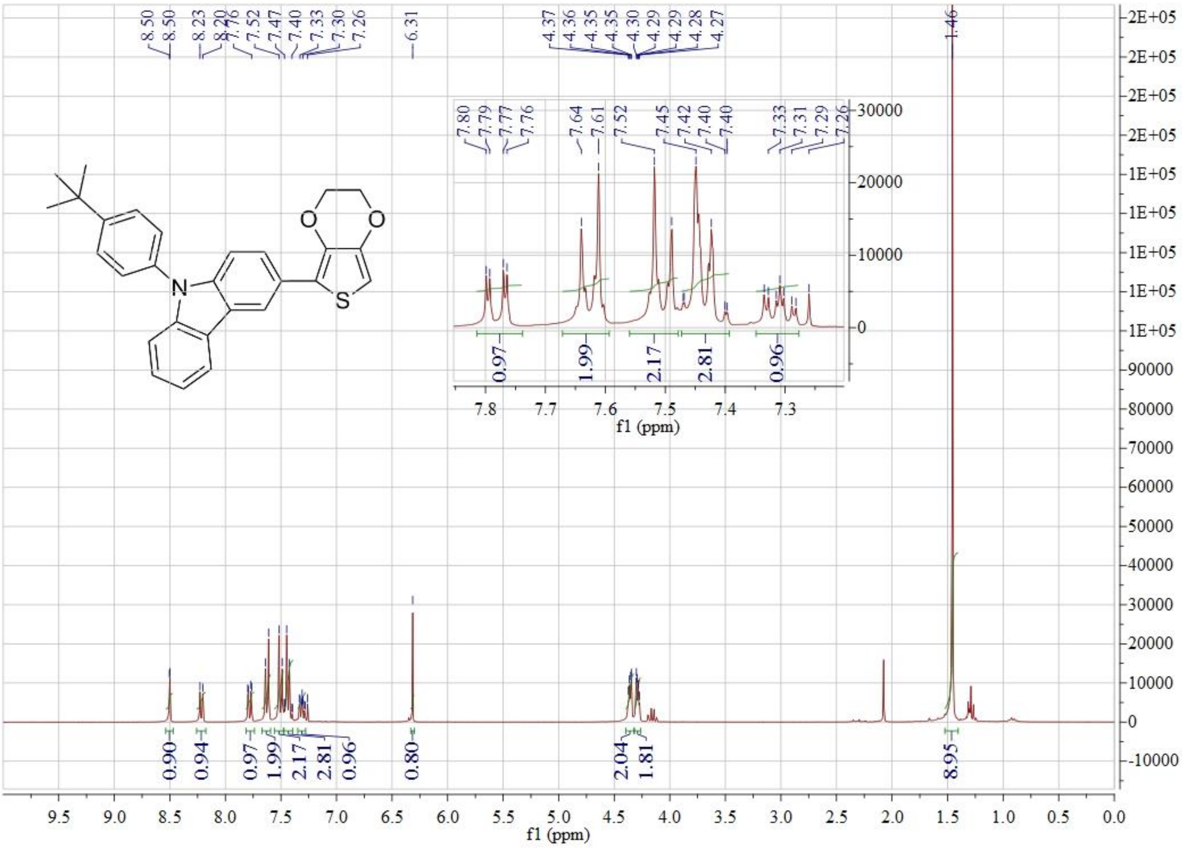


Figure S9. ^{13}C NMR Spectrum of **3b** (75 MHz, $CDCl_3$)

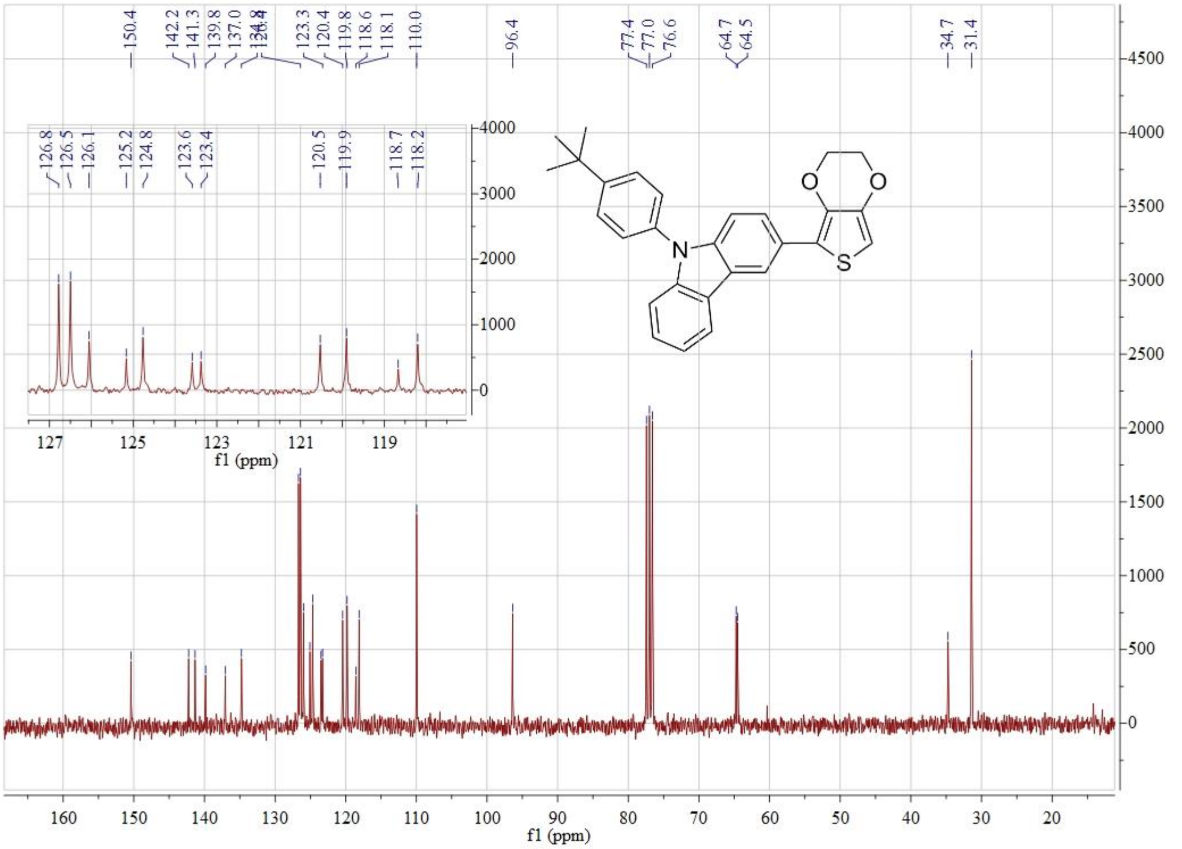


Figure S10. ^{1}H NMR Spectrum of **3c** (300 MHz, $CDCl_3$)

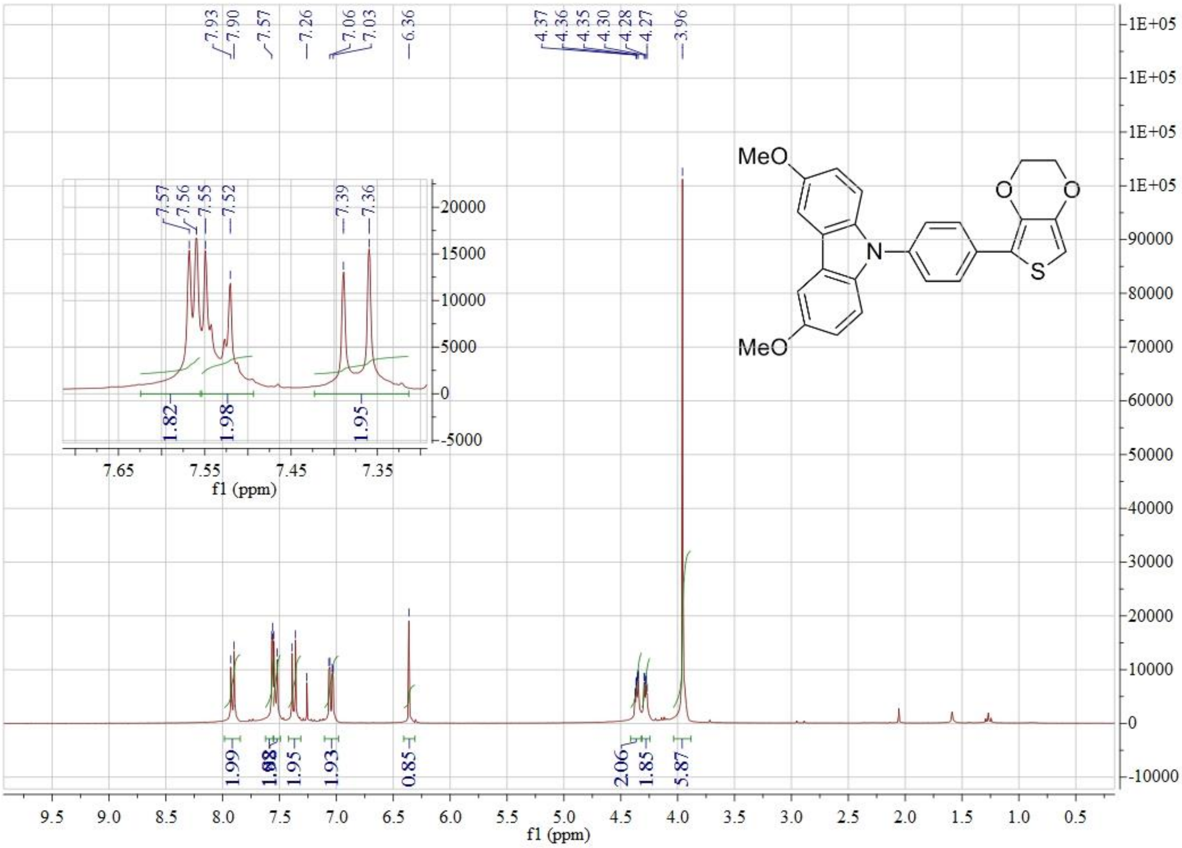


Figure S11. ^{13}C NMR Spectrum of **3c** (75 MHz, $CDCl_3$)

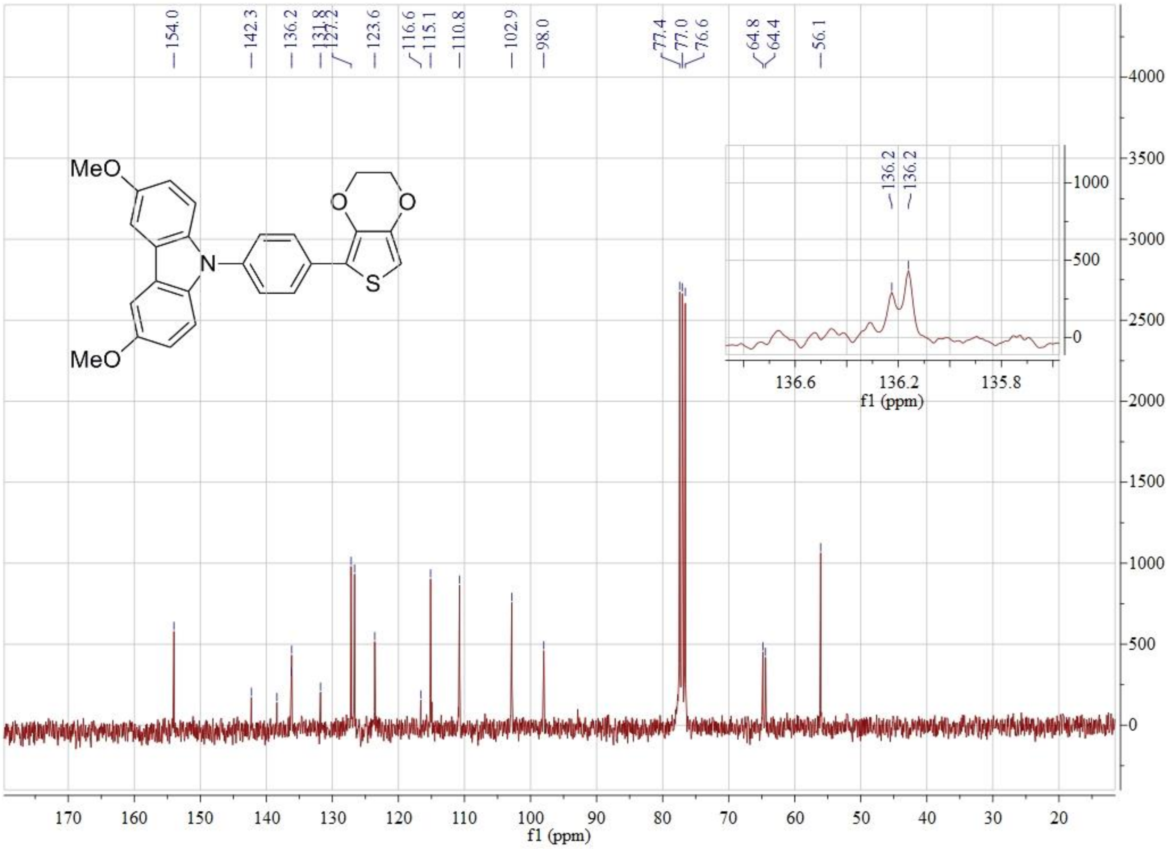


Figure S12. ^{1}H NMR Spectrum of **3d** (300 MHz, $CDCl_3$)

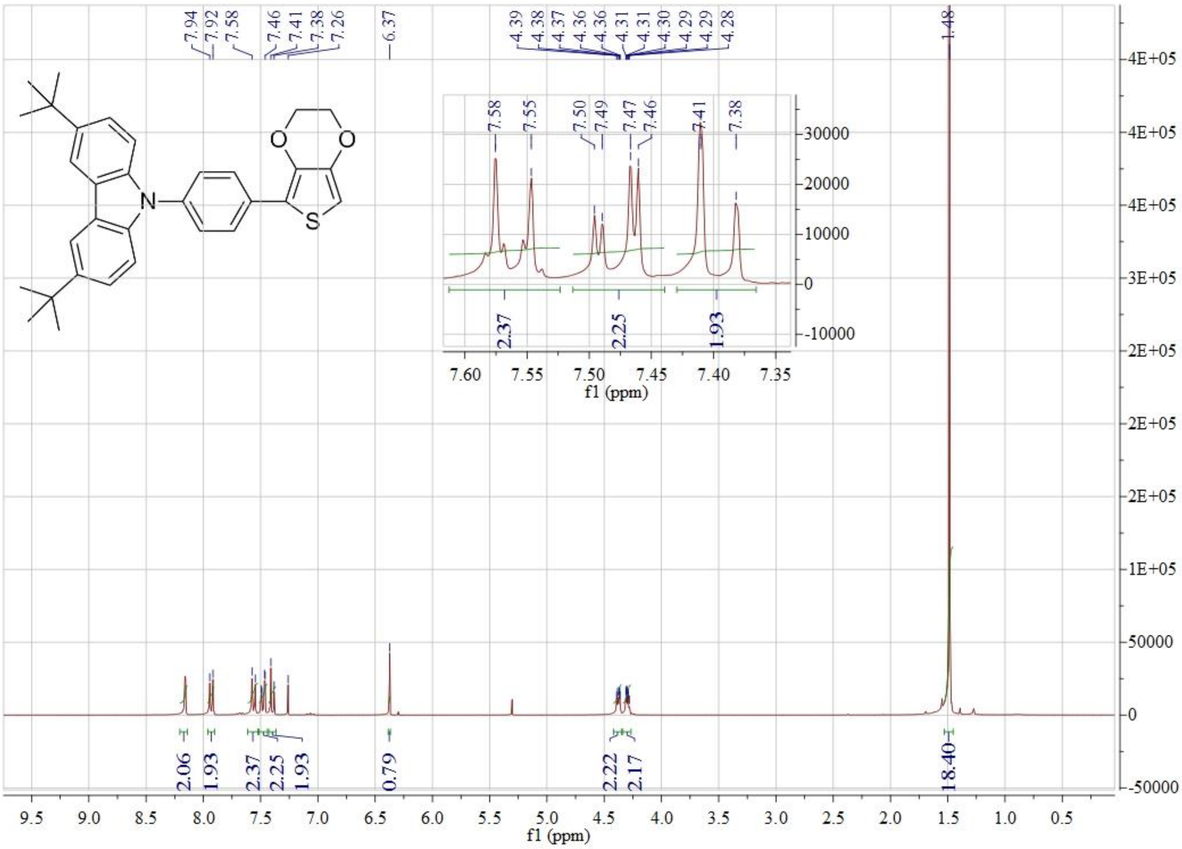


Figure S13. ^{13}C NMR Spectrum of **3d** (75 MHz, $CDCl_3$)

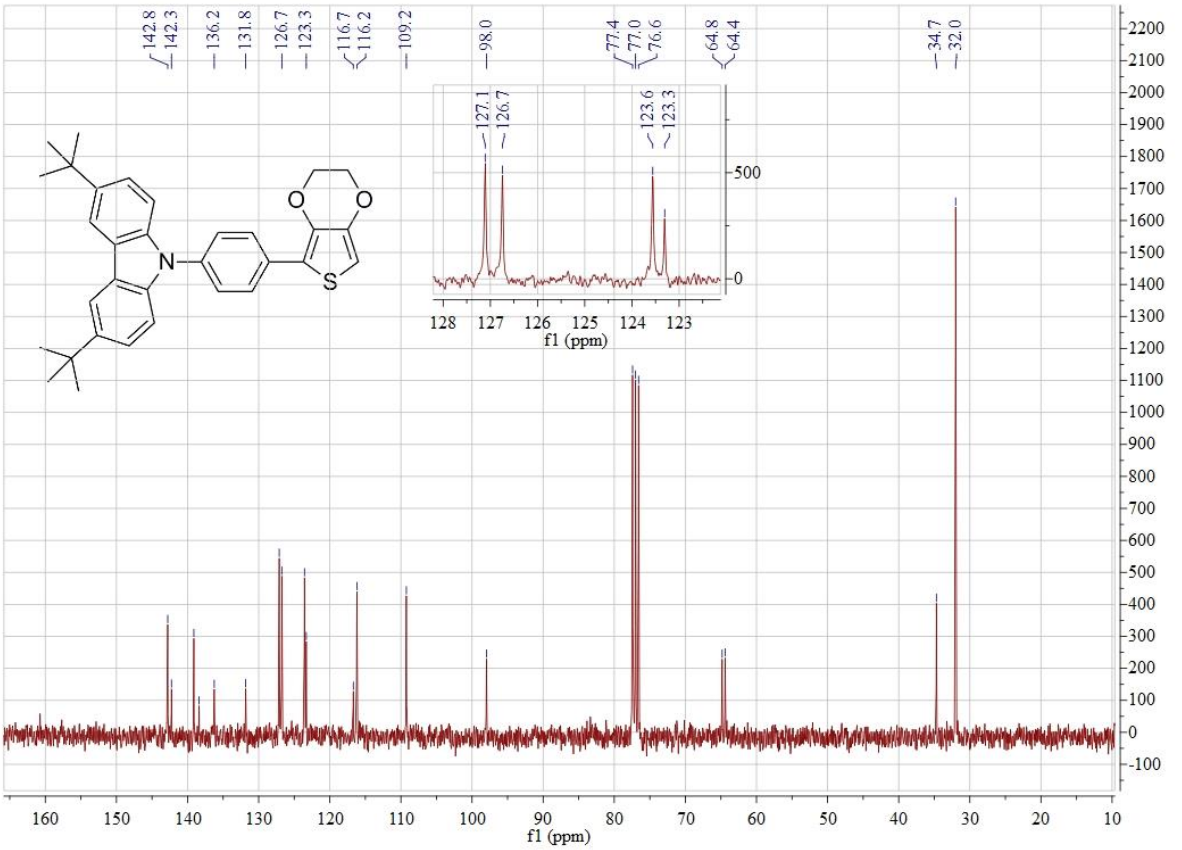


Figure S14. ^{1}H NMR Spectrum of **YC05** (300 MHz, CDCl$_3$)

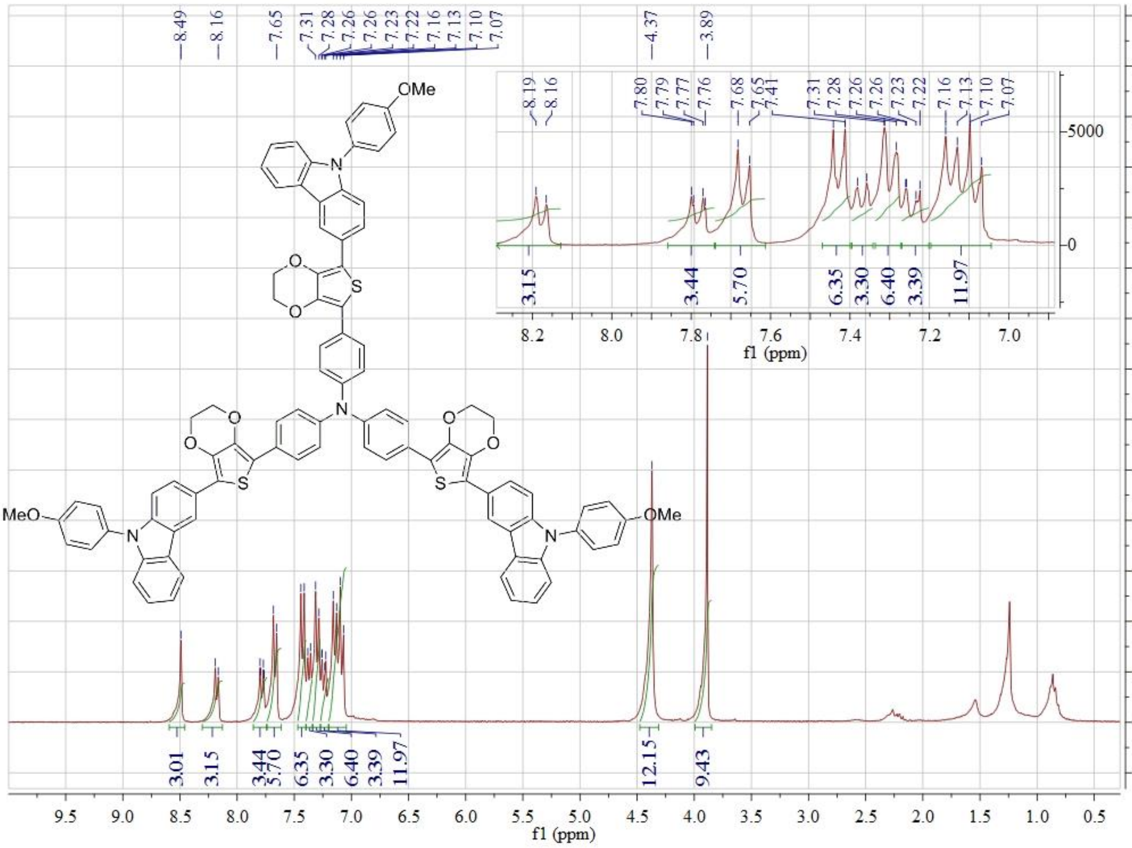


Figure S15. ^{13}C NMR Spectrum of **YC05** (75 MHz, CDCl$_3$)

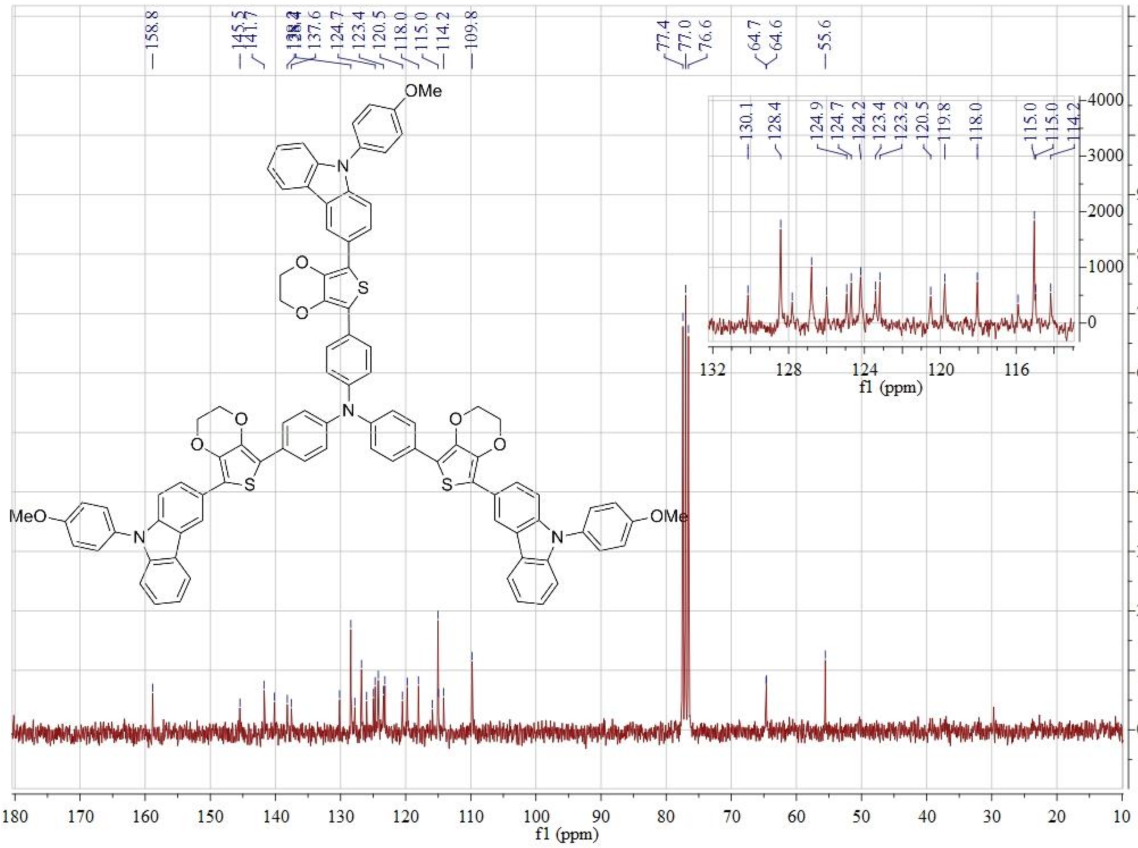


Figure S16. ^{1}H NMR Spectrum of **YC06** (500 MHz, CDCl$_3$)

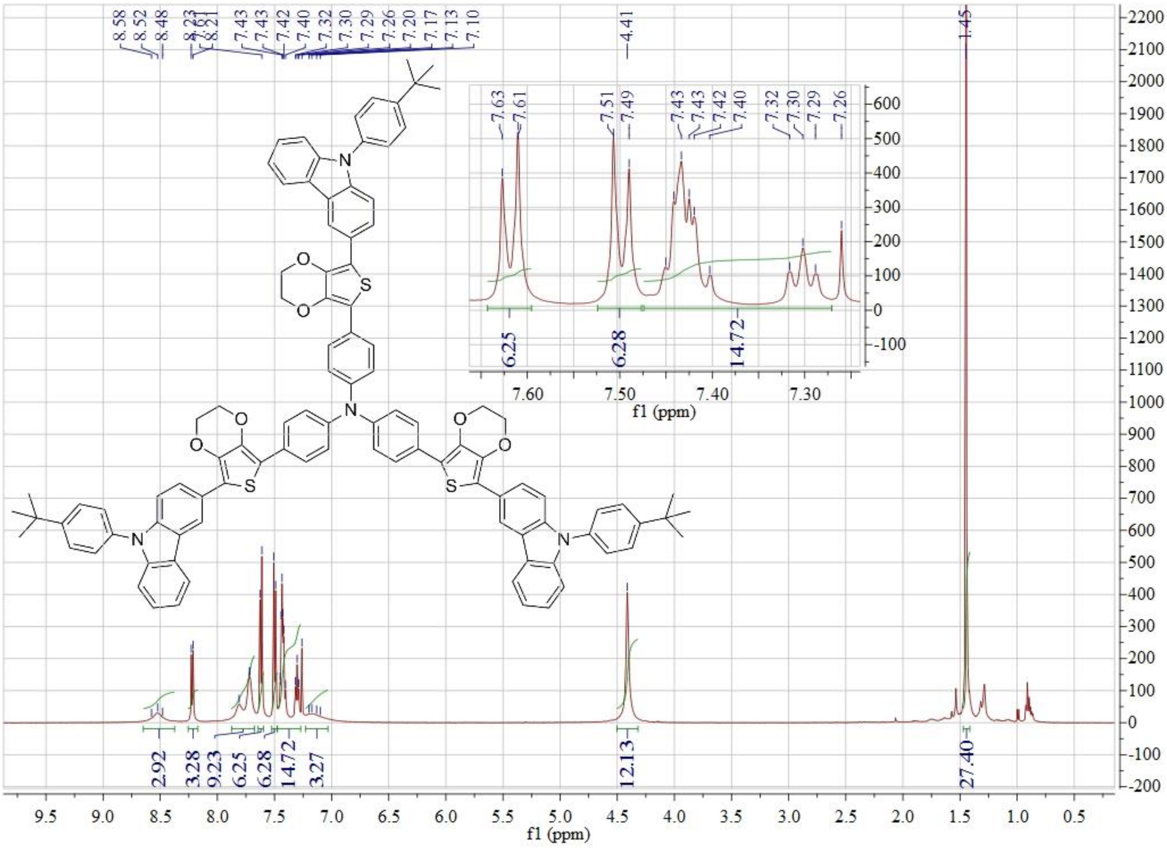


Figure S17. ^{13}C NMR Spectrum of **YC06** (150 MHz, CDCl$_3$)

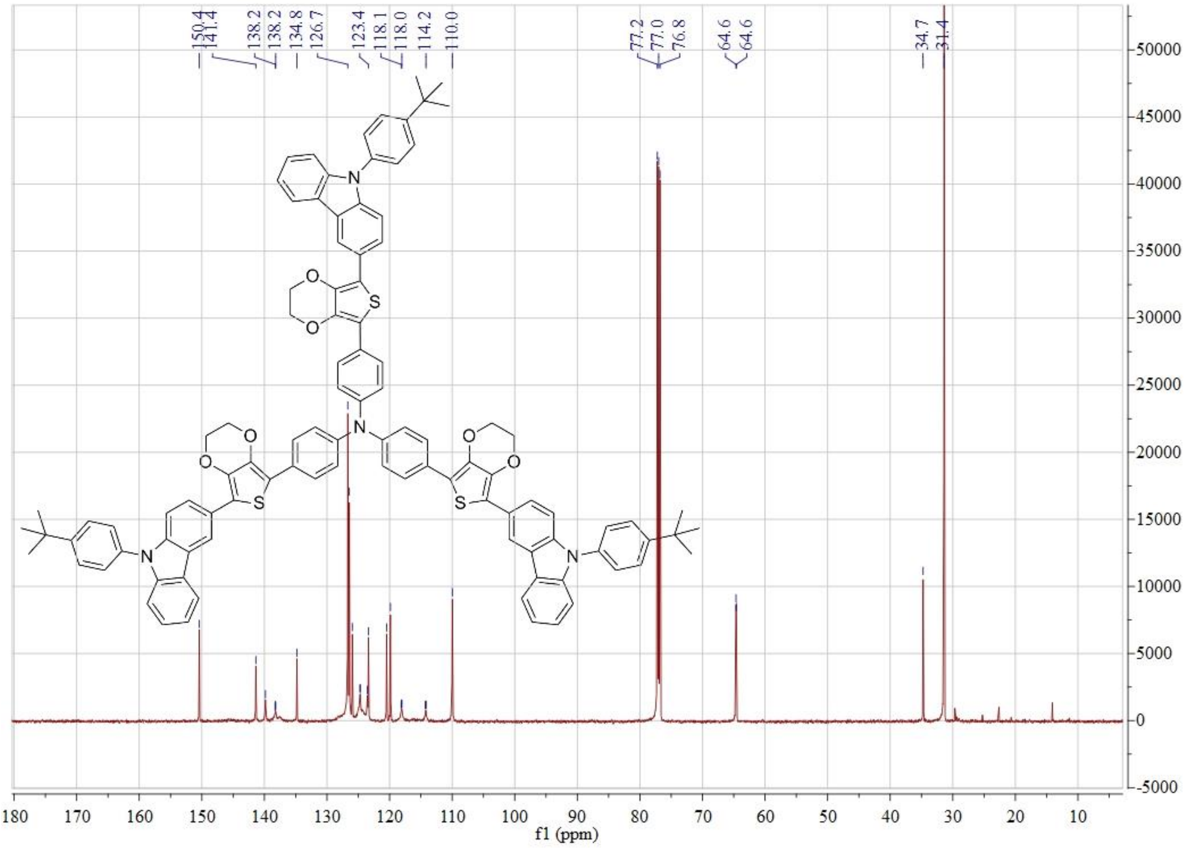


Figure S18. ^{1}H NMR Spectrum of **YC07** (500 MHz, $CDCl_3$)

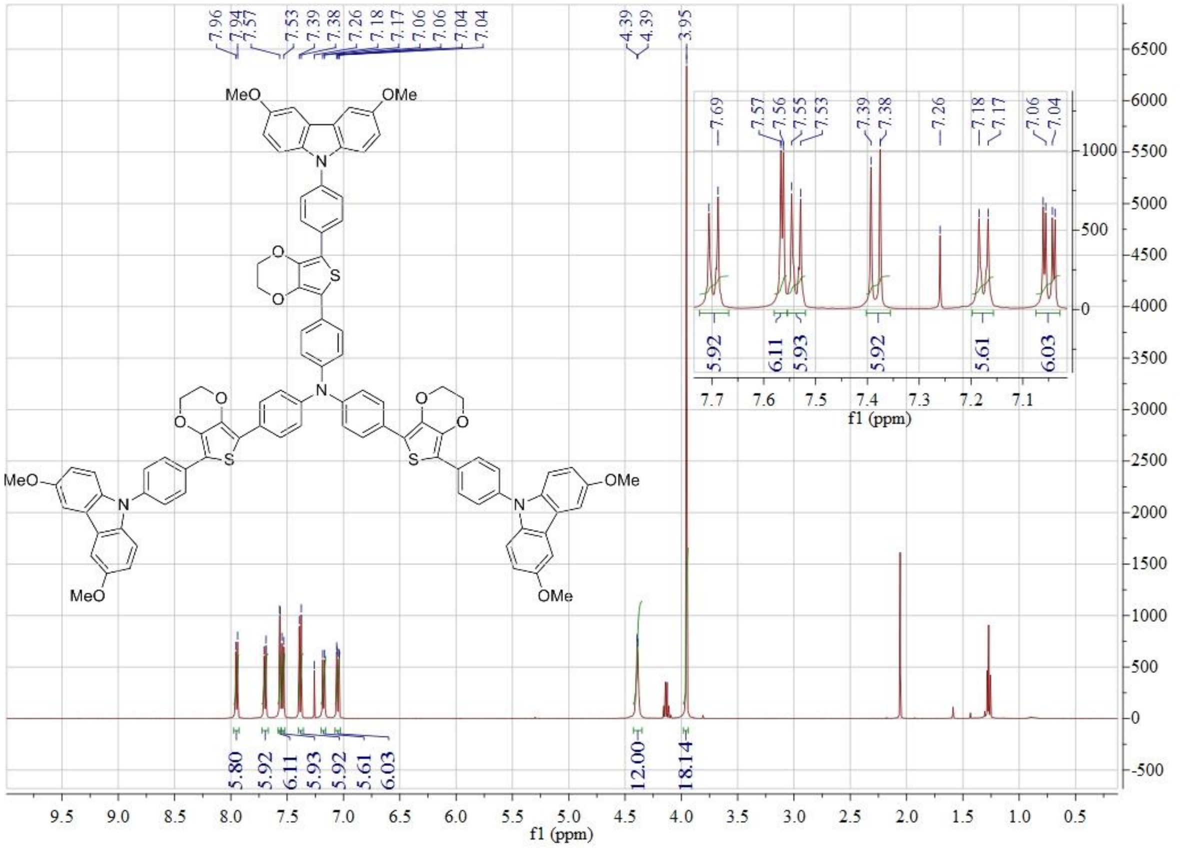


Figure S19. ^{13}C NMR Spectrum of **YC07** (125 MHz, $CDCl_3$)

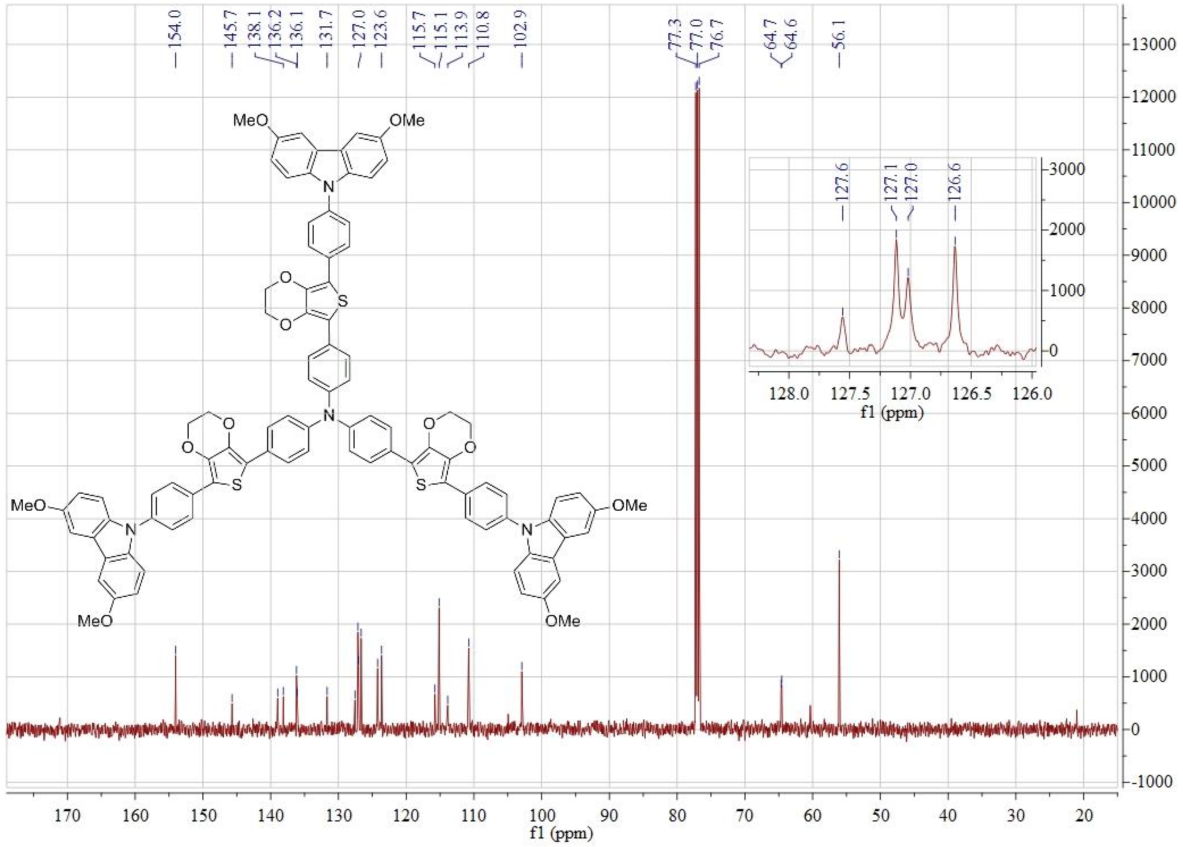


Figure S20. ^{1}H NMR Spectrum of **YC08** (500 MHz, CDCl$_3$)

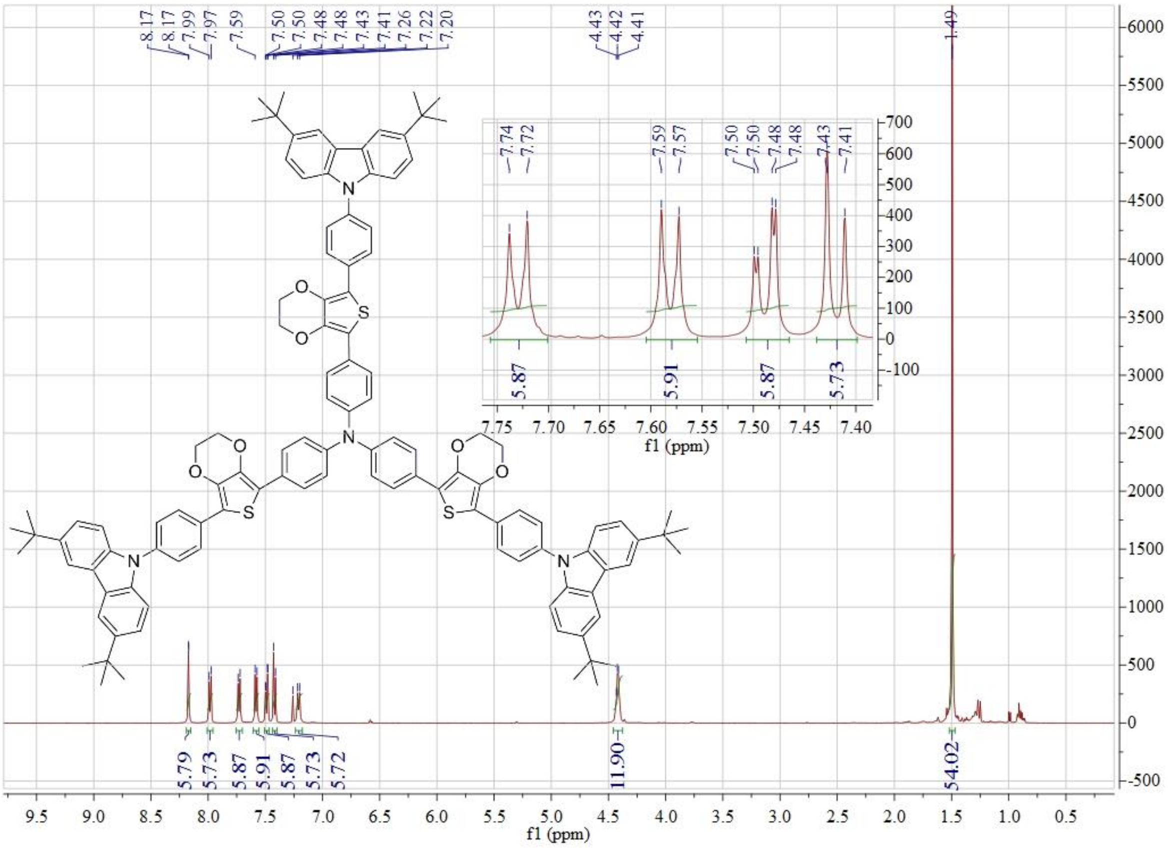


Figure S21. ^{13}C NMR Spectrum of **YC08** (125 MHz, CDCl$_3$)