

Efficient Buchwald-Hartwig amination protocol enables the synthesis of new branched and polymeric hole transport materials for perovskite solar cells

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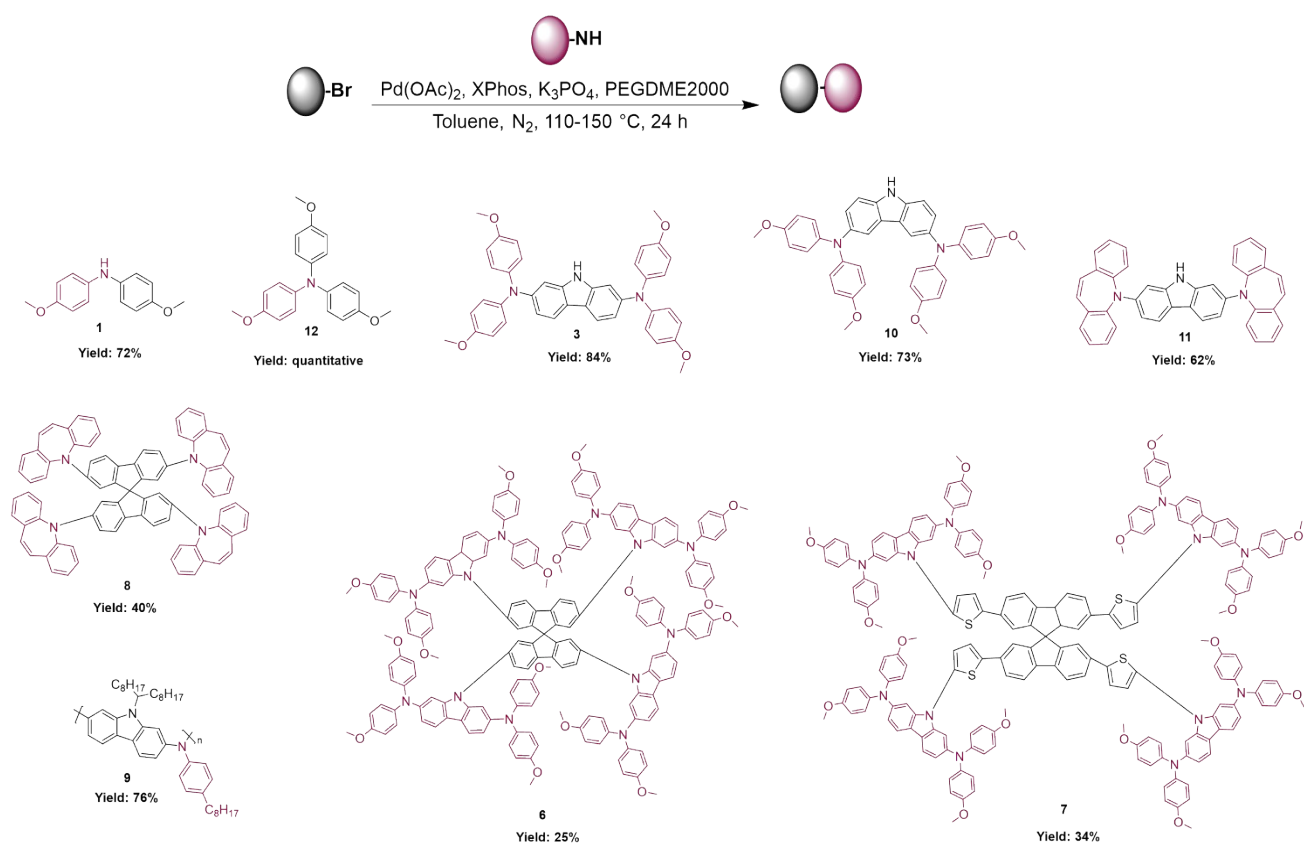
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Reagents and chemicals

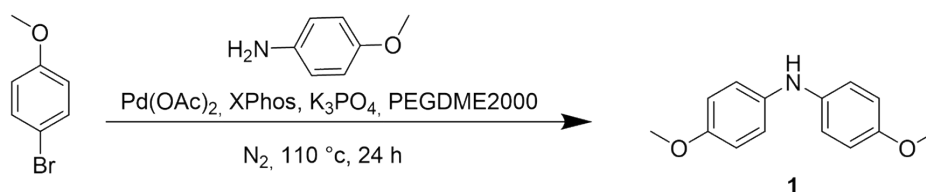
Starting materials for HTM syntheses were all commercially available. Reagents and solvents were bought from Fluorochem, Merck or Alfa Aesar. Filtration on silica gel is performed using Sigma-Aldrich high purity grade silica gel (pore size 60 Å, 220-440 mesh, 35-75 µm particle size) for flash column and Sigma-Aldrich high purity grade silica gel (pore size 60 Å, 70-230 mesh, 63-200 µm particle size) in case of column chromatography. Filtration on Celite is performed using Celite® 535 bought from Fluorochem. Filtration on carbon is performed using DARCO activated charcoal (moisture content <12%, 100 mesh particle size). Composition of eluents used in purification steps are indicated as volume/volume ratios. NMR spectra are collected on a Bruker NMR Avance 400 NEO. All reactions are carried on under nitrogen atmosphere by mean of a Schlenk line.

Synthesis of new HTMs



Scheme S1. Chemical structures of materials synthesized with the Buchwald-Hartwig approach described in this work

Synthesis of derivative 1



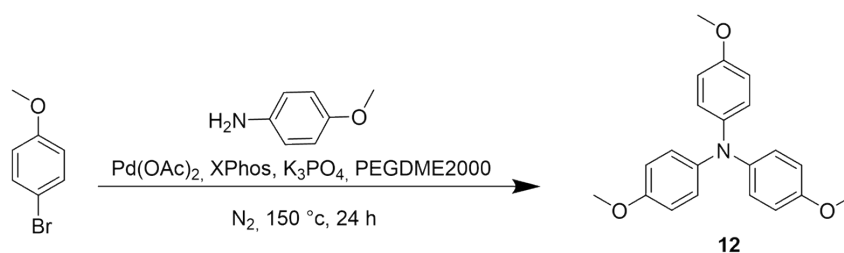
Scheme S2.

The reaction is performed under nitrogen atmosphere. 4-bromoanisole (373.00 mg, 2.00 mmol), p-anisidine (125.10 mg, 1.01 mmol), $\text{Pd}(\text{OAc})_2$ (9.01 mg, 0.04 mmol), XPhos (72.00 mg, 0.15 mmol), K_3PO_4 (636.01 mg, 3.00 mmol), and PEG 2000 dimethylether (6 wt% compared to base) are weighted in a 10 mL Schlenk tube.

The mixture is heated at $110\text{ }^\circ\text{C}$ for 24 hours. Reaction progress can be monitored by TLC (heptane/AcOEt 5:1). The mixture is diluted with toluene and filtered through a pad of celite. The filtrate is evaporated under reduced pressure. The solid is then extracted with DCM and water. The organic phase is evaporated under reduced pressure. The product is recovered by flash chromatography (heptane/AcOEt 5:1) as a white powder, **72% yield (165.10 mg, 0.72 mmol)**.

$^1\text{H NMR}$ (400 MHz, MeOD_3): δ 6.95-6.93 (d, $J=8.9$ Hz, 4H), δ 6.82-6.80 (d, $J=8.7$ Hz, 4H), δ 3.75 (s, 6H) ppm.

Synthesis of derivative 12



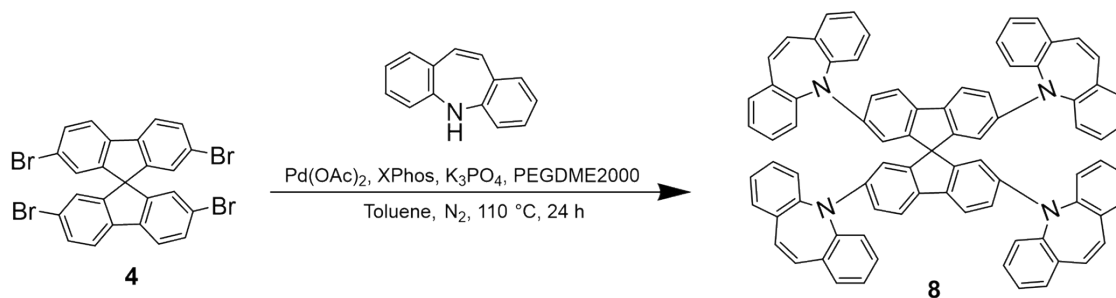
Scheme S3.

The reaction is performed under nitrogen atmosphere. 4-bromoanisole (187.02 mg, 1.00 mmol), p-anisidine (62.21 mg, 0.50 mmol), $\text{Pd}(\text{OAc})_2$ (5.06 mg, 0.02 mmol), XPhos (36.09 mg, 0.08 mmol), K_3PO_4 (318.10 mg, 1.50 mmol), and PEG 2000 dimethylether (6 wt% compared to base) are weighted in a 10 mL Schlenk tube. The mixture is heated at $150\text{ }^\circ\text{C}$ for 24 hours. Reaction progress can be monitored by TLC (heptane/AcOEt 7:3). The mixture is diluted with AcOEt and filtered through a pad of silica. The filtrate is evaporated under reduced pressure. The solid is then extracted with 50 mL of AcOEt and water (50 mL). The organic phase is evaporated under reduced pressure. Solid product, **quantitative yield (160.00 mg, 0.48 mmol)**.

$^1\text{H NMR}$ (400 MHz, CD_3OD): δ 6.93-9.79 (m, 12H), δ 3.77 (s, 9H) ppm.

Synthesis of spiro-core materials

Synthesis of derivative 8



Scheme S4.

The reaction is performed under nitrogen atmosphere. 2,2',7,7'-tetrabromo-9,9'-spirobifluorene (316.01 mg, 0.50 mmol), 5H-dibenzo[b,f]azepine (573.02 mg, 2.50 mmol), Pd(OAc)₂ (9.00 mg, 0.04 mmol), XPhos (38.01 mg, 0.08 mmol), K₃PO₄ (637.10 mg, 3.0 mmol), and PEG 2000 dimethylether (6 wt% compared to base) are weighted in a 10 mL Schlenk tube.

0.8 mL of toluene is added and the solution was heated at 110 °C for 24 hours. Reaction progress can be monitored by TLC (heptane/AcOEt 7:3). The mixture is diluted with toluene and filtered through a pad of silica. The filtrate was evaporated under reduced pressure. Solid powder is taken up with methanol (20 mL) and the precipitate was collected by filtration. The solid is then dispersed in 14 mL of ethyl acetate and the dispersion is heated at reflux for 10 minutes. The product is collected by hot filtration as a yellow powder, **40% yield (251.01 mg, 0.20 mmol)**.

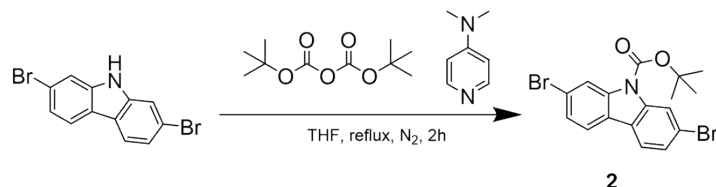
¹H NMR (400 MHz, C₆D₆): δ 7.11 (m, 8H), δ 7.04-7.01 (dd, J = 7.7, 1.4 Hz, 8H), δ 6.97-6.92 (m, 12H), δ 6.86-6.84 (td, J = 7.5, 1.1 Hz, 8H), δ 6.55 (s, 8H), δ 6.29-6.26 (dd, J = 8.6, 2.3 Hz, 4H), δ 6.01 (d, J = 2.3 Hz, 4H) ppm.

¹³C NMR (100 MHz, C₆D₆): δ 150.33, δ 147.63, δ 144.11, δ 136.35, δ 130.41, δ 130.18, δ 129.92, δ 129.26, δ 126.32, δ 118.32, δ 112.01, δ 108.17 ppm.

Synthesis of carbazole-core materials

The synthesis of carbazole-core materials (derivatives **3**, **10**, **11**) requires carbazole protection before performing the Buchwald-Hartwig cross-coupling.

Synthesis of derivative **2**

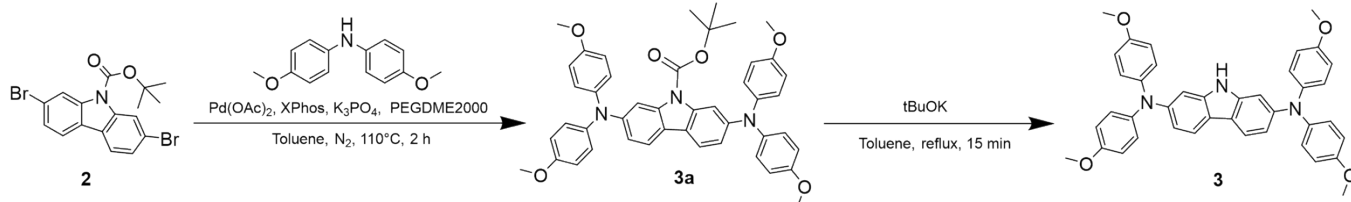


Scheme S5.

The reaction is performed under nitrogen atmosphere. 2,7-dibromocarbazole (13.15 g, 40.46 mmol) and di-tert-butyl dicarbonate (12.36 g, 56.64 mmol) are dispersed in 50 mL of anhydrous THF, then DMAP (0.47 g, 3.84 mmol) is added to the mixture. The solution is heated under reflux for two hours. Reaction progress can be monitored by TLC (heptane/AcOEt 7:3). After cooling, a white precipitate forms and is collected by filtration. The as obtained solid is washed with 100 mL of water, and dried until constant weight. White powder, **quantitative yield (16.92 g, 39.80 mmol)**.

¹H NMR (400 MHz, CDCl₃): δ 8.49 (d, $J = 1.4$ Hz, 2H), 7.80-7.78 (dd, $J = 8.3, 0.5$ Hz, 2H), 7.49-7.47 (dd, $J = 8.1, 1.6$ Hz, 2H), 1.77 (s, 9H) ppm.

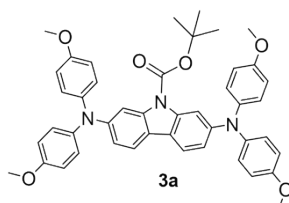
Synthesis of derivative **3**



Scheme S6.

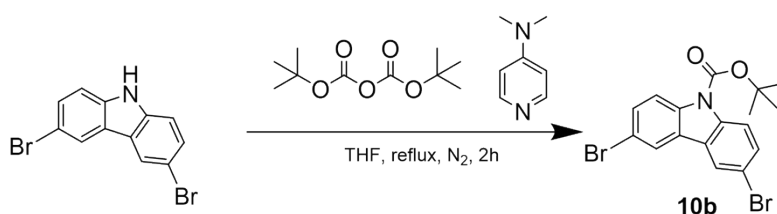
1) The reaction is performed with mechanical stirring under nitrogen atmosphere. Derivative **2** (10.01 g, 23.51 mmol), 4,4'-dimethoxydiphenylamine (13.43 g, 58.57 mmol), Pd(OAc)₂ (0.39 g, 1.76 mmol), XPhos (1.68 g, 3.52 mmol), K₃PO₄ (18.71 g, 88.12 mmol) and PEG dimethylether 2000 (6 wt% compared to base) are dispersed in 14 mL of toluene anhydrous. The mixture is heated at 110 °C for two hours. Reaction progress can be monitored by TLC (heptane/AcOEt 7:3). The mixture is diluted with toluene and filtered through a pad of celite. The filtrated is evaporated under reduced pressure. A mixture of intermediate **3a** and 4,4'-dimethoxydiphenylamine is recovered. Dark green powder (20.93 g).

¹H NMR (400 MHz, C₆D₆): δ 8.39 (s, 2H), δ 7.60-7.58 (d, $J = 8.3$ Hz, 2H), δ 7.22-7.19 (dd, $J = 8.6, 2.2$ Hz, 2H), δ 7.17-7.15 (m, 8H), δ 6.73-6.71 (m, 8H), δ 3.29 (s, 12 H), δ 1.15 (s, 9H) ppm.



- 2) To remove the protective group, the solid is dissolved in 300 mL of toluene and refluxed for 15 minutes while removing water with a Dean-Stark apparatus. Potassium tert-butoxide (7.40 g, 65.9 mmol) is added to the mixture and the reaction is performed under reflux for 15 minutes. A dispersion of yellow powder is obtained. The mixture is diluted with 60 mL of water. The phases are separated and the solvent is removed from the organic phase. The solid is crystallized with 100 mL of ethanol. Pale brown powder, **84% yield (12.24 g, 19.68 mmol)**.
- ¹H NMR (400 MHz, C₆D₆):** δ 7.74-7.72 (d, J= 8.7 Hz, 2H), 7.20-7.18 (m, 8H), 7.12-7.11 (d, J= 2.0 Hz, 2H), 6.91-6.90 (dd, J= 2.0, 0.4 Hz 2H), 6.78-6.76 (m, 8H), 6.31 ppm (s, 1H), 3.31 (s, 12H) ppm.

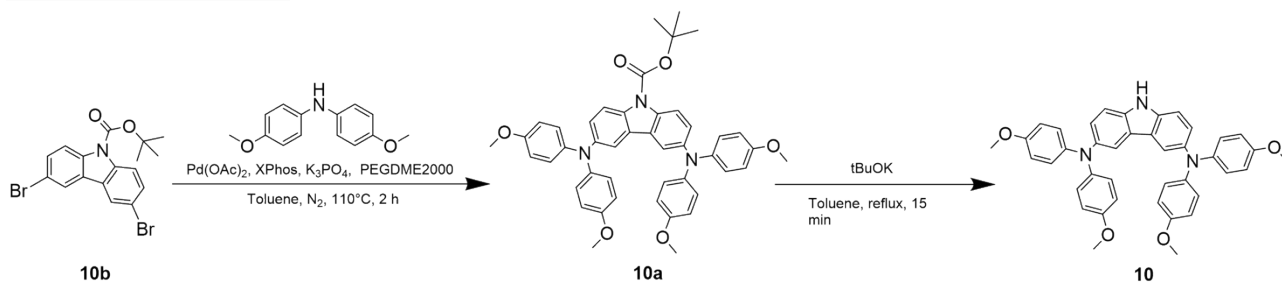
Synthesis of derivative 10b



Scheme S7.

The reaction is performed under nitrogen atmosphere. 3,6-dibromocarbazole (15.70 g, 48.30 mmol) and di-tert-butyl dicarbonate (13.09 g, 60.02 mmol) are dispersed in 30 mL of THF anhydrous, then DMAP (0.56 g, 4.64 mmol) is added to the starting mixture. The solution is heated under reflux for two hours. Reaction progress can be monitored by TLC (heptane/AcOEt 7:3). After cooling, a white precipitate is obtained. The residue is taken up with 100 mL of water and filtered. Yellow powder, **quantitative yield (20.41 g, 48.01 mmol)**.

Synthesis of derivative 10

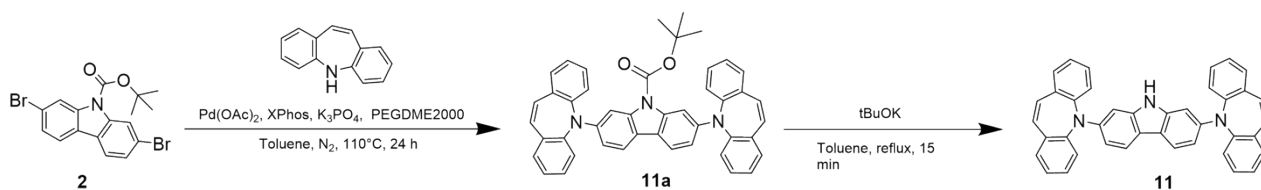


Scheme S8.

- 1) The reaction is performed with mechanical stirring under nitrogen atmosphere. Derivative **10b** (1.71 g, 4.00 mmol), 4,4'-dimethoxydiphenylamine (2.29 g, 10.88 mmol), Pd(OAc)₂ (67.01 mg, 0.32 mmol), XPhos (0.29 g, 0.60 mmol), K₃PO₄ (3.18 g, 15.98 mmol) and PEG dimethylether 2000 (6 wt% compared to base) are dispersed in 2.5 mL of toluene anhydrous. The mixture is heated at 110 °C for two hours. Reaction progress can be monitored by TLC (heptane/AcOEt 7:3). The mixture is diluted with toluene and filtered through a pad of silica gel. The filtrate is evaporated under reduced pressure. The solid is crystallized from heptane (20 mL) to afford a light yellow powder.
- 2) To remove the protective group and excess amine, the powder is heated at 180 °C for 2 h in a sublimation apparatus. The pure product is recovered as a yellow powder as the non-sublimated material, **73% yield (1.81 g, 2.91 mmol)**.

¹H NMR (400 MHz, THF): δ 7.66-7.65 (d, J= 2.2 Hz, 2H), δ 7.33-7.31 (dd, J= 8.6, 0.4 Hz, 2H), δ 7.13-7.10 (dd, J= 8.6, 2.2 Hz, 2H), δ 6.96-6.94 (m 8H), δ 6.78-6.75 (m, 8H), δ 3.73 (s, 12H) ppm.

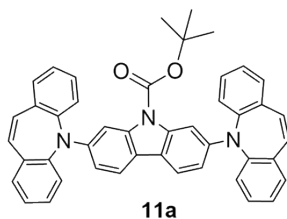
Synthesis of derivative 11



Scheme S9.

- 1) The reaction is performed with magnetic stirring under nitrogen atmosphere. Derivative **2** (0.21 g, 0.50 mmol), 5H-dibenzo[b,f]azepine (0.24 g, 1.25 mmol), Pd(OAc)₂ (8.40 mg, 0.04 mmol), XPhos (36.01 mg, 0.07 mmol), K₃PO₄ (0.39 g, 1.87 mmol) and PEG dimethylether 2000 (6 wt% with respect to the base) are dispersed in 0.3 mL of toluene anhydrous. The mixture is heated at 110 °C for 24 hours. Reaction progress can be monitored by TLC (heptane/AcOEt 7:3). The mixture is diluted with toluene and filtered through a pad of celite. The filtrate is evaporated under reduced pressure. The mixture of intermediate **11a** and 5H-dibenzo[b,f]azepine is recovered. Pale brown powder (0.45 g).

¹H NMR (400 MHz, C₆D₆): δ 7.47-7.44 (dd, J=7.9, 0.9 Hz, 4H), δ 7.30-7.29 (d, J=8.5 Hz, 2H), δ 7.19-7.17 (dd, J= 7.6, 1.6 Hz, 4H), δ 7.11-7.10 (d, J= 1.5 Hz, 2H), δ 7.02-6.98 (m, 6H), δ 6.53 (s, 4H), δ 6.47-6.47 (dd, J= 8.6, 2.1 Hz, 2H), δ 6.07 (s, 2H), δ 1.09 (s, 9H) ppm.

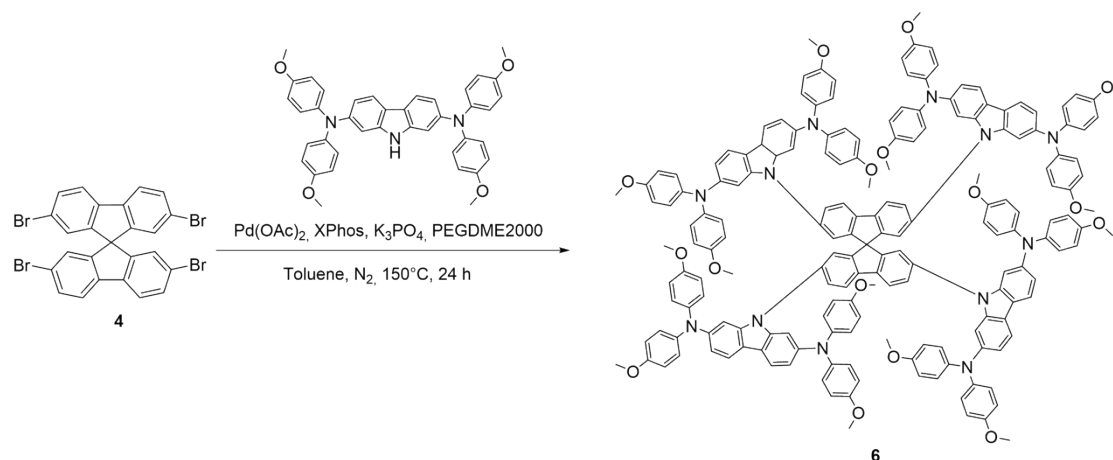


2) To remove the protective group, the solid is dissolved in 25 mL of toluene and refluxed for 15 minutes while removing water with a Dean-Stark apparatus. Potassium tert-butoxide (0.16 mg, 1.40 mmol) is added to the mixture and the reaction is performed under reflux for 15 minutes. The mixture is diluted with 20 mL of water. The phases are separated and the solvent of the organic phase is evaporated under reduced pressure. Solid powder is taken up with 15 mL of methanol and filtered. Pale brown powder, **62% yield (0.17 g, 0.31 mmol)**.

¹H NMR (400 MHz, C₆D₆): δ 7.51-7.49 (dd, J=7.7, 1.1 Hz, 4H), δ 7.44-7.42 (d, J=8.6 Hz, 2H), δ 7.24-7.20 (td, J= 7.4, 1.6 Hz, 4H), δ 7.17 (d, J= 1.6 Hz, 2H), δ 7.09-7.05 (m, 6H), δ 6.56 (s, 4H), δ 6.39-6.37 (dd, J= 8.6, 2.3 Hz, 2H), δ 6.08-6.07 (d, 2.0 Hz, 2H) ppm.

Synthesis of combined Spiro-carbazole HTMs

Synthesis of derivative 6



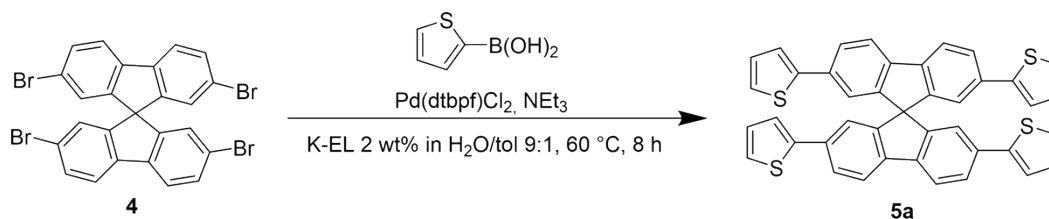
Scheme S10.

The reaction is performed under nitrogen atmosphere. 2,2',7,7'-tetrabromo-9,9'-spirobifluorene (316.00 mg, 0.50 mmol), N₂,N₂,N₇,N₇-tetrakis(4-methoxyphenyl)-9H-carbazole-2,7-diamine (1.55 g, 2.50 mmol), Pd(OAc)₂ (9.00 mg, 0.04 mmol), XPhos (38.01 mg, 0.08 mmol), K₃PO₄ (637.09 mg, 3.01 mmol), and PEG 2000 dimethylether (6 wt% with respect to the base) are weighted in a 10 mL Schlenk tube. Toluene (0.8 mL) is added and the solution is heated at 150 °C for 24 hours. Reaction progress can be monitored by TLC (heptane/AcOEt 1:1). The mixture is diluted with toluene and filtered through a pad of celite. The filtrate is evaporated under reduced pressure. The as obtained powder is purified by column chromatography with toluene/Et₂O 95:5 as eluent. Yellow powder, **25% yield (340.91 mg, 0.13 mmol)**.

¹H NMR (400 MHz, C₆D₆): δ 7.68-7.66 (d, J = 8.4 Hz, 8H), δ 7.42-7.40 (d, J = 8.1 Hz, 4H), δ 7.35-7.33 (dd, J = 8.2, 1.7 Hz, 4H), δ 7.24 (s, 8H), δ 7.04-7.02 (dd, J = 8.3, 1.9 Hz, 8H), δ 6.98 (s, 4H), δ 6.94-6.92 (d, J = 9.1 Hz, 32H), δ 6.56-6.54 (d, J = 8.7 Hz, 32H), δ 3.37 (s, 48H) ppm.

¹³C NMR (100 MHz, C₆D₆): δ 155.28, δ 148.99, δ 146.53, δ 142.03, δ 141.63, δ 138.62, δ 136.77, δ 125.15, δ 124.91, δ 122.02, δ 120.11, δ 119.56, δ 119.27, δ 117.72, δ 114.60, δ 105.69, δ 66.93, δ 54.72 ppm.

Synthesis of derivative 5a



Scheme S11.

2,2',7,7'-tetrabromo-9,9'-spirobifluorene (1.00 g, 1.58 mmol), 2-thienylboronic acid (1.01 g, 7.90 mmol) and Pd(dtbbpf)Cl₂ (82.01 mg, 0.01 mmol) are weighed in the reaction flask and 3.2 mL of Kolliphor EL 2 wt% in H₂O/toluene 9:1 v/v emulsion is added. The mixture is stirred and allowed to homogenize for 5 minutes before addition of the NEt₃ (0.96 g, 9.48 mmol). The reaction is quenched after 8 h of stirring at 60°C, extracted with CH₂Cl₂ and filtered over a pad of silica gel. The pure product is obtained in **98% yield (0.99 g, 1.55 mmol)**.

¹H-NMR (400 MHz, CDCl₃): δ 7.88-7.86 (dd, J = 8.0, 0.5 Hz, 4H), δ 7.67-7.65 (dd, J = 8.1, 1.6 Hz, 4H), δ 7.16-7.14 (m, 8H), δ 7.00 (dd, J = 1.7, 0.5 Hz, 4H), δ 6.95-6.93 (dd, J = 5.0, 3.6 Hz, 4H) ppm.

¹³C-NMR (100 MHz, CDCl₃): δ 149.38, δ 144.13, δ 140.63, δ 134.27, δ 127.87, δ 126.14, δ 124.71, δ 123.31, δ 121.41, δ 120.54, δ 65.91 ppm.

Synthesis of derivative 5

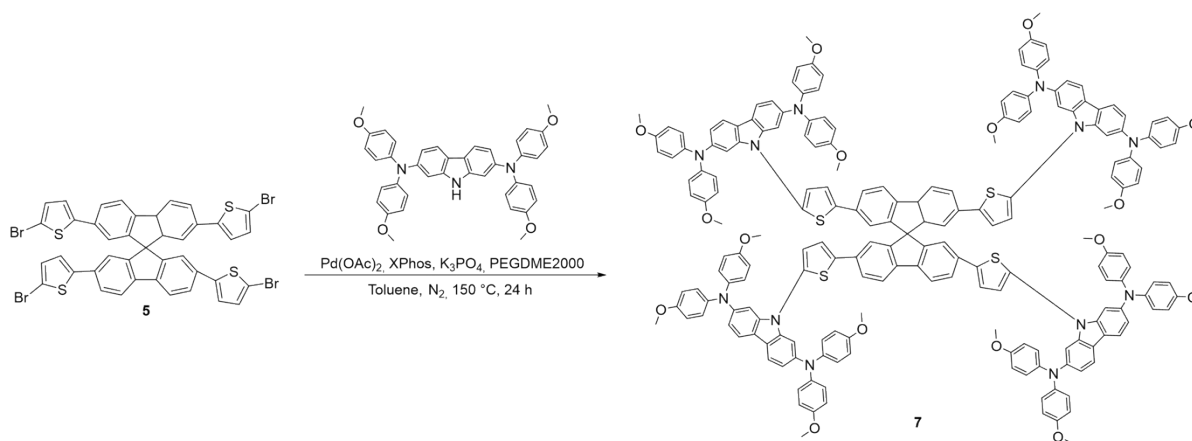


Scheme S12.

Derivative **5a** (0.90 g, 1.40 mmol) is dissolved in 30 mL of CHCl₃ and cooled to 0 °C with an ice bath. Then N-bromosuccinimide (NBS, 1.12 g, 6.29 mmol) is slowly added portion wise. The reaction is stirred in the dark for 24h. The mixture is washed 3 times with 30 mL of 5% solution of NaHCO₃ and then with 30 mL of deionized water. The crude is recrystallized in 40 mL of CHCl₃, cooling down the flask at -18 °C overnight. The pure product was collected by filtration as yellow powder. **68% yield (0.92 g, 0.95 mmol).**

¹H-NMR (400 MHz, toluene-d₈): δ 7.65-7.63 (d, J = 7.8 Hz, 4H), δ 7.41-7.39 (dd, J = 8.3, 1.9 Hz, 4H), δ 7.15 (d, J = 1.5 Hz, 4H), δ 6.46-6.45 (d, J = 3.9 Hz, 4H), δ 6.99-6.98 (d, J = 4.1 Hz, 4H) ppm.

¹³C-NMR (100 MHz, toluene-d₈): δ 149.76, δ 144.96, δ 140.85, δ 134.26, δ 130.78, δ 126.19, δ 123.57, δ 120.86, δ 120.76, δ 111.48, δ 66.27 ppm.



Scheme S13.

Synthesis of derivative 7

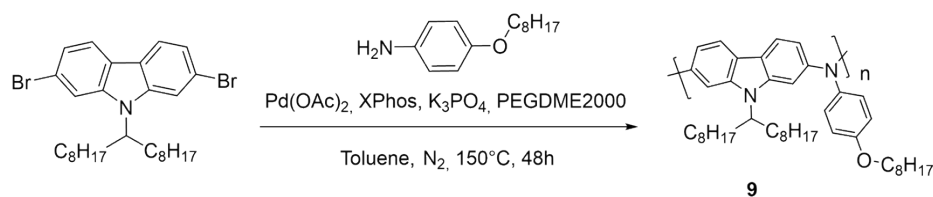
The reaction is performed under nitrogen atmosphere. 2,2',7,7'-tetrakis(5-bromo-thiophene-2-yl)-9,9'-spirobifluorene (250.01 mg, 0.26 mmol), N₂,N₂,N₇,N₇-Tetrakis(4-methoxyphenyl)-9H-carbazole-2,7-diamine (0.81 g, 1.30 mmol), Pd(OAc)₂ (5.00 mg, 0.02 mmol), XPhos (19.80 mg, 0.04 mmol), K₃PO₄ (331.01 mg, 1.00 mmol), and PEG 2000 dimethylether (6 wt% with respect to the base) are weighted in a 10 mL Schlenk tube. Toluene (0.4 mL) is added and the mixture is heated at 150 °C for 24 hours. Reaction progress can be monitored by TLC (heptane/AcOEt 1:1). The mixture is diluted with toluene and filtered through a pad of celite. The filtrated is evaporated under reduced

pressure. The as obtained powder is purified by column chromatography with toluene/Et₂O 97:3 as eluent. Yellow powder, **34% yield (282.01 mg, 0.09 mmol)**.

¹H NMR (400 MHz, THF): δ 8.00-7.98 (d, J= 8.1 Hz, 4H), δ 7.76-7.74 (d, J= 8.4 Hz, 4H), δ 7.56-7.54 (dd, J= 8.0, 1.1 Hz, 4H), δ 7.24 (s, 8H), δ 7.10 (d, J= 1.7 Hz, 12H), δ 7.06 (s, 4H), δ 6.99-6.97 (d, J= 8.7 Hz, 32H), δ 6.85-6.82 (m, 12H), δ 6.77-6.75 (d, J= 8.9 Hz, 32H), δ 3.67 (s, 48H) ppm.

¹³C NMR (100 MHz, THF): δ 155.74, δ 149.53, δ 147.06, δ 142.73, δ 141.49, δ 140.86, δ 140.77, δ 137.79, δ 134.19, δ 126.00, δ 125.58, δ 124.07, δ 122.48, δ 120.63, δ 120.36, δ 119.38, δ 118.27, δ 116.35, δ 114.31, δ 103.27, δ 54.55 ppm.

Polymerization test: synthesis of derivative 9



Scheme S14.

The polymerization is carried out in a Schlenk tube under magnetic stirring. 2,7-Dibromo-9-(1-octylonyl)-9H-carbazole (282.01 mg, 0.51 mmol), 4-(octyloxy)benzenamine (111.04 mg, 0.50 mmol), Pd(OAc)₂ (5.00 mg, 0.02 mmol), XPhos (19.78 mg, 0.04 mmol), K₃PO₄ (331.01 mg, 1.00 mmol), and PEG 2000 dimethylether (6 wt% with respect to the base) are weighted. Toluene (0.3 mL) was added and the mixture was heated at 150 °C. After stirring for 48 hours the polymer was precipitated in methanol (15 mL) and then submitted to Soxhlet extraction with MeOH, acetone and heptane in this order to remove the excess catalyst and oligomers. The polymer is recovered from the heptane extract by precipitation with methanol. Brown powder, **76% yield (238.01 mg, 0.38 mmol)**.

Mn (g/mol) 20410, Mw (g/mol) 35035, PDI 1.72.

NMR Spectra

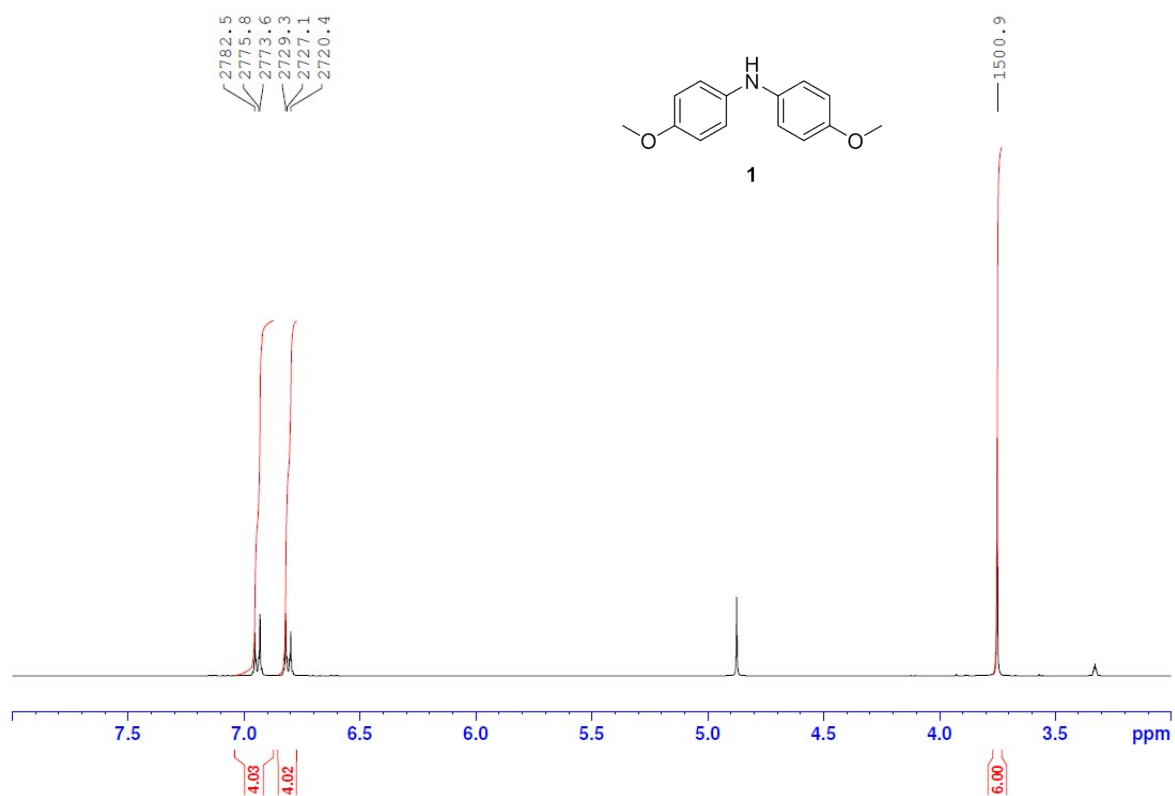


Figure S1. ¹H NMR of derivative 1 in CD₃OD

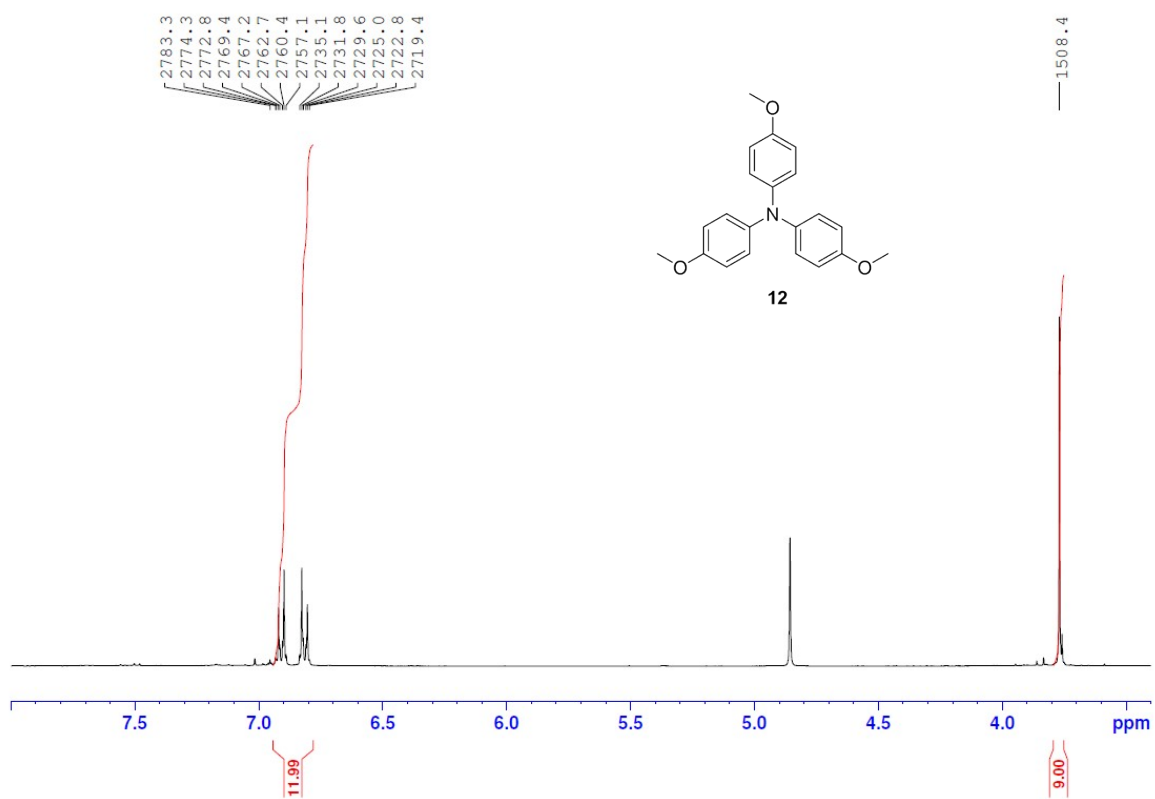
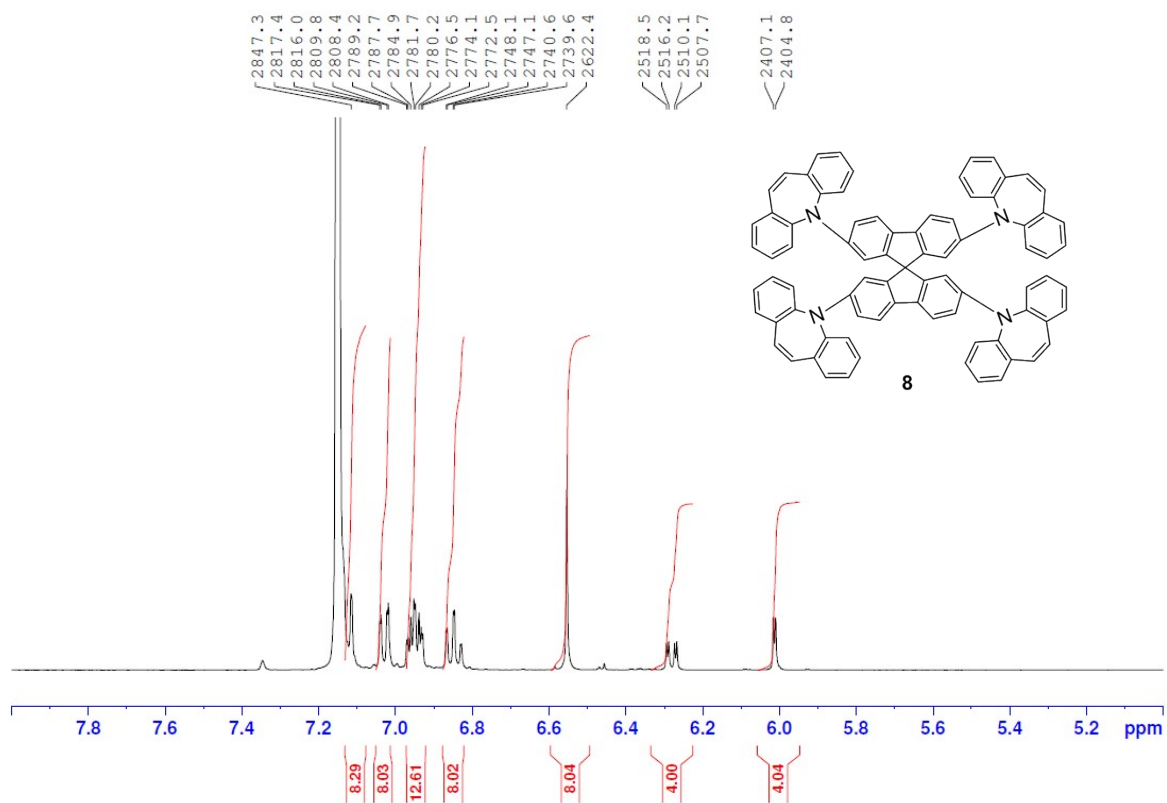


Figure S2. ^1H NMR of derivative 12 in CD_3OD



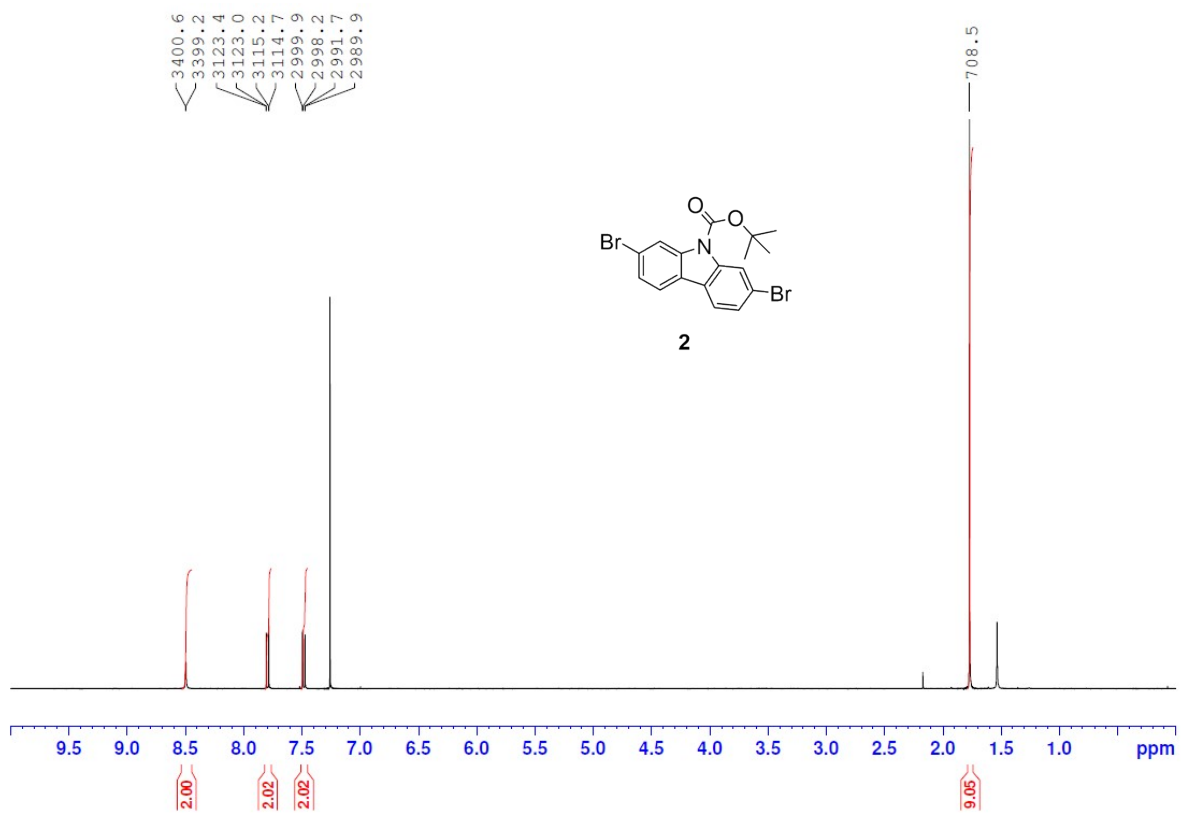


Figure S5. ¹H NMR of derivative 2 in CDCl₃

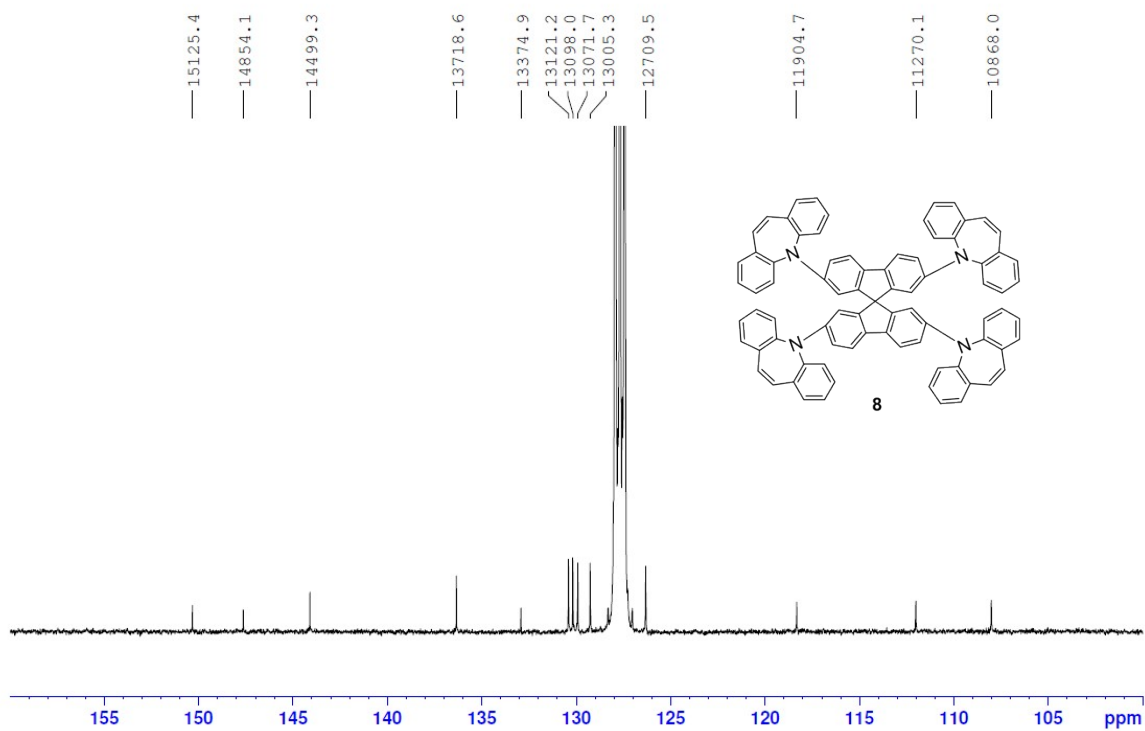


Figure S4. ¹³C NMR of derivative 8 in C₆D₆

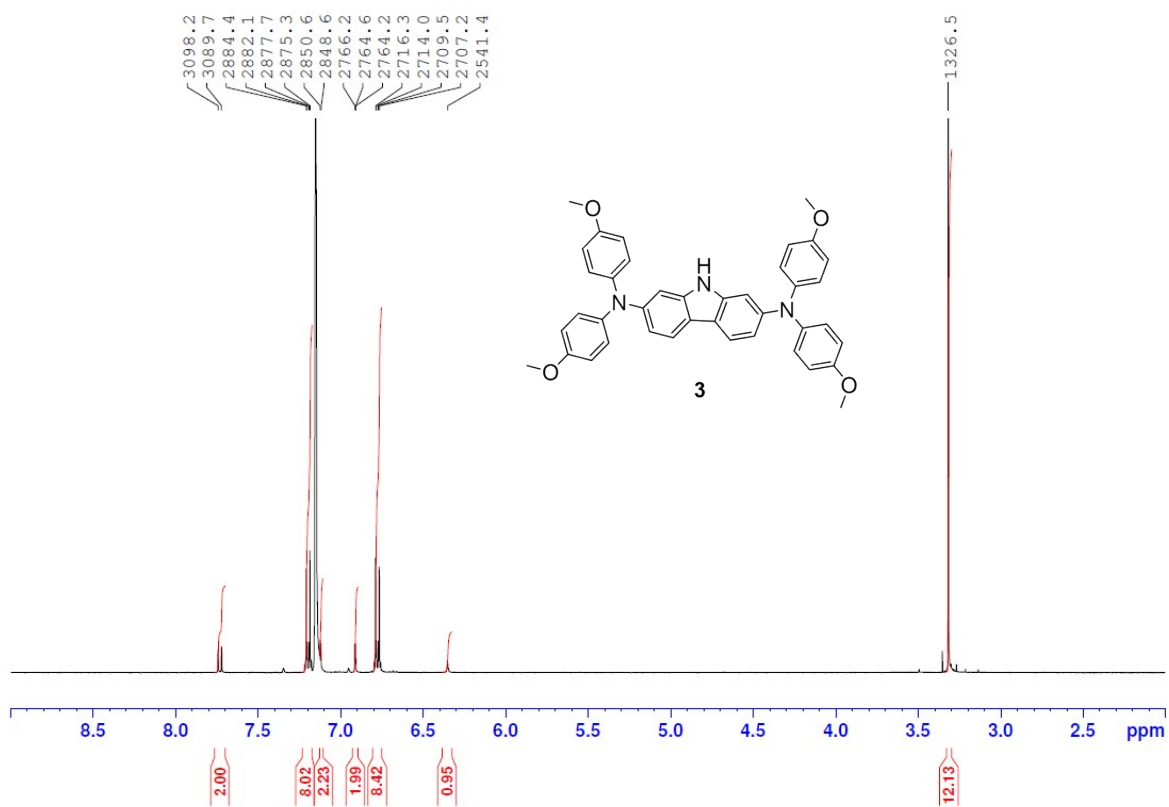


Figure S6. ¹H NMR of derivative 3 in C₆D₆

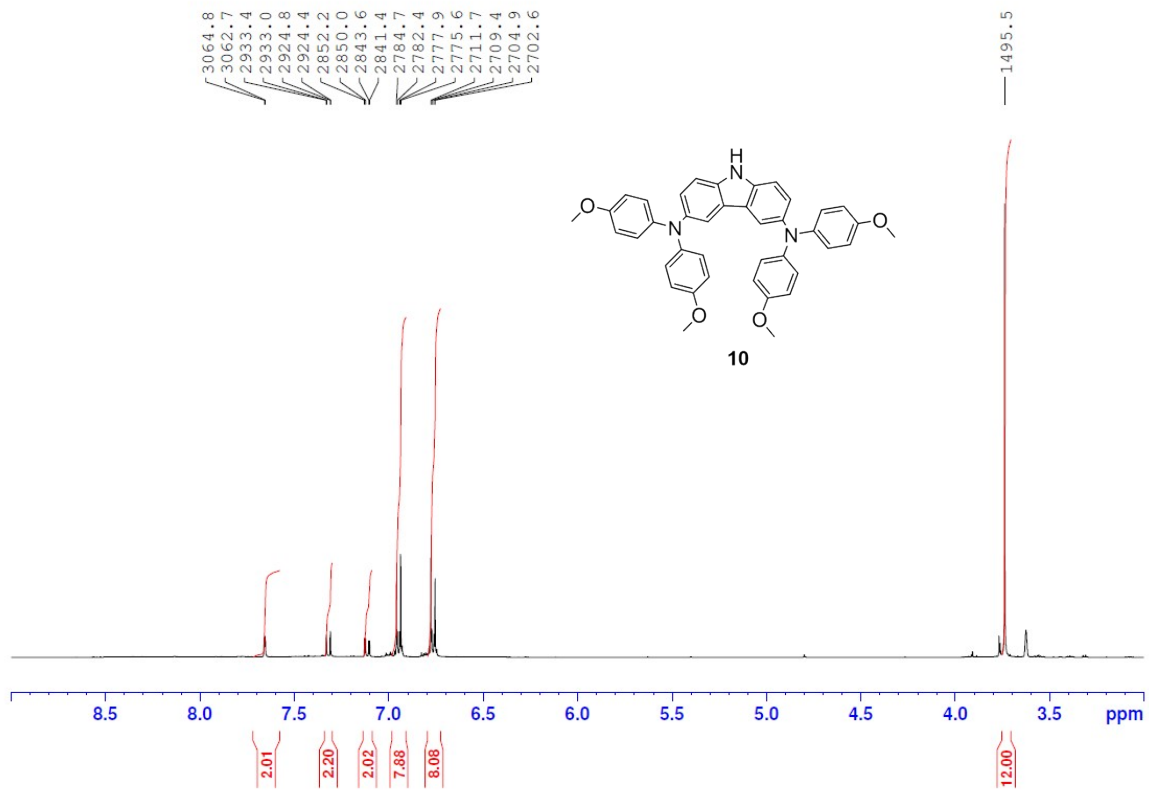


Figure S7. ¹H NMR of derivative 10 in THF

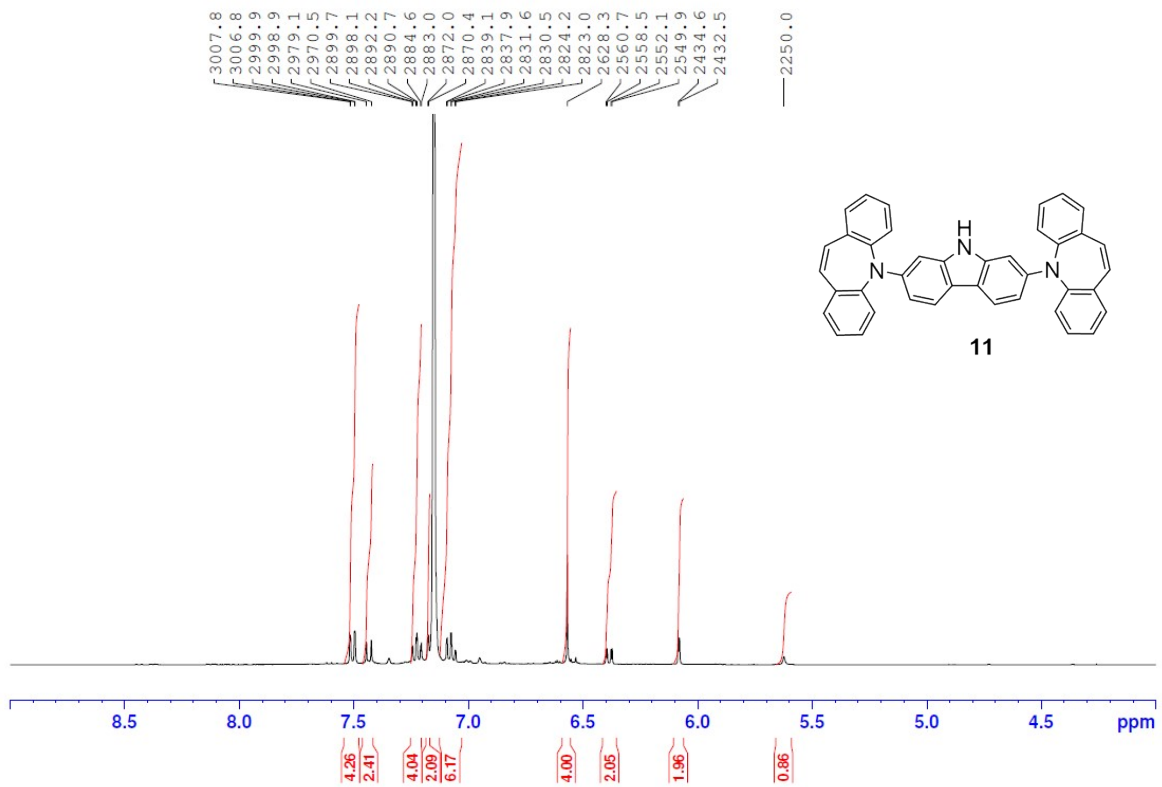


Figure S8. ¹H NMR of derivative 11 in C₆D₆

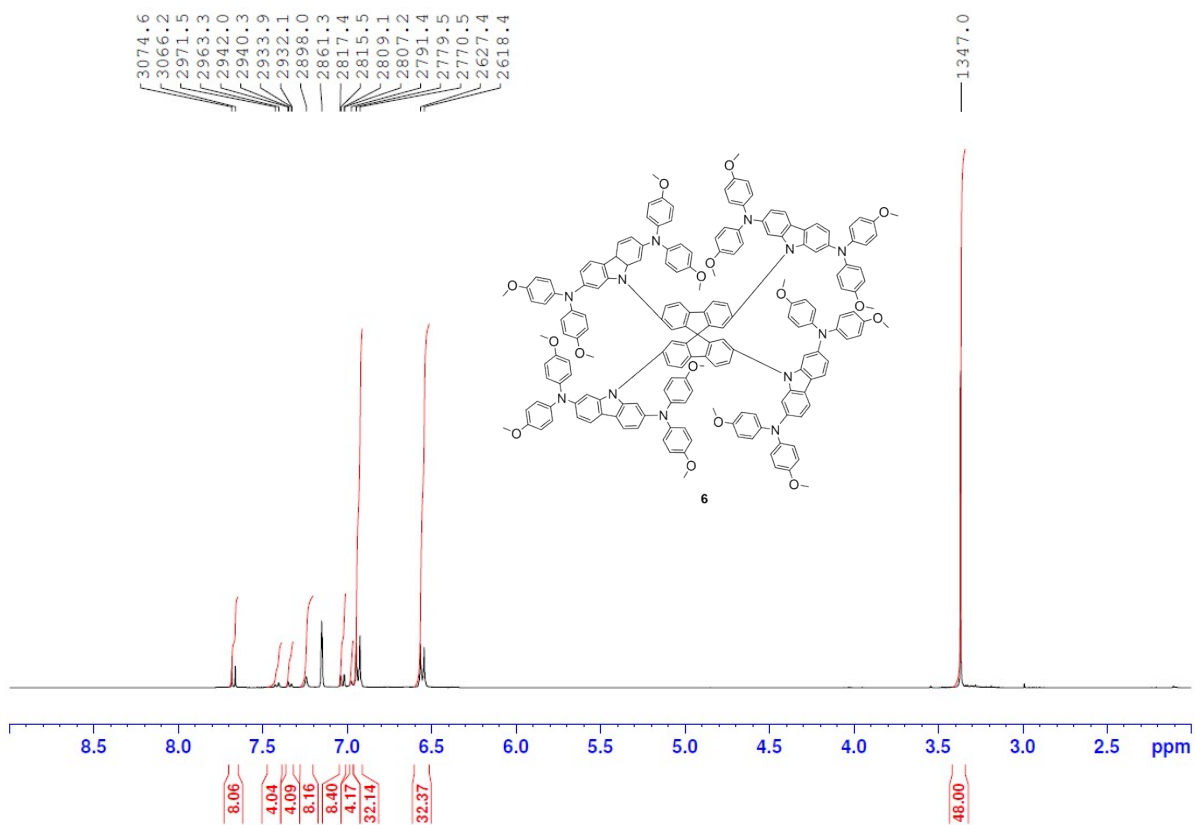


Figure S9. ^1H NMR of derivative 6 in C_6D_6

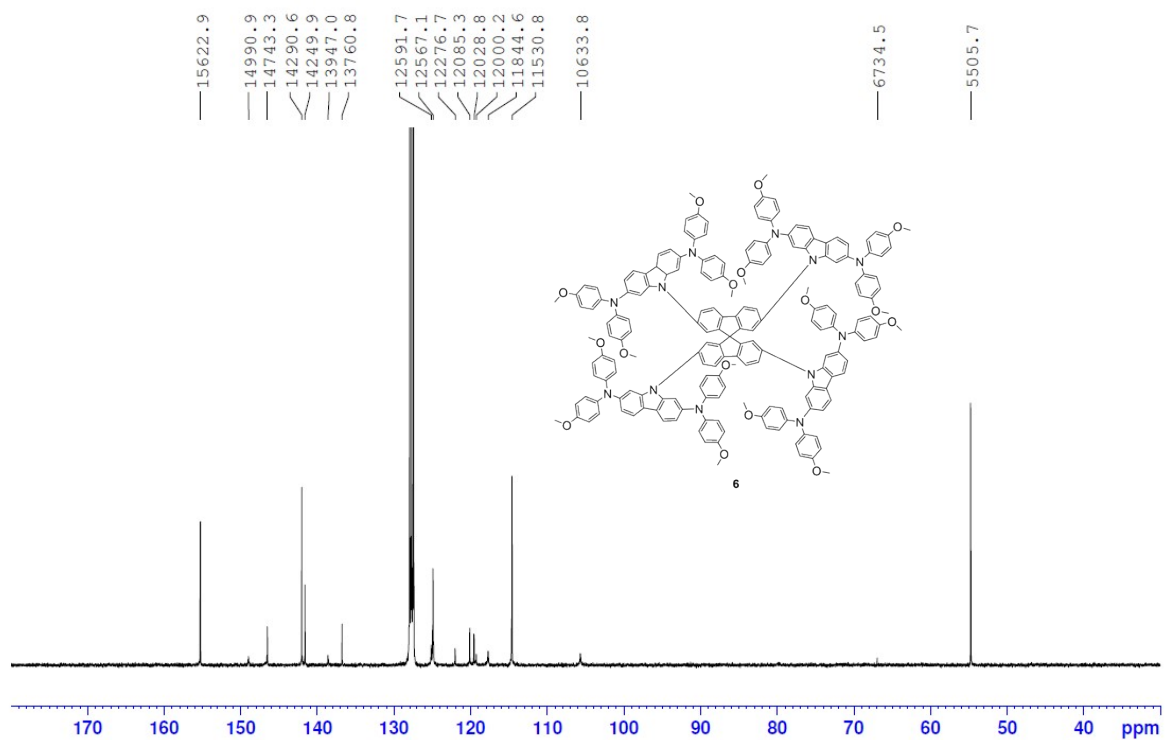


Figure S10. ^{13}C NMR of derivative 6 in C_6D_6

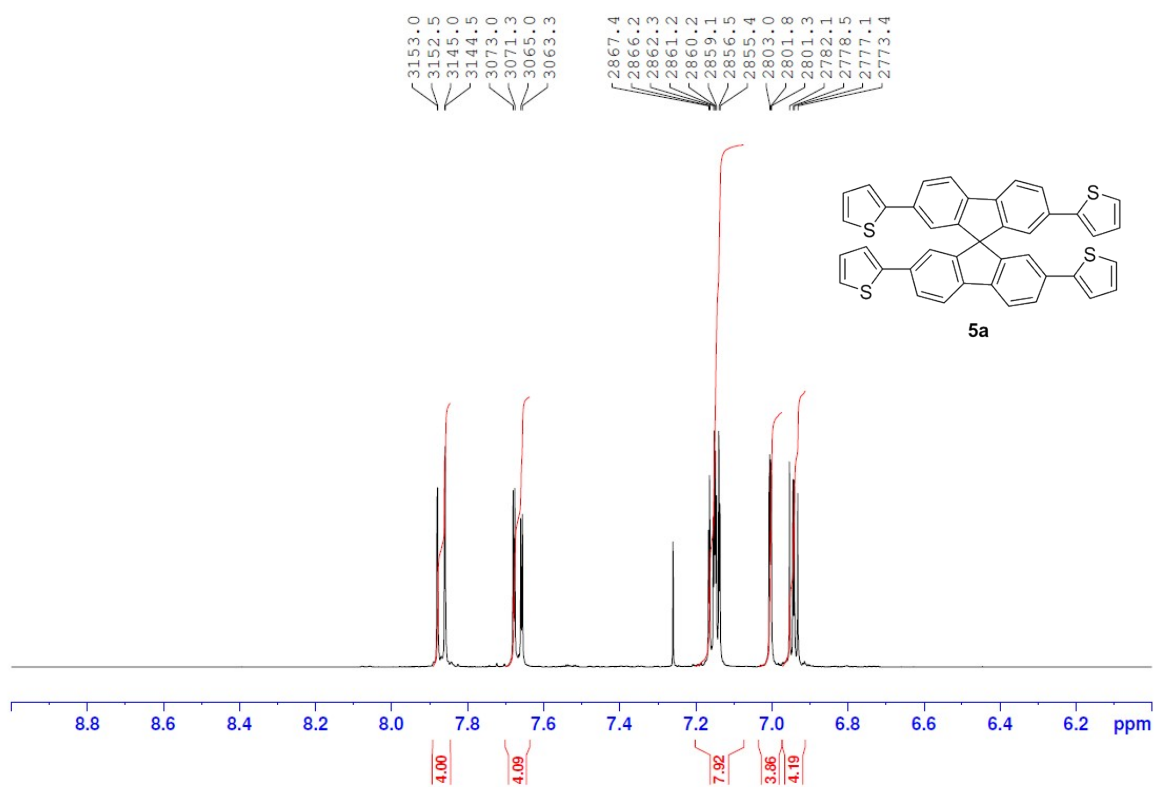


Figure S11. ^1H NMR of derivative 5a in CDCl_3

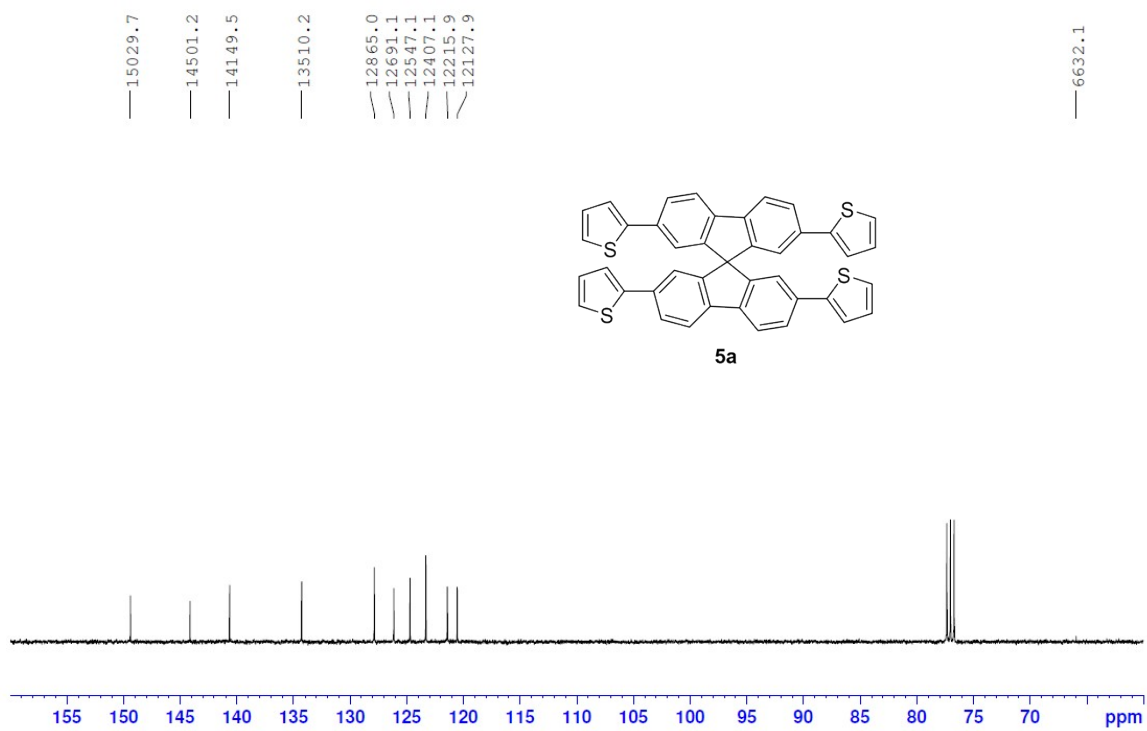


Figure S12. ^{13}C NMR of derivative 5a in CDCl_3

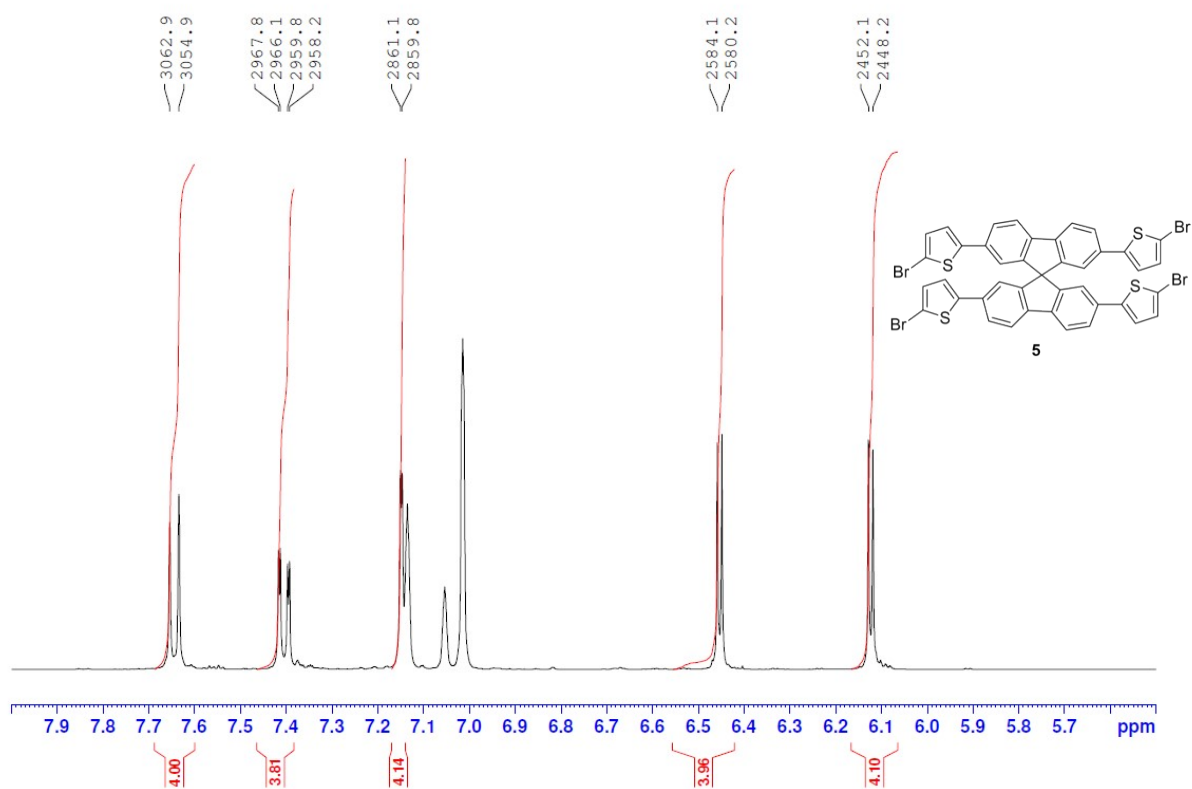


Figure S13. ^1H NMR of derivative 5 in toluene- d_8

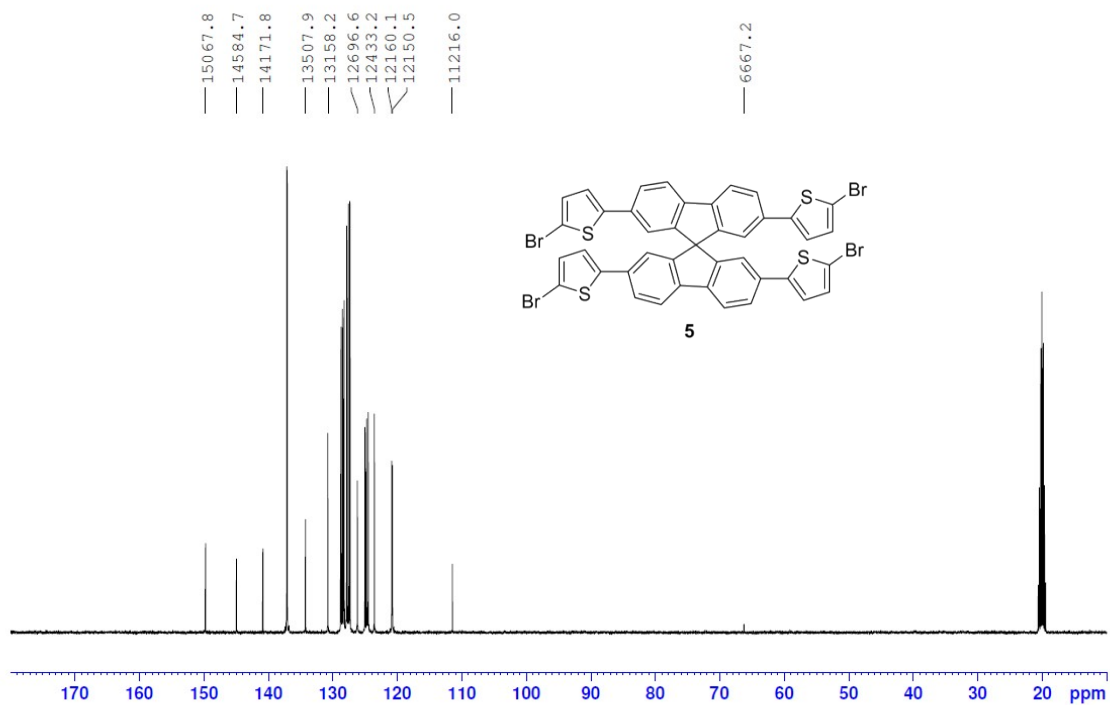


Figure S14. ^{13}C NMR of derivative 5 in toluene- d_8

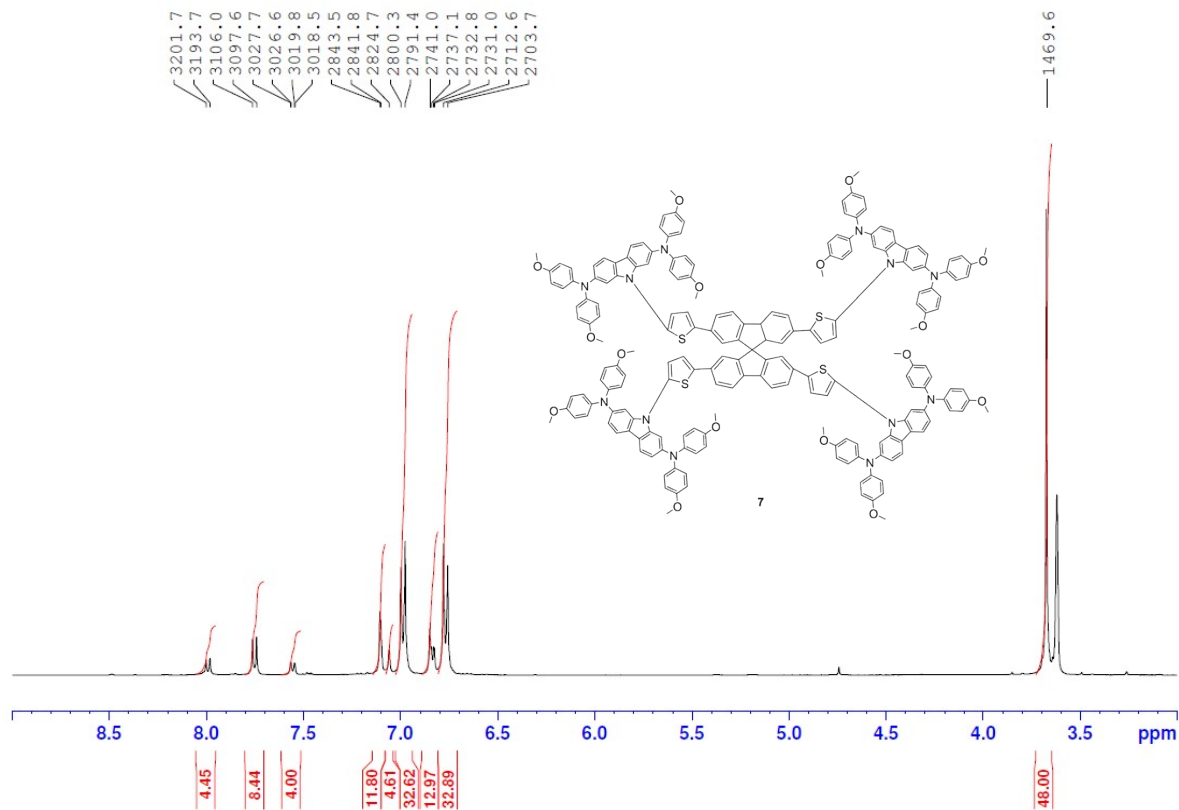


Figure S15. ¹H NMR of derivative 7 in THF

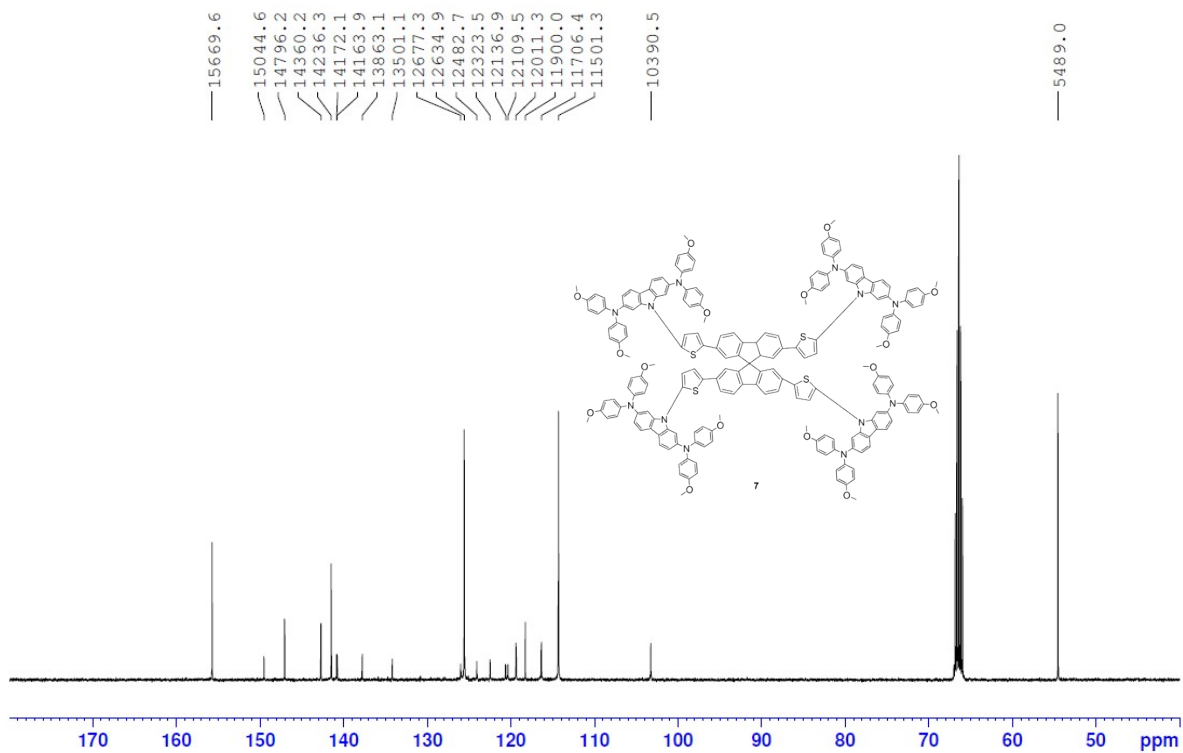


Figure S16. ¹³C NMR of derivative 7 in THF

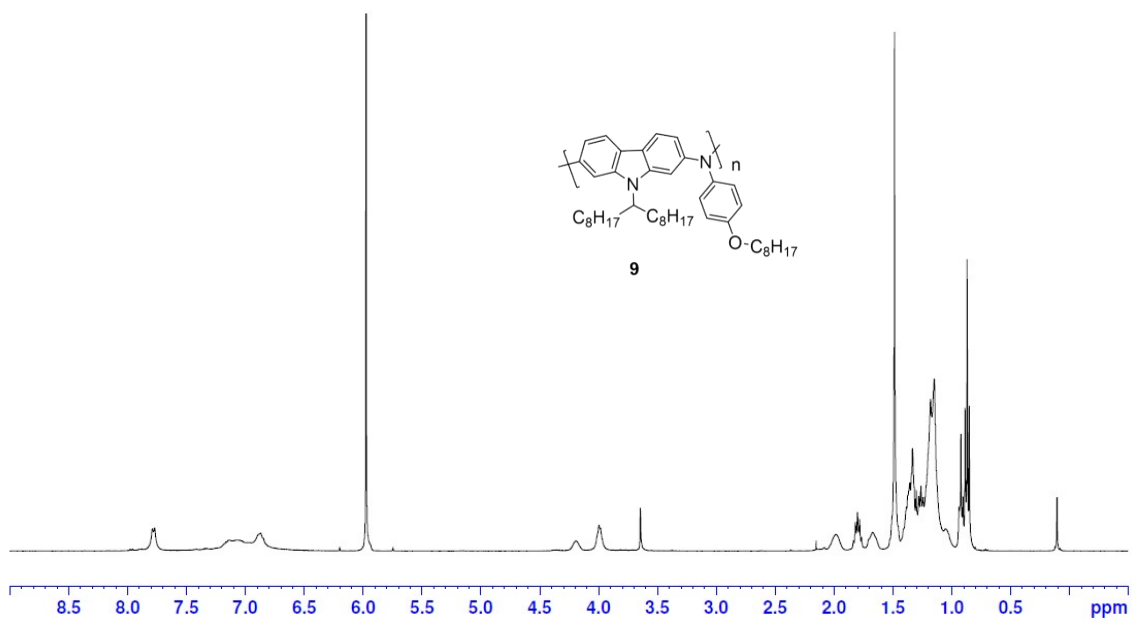


Figure S17. ^1H NMR of polymer 9 in 1,1,2,2-tetrachloroethane at 353 K

Thermal, optical, and electrochemical characterization of new materials

Methods

Differential pulsed voltammograms (DPV) and cyclic voltammetry (CV) of HTMs were carried out in N,N-dimethylformamide anhydrous 99.8% (Thermo Scientific) containing 0.1 M tetrabutylammonium hexafluorophosphate 99% (Sigma Aldrich) as the supporting electrolyte, in which the working electrode was a glassy carbon electrode (area=0.0707 cm²), the counter electrode was a Pt wire and the reference electrode was Ag/AgCl. The system was calibrated by ferrocene redox couple (0.391 mV vs Ag/AgCl)¹.

Absorption spectra were recorded on a Jasco V-570 UV-Vis-NIR spectrophotometer in the wavelength range from 200 to 600 nm with 200 nm/min as scanning speed. UV-Vis spectra of HTMs dichloromethane solutions were recorded at room temperature, with conventional 1 cm quartz cell.

Photoluminescence spectra (PL) of HTMs solutions were recorded on a Jasco FP-6200 Spectrofluorometer with a scanning rate of 500 nm/min in a 1 cm quartz cuvette. Excitation wavelength for each derivative was chosen as the maximum recorded for the corresponding absorption spectrum.

Differential Scanning Calorimetry (DSC) were recorded at 25-300 °C under nitrogen flow (80 mL/min) with a scanning rate of 10 °C/min using a DSC 1STARe system from METtler Toledo in aluminium crucibles. Calibration was performed with indium standard.

Thermogravimetric Analysis (TGA) were carried out on TGA/DSC STARe System (METtler TOLEDO). Method: 20 °C/min, N₂ flow 50 mL/min.

Characterization of 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenylamine)9,9'-spirobifluorene (Spiro-OMeTAD)

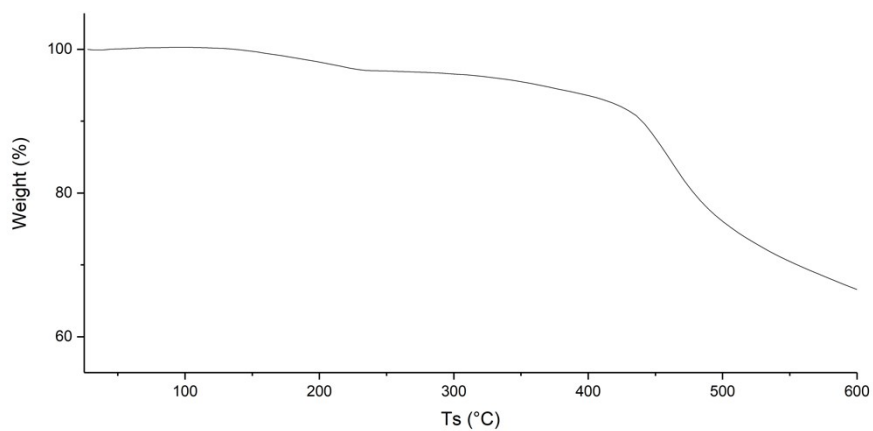


Figure S18. TGA curve of derivative Spiro-OMeTAD, temperature range: 25-600 °C

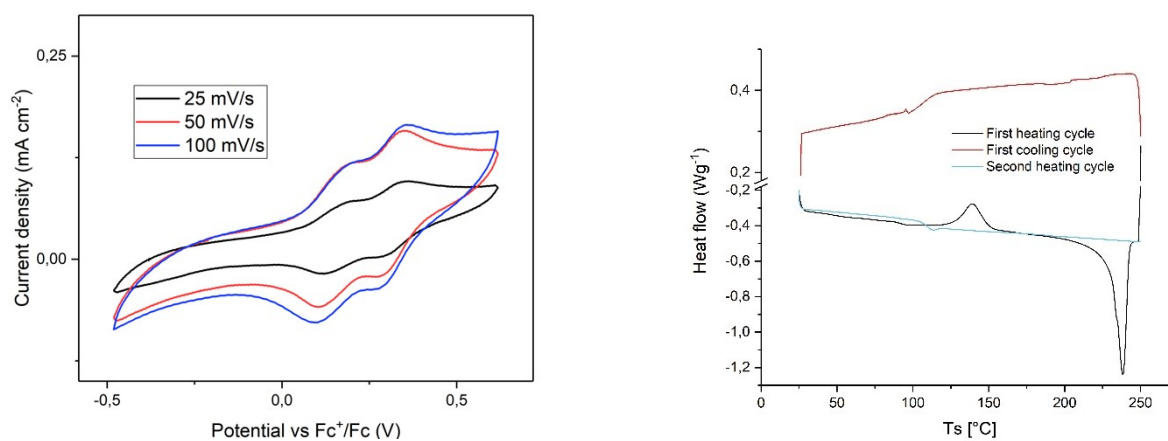


Figure S19. a) Cyclic voltammograms of Spiro O-MeTAD. Homo: -4.95 eV; b) DSC analysis of Spiro-OMeTAD with scan rate of 10 °C/min

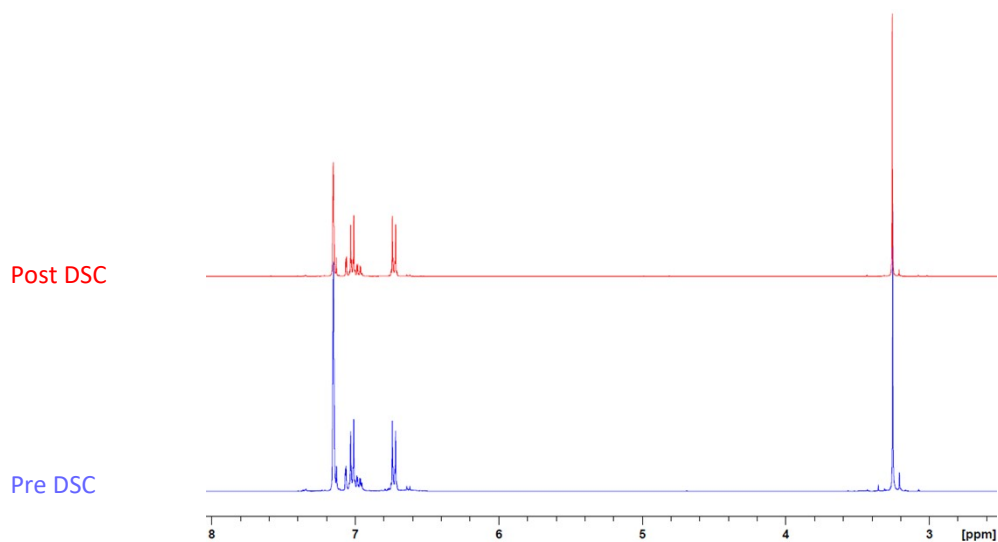
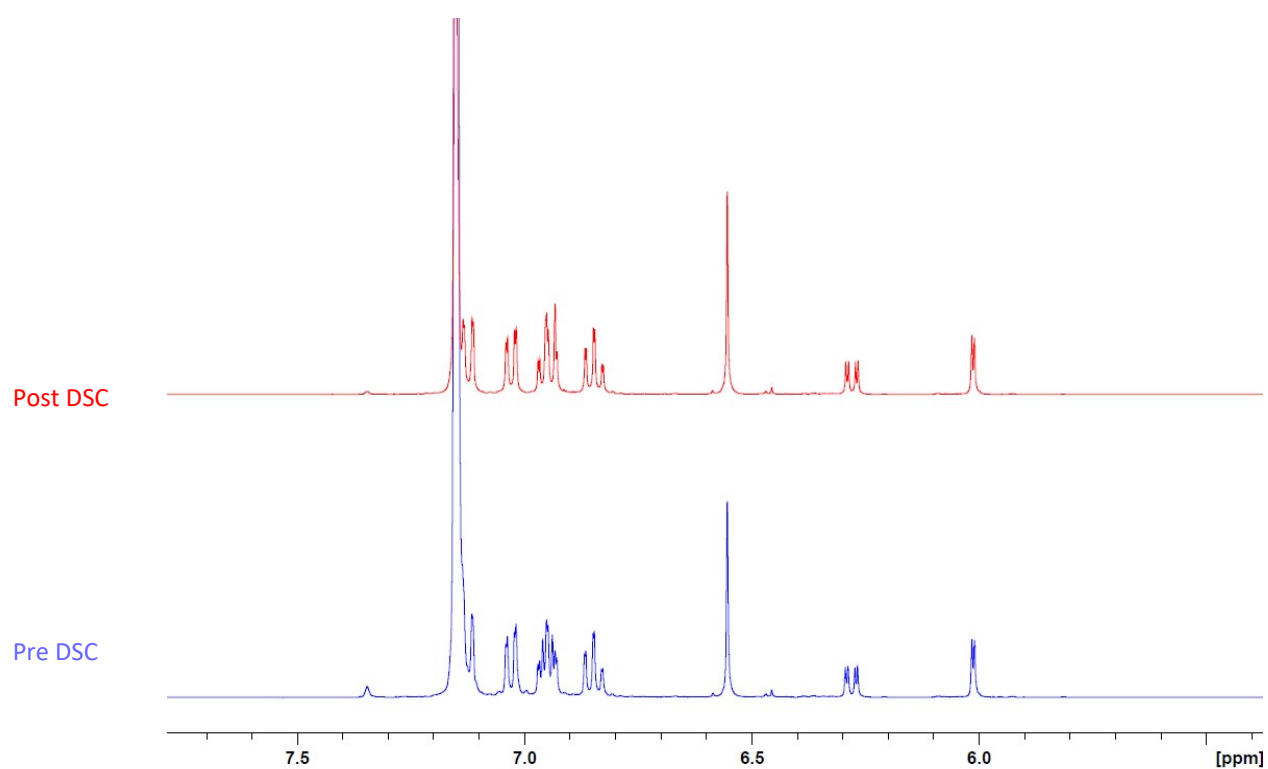
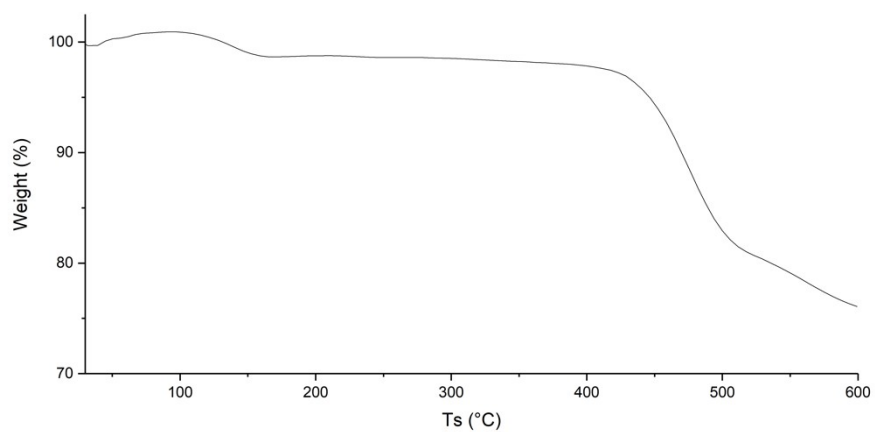
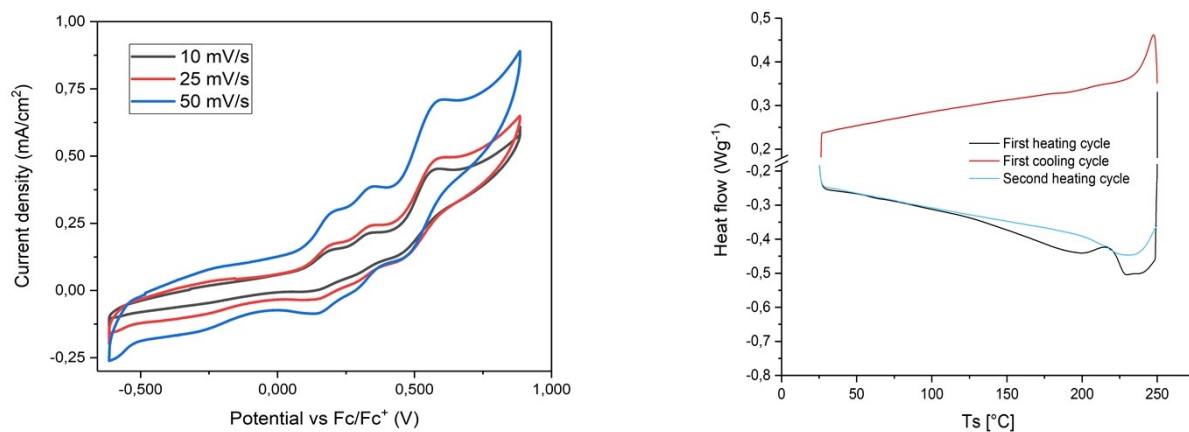


Figure S20. ¹H NMR spectra of Spiro-OMeTAD pre and post Differential Scanning Calorimetry analysis

Characterization of derivative 8



Characterization of derivative 11

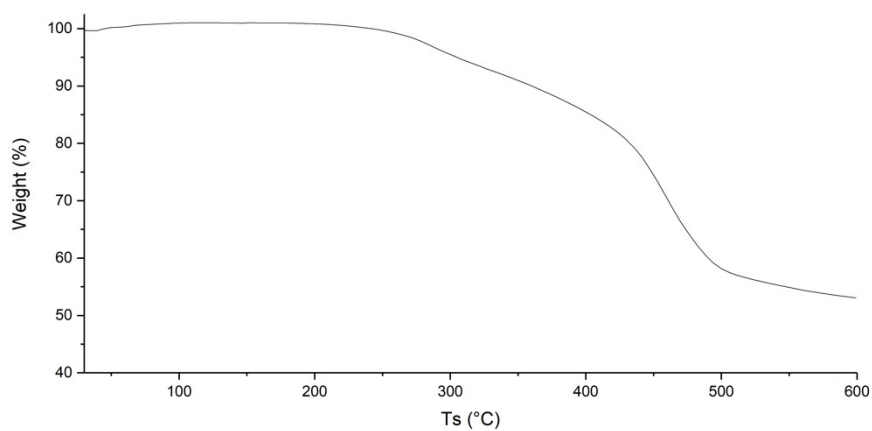


Figure S24. TGA curve of derivative 11, temperature range: 30-600 °C

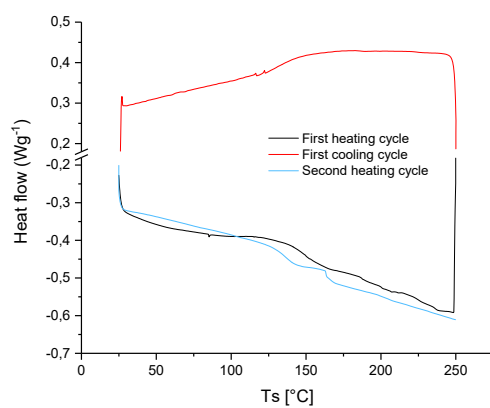


Figure S25. DSC analysis of derivative 11 with scan rate of 10 °C/min

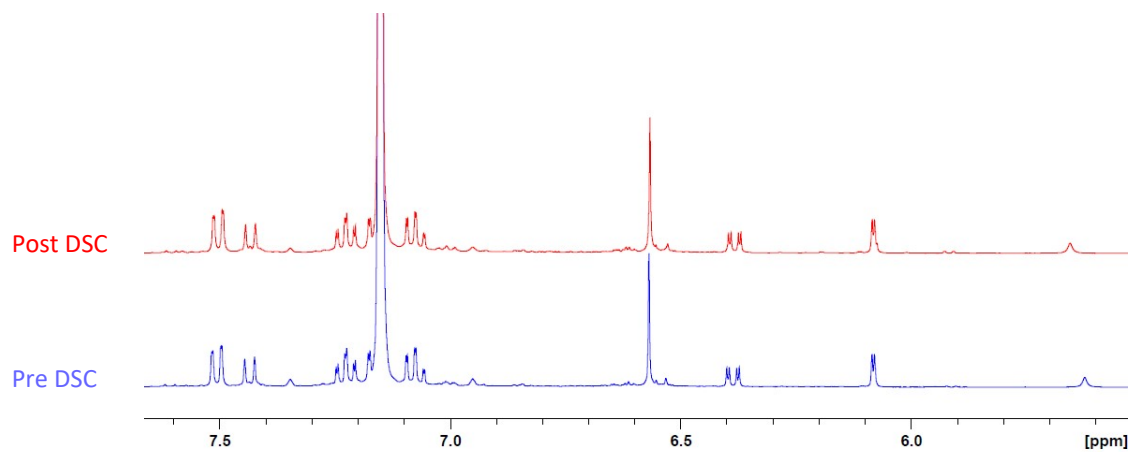
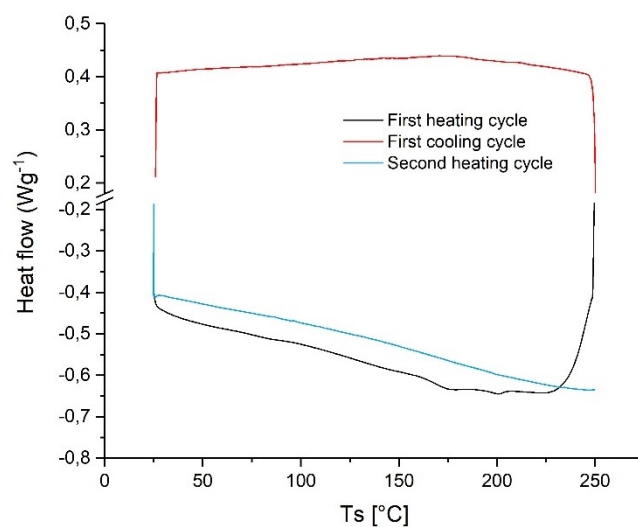
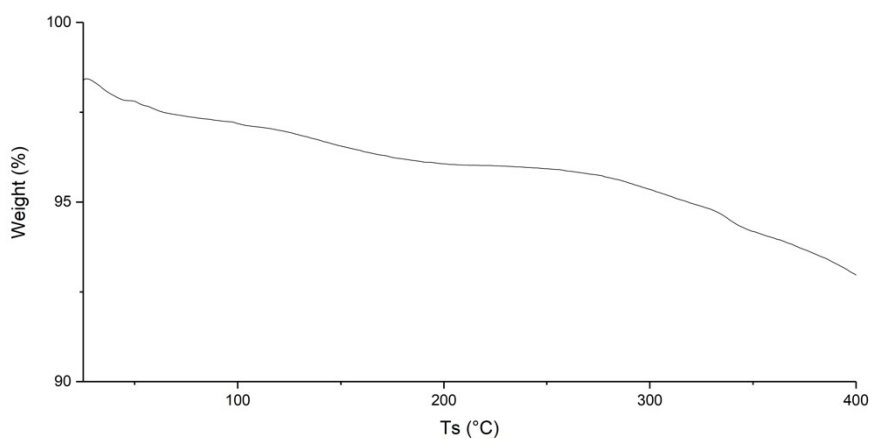
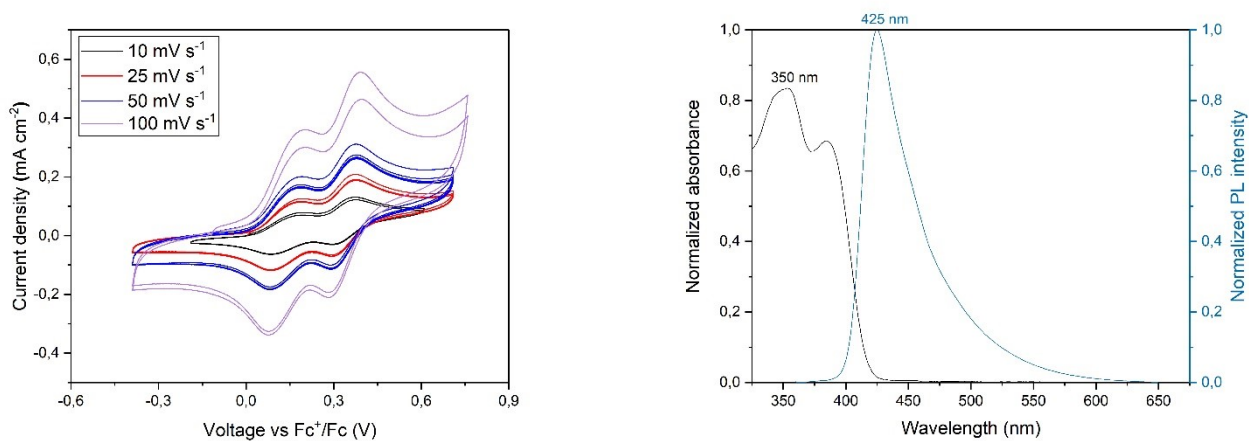


Figure S26. ¹H NMR spectra of derivative 11 pre and post Differential Scanning Calorimetry analysis

Characterization of derivative 6



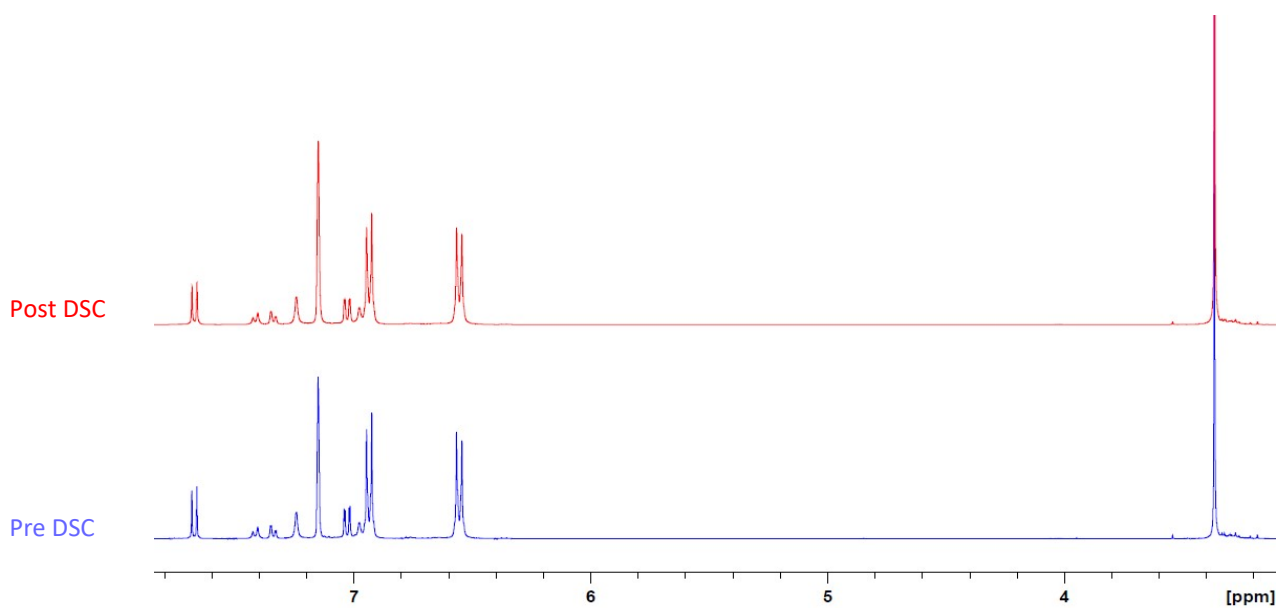


Figure S30. ¹H NMR spectra of derivative 6 pre and post Differential Scanning Calorimetry analysis

Characterization of derivative 7

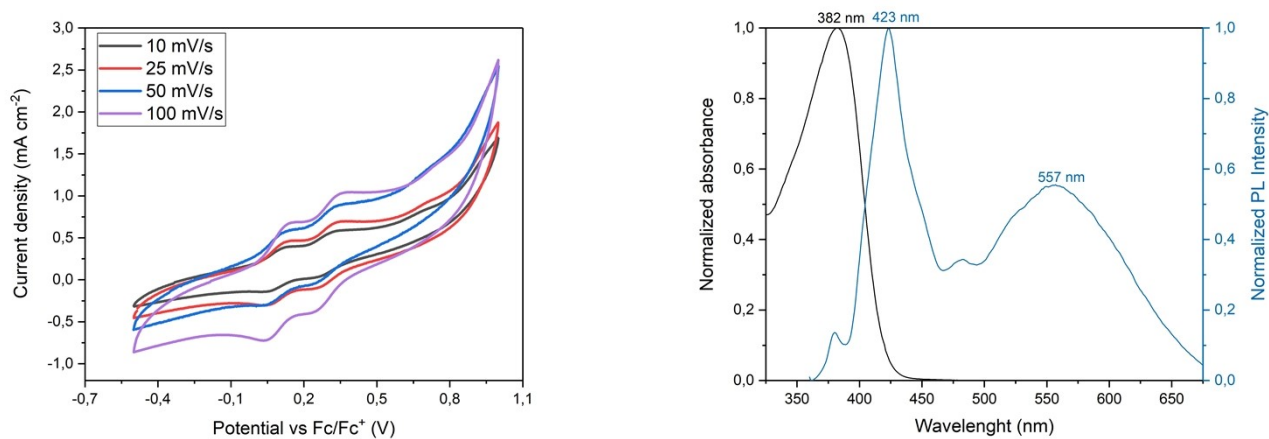


Figure S31. a) Cyclic voltammograms of derivative 7. HOMO: -4.80 eV; b) Absorption and photoluminescence spectra of derivative 7. Excitation wavelength: 382 nm

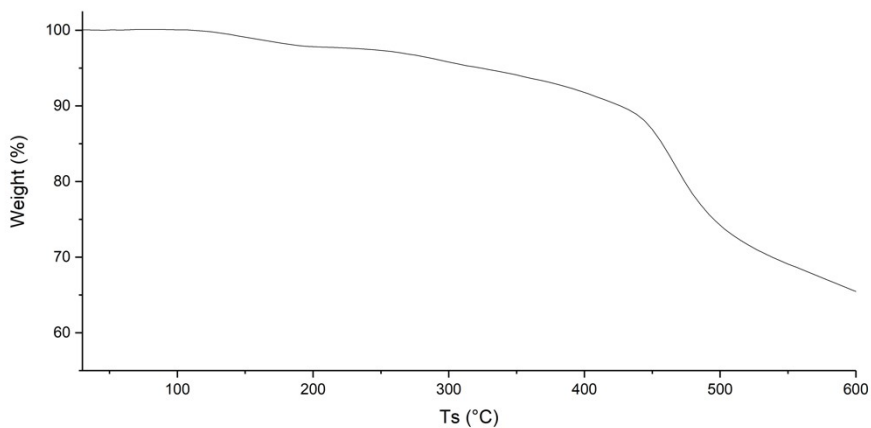


Figure S32. TGA curve of derivative 7, temperature range: 25-600 °C

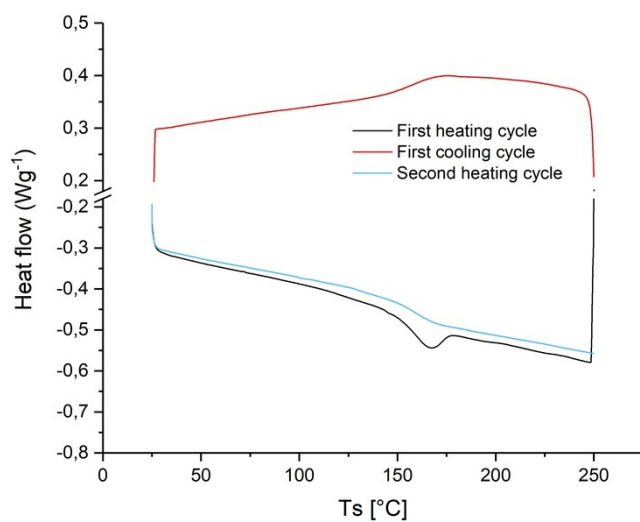


Figure S33. DSC analysis of derivative 7 with scan rate of 10 °C/min

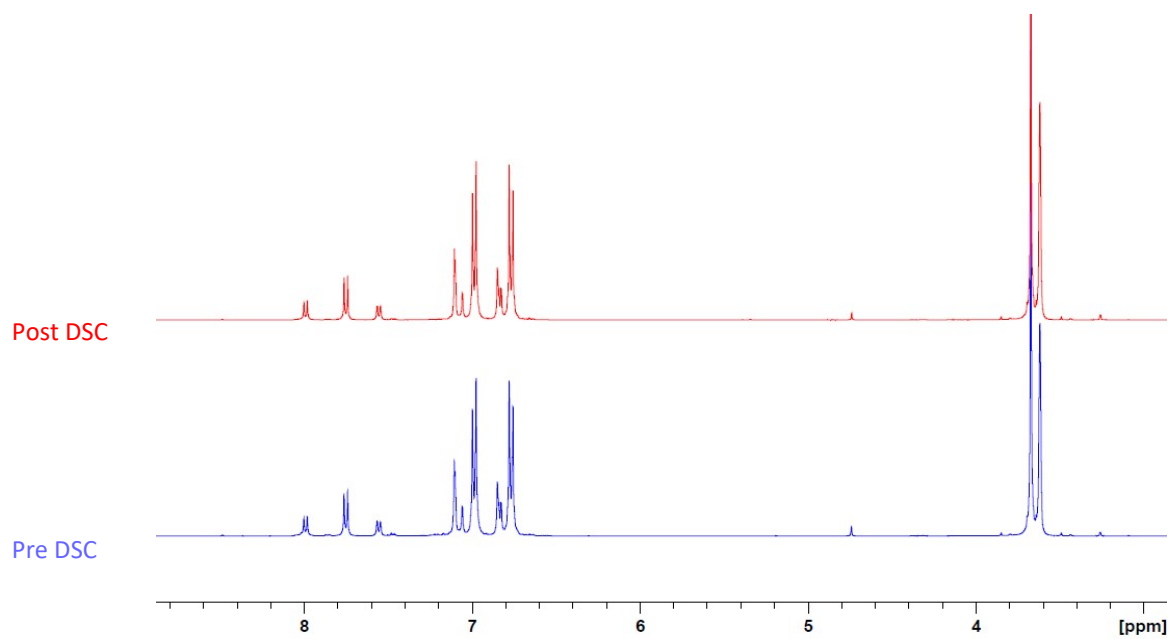


Figure S34. ¹H NMR spectra of derivative 7 pre and post Differential Scanning Calorimetry analysis

Characterization of derivative 9

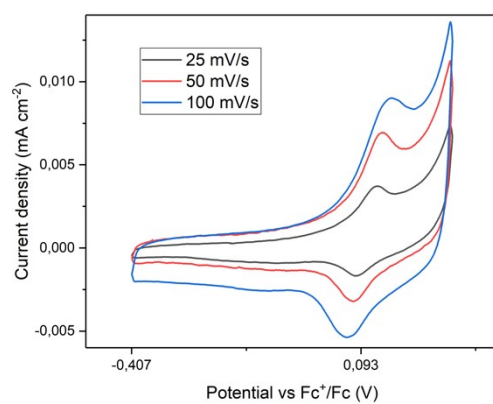


Figure S35. Cyclic voltammograms of derivative 9.
HOMO: -4.93 eV

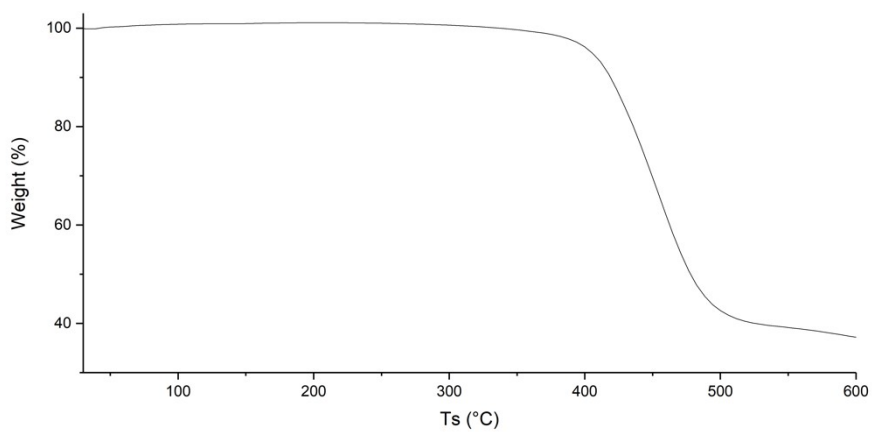


Figure S36. TGA curve of derivative 9, temperature range: 25-600 °C

Device preparation and characterization

Unless stated otherwise, solvent and reagents were purchased from Sigma Aldrich.

PSCs were fabricated with glass/ITO/SnO₂/Cs_{0.06}(MA_{0.16}FA_{0.78})_{0.94}Pb(I_{0.84}Br_{0.16})₃ (FAMACs)/HTM/Au architecture. Commercial Spiro-OMeTAD (from Borun New Material Technology LTD) was used for reference cells. Glass/ITO substrates (Kintec, 10 ohm/square) were patterned via a laser scribing process and cleaned in ultrasonic bath in acetone, 2-propanol, and deionised water for 10 minutes each. Before deposition of the ETL, glass/ITO substrates were subdued to UV irradiation for 10 min. SnO₂ was deposited by spin-coating a nanoparticle dispersion (15% in water, Alfa Aesar) at 6000 rpm for 35 s. Films were annealed at 100 °C for 45 min and subdued to UV irradiation for 10 min. Triple cation precursor solution containing FAI (1 M), PbI₂ (1.2 M), MABr (0.2 M), PbBr₂ (0.2 M) and CsI (0.08 M) was prepared in anhydrous DMF:DMSO 3.2:1 (v:v). The deposition was carried out in a nitrogen-filled glovebox by spin-coating the precursor solution at 4000 rpm for 23 s; 180 μL of chlorobenzene (CB) were dropped on the substrate 15 s before the end of the spin-coating process. Spiro-type HTM solutions were prepared by dissolving the compounds at a 73.42 mg/mL concentration in CB and stirred overnight at room temperature; 2 hours prior deposition, the HTM solutions were doped with 16.6 mL/mL LiTFSI stock solution (530 mg/mL in acetonitrile), 26.77 mL/mL TBP and 7.2 mL/mL cobalt (III) complex solution (FK209 from Lumtec). Derivative **6** devices were spin coated at 3000 rpm for 20 s, derivative **7** devices were spin coated at 4000 rpm for 20 s, whereas derivative **9** devices were spin coated at 4500 rpm for 20 s. Spiro-OMeTAD solution was spin coated at 3500 rpm for 20 s. Finally, a 100 nm thick Au electrode was deposited by thermal evaporation.

Devices were characterized under 1 sun (AM1.5G, 100 mWcm⁻²) at room temperature by means of a Keithley 2420 source meter and a ABET sun 2000 solar simulator as light source. During the measurements, the devices were masked with a black tape with 0.1 cm² aperture.

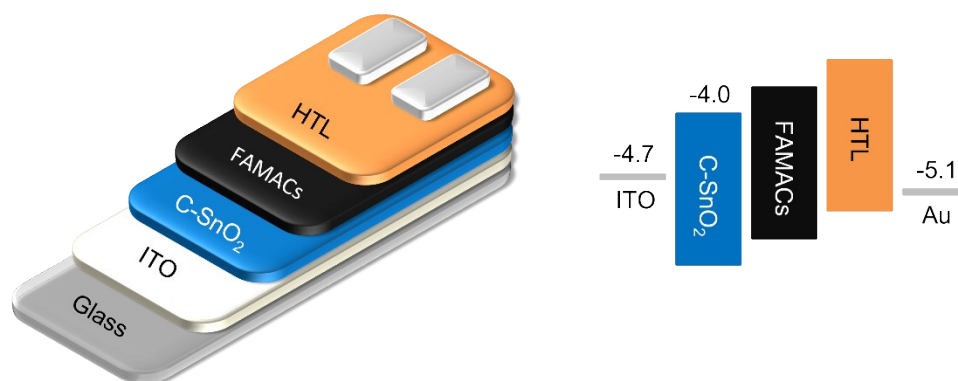


Figure S37. Schematic structure of fabricated perovskite solar cell (PSC) devices

Device HTL	Voc (V)	Jsc (mA/cm ²)	FF (%)	PCE (%)
Reference (Spiro O-MeTAD)	1.00±0.006 (1.01)	20.41±0.263 (20.91)	63.95±4.502 (69.33)	13.07±0.935 (14.60)
Derivative 6	0.94±0.076 (0.98)	18.68±0.302 (19.22)	70.66±4.244 (70.74)	12.43±0.818 (13.26)
Reference (Spiro O-MeTAD)	1.03±0.002 (1.05)	21.60±0.243 (21.68)	65.60±6.066 (75.02)	14.60±1.580 (17.23)
Derivative 7	1.03±0.004 (1.03)	21.00±0.264 (21.44)	70.98±3.458 (75.35)	15.38±0.800 (16.25)
Reference (Spiro O-MeTAD)	1.02±0.006 (1.03)	20.12±0.320 (20.58)	63.32±3.780 (67.46)	13.05±0.890 (14.29)
Polymer 9	0.92±0.006 (0.91)	18.79±0.690 (18.65)	63.28±2.800 (66.75)	10.96±0.380 (11.45)

Table S1. Photovoltaic parameters of PSCs based on the three new HTMs and reference Spiro-OMeTAD. In brackets, maximum values collected are reported.

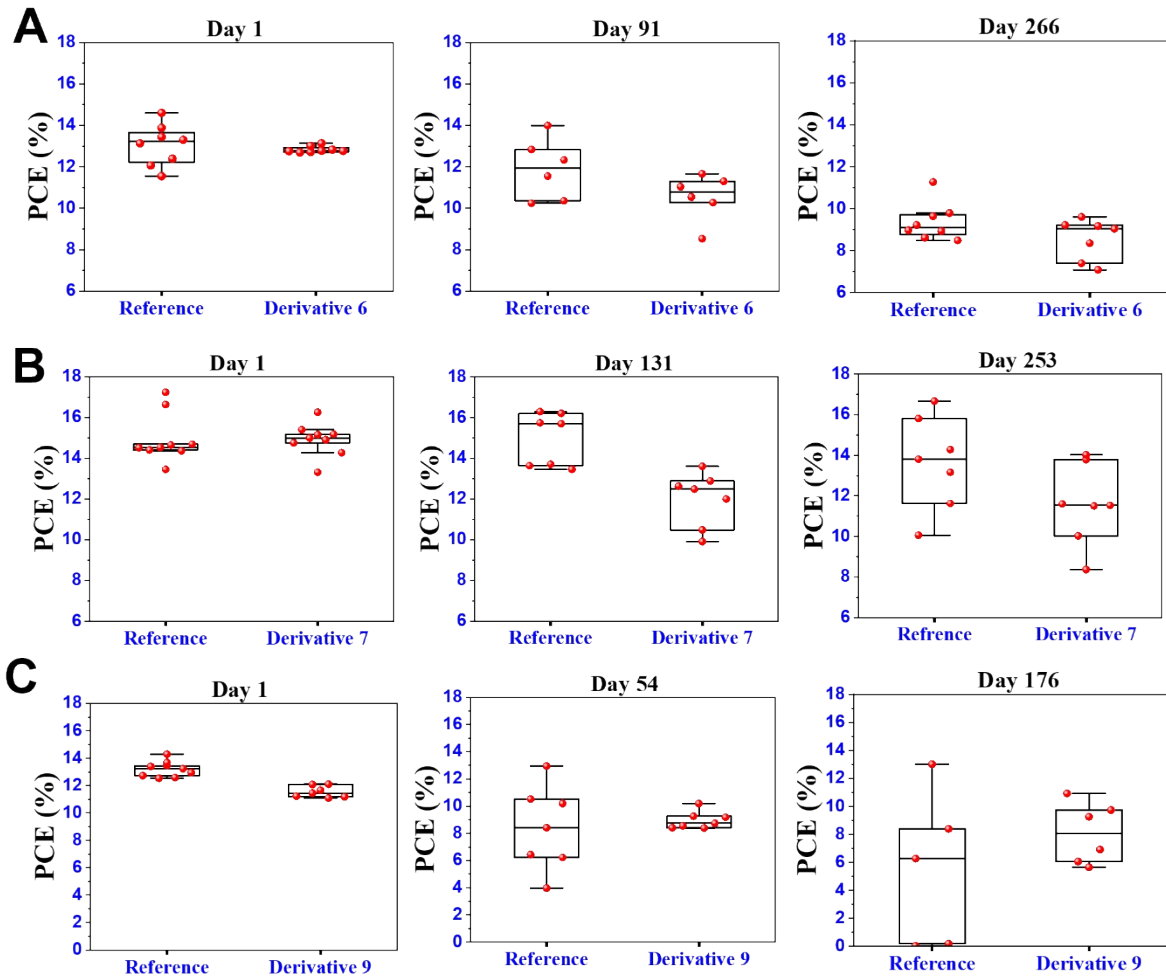


Figure S37. Box charts illustrating the statistical distribution of power conversion efficiency of perovskite solar cells. Photovoltaic parameters extracted from the reverse (RV) current-voltage scan (from V_{oc} to $V=0$). A) Reference Vs Derivative 6 at day 1, day 91, day 266, (B) Reference Vs Derivative 7 at day 1, day 131, day 253, (C) Reference Vs Derivative 9 at day 1, day 54 day 176, and Between measurements, samples were stored in the dark in a box with relative humidity (RH) in the 30%–40% range. Measurements were performed under standard test conditions (STC, 25 °C, 1000 W/m² irradiance, air mass 1.5 (AM1.5) spectrum), and the photovoltaic parameter was extracted from the reverse scan at a rate of 33 mV/s.

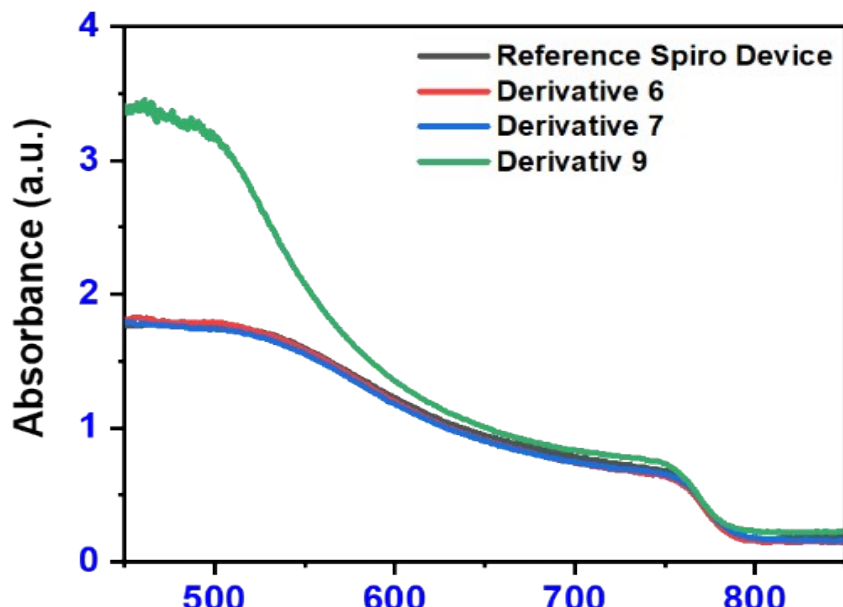


Figure S38: comparison of UV-Vis absorption spectra of various perovskite devices prepared with derivative **6** (red line), **7** (blue line), **9** (green line) and commercial Spiro-OMeTAD (black line).

External quantum efficiency (EQE) & integrated J_{sc}

The external quantum efficiency (EQE) of the cells was evaluated to analyse the different spectral conversion efficiency for the three different HTMs. As shown in Figure S39, the EQE spectra had similar shape for the three materials. EQEs above 80% were observed for Reference, Derivative 6 & Derivative 7 devices, while the Derivative 9 HTM delivered lower EQE. The integrated J_{sc} calculated from the EQE spectrum was within the experimental error for Reference cell (integrated J_{sc} =20.70 mW cm^{-2} , J_{sc} =20.91 mW cm^{-2} under the sun simulator), Derivative 6 (integrated J_{sc} = 19.22 mW cm^{-2} vs 19.22 mW cm^{-2}) shown in the figure 39A; figure 39B shows reference cell (integrated J_{sc} =20.98 mW cm^{-2} , J_{sc} =21.68 mW cm^{-2} under the sun simulator) and Derivative 7 (integrated J_{sc} = 20.89 mW cm^{-2} vs 21.44 mW cm^{-2}); whereas in figure 39C shows reference cell (integrated J_{sc} =20.72 mW cm^{-2} , J_{sc} =20.58 mW cm^{-2} under the sun simulator), Derivative 9 (integrated J_{sc} = 18.71 mW cm^{-2} vs 18.65 mW cm^{-2}).

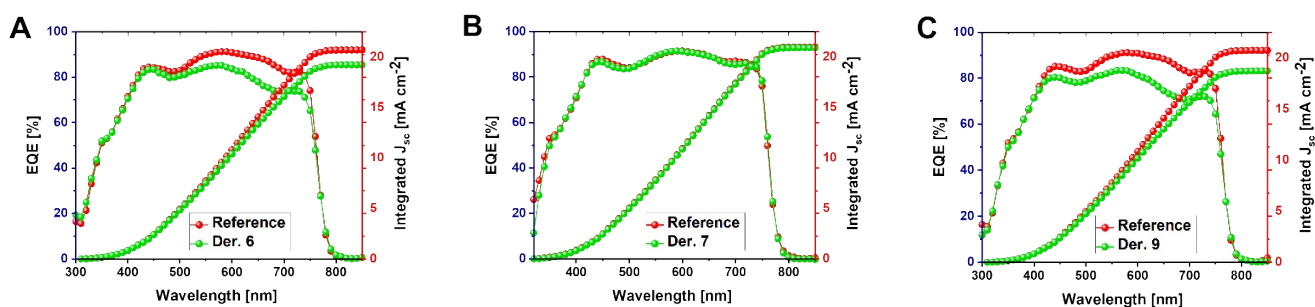


Figure S39. External quantum efficiency (EQE) and integrated short circuit current (J_{sc}) of glass/ITO/SnO₂/FAMACs/HTM/Au cells fabricated with various derivatives: the commercial one (“Reference”), derivative 6, derivative 7 and derivative 9.

Full references 29 and 31.

- **Reference 29.** T. J. Jacobsson, A. Hultqvist, A. García-Fernández, A. Anand, A. Al-Ashouri, A. Hagfeldt, A. Crovetto, A. Abate, A. G. Ricciardulli, A. Vijayan, A. Kulkarni, A. Y. Anderson, B. P. Darwich, B. Yang, B. L. Coles, C. A. R. Perini, C. Rehermann, D. Ramirez, D. Fairen-Jimenez, D. Di Girolamo, D. Jia, E. Avila, E. J. Juarez-Perez, F. Baumann, F. Mathies, G. S. A. González, G. Boschloo, G. Nasti, G. Paramasivam, G. Martínez-Denegri, H. Näsström, H. Michaels, H. Köbler, H. Wu, I. Benesperi, M. I. Dar, I. Bayrak Pehlivan, I. E. Gould, J. N. Vagott, J. Dagar, J. Kettle, J. Yang, J. Li, J. A. Smith, J. Pascual, J. J. Jerónimo-Rendón, J. F. Montoya, J.-P. Correa-Baena, J. Qiu, J. Wang, K. Sveinbjörnsson, K. Hirselandt, K. Dey, K. Frohna, L. Mathies, L. A. Castriotta, M. H. Aldamasy, M. Vasquez-Montoya, M. A. Ruiz-Preciado, M. A. Flatken, M. V. Khenkin, M. Grischek, M. Kedia, M. Saliba, M. Anaya, M. Veldhoen, N. Arora, O. Shargaieva, O. Maus, O. S. Game, O. Yudilevich, P. Fassel, Q. Zhou, R. Betancur, R. Munir, R. Patidar, S. D. Stranks, S. Alam, S. Kar, T. Unold, T. Abzieher, T. Edvinsson, T. W. David, U. W. Paetzold, W. Zia, W. Fu, W. Zuo, V. R. F. Schröder, W. Tress, X. Zhang, Y.-H. Chiang, Z. Iqbal, Z. Xie and E. Unger, *Nat. Energy*, 2022, **7**, 107–115.
- **Reference 31.** M. O. Reese, S. A. Gevorgyan, M. Jørgensen, E. Bundgaard, S. R. Kurtz, D. S. Ginley, D. C. Olson, M. T. Lloyd, P. Morvillo, E. A. Katz, A. Elschner, O. Haillant, T. R. Currier, V. Shrotriya, M. Hermenau, M. Riede, K. R. Kirov, G. Trimmel, T. Rath, O. Inganäs, F. Zhang, M. Andersson, K. Tvingstedt, M. Lira-Cantu, D. Laird, C. McGuinness, S. (Jimmy) Gowrisanker, M. Pannone, M. Xiao, J. Hauch, R. Steim, D. M. DeLongchamp, R. Rösch, H. Hoppe, N. Espinosa, A. Urbina, G. Yaman-Uzunoglu, J.-B. Bonekamp, A. J. J. M. van Breemen, C. Girotto, E. Voroshazi and F. C. Krebs, *Sol. Energy Mater. Sol. Cells*, 2011, **95**, 1253–1267.

References

1. Zhang, M. *et al.* Solar Energy Materials and Solar Cells Structure-performance relationship on the asymmetric methoxy substituents of spiro-OMeTAD for perovskite solar cells ☆. *Sol. Energy Mater. Sol. Cells* **176**, 318–323 (2018).