

## Electronic Supplementary Material

# The triple $\pi$ -bridge strategy for tailoring indeno[2,1-b]carbazole-based HTMs enables perovskite solar cells with efficiency exceeding 21%

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## 1. Base Characterization

### 1.1 NMR UV-vis and fluorescence.

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded with a Bruker-400MHz spectrometer. The absorption spectra of the solution of **M135-138** (dissolve in DCM) were recorded on a SHIMADZU UV-2600 spectrophotometer. Same samples of fluorescence measurements were obtained on a HITACHI F-4500 fluorescence spectrophotometer.

### 1.2 DPV DSC and TGA measurements

Differential pulse voltammetry (DPV) of **M135-138** were measured on a CHI660D electrochemical workstation, with a platinum electrode (counter electrode), Ag/AgCl electrode (reference electrode) and a glassy carbon disk (working electrode) at a scan rate of  $10 \text{ mVs}^{-1}$  in DCM solution of containing 0.1 M of  $n\text{-Bu}_4\text{NPF}_6$  and all potentials were reported against the ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) reference. Differential scanning calorimetry (DSC) was conducted on NETZSCH DSC 200 F3 differential scanning calorimeter at heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  under nitrogen atmosphere within temperature range of  $40 \text{ }^\circ\text{C}$  to  $210 \text{ }^\circ\text{C}$ . Thermogravimetric analysis (TGA) was conducted on NETZSCH TG209F3 thermogravimetric apparatus within temperature range of  $40 \text{ }^\circ\text{C}$  to  $500^\circ\text{C}$ .

### 1.3 Mobility Measurements

Hole mobilities of **M135-138** were measured by the space-charge-limited-current (SCLC) method with a device structure of ITO/PEDOT:PSS/HTMs/Ag. PEDOT:PSS was spin coated onto the ITO substrates and then annealed on a hotplate at  $120 \text{ }^\circ\text{C}$  for 30 min. Then, doped **M135-138** (in anhydrous chlorobenzene) was deposited via spin-

coating at 1000 rpm for 20 s. The best solution concentration of **M135**, **M136** and **M138** is 45 mM, and **M137** is only 20 mM due to poor solubility in chlorobenzene, with addition of 0.5 M Li-TFSI, 3.3 M TBP and 0.03 M FK209 solution. Finally, a 80 nm thick Ag back contact was deposited onto the HTM layer. The thicknesses of the HTMs were measured by using a Dektak profilometer. The classic Mott-Gurney equation (1) was used to determine the mobility.

$$J = 9\mu\epsilon_0\epsilon_r V^2 / (8d^3) \quad (1)$$

Here,  $\epsilon_r \approx 3$  is the average dielectric constant of the film,  $\epsilon_0$  is the permittivity of the free space,  $\mu$  is the carrier mobility,  $d$  is the thickness of the film, and  $V$  is the applied voltage.

#### 1.4 Conductivity Measurements

The conductivity of doped **M135-138** were determined by a two-contact electrical conductivity set-up. **M135-138** films were prepared by spin-coating a chlorobenzene solution onto ITO glass substrate via a spin speed of 1000 rpm for 20 s at room temperature. Then, 80 nm thick Au back contact was deposited by thermal evaporation. The thicknesses of the HTMs were measured by using a Dektak profilometer. The following equation (2) was used to determine the conductivity.

$$\sigma = d / (RS) \quad (2)$$

Here,  $S$  is the area of metal mask,  $R$  is the area of resistance,  $d$  is the thickness of HTM film.

## 2. Device Fabrication

### 2.1 Materials

FAI, MABr, FK209 and TiO<sub>2</sub> (DSL 18NR-T) were purchased from Dyesol. Indium tin oxide (ITO) coated glass, PbI<sub>2</sub> (99.999%) and PbBr<sub>2</sub> (99.999%) were purchased from TCI. Spiro-OMeTAD (99.5%) and PEDOT:PSS (Heraeus, Clevios PVP Al 4083) were purchased from p-OLED (China). Lithiumbis-(trifluoromethylsulfonyl)imide (Li-TFSI, 99%), 4-(tert-Butyl)pyridine (TBP, 99%), CsI (99%), were purchased from Energy Chemicals (China). Anhydrous DMSO (99.8%), DMF (99.8%) and chlorobenzene (99.8%) were purchased from Sigma Aldrich.

### 2.2 Devices Fabrication

We fabricated n-i-p PSCs with a structure of FTO/c-TiO<sub>2</sub>/meso-TiO<sub>2</sub>/CsFAMA/HTMs/Au to measure the photovoltaic performance of PSCs. The FTO substrates were etched by diluted HCl solution and little of zinc powder. Then ultrasonic cleaning 15 min in detergent, deionized water and ethanol, respectively. Then treatment with UV-ozone (20 min). A dense TiO<sub>2</sub> layer was deposited on glass substrates by spray pyrolysis using a 10 vol% titanium diisopropoxide bis(acetylacetonate) solution in ethanol at 460 °C. A mesoporous TiO<sub>2</sub> was coated on the dense TiO<sub>2</sub>/FTO substrate using a diluted TiO<sub>2</sub> paste (Dyesol DSL 18NR-T) with terpineol (1:3, mass ratio). After sintering the TiO<sub>2</sub> film on a hotplate at 460 °C for 30 min, the film was cooled to room temperature. The preparation method is: 1.30 M PbI<sub>2</sub>, 1.19 M FAI, 0.14 M PbBr<sub>2</sub>, 0.14 M MABr, and 0.07 M CsI were weighed in a bottle, then quickly transferred to the glove box. Under a nitrogen atmosphere in the glove box, add a mixed solvent with a

volume ratio of DMF: DMSO = 4:1. This resulting solution was stirred at 60 °C for 30 min to form  $(\text{FAPbI}_3)_{0.875}(\text{MAPbBr}_3)_{0.075}(\text{CsPbI}_3)_{0.05}(\text{PbI}_2)_{0.03}$ . Then deposited through a two-step spin coating program (10 s at 1000 rpm and 20 s at 6000 rpm) with dripping of 110  $\mu\text{L}$  chlorobenzene as anti-solvent during the second step, 5 s before the end. All the perovskite samples were thermally annealed at 100 °C for 1 h. The HTMs solution was spin-coated at 4000 rpm for 20 s to yield films. The doped **M135**, **M136** and **M138** chlorobenzene solution (45 mM) was prepared with addition of 12.5  $\mu\text{L}$  Li-TFSI (1.8 M in acetonitrile), 22.2  $\mu\text{L}$  TBP and 8.2  $\mu\text{L}$  FK209 (0.166 M in acetonitrile). The doped **M137** chlorobenzene solution (20 mM) was prepared with addition of 5.6  $\mu\text{L}$  Li-TFSI (1.8 M in acetonitrile), 9.9  $\mu\text{L}$  TBP and 3.6  $\mu\text{L}$  FK209 (0.166 M in acetonitrile). The doped spiro-OMeTAD/chlorobenzene (80 mg  $\text{mL}^{-1}$ ) solution was prepared with the same additives. Finally, 80 nm of gold was then evaporated onto the active layer under high vacuum (less than  $10^{-6}$  mbar).

### 3. Photovoltaic Performance Characterizations

Current-voltage characteristics were measured under 100  $\text{mW cm}^{-2}$  (AM 1.5 G illumination) using a Newport solar simulator (Oriel Sol 3A, USA). A monocrystalline silicon reference cell (Oriel P/N 91150 V, with KG-5 visible color filter) was used to calibrate the light source for an intensity of 100  $\text{mW cm}^{-2}$ . And the  $J$ - $V$  curves were recorded with a sourcemeter (Keithley 2400, USA). The cells were masked with a black metal mask limiting the active area to 0.09  $\text{cm}^2$  (Figure S4) and reducing the influence of the scattered light. Incident photon-to-current conversion efficiency (IPCE) spectra were recorded using a computer-controlled setup consisting of a Xenon light source

(Spectral Products ASB-XE-175), a monochromator (Spectra Products CM110), and a potentiostat (LabJack U6 DAQ board), calibrated by a certified reference solar cell (Fraunhofer ISE).

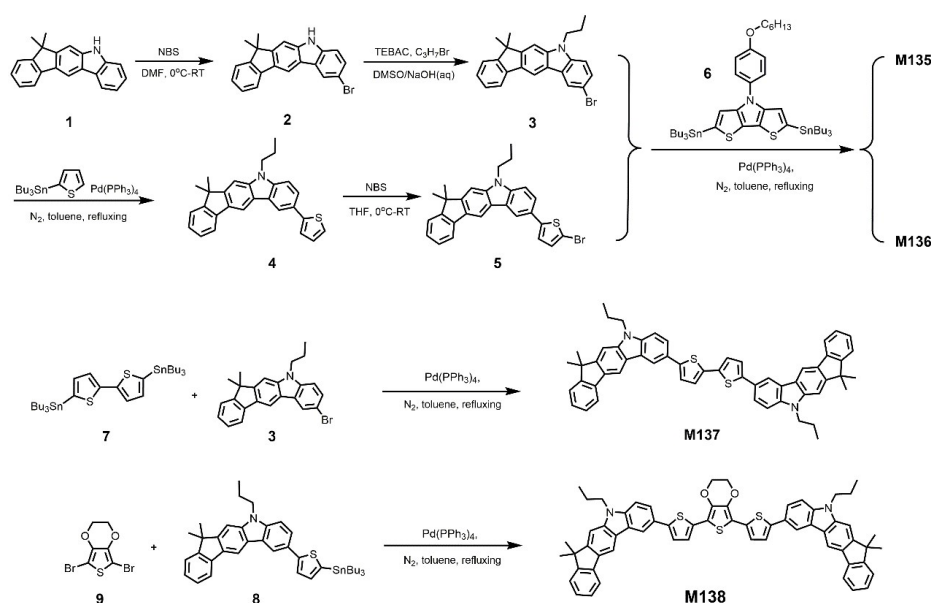
#### 4. Computational Details

In the simulation, Optimization and single point energy calculations are performed using the cam-B3LYP<sup>3</sup> and the 6-31G\*\* basis set for all atoms, without any symmetry constraints. All reported calculations were carried out by means of Gaussian 09.<sup>1</sup>

#### 5. Synthesis of HTMs

##### 5.1 Material

7,7-dimethyl-5,7-dihydroindeno[2,1-b]carbazole (compound **1**) raw material are purchased directly, 4-(4-(hexyloxy)phenyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (DTP) were synthesized according to reported literatures. DTP, 2,2'-bithiophene and compound **5** was allowed to react with *n*-BuLi/SnBu<sub>3</sub>Cl to produce compounds **6**, **7** and **8**, respectively.



**Scheme S1.** Synthesis routes of the HTMs **M135-138**.

## 5.2 Synthetic Procedures

### Synthesis of 2

Weigh compound **1** (1 g, 3.53 mmol) into a 100 mL round bottom flask, add 20 mL of DMF and stir to dissolve, add NBS (817 mg, 4.59 mmol) under ice bath conditions, the reaction system slowly from the ice bath to room temperature react for 6 hours. The reaction mixture was then poured into water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layer was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness. The product was directly used in the next reaction without purification.

### Synthesis of 3

Weigh compound **2** (1.28 g, 3.53 mmol) and TEBAC (40 mg, 0.18 mmol) into a 100 mL single-necked bottle, add 30 mL of dimethyl sulfoxide, stir to fully dissolve the raw materials, add 3 mL of an aqueous solution with a mass ratio of 1 g mL<sup>-1</sup> NaOH (DMSO: NaOH (aq) = 10:1), stirred vigorously for 30 min, then added C<sub>3</sub>H<sub>7</sub>Br (564 mg, 4.59 mmol), and stirred at room temperature overnight. The reaction mixture was then poured into water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layer was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness. The crude product was purified by silica gel column chromatography, and a mixed solvent with a volume ratio of DCM: PE = 1:10 was used as an eluent to obtain the product as a colorless oily liquid with a yield of 83% in two steps. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 8.63 (s, 1H), 8.41 (dd, *J* = 6.1, 1.9 Hz, 1H), 7.88 – 7.77 (m, 2H), 7.60 (d, *J* = 8.7 Hz, 1H), 7.56 – 7.53 (m, 1H), 7.53 (d, *J* = 2.1 Hz, 1H), 7.36 (t, *J* = 7.0 Hz, 1H), 7.27 (dt, *J* = 7.3, 3.7 Hz, 1H), 4.87 – 4.03 (m, 2H), 1.88 – 1.72 (m, 2H), 1.53 (s, 7H), 0.97 – 0.83 (m, 5H).



## Synthesis of 4

A two-necked flask containing Pd(PPh<sub>3</sub>)<sub>4</sub> (343 mg, 0.29 mmol), compound **3** (1.5 g, 3.71 mmol) and 2-tributylstannylthiophene (2.49 g, 6.68 mmol) and toluene (30 mL) equipped with a magnetic a N<sub>2</sub> purge, and a reflux condenser was heated at 110 °C for 12 h. The reaction mixture was then poured into water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layer was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness. The crude product was purified by silica gel column chromatography, and a mixed solvent with a volume ratio of DCM:PE = 1:10 was used as an eluent to obtain the product as a yellow oily liquid, and the yield was 87%. <sup>1</sup>H NMR (400 MHz, Acetone-*d*<sub>6</sub>): δ 8.66 (s, 1H), 8.53 (d, *J* = 1.4 Hz, 1H), 7.93 (d, *J* = 7.5 Hz, 1H), 7.83 – 7.71 (m, 2H), 7.57 (d, *J* = 8.5 Hz, 1H), 7.53 (d, *J* = 7.4 Hz, 1H), 7.49 – 7.46 (m, 1H), 7.41 – 7.34 (m, 2H), 7.31 – 7.25 (m, 1H), 7.14 (dd, *J* = 5.0, 3.6 Hz, 1H), 4.44 (t, *J* = 7.1 Hz, 2H), 1.95 (dt, *J* = 14.5, 7.3 Hz, 2H), 1.59 (s, 7H), 1.03 – 0.94 (m, 3H).

## Synthesis of 5

Compound **5** was synthesized by bromination of compound **4** with NBS in THF. Synthesis process refer to compound **2**. The product is a yellow oily liquid, and the yield was 87%.

## Synthesis of M135-138

**M135**: A two-necked flask containing Pd(PPh<sub>3</sub>)<sub>4</sub> (37 mg, 0.032 mmol), compound **6** (300 mg, 0.32 mmol) and compound **3** (388 mg, 0.96 mmol) and toluene (20 mL) equipped with a magnetic a N<sub>2</sub> purge, and a reflux condenser was heated at 110 °C overnight. The reaction mixture was then poured into water and extracted with CH<sub>2</sub>Cl<sub>2</sub>.

The combined organic layer was dried with anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated to dryness. The crude product was purified by silica gel column chromatography, and a mixed solvent with a volume ratio of DCM:PE = 1:3 was used as an eluent to obtain the product **M135** as a yellow solid, and the yield was 48%.  $^1\text{H}$  NMR (400 MHz, Acetone- $d_6$ )  $\delta$  8.60 (s, 1H), 8.37 (s, 1H), 7.90 (d,  $J$  = 7.3 Hz, 2H), 7.81 (d,  $J$  = 10.0 Hz, 1H), 7.66 (d,  $J$  = 10.9 Hz, 1H), 7.50 (d,  $J$  = 1.0 Hz, 2H), 7.36 (dd,  $J$  = 13.7, 7.4 Hz, 2H), 7.32 – 7.27 (m, 2H), 4.53 (t,  $J$  = 7.1 Hz, 2H), 4.45 (d,  $J$  = 7.2 Hz, 1H), 1.69 (d,  $J$  = 19.8 Hz, 1H), 1.64 – 1.59 (m, 6H), 1.56 (s, 7H), 0.88 (d,  $J$  = 6.6 Hz, 4H).  $^{13}\text{C}$  NMR (101 MHz, THF- $d_8$ )  $\delta$  = 157.96, 153.07, 144.44, 143.42, 141.55, 140.48, 140.02, 132.74, 131.53, 126.84, 125.84, 124.79, 123.65, 123.01, 122.46, 122.23, 118.98, 116.53, 115.37, 114.72, 111.44, 109.10, 106.63, 103.14, 68.07, 53.93, 46.43, 31.66, 29.33, 27.39, 25.83, 22.63, 22.26, 13.48, 11.00.

Synthesis process of **M136** and **M137** refer to **M135**.

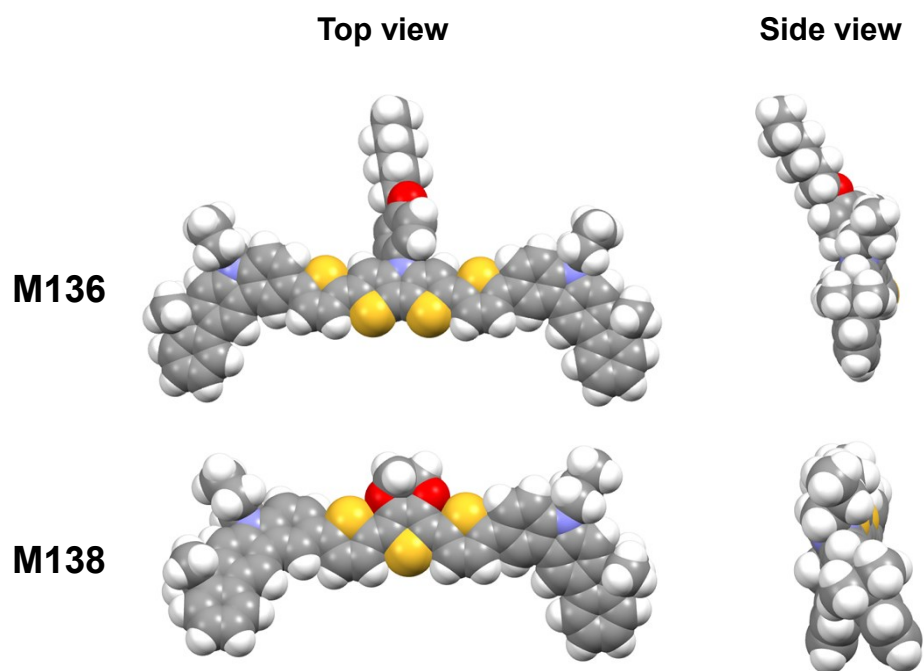
**M136**: Orange solid, the yield was 52%.  $^1\text{H}$  NMR (400 MHz, THF- $d_8$ )  $\delta$  = 8.59 (s, 2H), 8.51 (s, 2H), 7.90 (d,  $J$  = 7.5, 2H), 7.77 (d,  $J$  = 8.6, 2H), 7.67 (d,  $J$  = 8.7, 2H), 7.64 (s, 2H), 7.55 (d,  $J$  = 8.6, 2H), 7.49 (d,  $J$  = 7.3, 2H), 7.42 (d,  $J$  = 3.6, 2H), 7.35 (q,  $J$  = 7.3, 6H), 7.27 (d,  $J$  = 7.5, 2H), 7.22 (d,  $J$  = 8.3, 2H), 4.44 (t,  $J$  = 6.9, 4H), 4.14 (t,  $J$  = 6.4, 2H), 1.91 – 1.86 (m, 2H), 1.61 (s, 12H), 1.47 – 1.43 (m, 4H), 1.41 (d,  $J$  = 8.4, 2H), 1.33 (s, 4H), 1.08 – 1.00 (m, 9H).  $^{13}\text{C}$  NMR (101 MHz, THF- $d_8$ )  $\delta$  = 158.15, 153.12, 144.33, 141.54, 140.63, 139.97, 136.29, 135.77, 132.16, 131.63, 126.83, 125.89, 125.22, 124.59, 123.73, 122.98, 122.32, 119.00, 116.84, 115.44, 114.90, 111.42, 109.19, 107.57, 103.20, 46.44, 44.26, 31.65, 29.68, 29.29, 27.38, 25.80, 22.62, 22.25, 13.48,

10.98.

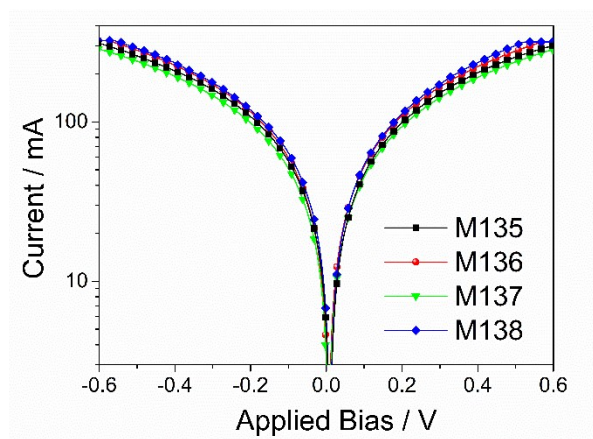
**M137**: Yellow solid, the yield was 44%.  $^1\text{H}$  NMR (400 MHz,  $\text{THF-}d_8$ )  $\delta$  = 8.60 (s, 2H), 8.53 (d,  $J$  = 1.3, 2H), 7.91 (d,  $J$  = 7.4, 2H), 7.79 (d,  $J$  = 10.2, 2H), 7.65 (s, 2H), 7.58 (d,  $J$  = 8.5, 2H), 7.49 (d,  $J$  = 7.4, 2H), 7.44 (d,  $J$  = 3.7, 2H), 7.36 (t,  $J$  = 7.4, 2H), 7.31 (d,  $J$  = 3.7, 2H), 7.26 (t,  $J$  = 7.1, 2H), 4.46 (t,  $J$  = 7.1, 4H), 1.76 (s, 12H), 1.62 (s, 4H), 1.06 (t,  $J$  = 7.4, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{THF-}d_8$ )  $\delta$  = 153.12, 144.34, 141.55, 140.64, 139.97, 135.49, 131.62, 126.84, 125.89, 125.31, 123.89, 123.63, 123.10, 122.32, 119.01, 116.89, 111.43, 109.20, 103.20, 46.44, 44.26, 27.38, 22.25, 10.99.

**M138**: A two-necked flask containing  $\text{Pd}(\text{PPh}_3)_4$  (58 mg, 0.05 mmol), compound **9** (150 mg, 0.5 mmol) and compound **8** (1.04 g, 1.5 mmol) and toluene (20 mL) equipped with a magnetic stirrer, a  $\text{N}_2$  purge, and a reflux condenser was heated at 110 °C overnight. The reaction mixture was then poured into water and extracted with  $\text{CH}_2\text{Cl}_2$ . The combined organic layer was dried with anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated to dryness. The crude product was purified by silica gel column chromatography, and a mixed solvent with a volume ratio of  $\text{DCM:PE}$  = 1:3 was used as an eluent to obtain the product **M138** as an orange solid, and the yield was 57%.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  = 8.74 (s, 2H), 8.53 (d,  $J$  = 1.5, 2H), 7.92 (d,  $J$  = 7.6, 2H), 7.84 (s, 2H), 7.81 – 7.77 (m, 2H), 7.67 (d,  $J$  = 8.6, 2H), 7.55 (t,  $J$  = 5.9, 4H), 7.38 (t,  $J$  = 7.4, 2H), 7.29 (dd,  $J$  = 5.5, 4H), 4.55 (s, 4H), 4.45 (t, 4H), 1.56 (s, 12H), 1.23 (s, 4H), 0.94 (t,  $J$  = 7.4, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2\text{-}d_2$ )  $\delta$  = 153.28, 153.27, 144.01, 141.43, 140.53, 139.74, 137.67, 132.54, 132.22, 132.11, 131.48, 128.97, 128.57, 128.45, 128.16, 127.09, 126.22, 125.31, 123.89, 123.42, 123.33, 122.56, 122.19, 122.06, 119.19, 117.04,

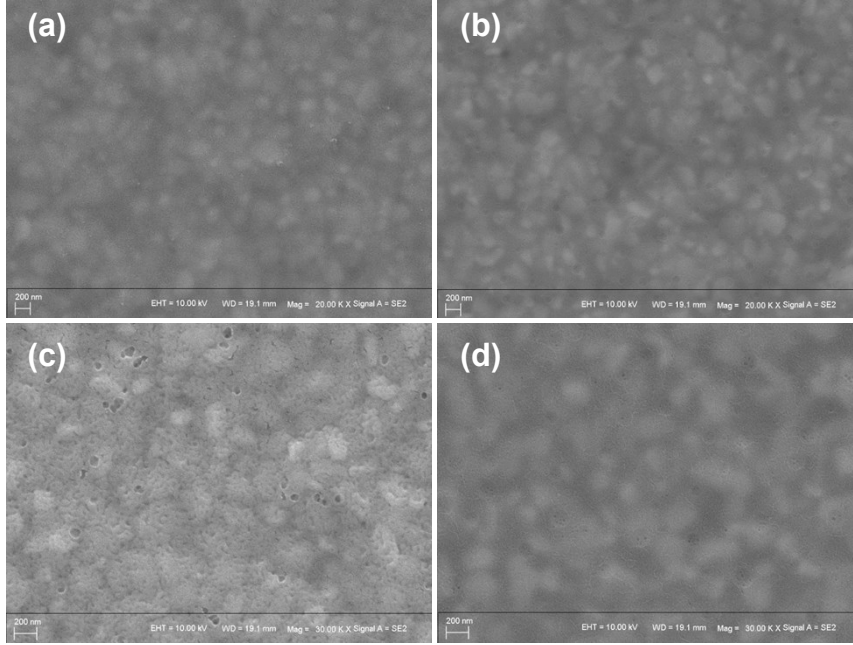
109.32, 103.34, 65.21, 46.70, 44.86, 27.87, 22.35, 11.58.



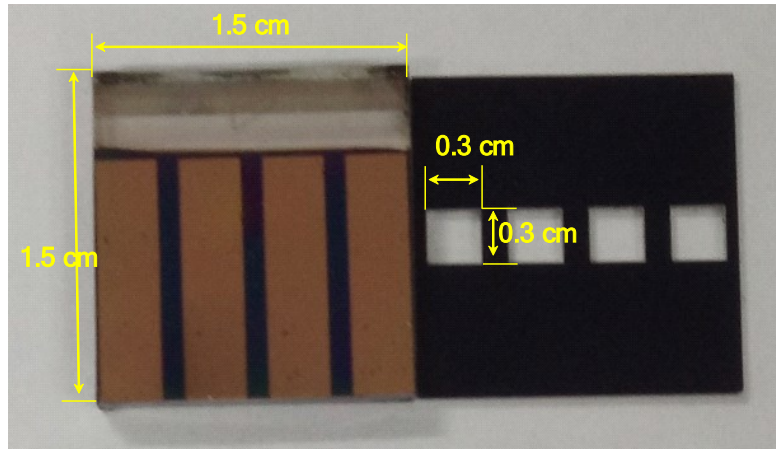
**Figure S1.** Top view and side view of M136 and M138.



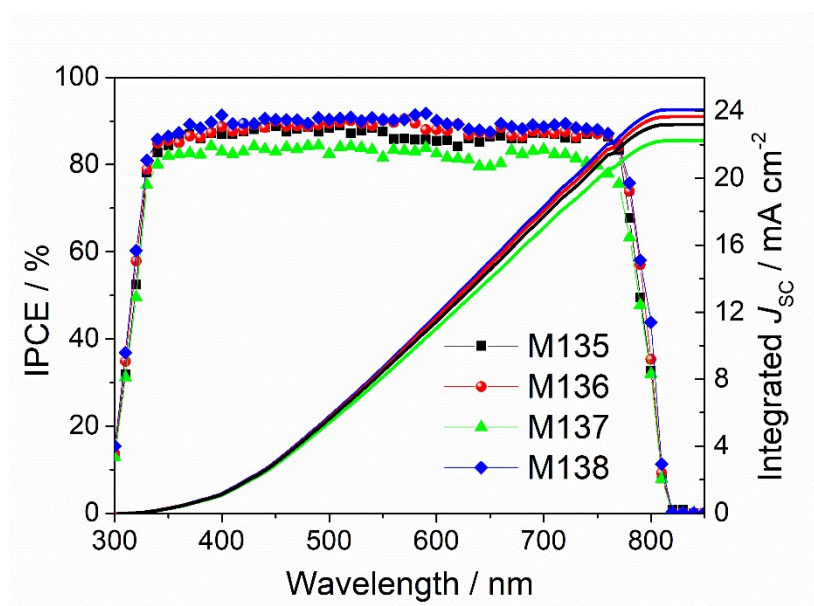
**Fig. S2.** Current–voltage characteristics of films based on the M135-138.



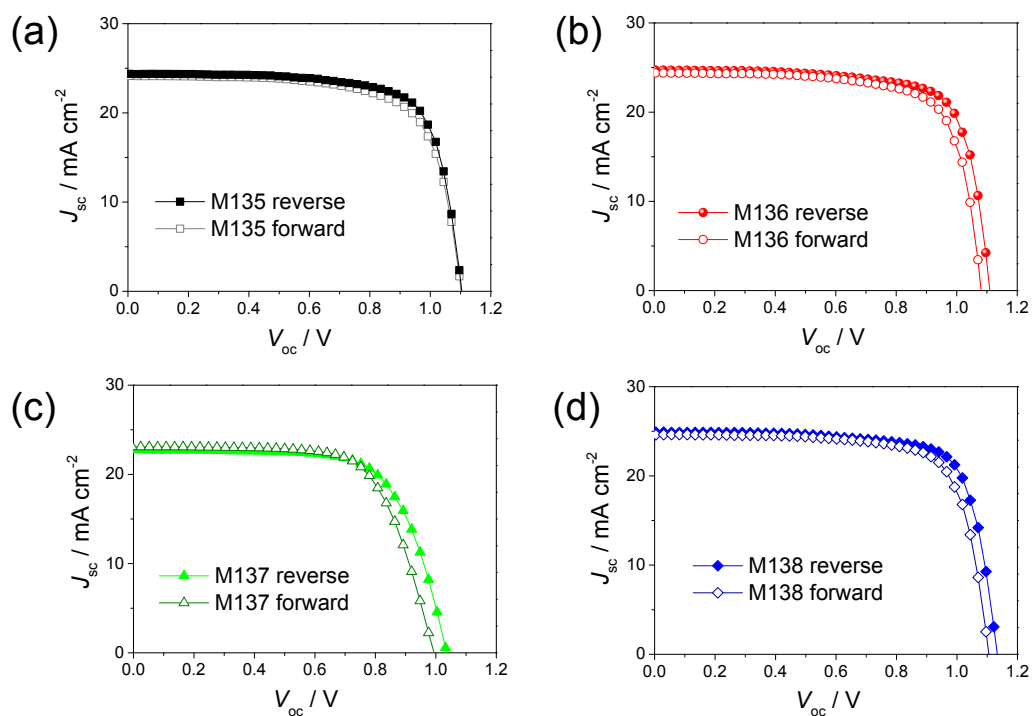
**Fig. S3.** SEM top images of devices fabricated with the M135 (a), M136 (b), M137 (c) and M138 (d).



**Figure S4.** The devices we fabricated and the black metal mask with an active area of  $0.09 \text{ cm}^2$ .

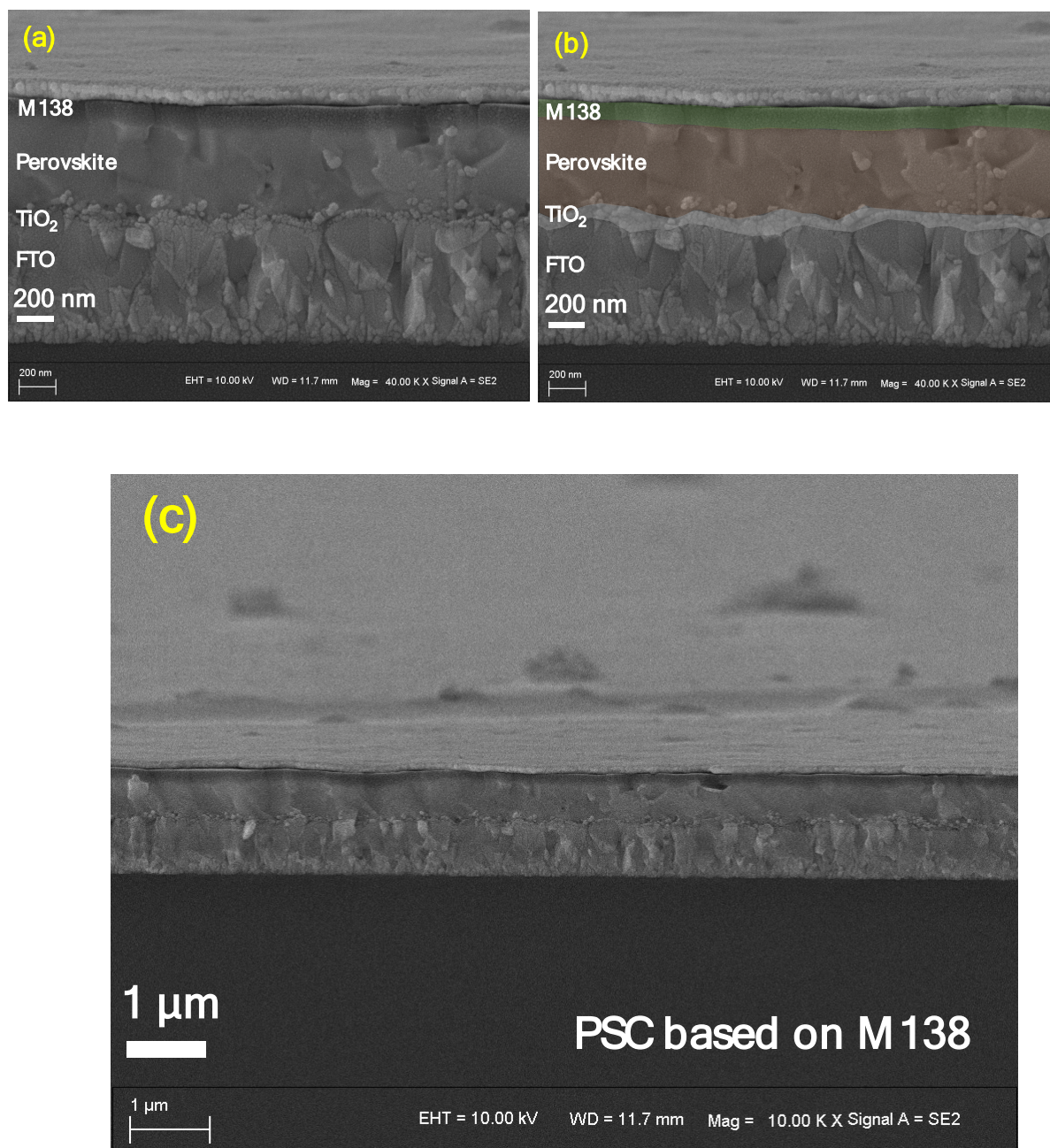


**Figure S5.** IPCE and integrated  $J_{sc}$  versus wavelength spectra of fabricated PSCs.

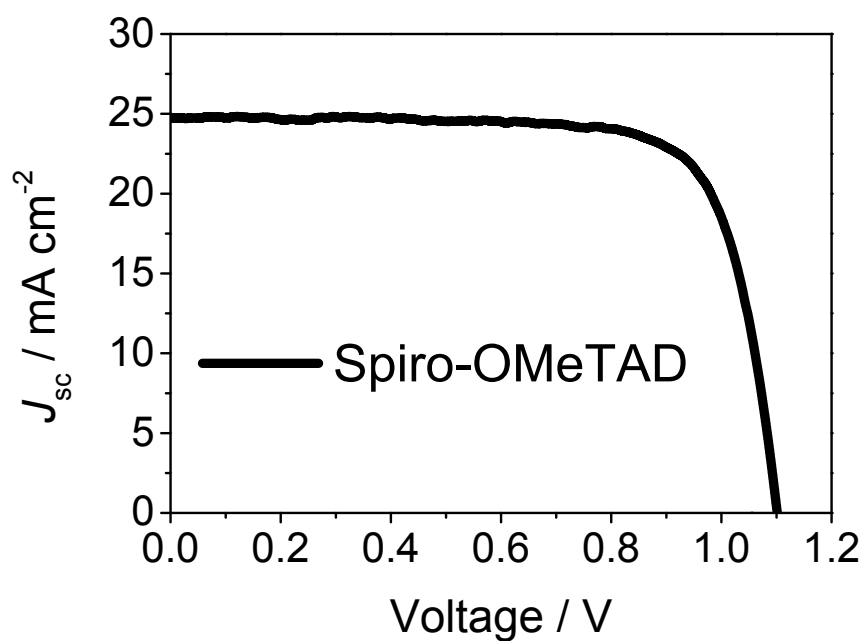


**Figure S6.**  $J$ - $V$  curves for PSCs employing different HTMs in the different scanning directions.

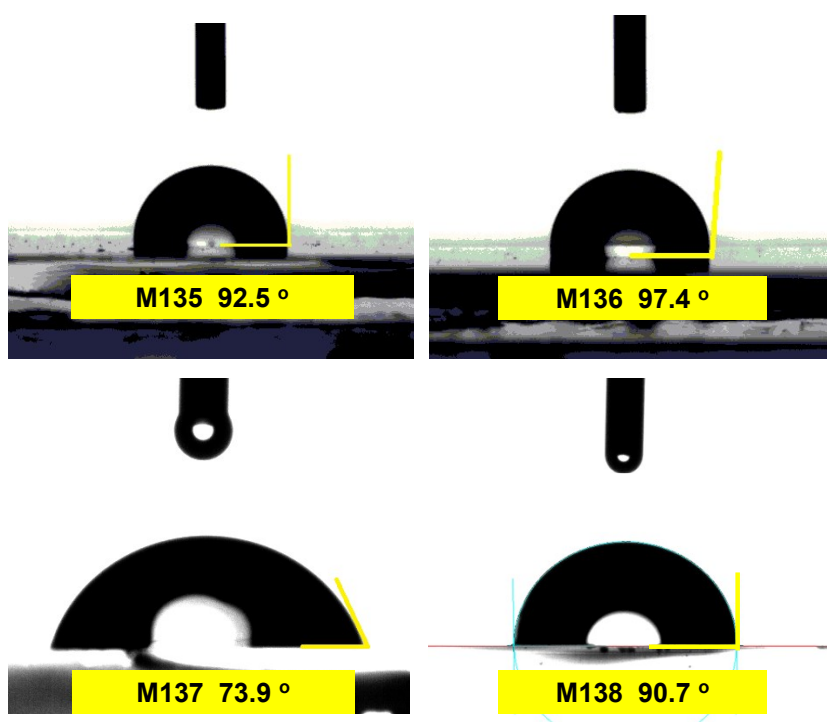




**Figure S7.** The cross-section view of the device based on M138 without (a) and with colored sign (b). The cross-section view of the device based on M138 with a large scale (c).

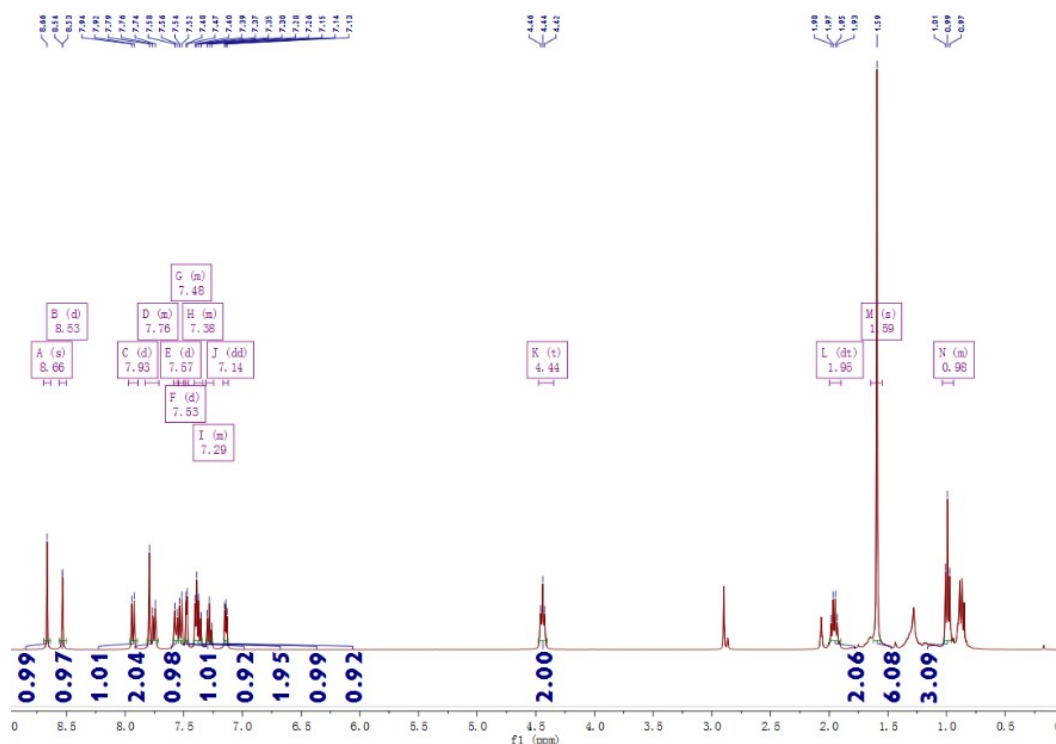
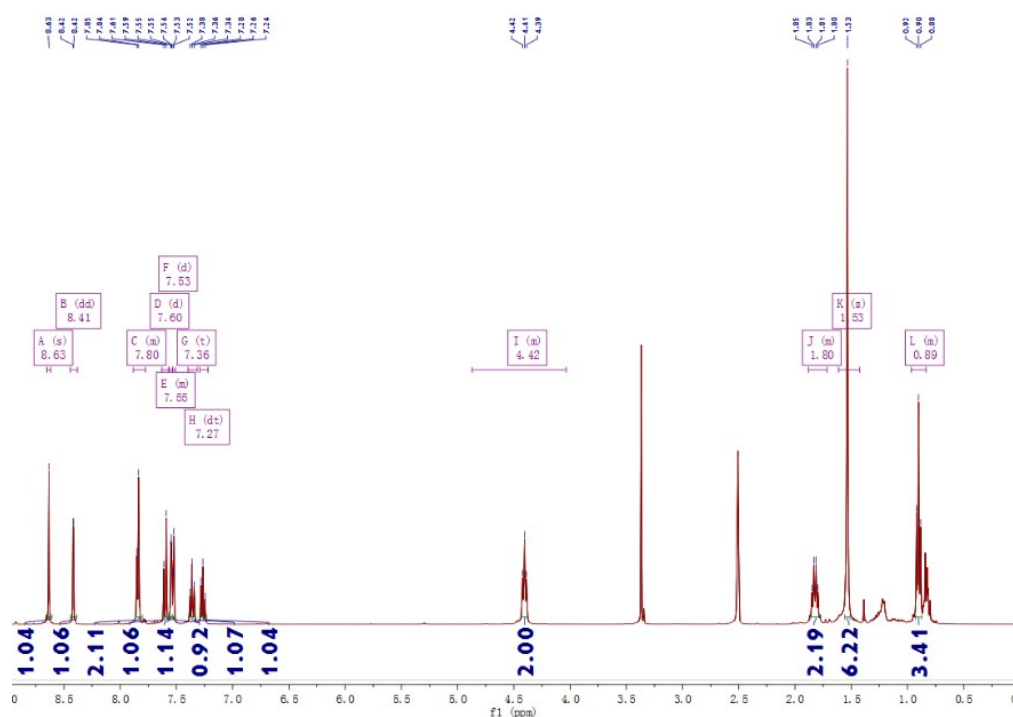


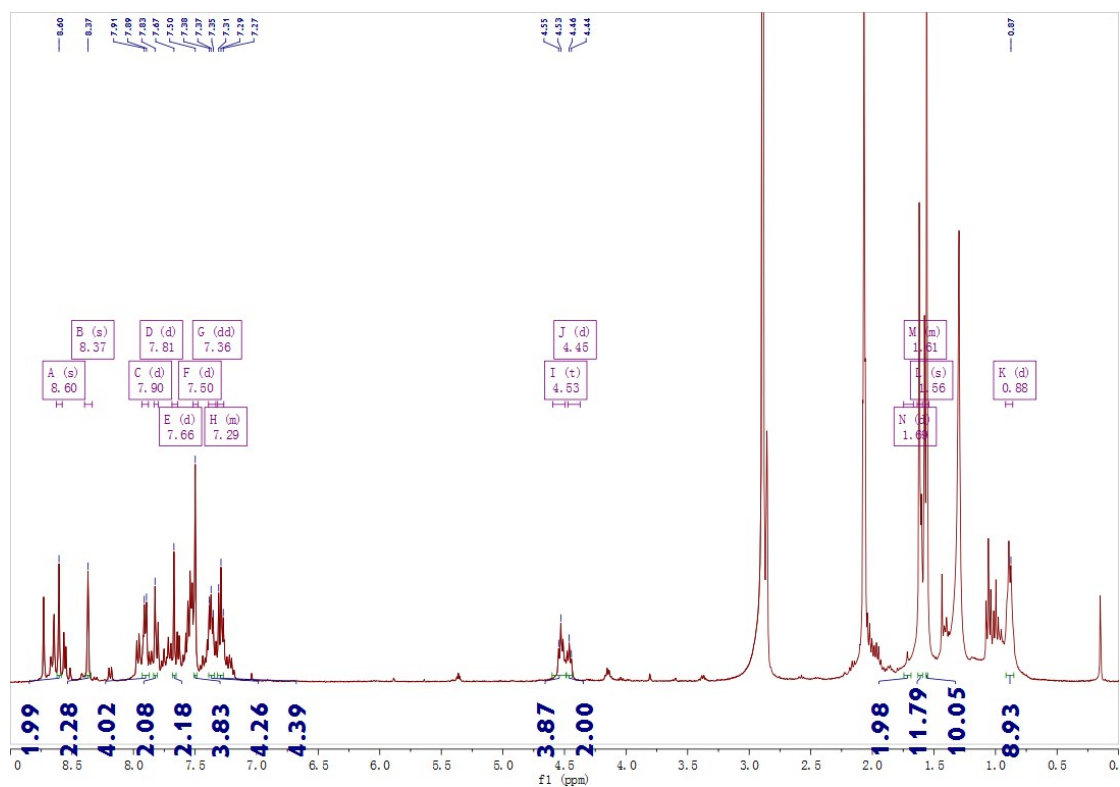
**Figure S8.** The reverse scanning  $J$ - $V$  curves for the best performing devices based on Spiro-OMeTAD.



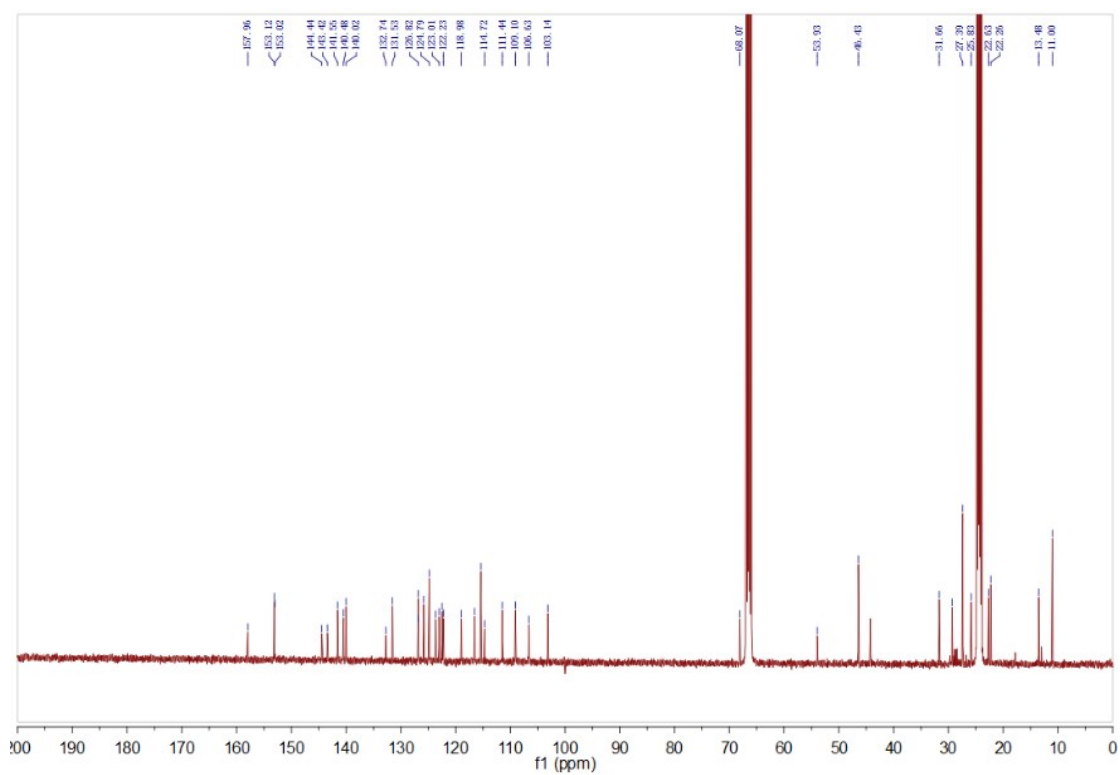
**Figure S9.** Water contact angle measurements of perovskite/HTMs.



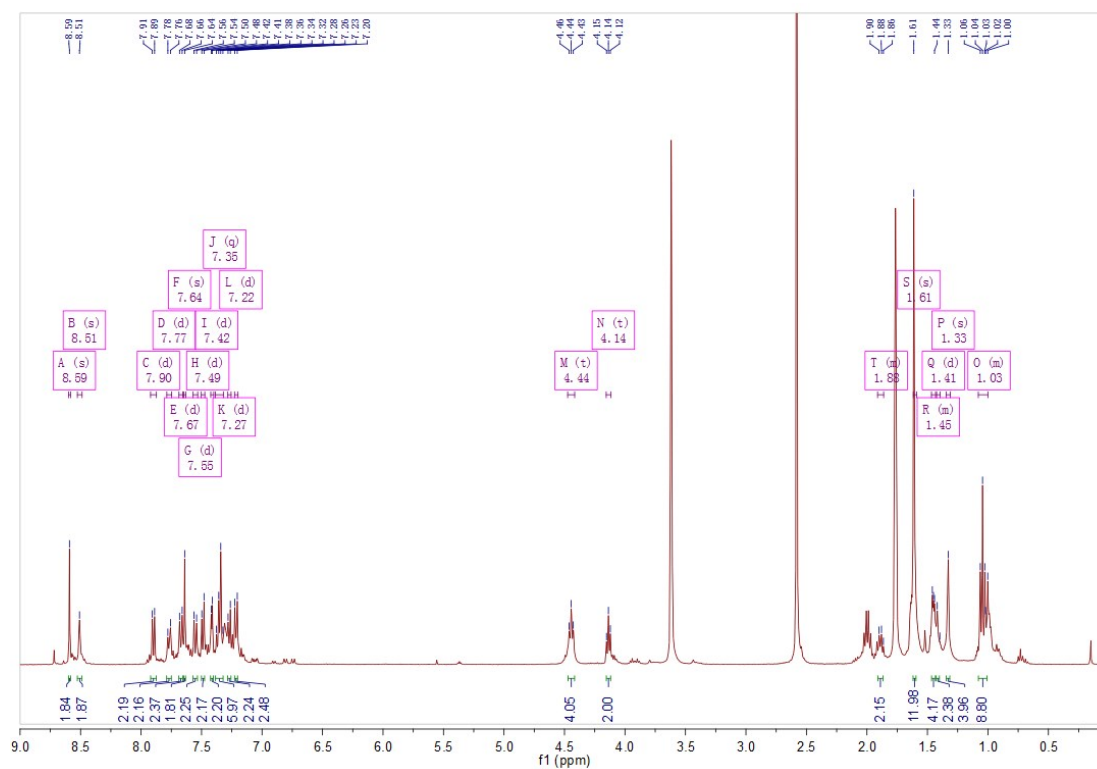




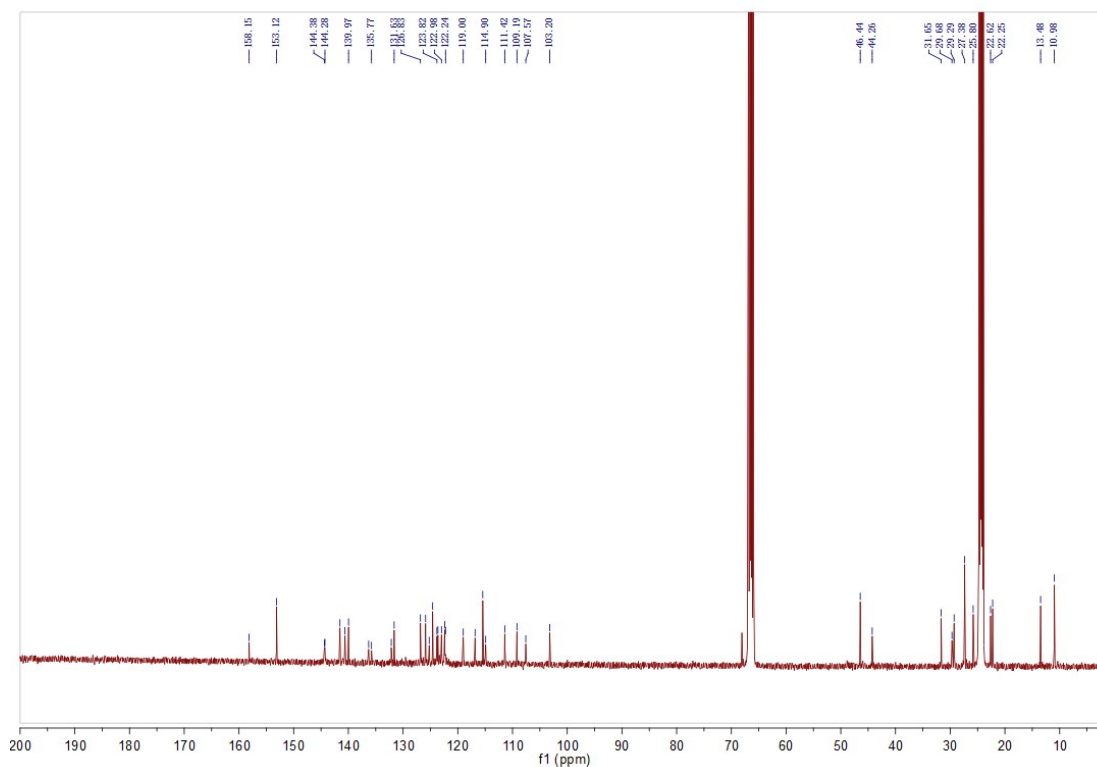
**Figure S11.  $^1\text{H}$  NMR (Acetone- $d_6$ ) spectrum of M135**



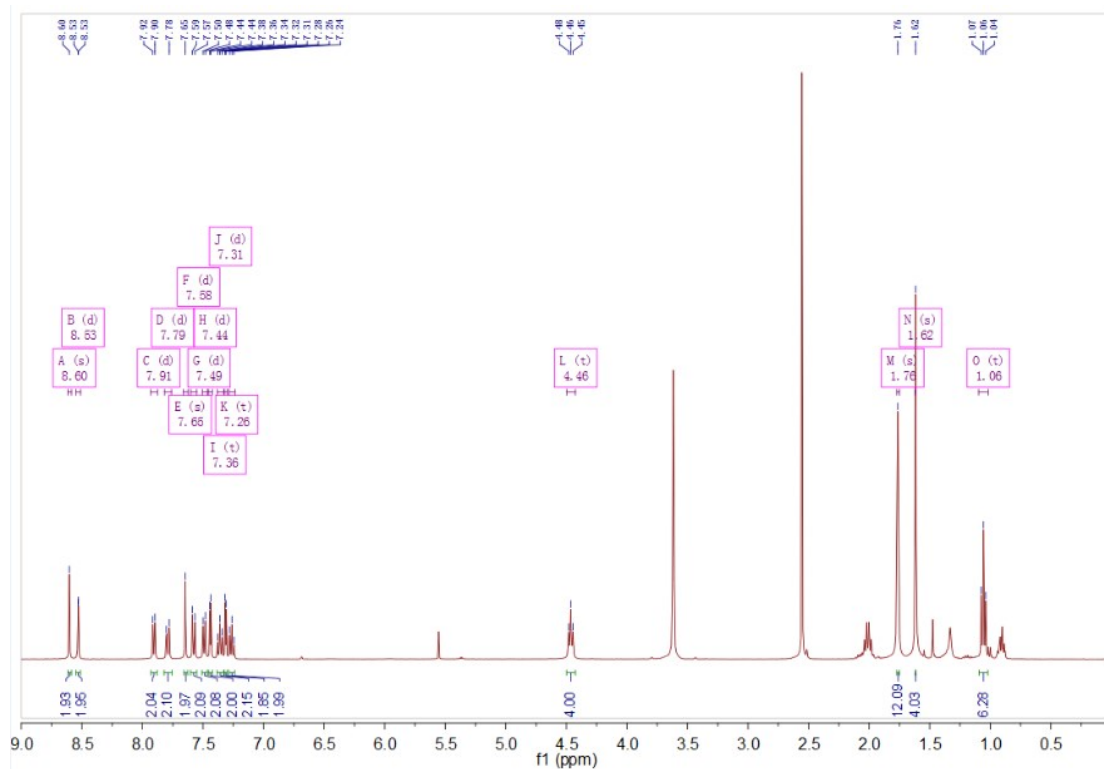
**Figure S12.  $^{13}\text{C}$  NMR (THF- $d_8$ ) spectrum of M135**



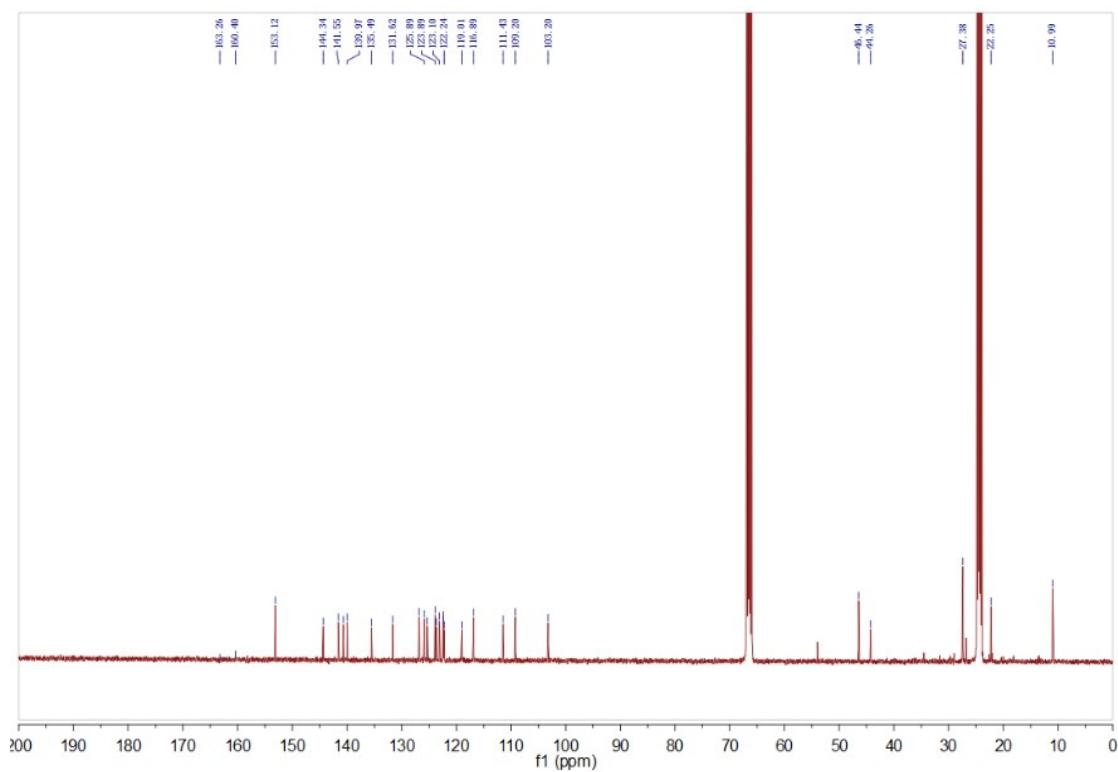
**Figure S13.**  $^1\text{H}$  NMR ( $\text{THF-}d_8$ ) spectrum of **M136**



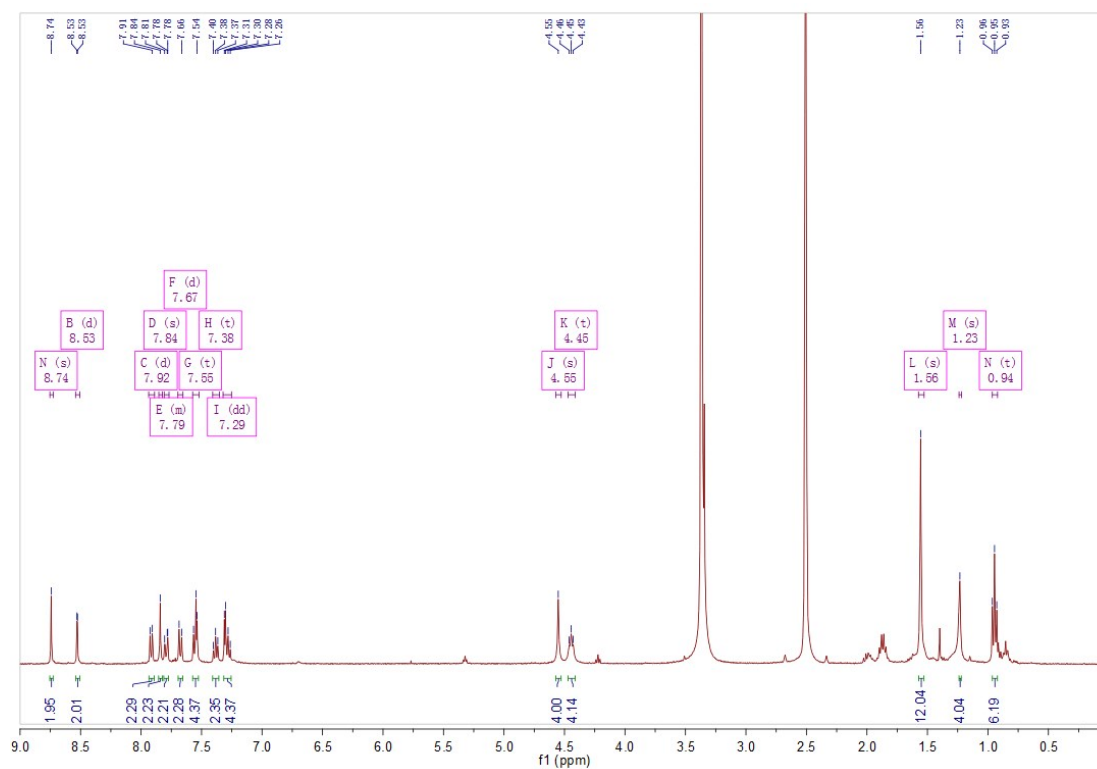
**Figure S14.**  $^{13}\text{C}$  NMR ( $\text{THF-}d_8$ ) spectrum of **M136**



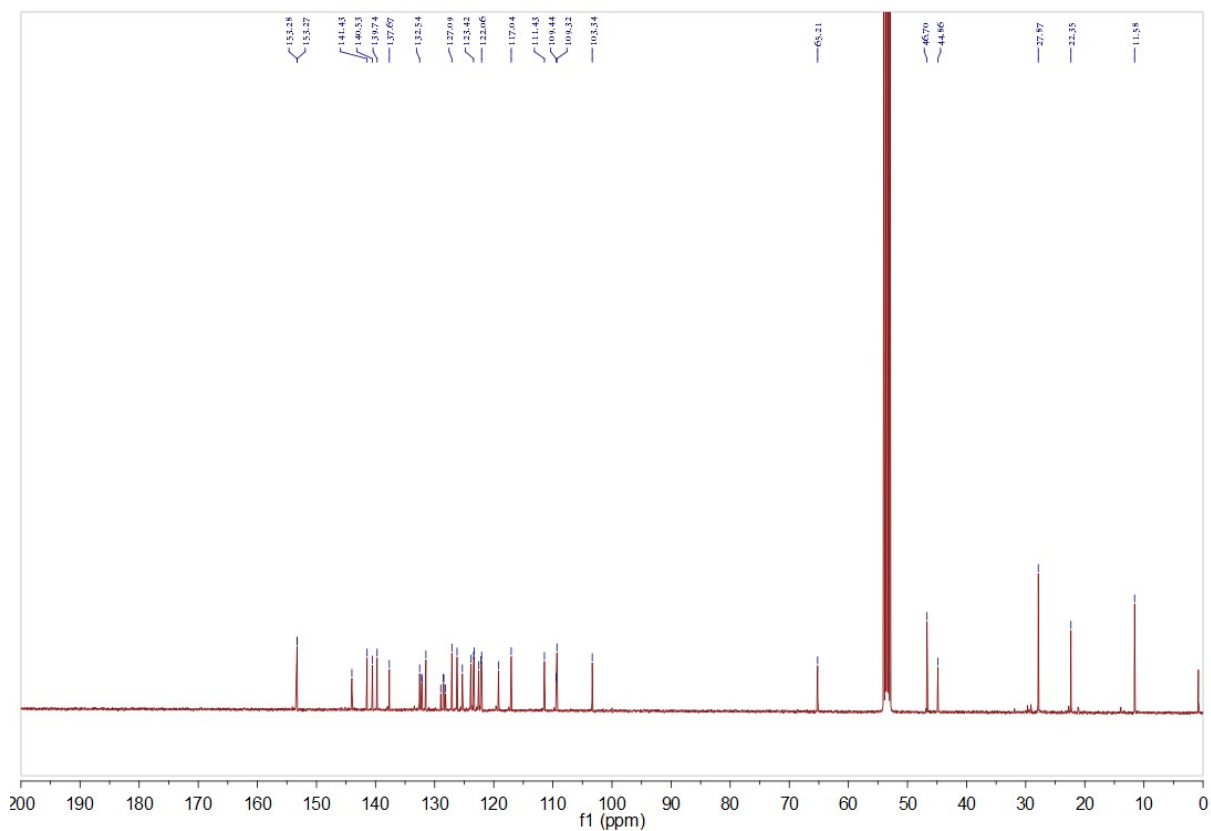
**Figure S15.  $^1\text{H}$  NMR (THF- $d_8$ ) spectrum of M137**



**Figure S16.  $^{13}\text{C}$  NMR (THF- $d_8$ ) spectrum of M137**



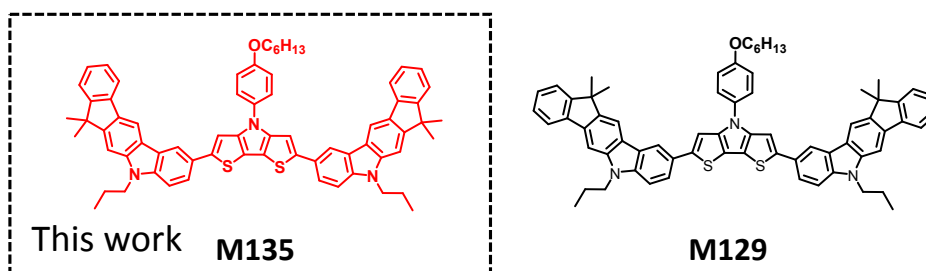
**Figure S17.  $^1\text{H}$  NMR ( $\text{THF}-d_8$ ) spectrum of M138**



**Figure S18.  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) spectrum of M138**

**Table S1.** Photovoltaic parameters of the best PSC devices (FTO/c-TiO<sub>2</sub>/meso-TiO<sub>2</sub>/CsFAMA/HTMs/Au) based on M135 and M129.

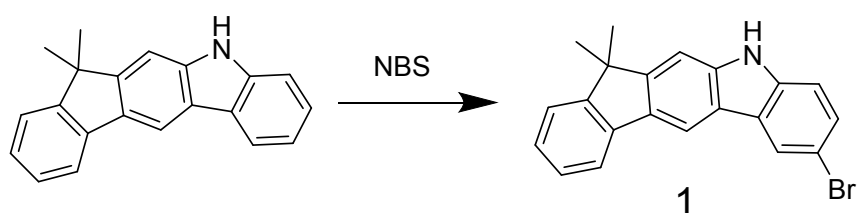
HTMs	$J_{SC} / \text{mA cm}^{-2}$	$V_{OC} / \text{V}$	FF	PCE / %
M135	24.41	1.10	0.74	19.86
M129	24.30	1.12	0.75	20.41



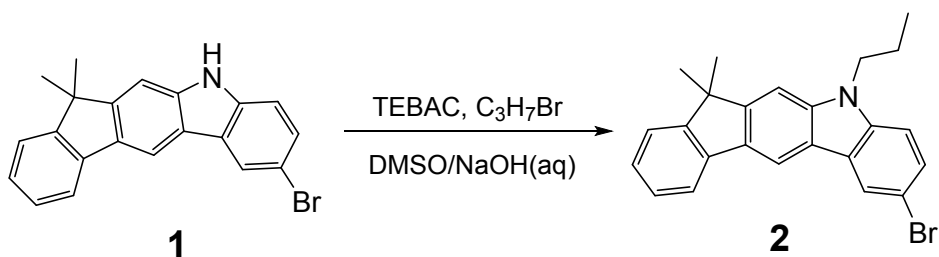
**Table S2.** TRPL time of the HTMs **M135-138**

	M135	M136	M137	M138
T <sub>1</sub> (ns)	133.8595	1.5247	213.5583	0.58783
T <sub>2</sub> (ns)	0.77841	32.5534	3.70971	83.68022
average T(ns)	101.61	29.15	198.5	25.68
A1	0.05796	2.32139	0.53486	5.54453
A2	3.19003	0.87897	2.35767	0.07283

## The cost analysis of **M138** synthesis

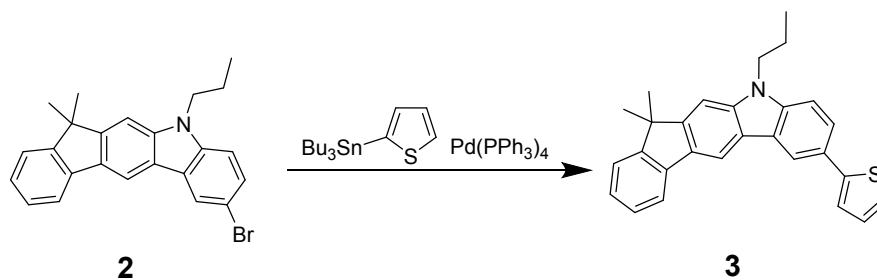


Reagent	Amount/g	Amount/mL	Price/g or mL	Total price/RMB
indeno[2,1-b]carbazole	5		100.46	502.3
NBS	3.3		0.174	0.57
DMF		30	0.0375	1.12
dichloromethane		50	0.02	1
Total cost	504.99			
Amount <b>1</b>	6.3 g			
COST for <b>1</b>	80.16 RMB g <sup>-1</sup> or 12.4 \$ g <sup>-1</sup>			

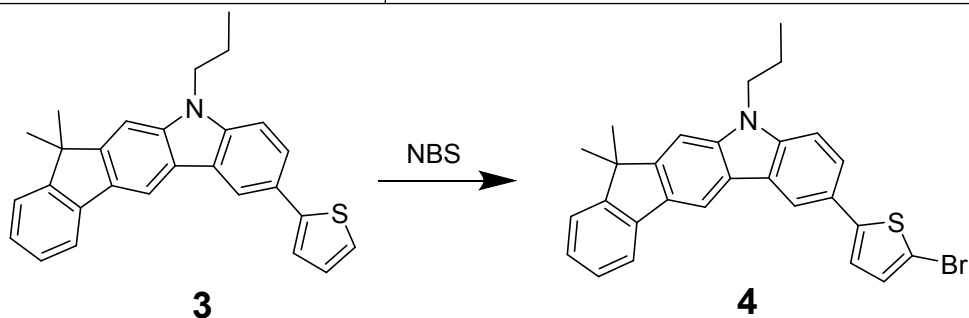


Reagent	Amount/g	Amount/mL	Price/g or mL	Total price/RMB
<b>1</b>	6.3		80.16	505
1-Bromopropane	2.56		0.253	0.648
NaOH	4		0.088	0.352
DMSO		40	0.2	8
TEBAc	0.08		1.2	0.096
Silica gel	80		0.036	2.88
Petroleum ether60-90 °C		600	0.022	13.2
dichloromethane		50	0.02	1
Total cost	531.18			
Amount <b>2</b>	6.88 g			

COST for <b>2</b>	77.21 RMB g <sup>-1</sup> or 11.94 \$ g <sup>-1</sup>
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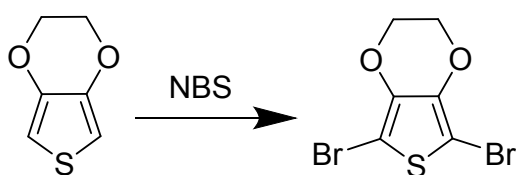
Reagent	Amount/g	Amount/mL	Price/g or mL	Total price/RMB
<b>2</b>	6.88		77.21	531.18
2-(Tributylstannyl)thiophene	9.52		2.96	28.18
Pd(PPh <sub>3</sub> ) <sub>4</sub>	0.95		44	41.8
Toluene		70	0.1	7
Silica gel	150		0.036	5.4
Petroleum ether 60-90 °C		1000	0.022	22
dichloromethane		120	0.02	2.4
Total cost	637.96			
Amount <b>3</b>	6.89 g			
COST for <b>3</b>	92.59 RMB g <sup>-1</sup> or 14.32 \$ g <sup>-1</sup>			



Reagent	Amount/g	Amount/mL	Price/g or mL	Total price/RMB
<b>3</b>	6.89		92.59	637.96
NBS	3.62		0.174	0.63
THF		40	0.2	8



Silica gel	200		0.036	7.2
Petroleum ether60-90 °C		500	0.022	11
dichloromethane		100	0.02	2
Total cost	666.79			
Amount <b>4</b>	7.84 g			
COST for <b>4</b>	85.05 RMB g <sup>-1</sup> or 13.15 \$ g <sup>-1</sup>			



**5**

Reagent	Amount/g	Amount/mL	Price/g or mL	Total price/RMB
3,4-Ethylenedioxythiophene	1		4	4
NBS	2.75		0.174	0.48
THF		15	0.2	3
Silica gel	30		0.036	1.08
Petroleum ether60-90 °C		100	0.022	2.2
dichloromethane		10	0.02	0.2
Total cost	10.96			
Amount <b>5</b>	1.9 g			
COST for <b>5</b>	5.77 RMB g <sup>-1</sup> or 0.89 \$ g <sup>-1</sup>			

### M138

Regent	Amount/g	Amount/mL	Price/g or mL	Total price/RMB
<b>4</b>	1.5		85.05	127.57
n-BuLi (2.5mol / L)		1.5	0.28	0.42
Sn(But) <sub>3</sub> Cl	1.2		1.09	1.38
THF		10	0.2	2
<b>5</b>	0.3		5.77	1.73
Pd(PPh <sub>3</sub> ) <sub>4</sub>	0.09		44	3.96
Toluene		15	0.1	1.5
Silica gel	200		0.036	7.2
Petroleum ether 60-90 °C		1000	0.022	22
dichloromethane		600	0.02	12
Total cost	179.76			
Amount <b>M138</b>	0.54 g			
COST for <b>M138</b>	332.89 RMB g <sup>-1</sup> or 51.49 \$ g <sup>-1</sup>			

## References

[1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. M. a, G. A. Petersson, H. Nakatsuji, M. Caricato, X. L. and, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. H. a. M. E. a. K. T. a. R. F. a. J. H. a. M. I. a. T. N. a. Y. H. a. O. K. and H. Nakai and T. Vreven and Montgomery, Jr., J. A. and J. E. Peralta and F. Ogliaro and M. Bearpark and J. J. Heyd and E. Brothers and K. N. Kudin and V. N. Staroverov and R. Kobayashi and J. Normand and K. Raghavachari and A. Rendell and J. C. Burant and S. S. Iyengar and J. Tomasi and M. Cossi and N. Rega and J. M. Millam and M. Klene and J. E. Knox and J. B. Cross and V. Bakken and C. Adamo and J. Jaramillo and R. Gomperts and R. E. Stratmann and O, Gaussian Inc. Wallingford CT 2009.