

## Supplementary Information

### Thieno-imidazole based small molecule hole transport materials for dopant-free, efficient inverted (p-i-n) perovskite solar cells

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## General Information

All chemicals and reagents were procured from commercial vendors and used directly without further purification unless otherwise specified. The solvents such as  $\text{CH}_2\text{Cl}_2$ , THF, and DMF were dried using VAC purifier (VAC 103991, Vacuum Atmospheres). All the other solvents were of HPLC grade. Air-sensitive reactions were carried out under argon atmosphere. The reaction progresses were monitored by thin layer chromatography (TLC) using aluminum coated Merck Kieselgel 60 F254 plates and developed with  $\text{I}_2$  or UV light. Silica gel (Scharlau 60, 230-240 mesh) was utilized for flash chromatography. All the intermediates and final compounds were characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra using a Bruker Avance 500 MHz spectrometer. Coupling constants (J) and chemical shifts ( $\delta$ ) are denoted with Hz and ppm, respectively. Multiplicities were reported as: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, b = broad. UV-Vis solution spectra were recorded on a Shimadzu UV3600 UV-vis-NIR spectrophotometer. The UV-Vis film were recorded on JASCO V-730 spectrophotometer with film thickness (measured by ellipsometer-Woollam M-2000VI) of PEDOT:PSS = 40.70 nm; Spiro = 23.90 nm; Al109 = 2.23 nm, Al112 = 1.78 nm. Mass spectra Matrix assisted Laser desorption ionization (coupled to a Time-of-Flight analyzer) experiments (MALDI-TOF) were recorded on a Bruker Daltonics flexAnalysis spectrometer. Cyclic voltammetry (CV) experiments were performed using CHI 627C electrochemical setup consisting of a conventional single-compartment three-electrode cell. A glassy carbon electrode, a silver wire ( $\text{Ag}/\text{AgNO}_3$  in acetonitrile), and a Pt wire were employed as the working electrode, the reference electrode, and the counter-electrode, respectively. While, 0.1 M tetrabutylammonium hexafluorophosphate was utilized as the supporting electrolyte. A scan rate of  $50 \text{ mVs}^{-1}$  was typically used to record the cyclic voltammograms. After measurement, ferrocene was added as the internal reference for calibration. Thermogravimetric analysis (TGA) was performed using a TA Instruments TGAQ500 with a ramp of  $10 \text{ }^\circ\text{C}/\text{min}$  under  $\text{N}_2$  from 100 to  $600 \text{ }^\circ\text{C}$ . DSC was run on a Discovery DSC from TA instruments. Two cycles were recorded under nitrogen, heating (until  $400 \text{ }^\circ\text{C}$ ) and cooling ( $50 \text{ }^\circ\text{C}$ ) at  $10 \text{ }^\circ\text{C}/\text{min}$  of scanning rate.

## Device Fabrication

Perovskite solar cells (PSCs) with a p-i-n structure were fabricated with a configuration of ITO/HTMs/perovskite/PCBM/BCP/Ag. ITO glass was cleaned by sequentially washing with detergent, deionized water, acetone, and isopropanol. The substrates were dried with  $\text{N}_2$  and cleaned by UV ozone for 15 min. After transferring the substrates to a glovebox, Al109, Al112, PEDOT:PSS, and spiro-OMeTAD films were fabricated separately.<sup>S1, S2</sup> Al109 and Al112 HTMs with a concentration of 1.0 mg/mL in chlorobenzene:DMF (99.5%:0.5%) were spin coated on the clean ITO substrates at a rate of 3000 rpm for 40 s and the substrates were annealed at  $80 \text{ }^\circ\text{C}$  for 20 min. The stock solution of PEDOT:PSS was filtered through a  $0.22 \text{ } \mu\text{m}$  PVDF, spin coated on the ITO at 3500 rpm for 40 s and subsequently heated at  $140 \text{ }^\circ\text{C}$  for 10 min. For PSC based on Spiro-OMeTAD,<sup>S2</sup> a solution of 10 mg/mL in chlorobenzene was spin coated on ITO at a rate of 3000 rpm for 30 s and subsequently dried at  $60 \text{ }^\circ\text{C}$  for 10 min. A mixture of  $\text{PbI}_2$  (345.75 mg), MAI (119.25 mg), DMSO ( $159.23 \text{ } \mu\text{L}$ ), DMF ( $580.7 \text{ } \mu\text{L}$ ) was stirred at  $50 \text{ }^\circ\text{C}$  to obtain a homogenous perovskite solution. The prepared perovskite solution ( $80 \text{ } \mu\text{L}$ )

was spin coated on the HTM layer at different rates, 1000 rpm for 10 s and 5000 rpm for 20 s, and 105  $\mu\text{L}$  of toluene was dropped on the perovskite layer in the last 3 s of the procedure. Afterwards, the as prepared films were annealed at 60 °C for 2 min and 100 °C for 3 min. After cooling down, 50  $\mu\text{L}$  of [6,6]-phenyl-C61-butyric acid methyl ester (PCBM, 20 mg/mL in chlorobenzene) filtered through a 0.45  $\mu\text{m}$  PTFE, was spin-coated at 1000 rpm for 60 s and allowed to stand for 30 min to dye the solvent. A ~5 nm thick finishing BCP (bathocuproine) layer was vapor deposited on the top of PC61BM layer. Finally, a 100 nm thick Ag electrode was deposited by thermal evaporation in a vacuum deposition chamber (background pressure  $\approx 5 \times 10^{-6}$  torr).

### Device Characterization

The *J-V* characteristics were measured with Keithley 2400 measurement source units with the devices maintained at room temperature in glove-box. The photovoltaic response was measured under a calibrated solar simulator (Enli Technology) at 100 S15  $\text{mW cm}^{-2}$ , and the light intensity was calibrated with a standard photovoltaic reference cell. The EQE spectrum was measured using a QE-R Model of Enli Technology. Top-view morphology and cross-section SEM was characterized by Hitachi S-4800 scanning electron microscope. The X-ray diffraction patterns were obtained using a BRUKER ECO D8 series. Time PL spectra were measured using a Spectrometer (iHR320, HIRIBA scientific) and 405 nm pulsed laser was used as excitation source for the measurement.

### Experimental Procedures

#### *Synthesis of compound 3*

To a stirred solution of compound **1** (2.00 g, 10.85 mmol) and compound **2** (1.70 g, 11.94 mmol) in acetonitrile (40 mL) was added TEA (3.00 mL, 21.70 mmol) at room temperature. The reaction mixture was heated to 80 °C and stirred for 16 h at the same temperature. Reaction progress was monitored by TLC (EtOAc/hexanes). After completion of reaction, the mixture was allowed to cool to room temperature. The product was precipitated out from the reaction mixture as yellow crystals which were filtered off using Buckner funnel, washed with cold acetonitrile (5 mL), and dried under vacuum to afford compound **3** as shiny yellow flakes (2.34 g, 70%).

$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78-7.73 (m, 5H), 7.62 (d,  $J = 3.5$  Hz, 1H), 7.23 (d,  $J = 4.0$  Hz, 1H), 6.17 (s, 1H), 4.20-4.07 (m, 4H).

$^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  148.74, 138.32, 137.86, 136.71, 133.95, 132.95, 126.90, 126.29, 118.33, 117.23, 112.51, 106.74, 99.89, 65.56.

HRMS (FAB) calcd for  $\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_2\text{S}$   $[\text{M}]^+$  308.0619, found: 308.0607.

#### *Synthesis of compound 4*

To a solution of compound **3** (2.00 g, 6.485 mmol) in acetone (20 mL) was added 5% aqueous HCl (5 mL) dropwise at room temperature. A yellow color precipitate was started forming while adding the acid. The yellow turbid reaction mixture was stirred at room temperature for 1 h. The yellow precipitate was

filtered off, washed with water, and dried under vacuum to give compound **4** as yellow powdered solids (1.43 g, 84%).

<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 10.04 (s, 1H), 8.60 (s, 1H), 8.12 (d, *J* = 4.0 Hz, 1H), 8.02-7.95 (m, 4H), 7.91 (d, *J* = 4.0 Hz, 1H).

HRMS (FAB) calcd for C<sub>15</sub>H<sub>9</sub>N<sub>2</sub>O<sub>5</sub> [M+H]<sup>+</sup> 265.0430, found: 265.0423.

#### *Synthesis of compound 7*

A mixture of compound **5** (11.95 g, 17.67 mmol), compound **6** (2.34 g, 7.06 mmol), and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (248 mg, 0.353 mmol) in THF (71 mL) in a round bottom flask was purged with argon and the reaction mixture was refluxed for 12 h under argon atmosphere. After completion, the solvent was evaporated by rotary evaporator under reduced pressure. The product was crashed out from the crude residue by EtOAc/hexanes system. This procedure was repeated three times to afford a black solid **7** (6.6 g, 99%)

<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 7.69 (d, *J* = 3.9 Hz, 2H), 7.54 (d, *J* = 8.7 Hz, 4H), 7.49 (d, *J* = 2.0 Hz, 2H), 7.09 (d, *J* = 8.8 Hz, 8H), 6.94 (d, *J* = 8.8 Hz, 8H), 6.75 (d, *J* = 8.7 Hz, 4H), 3.75 (s, 12H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 156.52, 151.02, 149.61, 140.12, 135.00, 133.66, 132.40, 127.22, 126.89, 125.67, 124.26, 122.65, 119.63, 114.96, 55.60.

HRMS (FAB) calcd for C<sub>52</sub>H<sub>40</sub>N<sub>4</sub>O<sub>8</sub>S<sub>3</sub> [M]<sup>+</sup> 944.2008, found: 944.2017.

#### *Synthesis of compound 8*

To a mixture of compound **7** (1.5 g, 1.59 mmol), NH<sub>4</sub>Cl (4.2 g, 79.5 mmol), and Fe powder (3.5 g, 63.6 mmol) in a 250 mL round bottom flask, was added H<sub>2</sub>O (10.5 mL), EtOH (21 mL), EtOAc (42 mL), and THF (42 mL). The reaction mixture was then stirred at 70 °C under argon for 5 h. After cooling the solution to room temperature, the metal catalyst was filtered through Celite, and the filtrate was evaporated under reduced pressure. The residue was dissolved into EtOAc and washed with water. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated to obtain the crude solid which was purified by column chromatography (EtOAc/hexane = 4:6) to afford the diamine **8** as a dark solid (1.13 g, 81%).

<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 7.45 (d, *J* = 8.7 Hz, 4H), 7.29 (d, *J* = 3.9 Hz, 2H), 7.12 (d, *J* = 3.9 Hz, 2H), 7.05-7.03 (m, 8H), 6.93-6.92 (m, 8H), 6.77 (d, *J* = 8.7 Hz, 4H), 5.09 (s, 4H), 3.75 (s, 12H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 156.02, 148.21, 142.76, 140.65, 134.07, 133.53, 126.69, 126.21, 124.56, 122.26, 120.58, 114.79, 110.60, 55.52.

HRMS (FAB) calcd for C<sub>52</sub>H<sub>44</sub>N<sub>4</sub>O<sub>4</sub>S<sub>3</sub> [M]<sup>+</sup> 884.2525, found: 884.2533.

#### *Synthesis of compound AI109*

To an argon purged round bottom flask was added diamine (**8**) (1.00 g, 1.13 mmol), compound **9**<sup>S3</sup> (213 mg, 1.13 mmol), Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> (236 mg, 1.24 mmol), and DMF (5.65 mL). The reaction mixture was stirred at 60 °C for 1 h and then at 75 °C for 5 h under argon. After the reaction is completed, the solvent was evaporated under reduced pressure and the residue was worked up with EtOAc and water. The organic

layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated. The crude residue was purified by column chromatography (10-50% EtOAc in hexanes) to yield the product which was recrystallized from EtOAc/hexanes to afford the pure **AI109** as a black solid (487 mg, 41%)

<sup>1</sup>H NMR (500 MHz, *d*<sub>6</sub>-DMSO): δ (ppm): 12.71 (br, 1H), 8.72 (s, 1H), 8.18 (d, *J* = 4.00 Hz, 1H), 7.99 (d, *J* = 4.00 Hz, 1H), 7.46-7.33 (br, 8H), 7.06 (d, *J* = 9.00 Hz, 8H), 6.94 (d, *J* = 9.00 Hz, 8H), 6.79 (d, *J* = 8.50 Hz, 4H), 3.76 (s, 12H).

<sup>13</sup>C NMR (125 MHz, *d*<sub>6</sub>-DMSO): δ (ppm): 156.38, 155.28, 152.80, 148.32, 148.03, 143.02, 142.63, 141.91, 140.92, 140.19, 137.33, 134.90, 132.95, 132.69, 129.59, 127.28, 126.43, 125.61, 125.48, 123.58, 119.69, 115.44, 114.73, 114.01, 104.28, 77.32, 55.70

HRMS (MALDI): *m/z*: calculated for C<sub>61</sub>H<sub>45</sub>N<sub>6</sub>O<sub>4</sub>S<sub>4</sub>, [M+H]<sup>+</sup>: 1053.2380;found: 1053.2358.

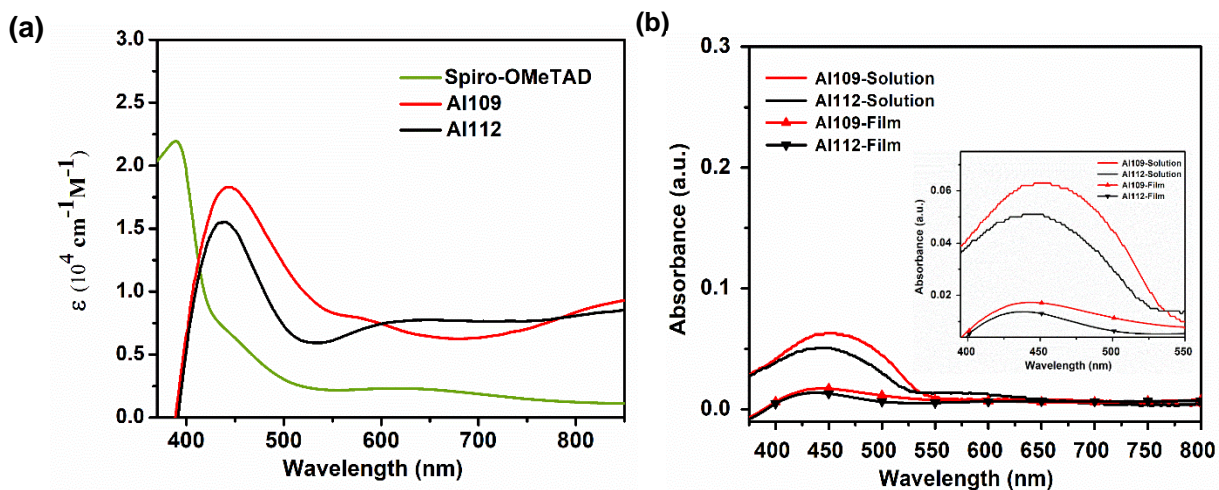
#### *Synthesis of compound AI112*

Diamine (**8**) (500 mg, 0.564 mmol), compound **4** (149 mg, 0.564 mmol), and Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> (112 mg, 0.593 mmol), were dissolved in DMF (3.0 mL) and the reaction mixture was stirred at 75 °C for 3 h followed by stirring at 90 °C for 48 h under argon. After completion of the reaction, the solvent was evaporated under reduced pressure and the residue was dissolved in EtOAc, and washed with water. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated. The crude residue was purified by column chromatography (20-30% EtOAc in hexanes) to yield the product which was recrystallized from EtOAc/hexanes to afford the pure **AI112** as a dark solid (355 mg, 55%)

<sup>1</sup>H NMR (500 MHz, *d*<sub>6</sub>-DMSO): δ (ppm): 12.63 (s, 1H), 8.55 (s, 1H), 8.15 (d, *J* = 4.0 Hz, 1H), 8.00-7.93 (m, 4H), 7.90 (d, *J* = 4.0 Hz, 1H), 7.49-7.46 (m, 6H), 7.42 (dd, *J* = 3.5 Hz, 2H), 7.06 (d, *J* = 9.0 Hz, 8H), 6.93 (d, *J* = 9.0 Hz, 8H), 6.78 (d, *J* = 8.0 Hz, 4H), 3.75 (s, 12H).

<sup>13</sup>C NMR (125 MHz, *d*<sub>6</sub>-DMSO): 155.92, 147.92, 142.14, 139.69, 137.68, 137.58, 136.39, 134.61, 132.99, 132.53, 132.21, 129.01, 126.82, 126.21, 125.97, 125.31, 125.01, 124.91, 123.19, 123.03, 119.23, 118.40, 117.25, 114.98, 112.95, 111.12, 105.92, 103.53, 55.22.

HRMS (MALDI): *m/z*: calculated for C<sub>67</sub>H<sub>48</sub>N<sub>6</sub>O<sub>4</sub>S<sub>4</sub>, [M+H]<sup>+</sup>: 1128.2620;found: 1128.2648.

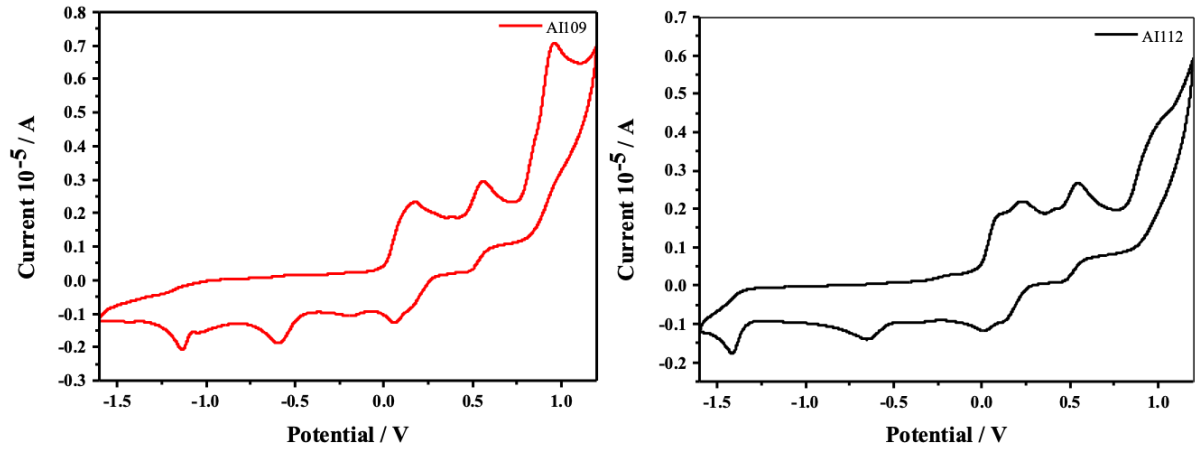


**Figure S1** (a) UV-vis absorption spectra of **AI109**, **AI112**, and **Spiro-OMeTAD** in chlorobenzene. (b) UV-vis absorption spectra of **AI109** and **AI112** solution ( $\text{CHCl}_3$ ) and film.

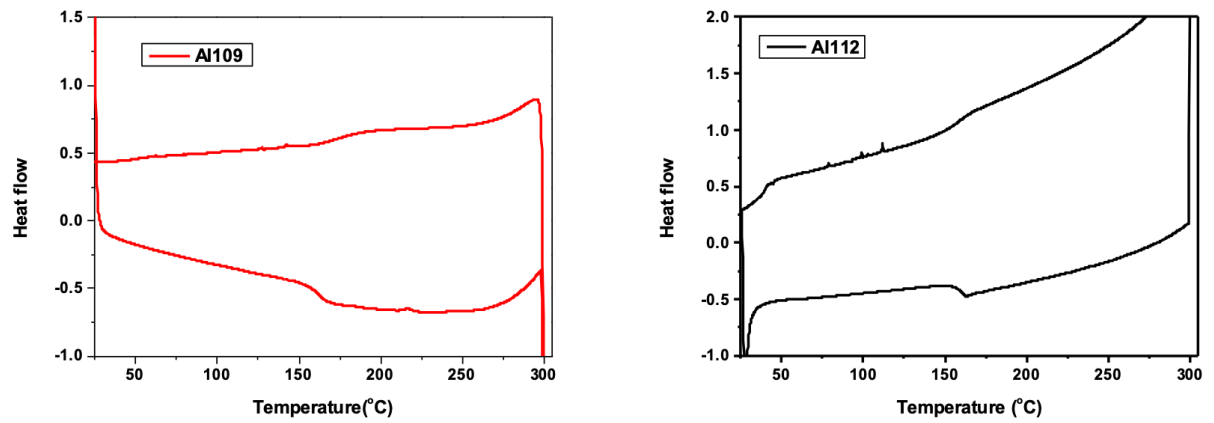
**Table S1. Optical, electronic, and hole mobility properties of HTMs**

HTM	$\lambda_{\text{max}}^a$ (nm)	$E_{\text{HOMO}}^b$ (eV)	$E_{\text{LUMO}}^c$ (eV)	$E_{0-0}^d$ (eV)	Hole mobility ( $\text{cm}^2 \text{V}^{-1} \text{S}^{-1}$ )
<b>AI109</b>	442	-5.14	-2.85	2.29	$3.59 \times 10^{-4}$
<b>AI112</b>	438	-5.12	-2.69	2.43	$4.21 \times 10^{-4}$
<b>PEDOT:PSS</b>	--	-5.10	-1.5	3.60	$3.15 \times 10^{-4}$
<b>Spiro-OMeTAD</b>	389	-5.21	-2.42	2.79	$2.55 \times 10^{-4}$

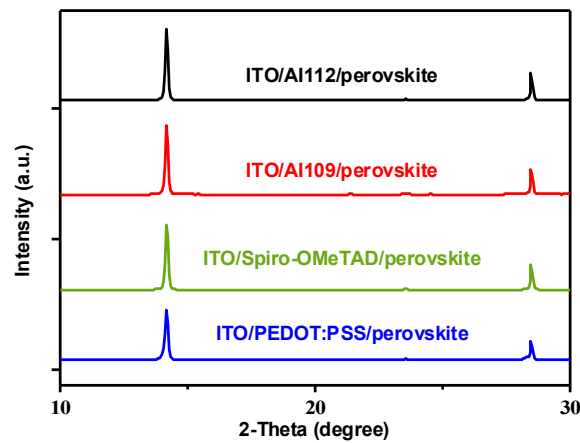
<sup>a</sup>Measured in chlorobenzene. <sup>b</sup> $E_{\text{HOMO}} = -(5.1 + E_{1/2} - E_{\text{Fc}}^{1/2})$  eV. <sup>c</sup> $E_{\text{LUMO}} = E_{\text{HOMO}} - E_{0-0}$  <sup>d</sup>The band gap,  $E_{0-0}$ , was estimated from the onset of solution absorption spectrum. The HOMO and LUMO values of PEDOT:PSS and spiro-OMeTAD were referenced from previous report. <sup>55, 56</sup>



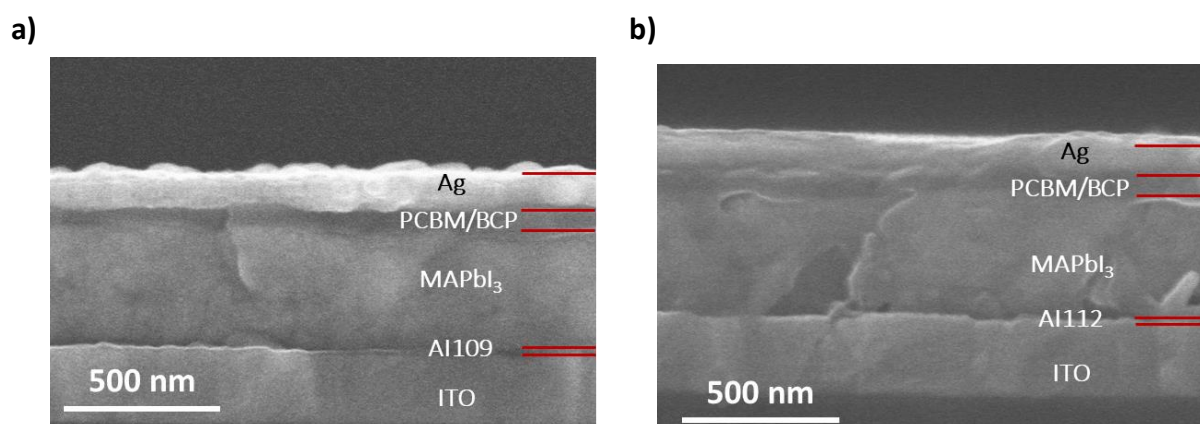
**Figure S2.** Cyclic voltammograms of Al-HTMs.



**Figure S3.** DSC curves of Al109 and Al112.



**Figure S4.** X-Ray diffraction peaks of perovskite films on different HTMs.



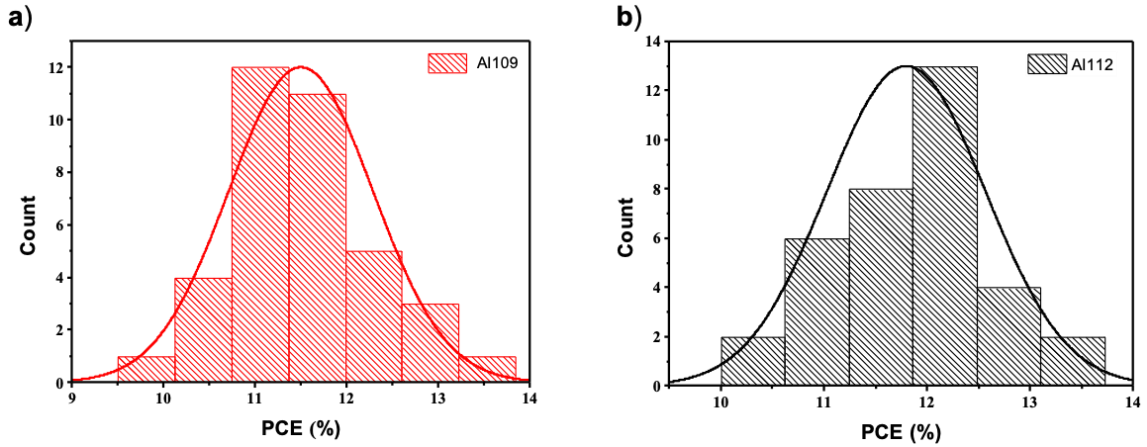
**Figure S5.** Cross section scanning electron microscopy (SEM) images of the PSC devices based on a) **AI109** and b) **AI112**.

**Table S2.** Performance metrics of PSCs based on **AI109** using the configuration of ITO/Al-  
HTM/MAPbI<sub>3</sub>/PCBM/Ag and at various concentrations.<sup>a</sup>

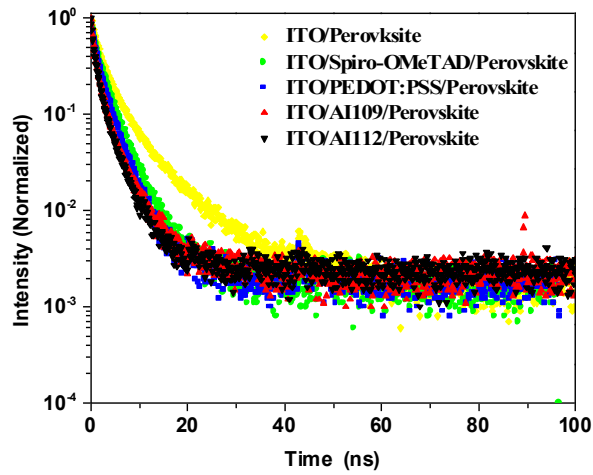
<b>AI109</b>	Thickness (nm)	Voc (V)	J <sub>sc</sub> (mA cm <sup>-2</sup> )	FF	η (%)
No HTM	---	0.95	9.92	37.92	3.57
0.47 mM (0.5 mg mL <sup>-1</sup> )	1.39	0.95	17.74	61.64	10.38
0.95 mM (1.0 mg mL <sup>-1</sup> )	2.23	0.98	16.47	65.49	10.62
1.42 mM (1.5 mg mL <sup>-1</sup> )	3.34	0.95	16.35	65.27	10.15
1.89 mM (2.0 mg mL <sup>-1</sup> )	4.04	0.94	17.52	61.03	10.04
2.37 mM (2.5 mg mL <sup>-1</sup> )	5.08	0.92	16.24	67.39	10.02

[a] The average photovoltaic parameters were obtained from 6 separate cells based on each concentration of HTM.

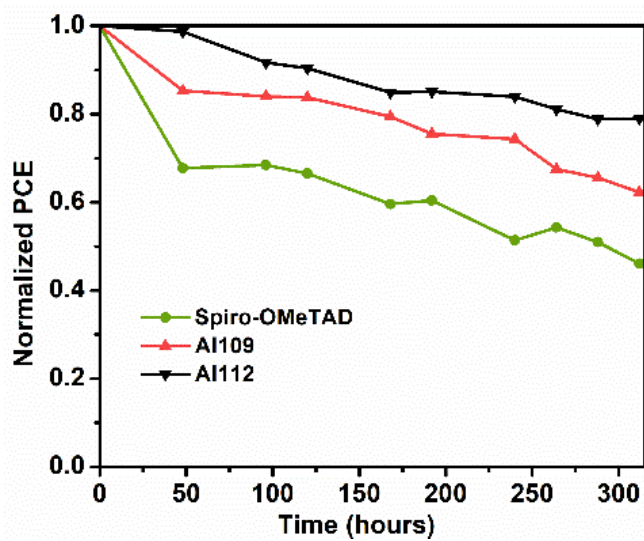




**Figure S6.** Efficiency histograms of PSC devices based on a) Al109 and b) Al112.



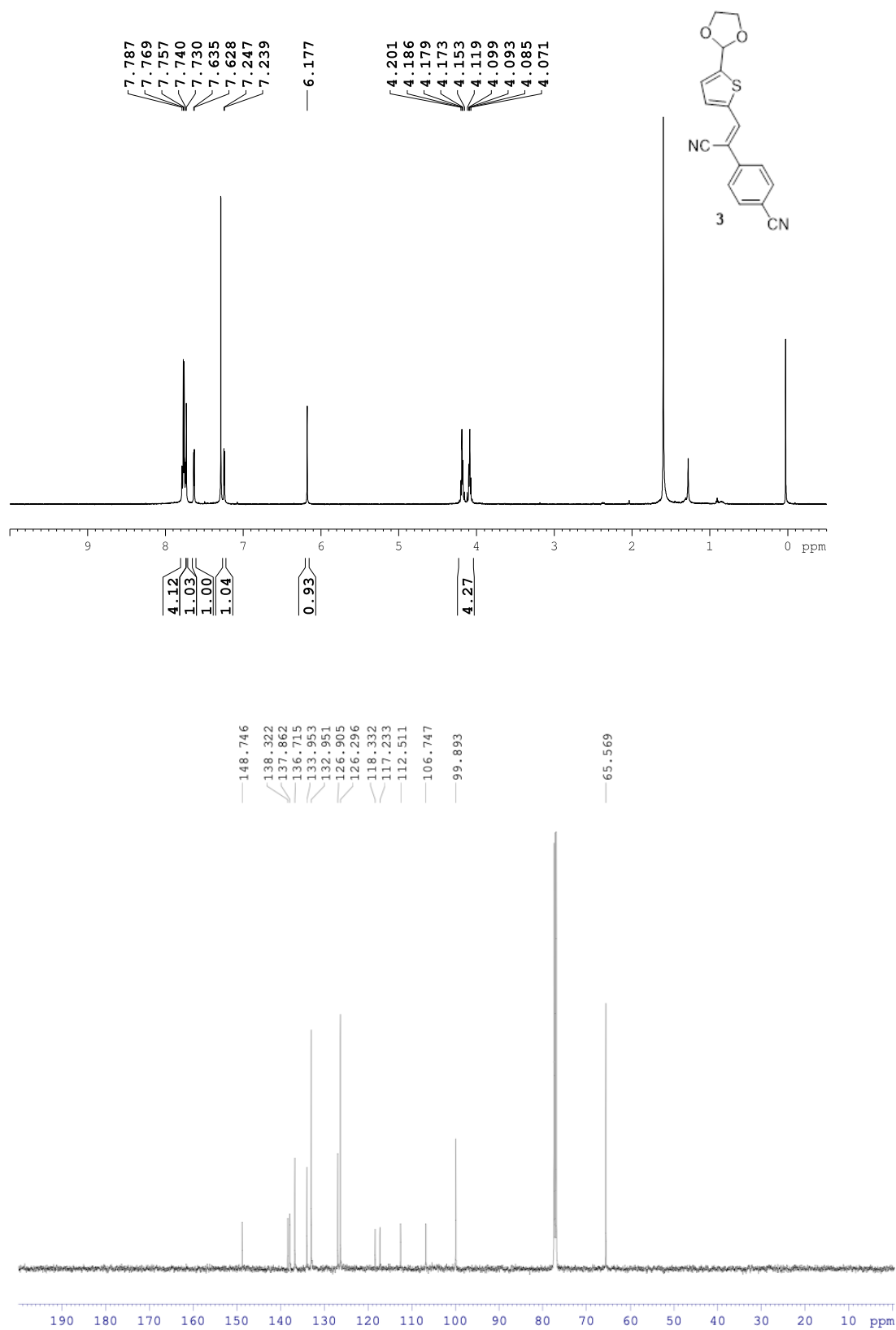
**Figure S7.** TRPL spectra of perovskite films with or without HTMs.



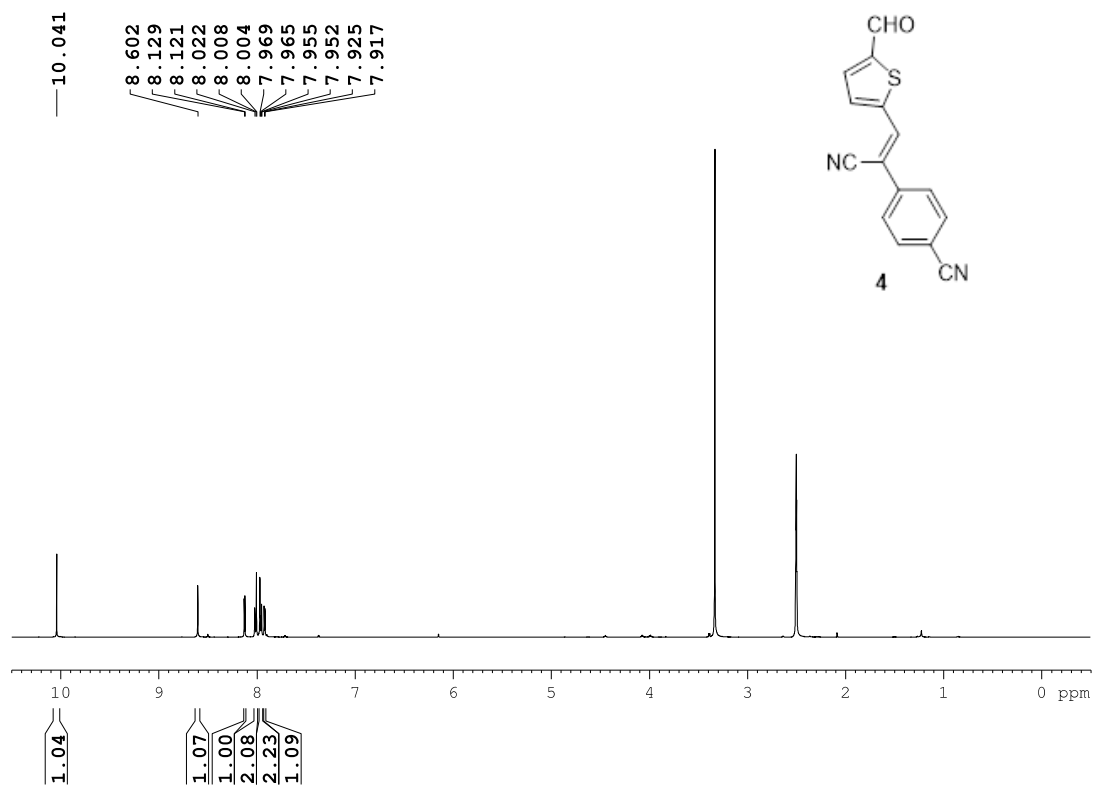
**Figure S8.** The stability testings of the PSCs incorporated with Spiro-OMeTAD, Al109, and Al112 measured under ambient conditions.

**$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of intermediates and final compounds.**

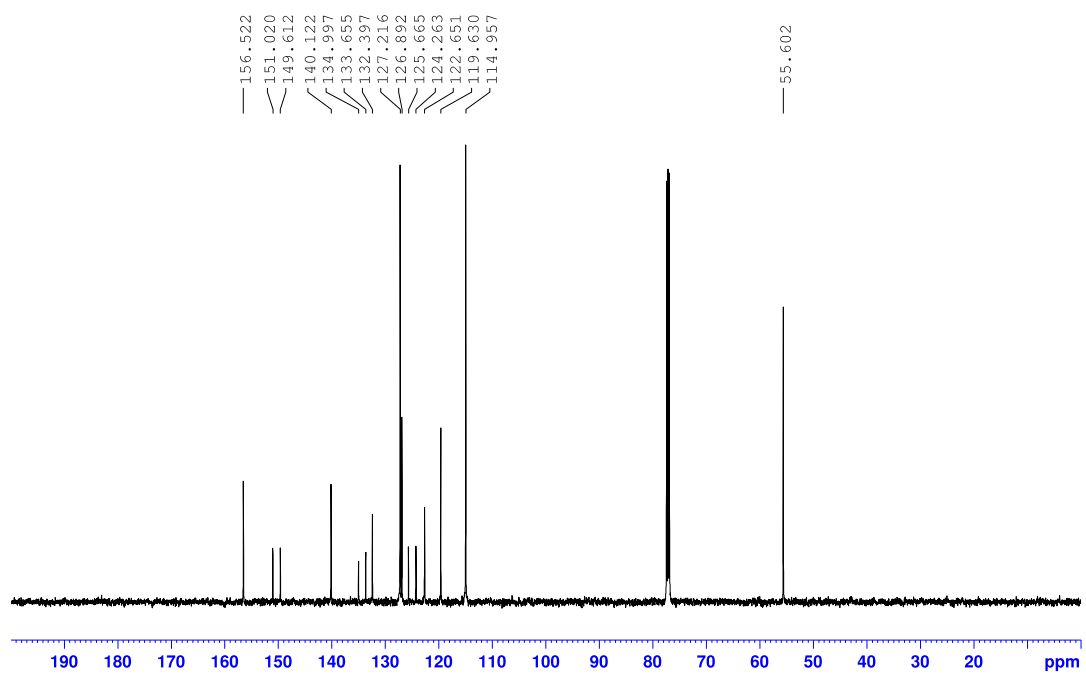
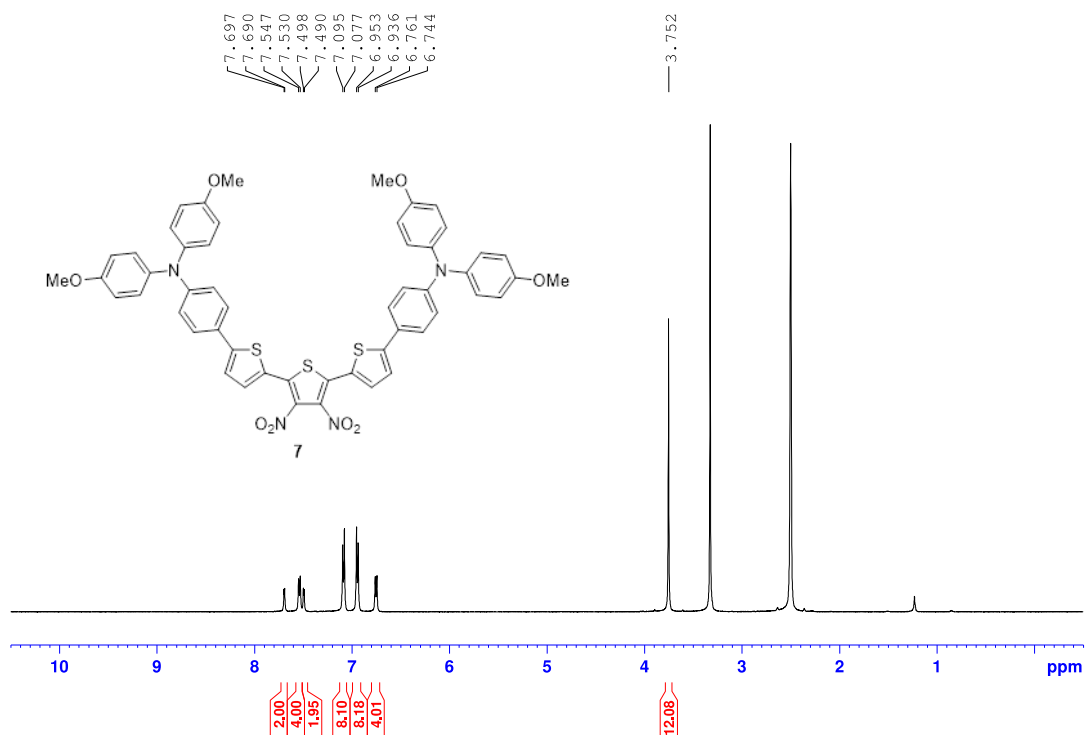
**1.  $^1\text{H}$  (500 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectra of compound 3.**



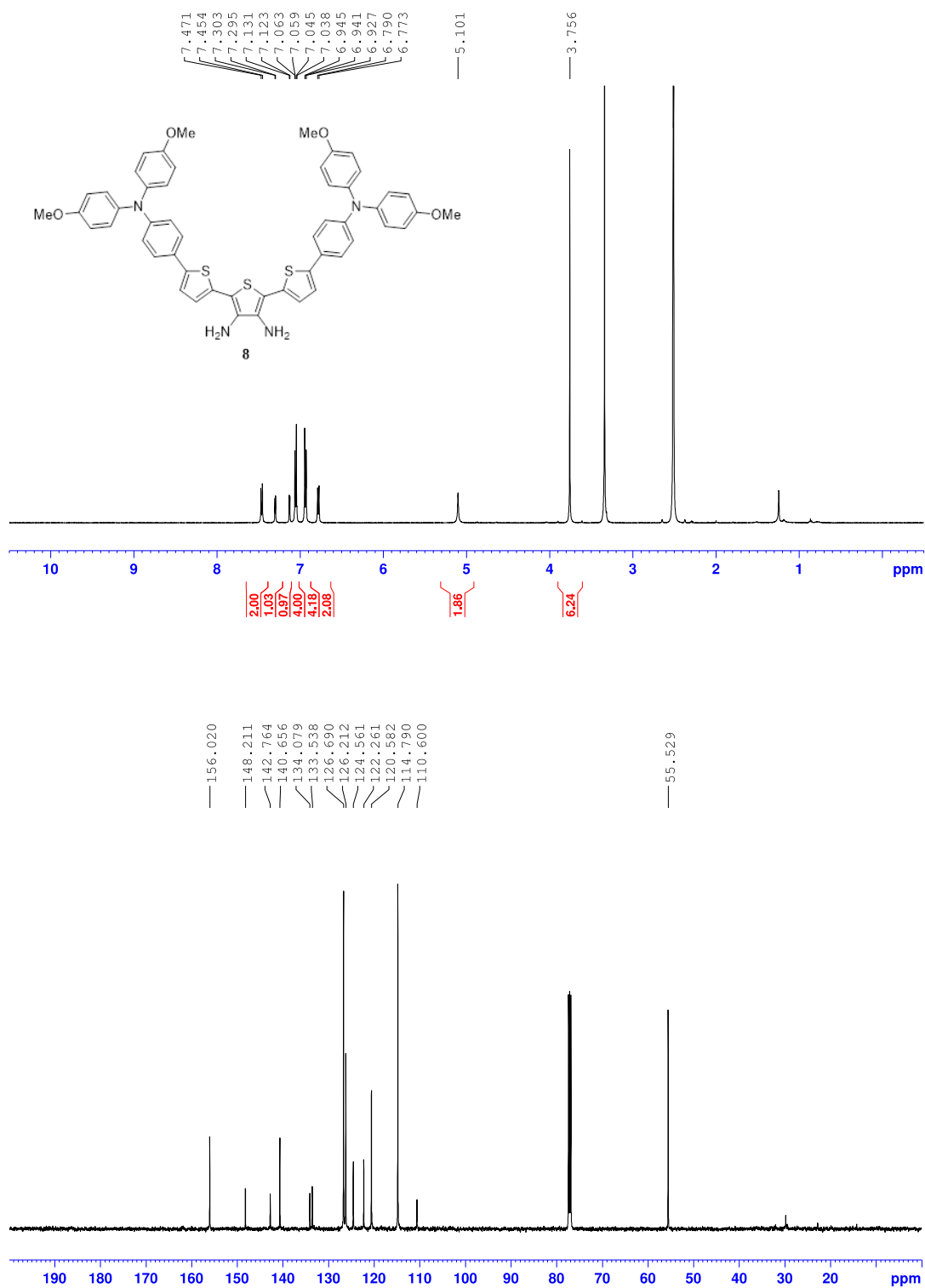
2. <sup>1</sup>H (500 MHz, DMSO) spectrum of compound 4.



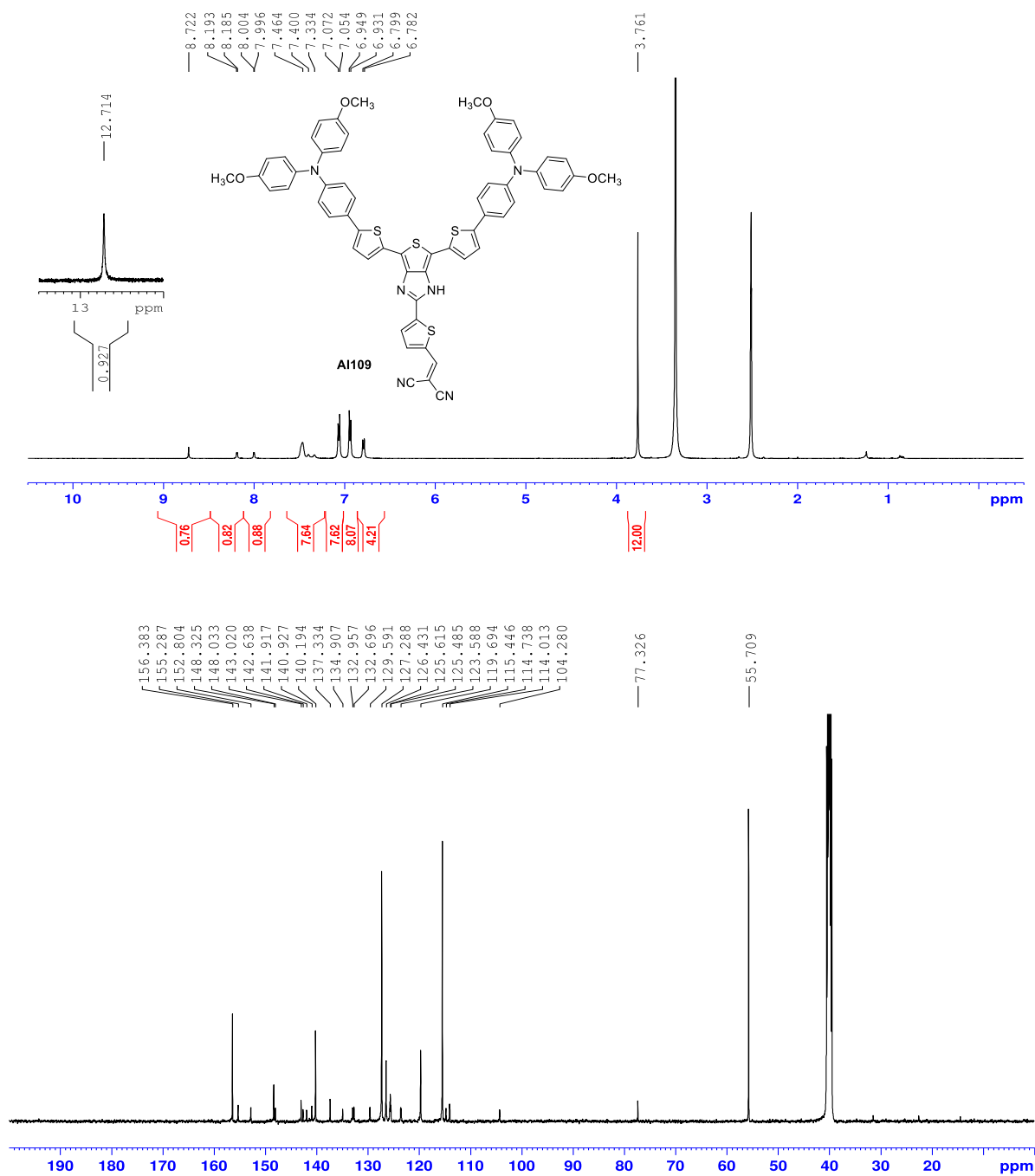
3.  $^1\text{H}$  (500 MHz, DMSO) and  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectra of compound 7.



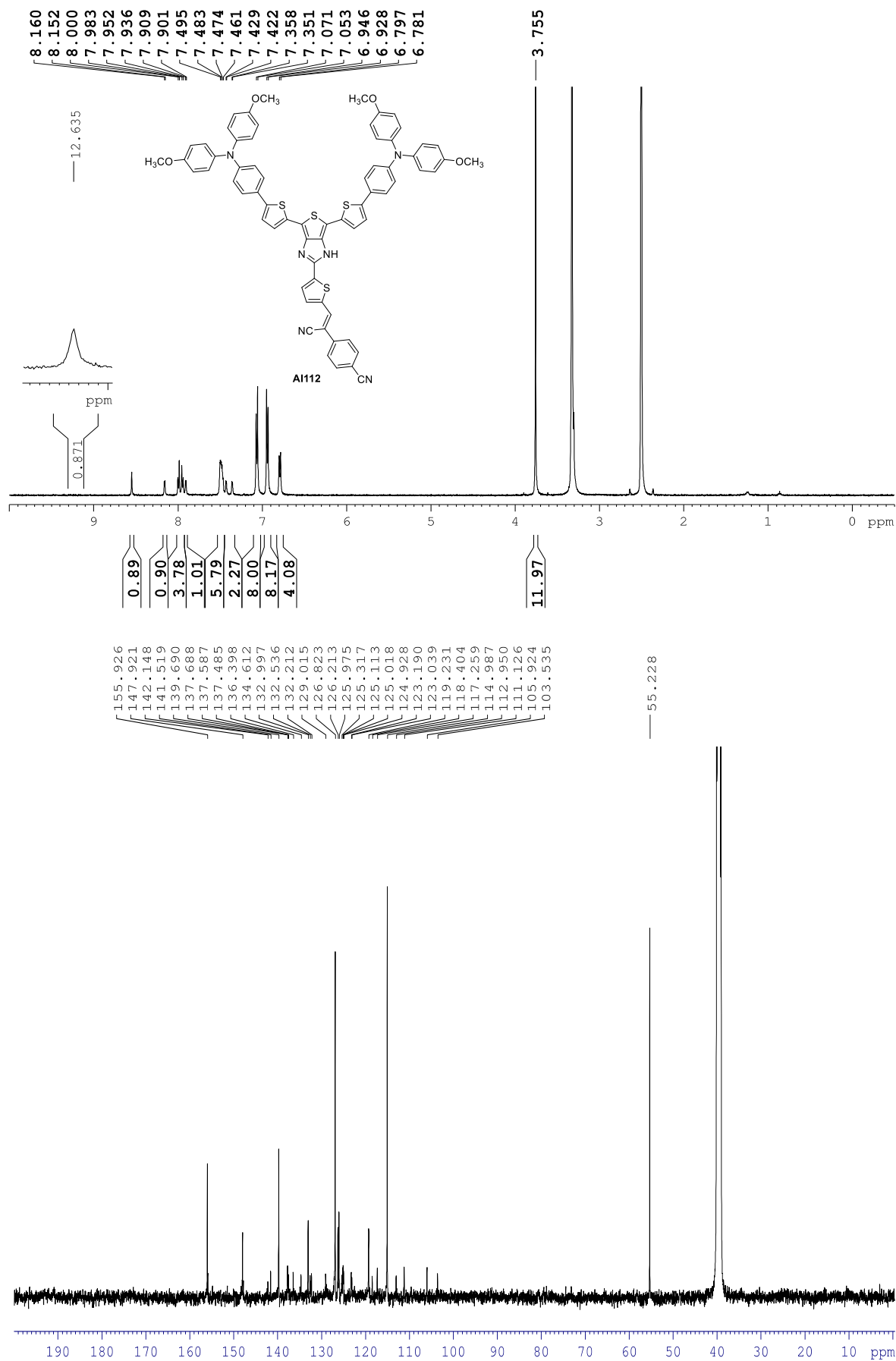
4.  $^1\text{H}$  (500 MHz, DMSO) and  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectra of compound 8.



5.  $^1\text{H}$  (500 MHz,  $\text{DMSO-}d_6$ ) and  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-}d_6$ ) spectra of A1109.



6.  $^1\text{H}$  (500 MHz,  $\text{DMSO-d}_6$ ) and  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-d}_6$ ) spectra of A1112.



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