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Supporting Information

Benzothiazole-based Arylamines as Hole Transporting Materials for Perovskite Solar Cells

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Experimental section

Materials. Formamidinium iodide (FAI, 99.99%), methylammonium chloride (MACl, 99.99%), methylammonium bromide (MABr, 99.99%), phenethylammonium iodide (PEAI) and tris(2-(1*H*-pyrazol-1-yl)-4-*tert*-butylpyridine)cobalt tri[bis(trifluoromethanesulfonyl)imide] ([PrazPy]$_3$Co(III)[TFSI]$_3$, FK 209) were purchased from Greatcell Solar Materials (Australia). Lead iodide (PbI_2, 99.99%) and lead bromide ($PbBr_2$, 99.99%) were purchased from Tokyo Chemical Industry (TCI). Tin(II) chloride dihydrate ($SnCl_2 \cdot 2H_2O$, 99.99%), lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI), urea (99.5%), thioglycolic acid (99%), potassium chloride (KCl, 99%) and dimethyl sulfoxide (DMSO, 99.9%, anhydrous) were purchased from Sigma-Aldrich. Dimethylformamide (DMF), acetonitrile (ACN), chlorobenzene (CB, 99%), 4-*tert*-butylpyridine (tBP), diethyl ether (99.5%), dichloromethane (CH_2Cl_2, 99%, extra dry over molecular sieve) and hydrochloric acid (HCl, 37% solution in water) were purchased from Thermo Fisher Scientific. Spiro-OMeTAD was purchased from Borun New Material Technology. All reagents and solvents were used as received without further purification.

Preparation of the HTM solutions. The HTM solutions were prepared by mixing the HTM (V1670, V1671 or V1672), 14 μL Li-TFSI (517 mg/mL in ACN), 30 μL tBP and 11 μL [PrazPy]$_3$Co(III)[TFSI]$_3$ (376 mg/mL in ACN) in 1000 μL mixed CB and CH_2Cl_2 (v:v = 1:1) solution. The solution was filtered through a 0.22 μm PTFE filter before use.

Preparation of the Spiro-OMeTAD solution. The Spiro-OMeTAD solution was prepared by mixing 120 mg Spiro-OMeTAD, 28 μL Li-TFSI (517 mg/mL in ACN), 48 μL tBP and 22 μL $[PrazPy]_3Co(III)[TFSI]_3$ (376 mg/mL in ACN) in 1536 μL CB. The solution was filtered through a 0.22 μm PTFE filter before use.

Fabrication of PSCs. Scribed FTO glass substrates were sonicated in deionized water, acetone and isopropanol sequentially. Each step lasts 20 minutes. The substrates were dried and treated with UV-O_3 for 20 minutes before use. The 4 h chemical bath deposition (CBD) SnO_2 ETLs were deposited on FTO substrates according to the previous report.[1] FTO/SnO_2 substrates were treated with UV-O_3 for 30 minutes before use. Next, 40 mM KCl water solution was spin-coated onto the substrates at 3000 rpm for 30 s. The substrates were annealed at 150 °C for 15 minutes. The perovskite solution was prepared by dissolving 4.5 mg $PbBr_2$, 1.4 mg MABr, 33.7 mg MACl, 240.7 mg FAI and 705.3 mg PbI_2 in 1 mL mixed solvent (DMF:DMSO=8:1).[2] The relative humidity (RH) of the lab was kept below 40%. Then 30 μL perovskite precursor solution was spin-coated onto the FTO/SnO_2 substrate at 1000 rpm with an acceleration of 2000 rpm s^{-1} for 10 s, and continuously at 5000 rpm with an acceleration of 2000 rpm s^{-1} for 30 s. During the second step, 600 μL diethyl ether as anti-solvent was quickly dropped onto the substrate centre after 15 s. Thereafter, the perovskite films were annealed on the hotplate at 100 °C for 40 minutes. After cooling to room temperature, 30 μL PEAI solution prepared by dissolving 3 mg PEAI in 1 mL IPA was rapidly dropped onto the substrate centre at 4000 rpm for 12 s. Then HTM or Spiro-OMeTAD solution was spin-coated onto the substrate at 4000 rpm for 20 s. The substrates were stored inside a dry air box (RH < 5%) overnight. Finally, a 70 nm thick gold electrode was deposited by thermal evaporation under a high vacuum of 10^{-5} Pa.

Characterization of the PSCs. PSC measurements were performed using an Oriel solar simulator (450 W xenon, AAA class). The light intensity was calibrated with a Si reference solar cell equipped with an IR-cutoff filter (KG3, Newport). $J-V$ characteristics of the PSCs were obtained by applying an external voltage bias while measuring the current response with a digital source meter (Keithley 2400).[3] The voltage scan rate was 100 $mV\cdot s^{-1}$ and no device preconditioning was applied before starting the measurements. The PSCs were masked with an active area of 0.09 cm^2 to fix the active area and reduce the influence of the scattered light. The EQEs of PSCs were measured with an IQE200B (Oriel) without bias light. For stability tests, unencapsulated PSCs were evaluated at the MPP using a light-emitting diode lamp of a constant illumination of 100 $mW\cdot cm^{-2}$ (intensity verified with a reference Si-photodiode) under N_2 atmosphere at room temperature.

SEM. Surface and cross-sectional SEM images of samples grounded were obtained with a Zeiss Gemini SEM 300. The samples were deposited 10 nm gold before measurement.

UPS. UPS measurements were conducted on a Kratos Axis Supra instrument with a He-I source energy of 21.22 eV. Samples were grounded before measurement. The WFs of samples were calculated using $\Phi = 21.22 - E_{cutoff}$. The VBMs were obtained by the formula of VBM = 21.22 eV $- E_{cutoff} + E_{onset}$.

Ultraviolet-visible absorption, Photoluminescence and TRPL spectroscopy. Absorption spectra of the HTM solutions in cuvettes were recorded with using a UV-vis spectrometer (Cary 500, Varian). PL spectra of the HTM solutions in cuvettes were measured using a Cary Eclipse (Agilent) fluorescence spectrometer with a 405 nm excitation. TRPL curves of samples were measured using a LifeSpec II fluorescence spectrometer with a 506 nm picosecond-pulsed diode laser (EPL-510, Edinburgh Instruments). The fluence and repetition for the TRPL measurement is 5 nJ cm^{-2} and 100 kHz, respectively. During TRPL measurements, the bandwidth was adjusted, ensuring that the signal rate of the sample is lower than 5% of the source repetition rate (under TCSPC diode, in Hz), therefore, preventing carrier accumulation.

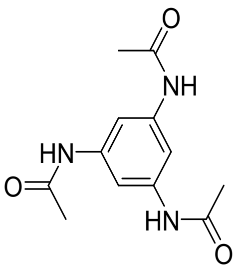
Thermal properties measurements. The transformations of thermal changes of target materials were recorded with a TA Instruments Q10 differential scanning calorimeter in a nitrogen atmosphere. From the obtained thermal curves, the glass transition temperature of the materials is determined. Heating and cooling mode reaches 10 °C/min. The destruction temperatures of the new compounds were recorded by TA Instruments Q50 by thermogravimetric analysis in a nitrogen atmosphere. The decomposition temperature of a compound is recorded when the weight loss is 5%. Heating mode 10 °C/min.

Ionization potential measurements. The solid-state ionization potential (I_p) was measured according to the electron photoemission in air method by dissolving HTMs in THF and coating layers of 0.5−1 µm thickness on Al plate, which was pre-coated with methylmethacrylate and methacrylic acid copolymer adhesive layer (~0.5 µm thick). Samples were illuminated with monochromatic light originating from the quartz monochromator with deuterium lamp. The power of incident light beam was $(2-5)\cdot 10^{-8}$ W. Negative voltage of –300 V was supplied to the sample substrate. Counter-electrode with the 4.5×15 mm^2 slit for illumination was placed at 8 mm distance from the sample surface. For the photocurrent measurement, the counter-electrode was connected to the input of the BK2-16 type electrometer working in the open input regime. Strength of photocurrent in the circuit under illumination was 10^{-15}–10^{-12} A. The photocurrent I depends on the incident light photon energy $h\nu$. The $I^{0.5} = f(h\nu)$ dependence was plotted. The dependence of the photocurrent on incident light quanta energy is described by a linear relationship between $I^{0.5}$ and $h\nu$ near the threshold. The linear part of this dependence was extrapolated to the $h\nu$ axis and I_p value was determined as the photon energy at the interception point.

Hole drift mobility measurements. Samples were prepared by spin-coating the HTM solution on the polyester film with a conductive Al layer. The thickness of spin-coated layer was 5–10 µm. Hole drift mobility was measured by xerographic time of flight technique (XTOF). Electric field was created by positive corona charging. Charge carriers were generated at the layer surface by illumination with pulses of nitrogen laser (pulse duration 2 ns, wavelength 337 nm). The layer surface potential decreased up to 1–5 % of initial potential before illumination as a result of pulse illumination. Capacitance probe connected to the wide frequency band electrometer measured the speed of the surface potential decrease dU/dt. Transit time t_t was determined by the kink on the curve of the dU/dt transient in double logarithmic scale. Drift mobility was calculated according to the formula $\mu = d^2/U_0 t_t$, here d – layer thickness, U_0 –surface potential at the moment of illumination.

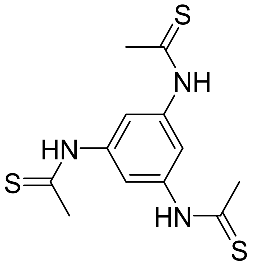
General synthesis procedures. Chemicals required for the synthesis were purchased from Sigma-Aldrich, TCI Europe or BLDpharm and used as received. Reactions were monitored by thin-layer chromatography on ALUGRAM SIL G/UV254 plates and developed with UV light. Silica gel (grade 9385, 230-400 mesh, 60 Å, Aldrich) was used for column chromatography. ^{1}H NMR spectra were recorded at 400 MHz on a Bruker Avance III spectrometer with a 5 mm double resonance broad band BBO z-gradient room temperature probe, ^{13}C NMR spectra were collected using the same instrument at 101 MHz. The chemical shifts, expressed in ppm, were relative to tetramethylsilane (TMS), using the residual solvent peak as internal standard. All the NMR experiments were performed at 25 °C. Elemental analysis was performed with an Exeter Analytical CE-440 elemental analyzer, Model 440 C/H/N. Mass Spectrometry was performed on a Waters SQ Detector 2 Spectrometer using the electrospray ionization (ESI) technique.

N,*N*',*N*''-(benzene-1,3,5-triyl)triacetamide (1)



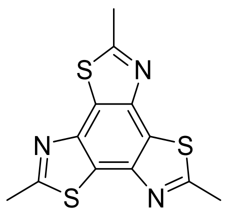
Benzene-1,3,5-triamine trihydrochloride (1.63 g, 7 mmol) was dissolved in dry THF (100 mL) under an argon atmosphere. To the resulting solution acetic anhydride (2.3 mL, 24.5 mmol) and 4-dimethylaminopyridine (0.17 g, 1.4 mmol) were added. The reaction mixture was stirred at 65 °C under an argon atmosphere for 72 h. After completion of the reaction (TLC, acetone:*n*-hexane, 3:2, v:v), the solvent was distilled off under reduced pressure. The crude product was purified by column chromatography (acetone:*n*-hexane, 4:1, v:v). The resulting product was used for the further synthesis without additional purification. Yield 1.28 g (73.3%). ^{1}H NMR (400 MHz, DMSO–d_6) δ, ppm: 9.91 (s, 3H); 7.61 (s, 3H); 2.01 (s, 9H). ^{13}C NMR (101 MHz, DMSO–d_6) δ, ppm: 168.32; 139.56; 104.8; 24.03. Anal. Calcd. For $C_{12}H_{15}N_3O_3$, %: C, 57.82; H, 6.07; N, 16.86. Found, %: C, 57.91; H, 6.15; N, 16.98. $C_{12}H_{15}N_3O_3[M^+]$ exact mass = 249.11, MS (ESI) = 247.99.

N,*N*',*N*''-(benzene-1,3,5-triyl)triethanethioamide (2)



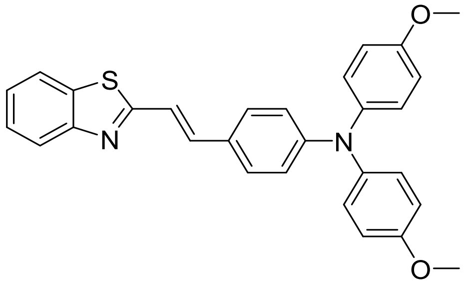
In a glass vessel for microwave reactor, the **1** (0.15 g, 0.6 mmol) was dissolved in dry THF (12 mL). To the resulting solution Lawesson's reagent (0.4 g, 0.99 mmol) was added, and the reaction mixture was exposed to microwave irradiation for 30 min at 100 °C. After completion of the reaction (TLC, acetone:*n*-hexane, 2:3, v:v), the mixture was cooled down and extracted with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent was distilled off under reduced pressure. The crude product was purified by column chromatography (acetone:*n*-hexane, 3:7, v:v). The resulting product was used for the further synthesis without additional purification. Yield 0.12 g (65.4%). ^{1}H NMR (400 MHz, THF–d_8) δ, ppm: 10.80 (s, 3H); 8.56 (s, 3H); 2.62 (s, 9H). ^{13}C NMR (101 MHz, THF–d_8) δ, ppm: 200.41; 141.09; 114.12; 36.21. Anal. Calcd. For $C_{12}H_{15}N_3S_3$, %: C, 48.46; H, 5.08; N, 14.13. Found, %: C, 48.55; H, 5.06; N, 14.04. $C_{12}H_{15}N_3S_3[M^+]$ exact mass = 297.04, MS (ESI) = 297.57.

2,5,8-trimethylbenzo[1,2-*d*:3,4-d':5,6-*d*'']tris(thiazole) (3)



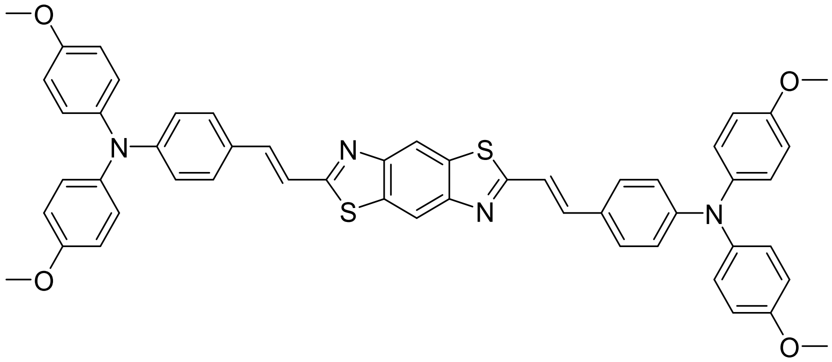
To a 20% aqueous solution of $K_3[Fe(CN)_6]$ (27.7 mL, 6.91 g, 21 mmol), the solution of **2** (0.89 g, 3 mmol) in 10% aqueous solution of NaOH (19.5 mL, 2.2 g, 54 mmol) was added dropwise into the mixture. The reaction mixture was stirred at room temperature for 3 h. After completion of the reaction (TLC, acetone:*n*-hexane, 2:3, v:v), the mixture was cooled down and extracted with chloroform. The organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent was distilled off under reduced pressure. The crude product was purified by column chromatography (chloroform:methanol:*n*-hexane, 50:1:74, v:v). The resulting product was used for the further synthesis without additional purification. Yield 0.41 g (46.7%). ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 2.96 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ, ppm: 168.16; 145.48; 125.17; 20.22. Anal. Calcd. For $C_{12}H_9N_3S_3$, %: C, 49.46; H, 3.11; N, 14.42. Found, %: C, 49.38; H, 3.07; N, 14.43. $C_{12}H_9N_3S_3[M^+]$ exact mass = 291.00, MS (ESI) = 291.73.

4-(2-(benzo[*d*]thiazol-2-yl)vinyl)-*N*,*N*-bis(4-methoxyphenyl)aniline (V1670)



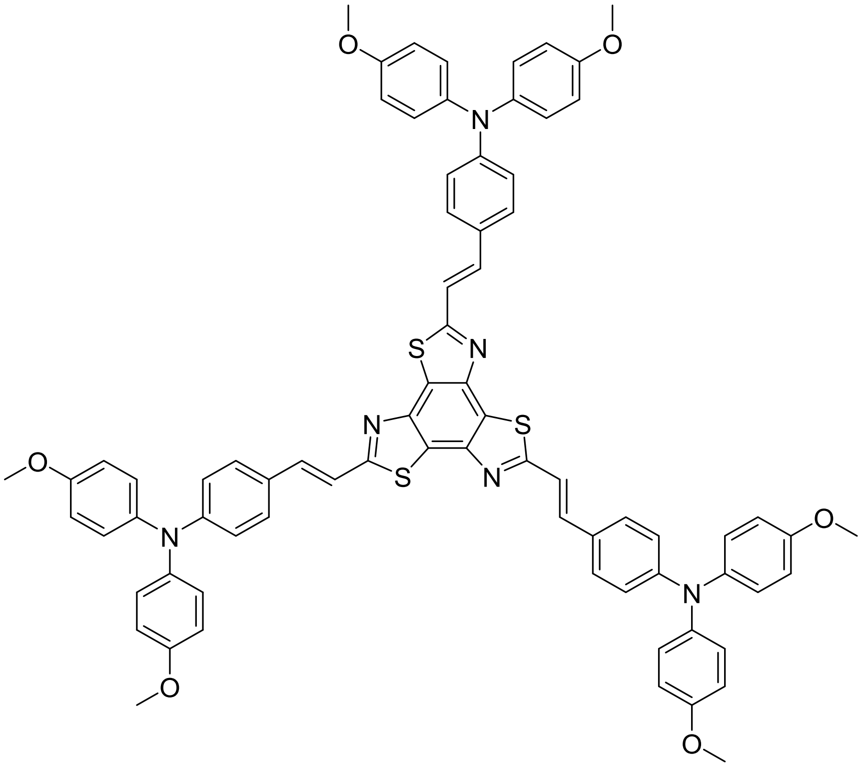
Sodium hydride (0.07 g, 3 mmol) was dispersed in dry THF (8 mL) under argon atmosphere. To the resulting suspension was added solution of 2-methylbenzothiazole (0.15 g, 1 mmol) in THF (5 mL) and resulting mixture was stirred for an hour at room temperature. Then solution of 4-[bis(4-methoxyphenyl)amino]benzaldehyde (0.43 g, 1.3 mmol) in THF (13 mL) was added dropwise into the mixture. The reaction mixture was stirred at 65 °C under an argon atmosphere for 6 h. After completion of the reaction (TLC, acetone:*n*-hexane, 1:5, v:v), the mixture was cooled down and extracted with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent was distilled off under reduced pressure. The crude product was purified by column chromatography (acetone:*n*-hexane, 3:22, v:v). Water was poured onto the crude residue. The formed precipitate was filtered off, washed with water, and dried. Yield 0.29 g (62.7%). ^{1}H NMR (400 MHz, acetone–d_6) δ, ppm: 7.98 (d, J = 7.9 Hz, 1H); 7.91 (d, J = 8.1 Hz, 1H); 7.59–7.52 (m, 3H); 7.48 (t, J = 7.7 Hz, 1H); 7.38 (t, J = 7.6 Hz, 1H); 7.31 (d, J = 16.2 Hz, 1H); 7.13 (d, J = 8.5 Hz, 4H); 6.95 (d, J = 8.5 Hz, 4H); 6.83 (d, J = 8.3 Hz, 2H); 3.81 (s, 6H). ^{13}C NMR (101 MHz, acetone–d_6) δ, ppm: 168.05; 157.84; 155.16; 151.15; 140.70; 138.41; 135.17; 129.52; 128.41; 127.61; 127.08; 125.88; 123.33; 122.51; 119.41; 119.32; 115.79; 55.76. Anal. Calcd. For $C_{29}H_{24}N_2O_2S$, %: C, 74.97; H, 5.21; N, 6.03. Found, %: C, 74.85; H, 5.03; N, 6.21. $C_{29}H_{24}N_2O_2S[M^+]$ exact mass = 464.16, MS (ESI) = 464.29.

4,4'-(benzo[1,2-*d*:4,5-*d'*]bis(thiazole)-2,6-diylbis(ethene-2,1-diyl))bis(*N*,*N*-bis(4-methoxyphenyl)aniline) (V1671)



Sodium hydride (0.07 g, 3 mmol) was dispersed in dry THF (8 mL) under argon atmosphere. To the resulting suspension was added solution of 2,6-dimethylbenzo[1,2-*d*:4,5-*d'*]bisthiazole (0.11 g, 0.5 mmol) in THF (11 mL) and resulting mixture was stirred for an hour at room temperature. Then solution of 4-[bis(4-methoxyphenyl)amino]benzaldehyde (0.43 g, 1.3 mmol) in THF (13 mL) was added dropwise into the mixture. The reaction mixture was stirred at 65 °C under an argon atmosphere for 48 h. After completion of the reaction (TLC, acetone:*n*-hexane, 1:5, v:v), the mixture was cooled down and extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent was distilled off under reduced pressure. The crude product was purified by column chromatography (chloroform:*n*-hexane, 1:1, v:v). The resulting product was crystallized from tetrahydrofuran/methanol 1:2 mixture. The precipitate was filtered off, washed with methanol, and dried. Yield 0.33 g (77.2%). ^1H NMR (400 MHz, THF–d_8) δ, ppm: 8.36 (s, 2H); 7.55–7.43 (m, 6H); 7.31 (d, J = 16.0 Hz, 2H); 7.08 (d, J = 8.3 Hz, 8H); 6.91–6.82 (m, 12H); 3.77 (s, 12H). ^{13}C NMR (101 MHz, THF–d_8) δ, ppm: 168.57; 157.93; 153.44; 151.20; 140.95; 138.78; 134.69; 129.46; 128.22; 128.05; 119.78; 119.75; 115.66; 115.39; 55.66. Anal. Calcd. For $C_{52}H_{42}N_4O_4S_2$, %: C, 73.39; H, 4.97; N, 6.58. Found, %: C, 73.52; H, 4.84; N, 6.49. $C_{52}H_{42}N_4O_4S_2[M^+]$ exact mass = 850.26, MS (ESI) = 850.75.

4,4',4''-(benzo[1,2-*d*:3,4-d':5,6-*d''*]tris(thiazole)-2,5,8-triyltris(ethene-2,1-diyl))tris(*N*,*N*-bis(4-methoxyphenyl)aniline) (V1672)



Sodium hydride (0.11 g, 4.5 mmol) was dispersed in dry THF (12 mL) under argon atmosphere. To the resulting suspension was added solution of **3** (0.15 g, 0.5 mmol) in THF (21.9 mL) and resulting mixture was stirred for an hour at room temperature. Then solution of 4-[bis(4-methoxyphenyl)amino]benzaldehyde (0.65 g, 1.95 mmol) in THF (19.5 mL) was added dropwise into the mixture. The reaction mixture was stirred at 65 °C under an argon atmosphere for 120 h. After completion of the reaction (TLC, tetrahydrofuran:ethyl acetate:*n*-hexane, 4:4:17, v:v), the mixture was cooled down and extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent was distilled off under reduced pressure. The crude product was purified by column chromatography (chloroform:*n*-hexane, 13:7, v:v). The resulting product was crystallized from tetrahydrofuran/methanol 1:1 mixture. The precipitate was filtered off, washed with methanol, and dried. Yield 0.39 g (62.3%). ^{1}H NMR (400 MHz, THF–d_8) δ, ppm: 7.63 (d, J = 16.0 Hz, 3H); 7.48 (d, J = 8.3 Hz, 6H); 7.37 (d, J = 16.0 Hz, 3H); 7.09 (d, J = 8.3 Hz, 12H); 6.92–6.83 (m, 18H); 3.78 (s, 18H). ^{13}C NMR (101 MHz, THF–d_8) δ, ppm: 169.01; 157.93; 151.16; 147.80; 140.97; 138.09; 129.49; 128.24; 128.07; 125.03; 119.75; 119.09; 115.66; 55.67. Anal. Calcd. For $C_{75}H_{60}N_6O_6S_3$, %: C, 72.79; H, 4.89; N, 6.79. Found, %: C, 72.85; H, 4.81; N, 6.88. $C_{75}H_{60}N_6O_6S_3[M^+]$ exact mass = 1236.37, MS (ESI) = 1237.80.

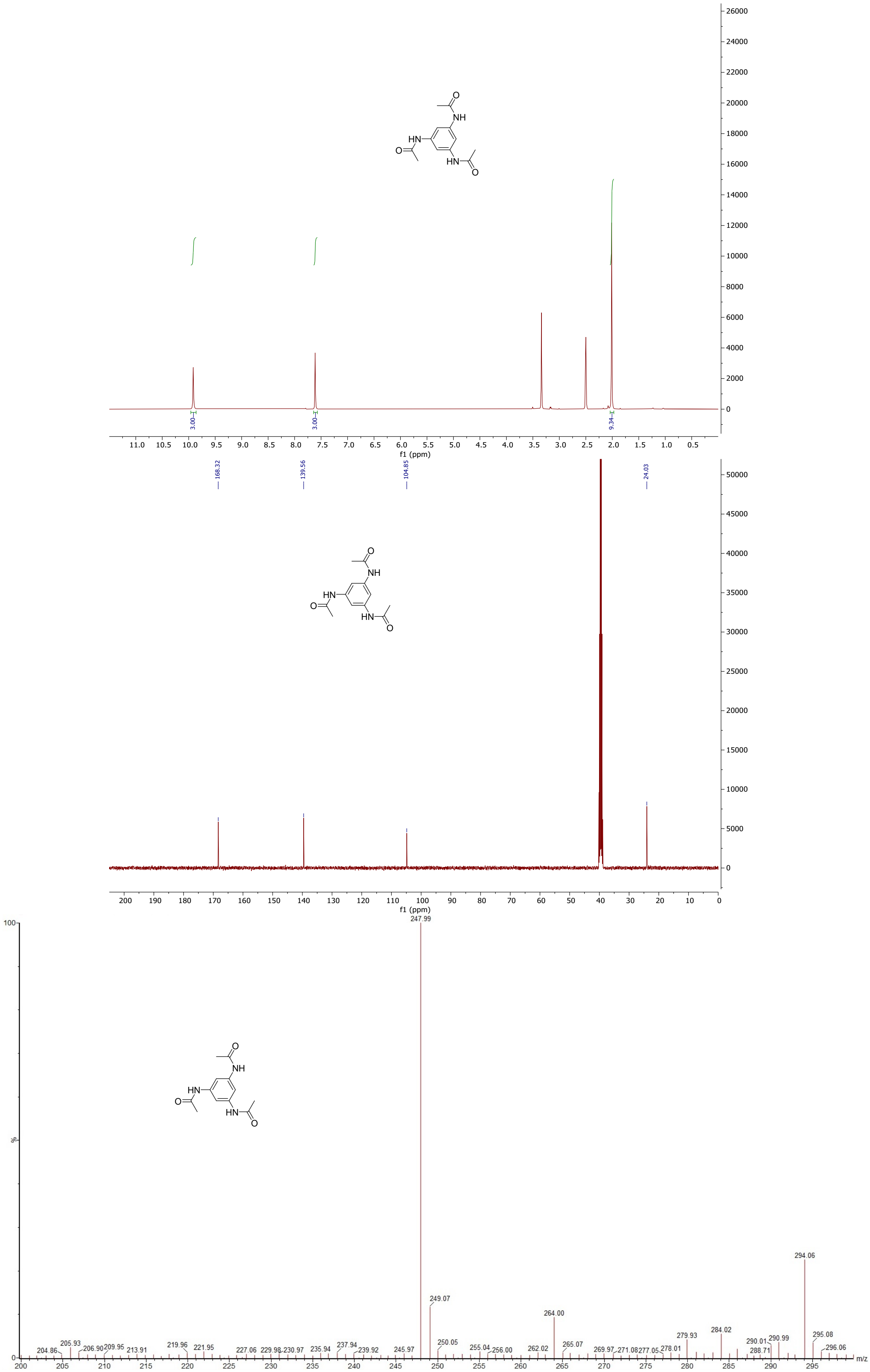


Figure S1. ^{1}H, ^{13}C NMRs and MS spectra of **1**.

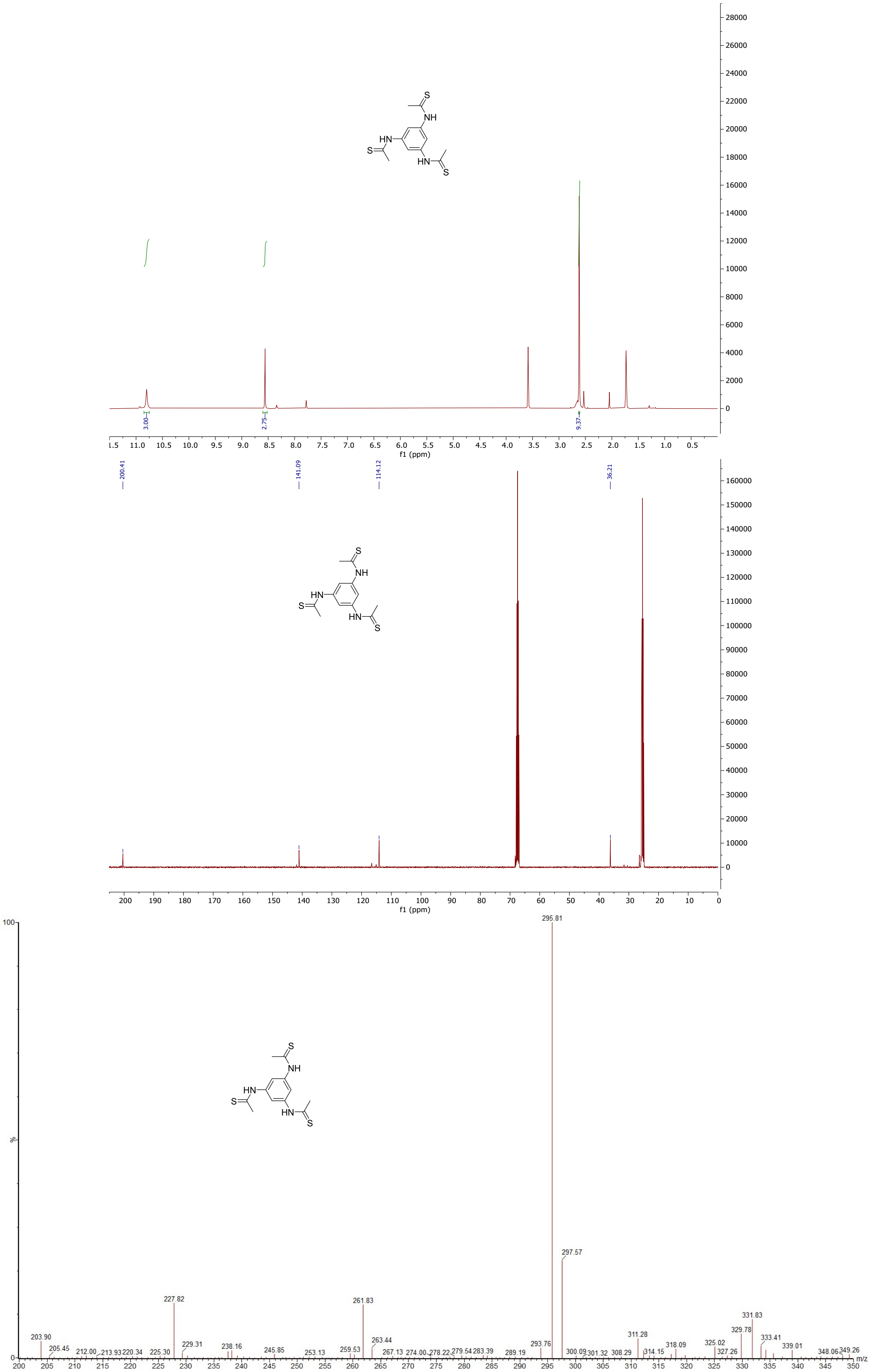


Figure S2. ^{1}H, ^{13}C NMRs and MS spectra of **2**.

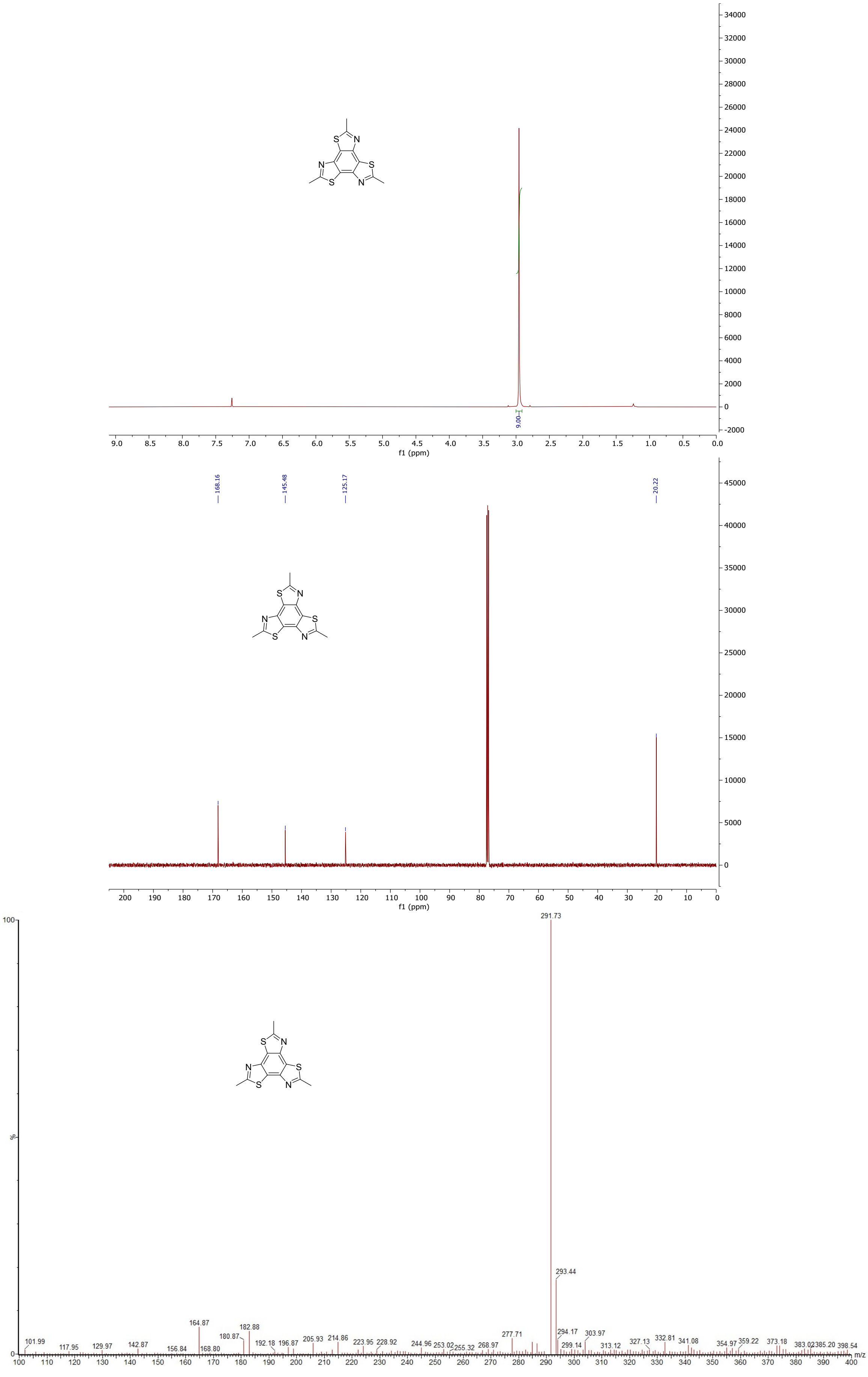


Figure S3. ^{1}H, ^{13}C NMRs and MS spectra of **3**.

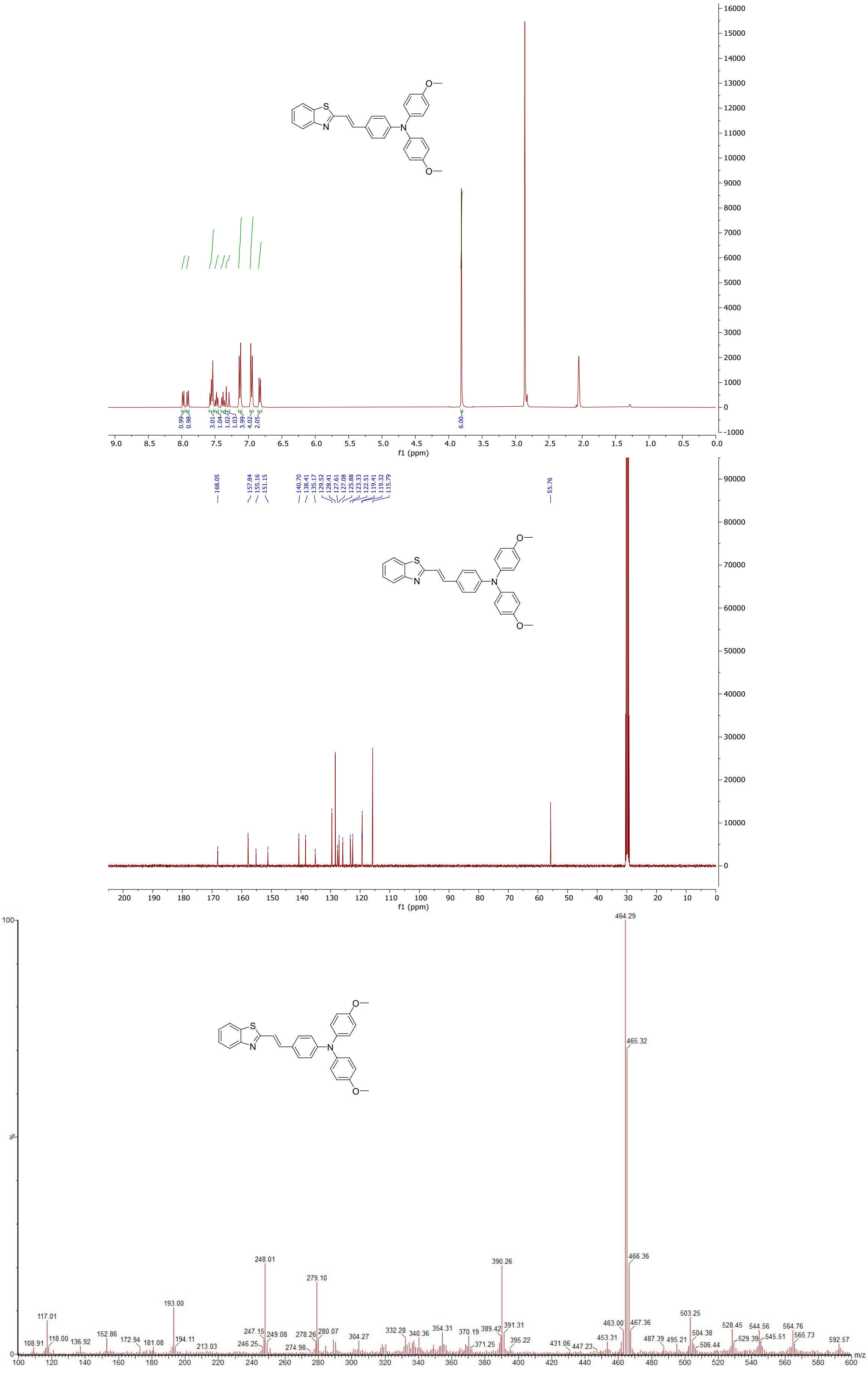


Figure S4. ^{1}H, ^{13}C NMRs and MS spectra of **V1670**.

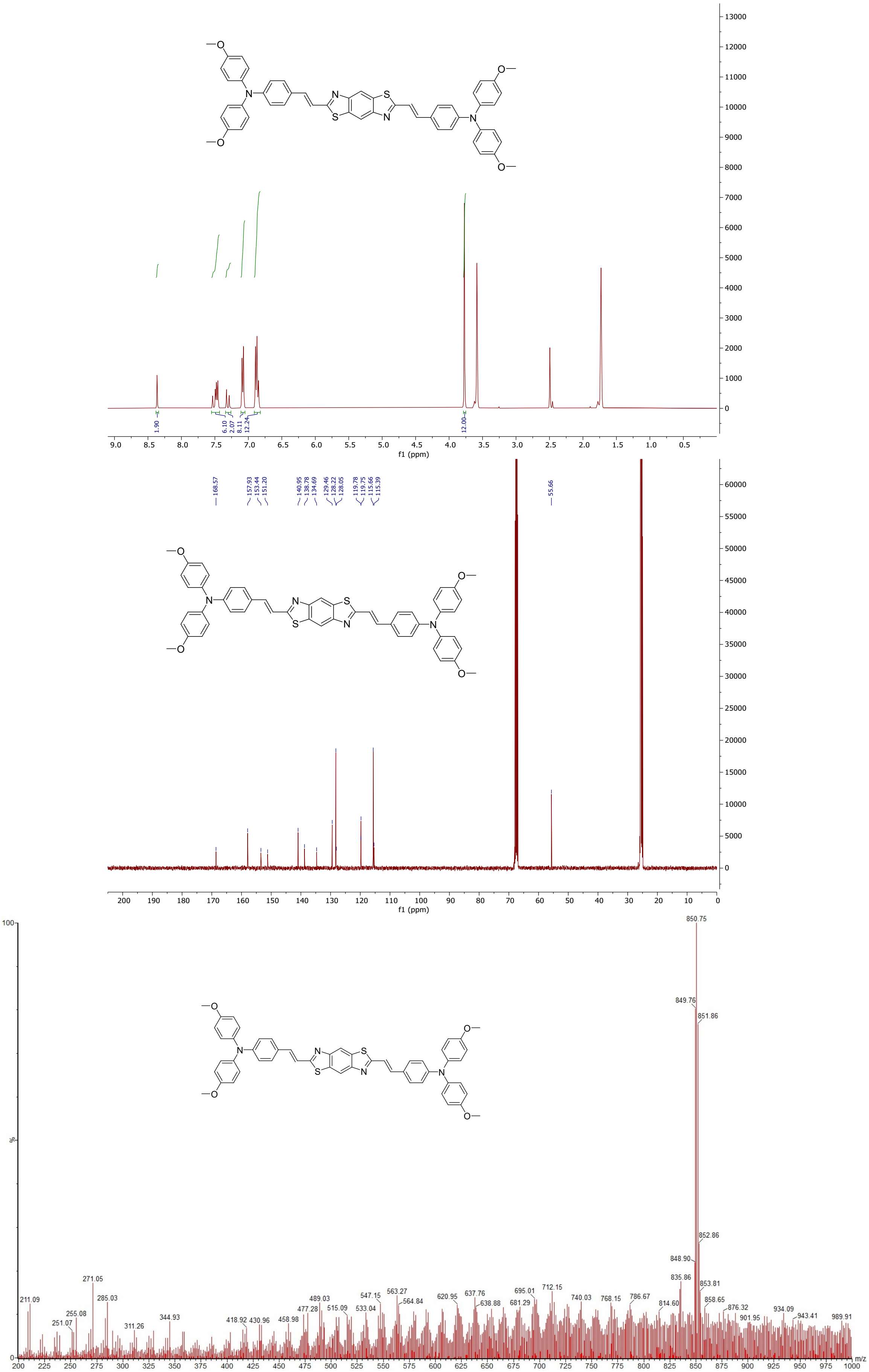


Figure S5. ^{1}H, ^{13}C NMRs and MS spectra of **V1671**.

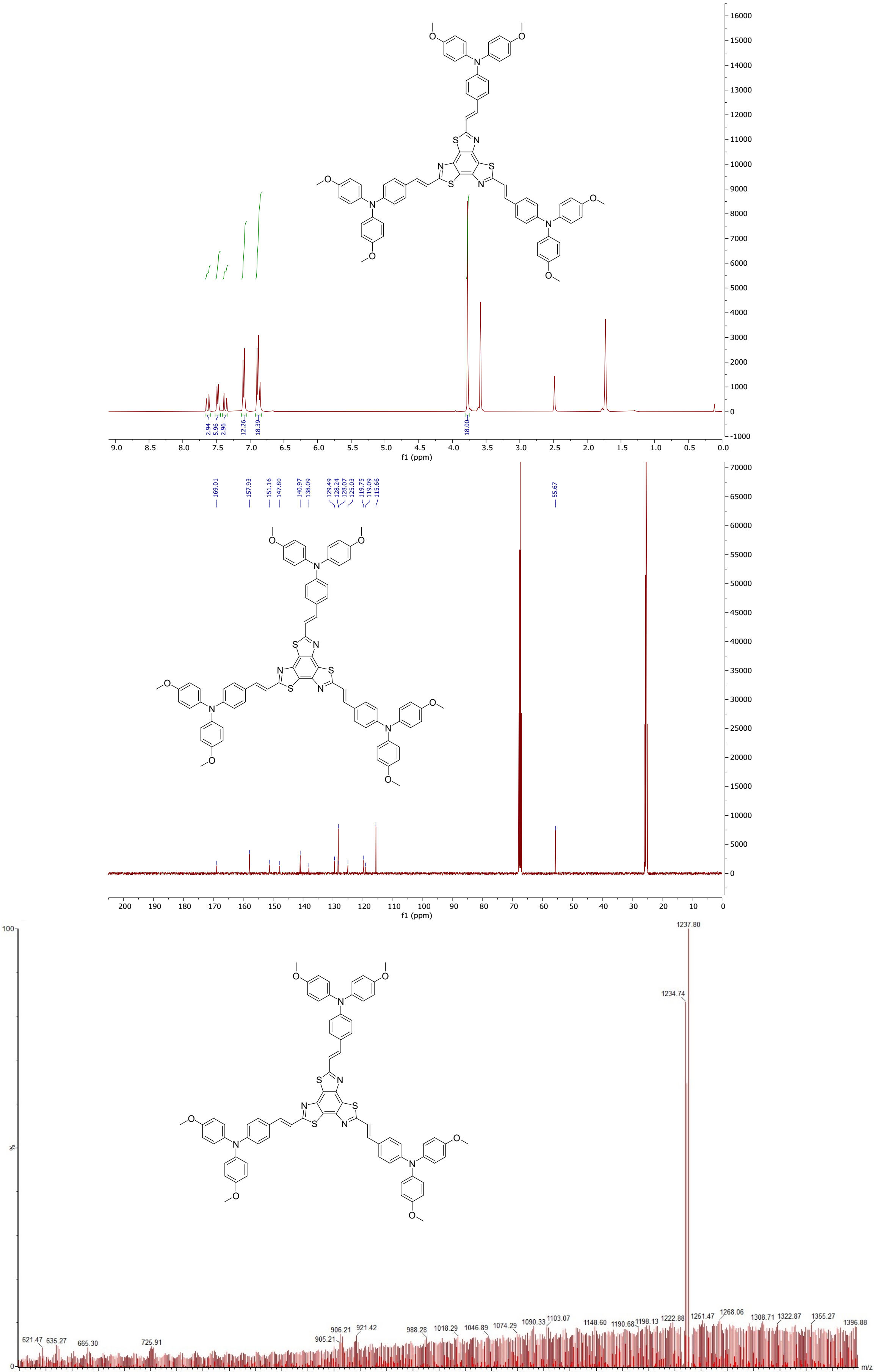


Figure S6. ^{1}H, ^{13}C NMRs and MS spectra of **V1672**.

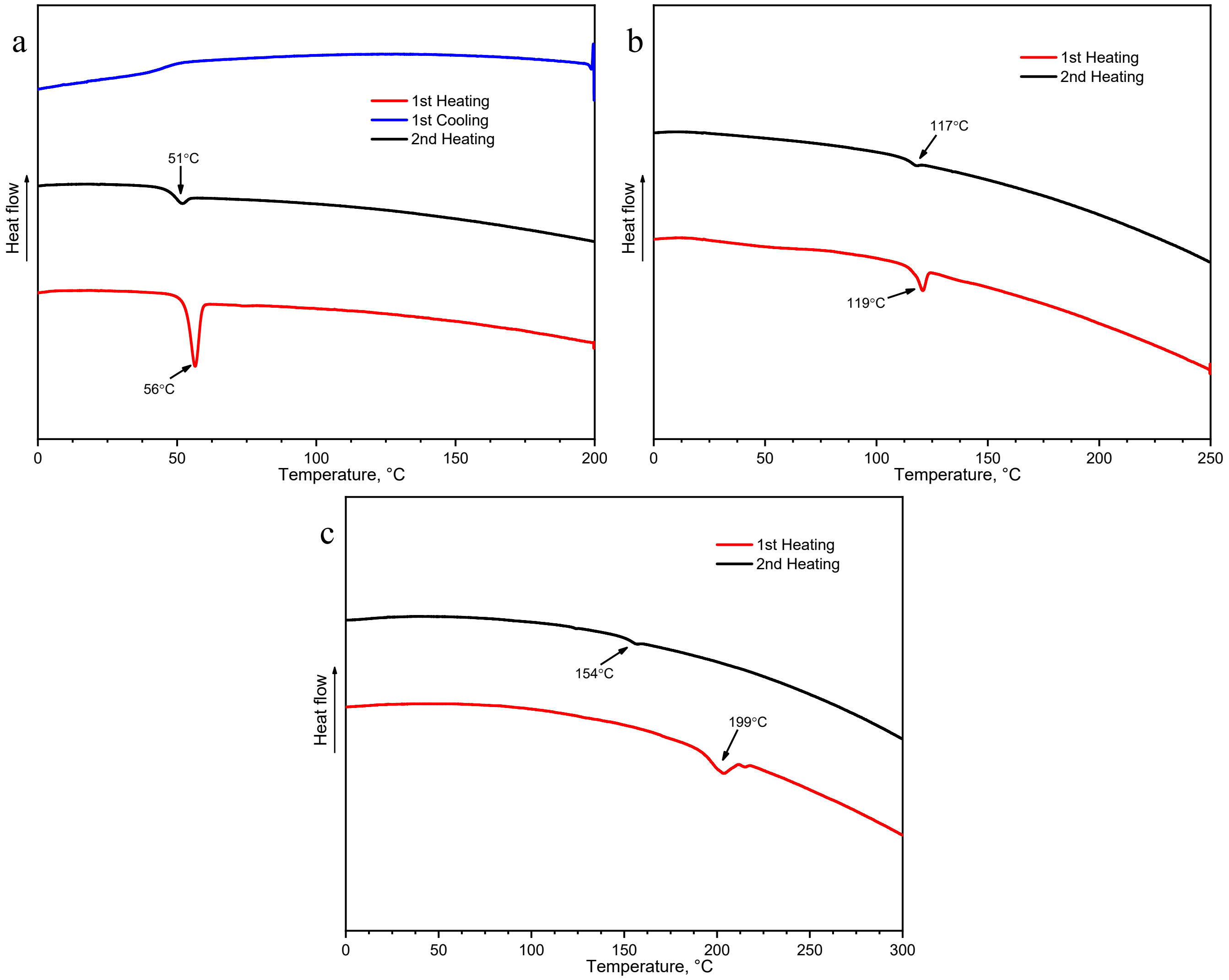


Figure S7. DSC heating curves for the first and second scan of **V1670** (a), **V1671** (b), and **V1672** (c) (heating rate of 10 °C/min, N_2 atmosphere, the y-axis is showing a heat flux).

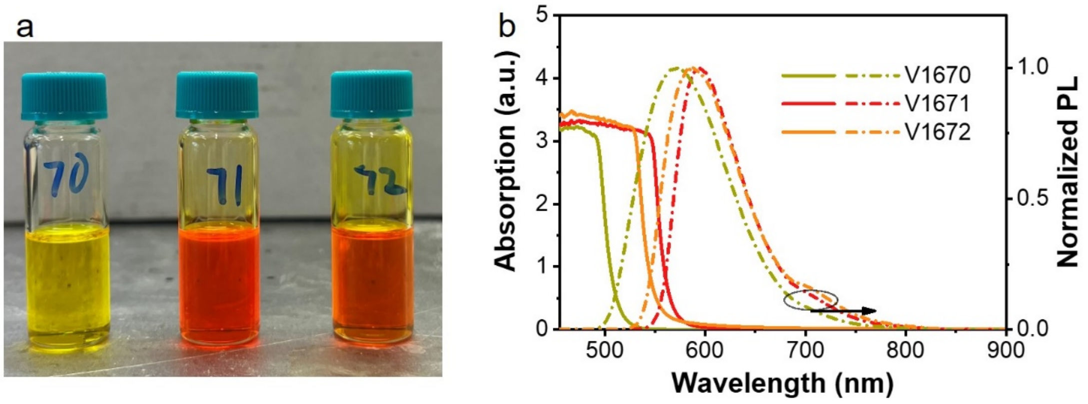


Figure S8. (a) A picture of **V1670**, **V1671** and **V1672** solutions in CB and CH_2Cl_2 (1:1 in volume) and the concentration is 3.3 mM. (b) Absorption and normalized PL spectra of the **V1670**, **V1671** and **V1672** solutions in (a). The PL peaks of the **V1670**, **V1671** and **V1672** solutions are 572 nm (FWHM of 101.3 nm), 593 nm (FWHM of 73.8 nm) and 588 nm (FWHM of 87.5 nm), respectively.

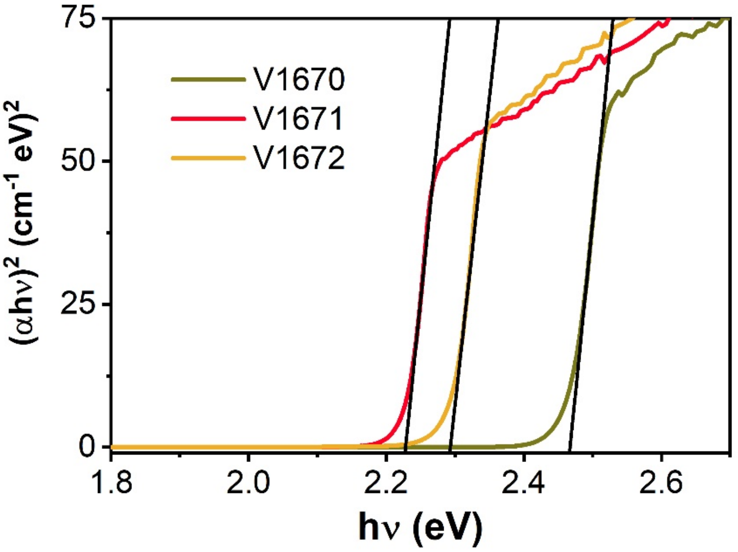


Figure S9. The optical bandgaps of the **V1670**, **V1671** and **V1672** HTMs are 2.46, 2.23 and 2.29 eV, respectively.

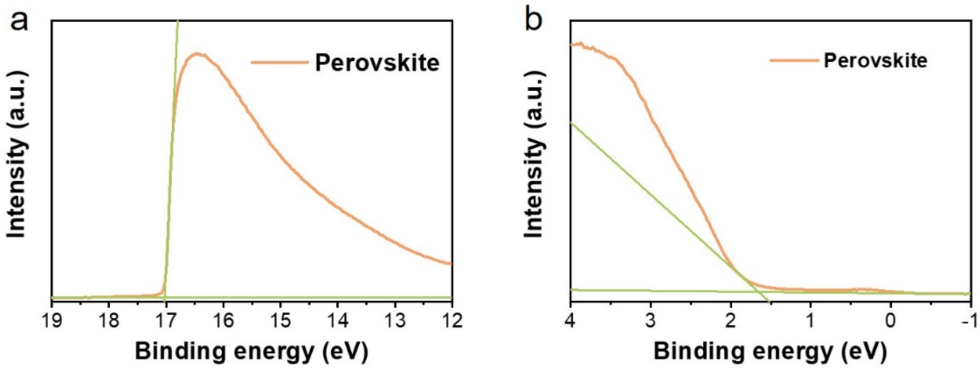


Figure S10. UPS and valence band spectra of the (a and b) perovskite films deposited on the FTO/SnO_2 substrates. The optical bandgap of the perovskite film is 1.53 eV.

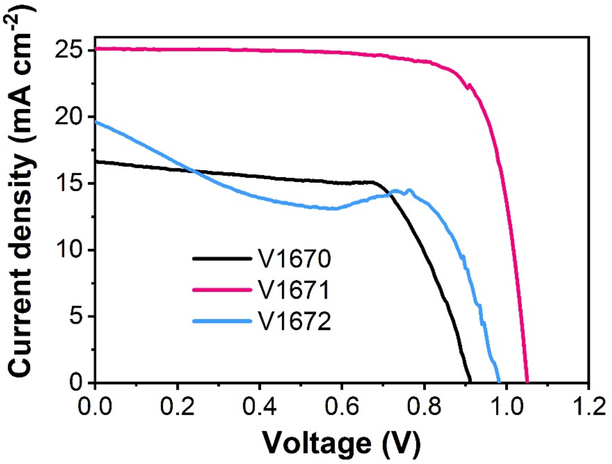


Figure S11. The current density-voltage curves of PSCs based on the same concentration of **V1670**, **V1671** and **V1672** HTMs solutions (25 mg/mL).

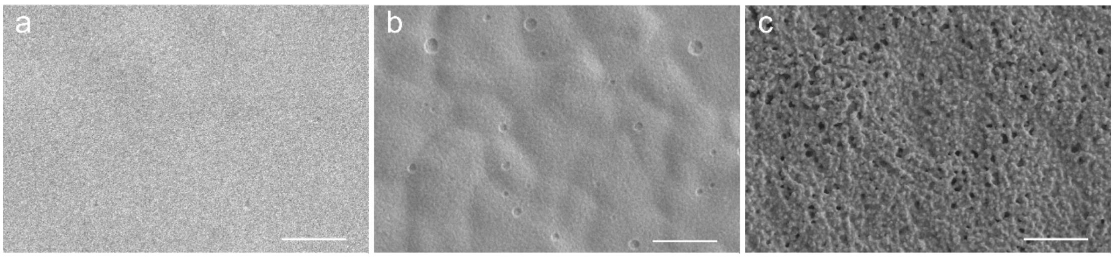


Figure S12. Top-view SEM images of (a) **V1670**, (b) **V1671** and (c) **V1672** HTMs films. The scale bar is 1 µm. The solution concentration for them is 25 mg/mL.

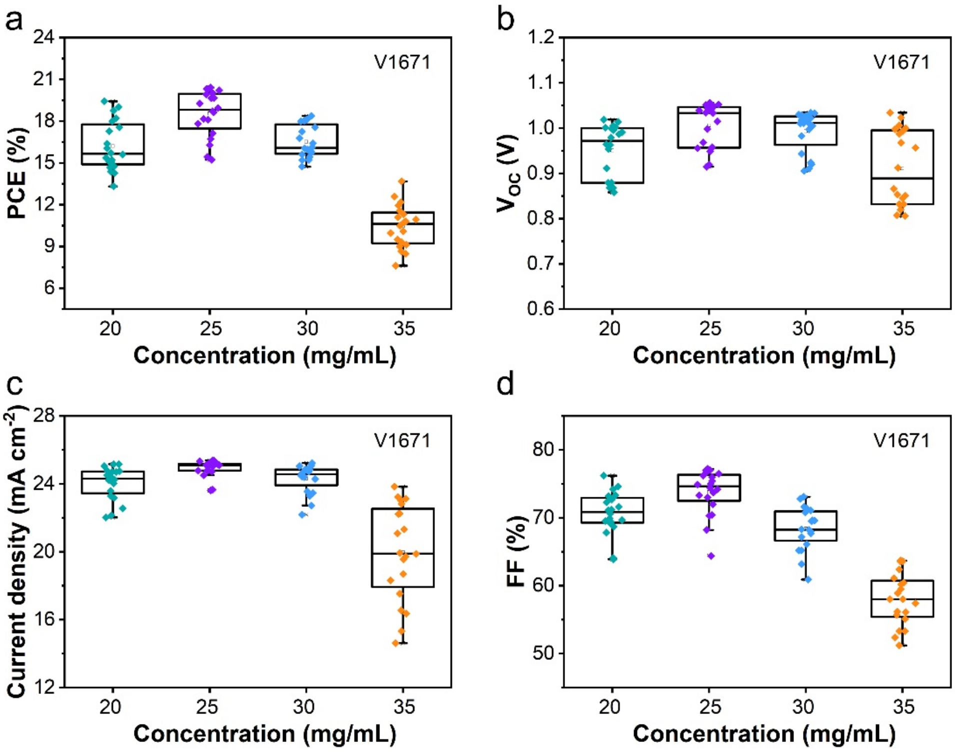


Figure S13. Statistical photovoltaic parameters of PSCs based on **V1671** HTM with different concentrations. (a) PCE, (b) V_{OC}, (c) current density and (d) FF. Each condition has 20 devices.

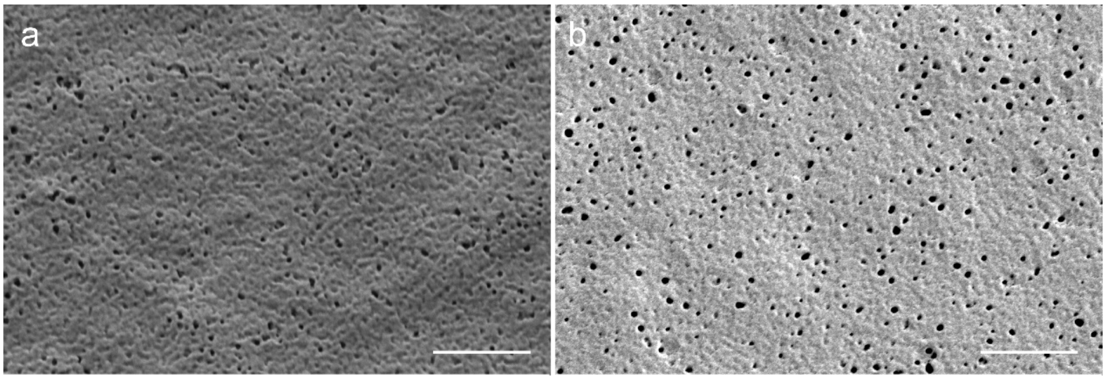


Figure S14. Top-view SEM images of **V1671** HTM films with different solution concentrations of (a) 20 mg/mL and (b) 30 mg/mL. The scale bar is 1 µm.

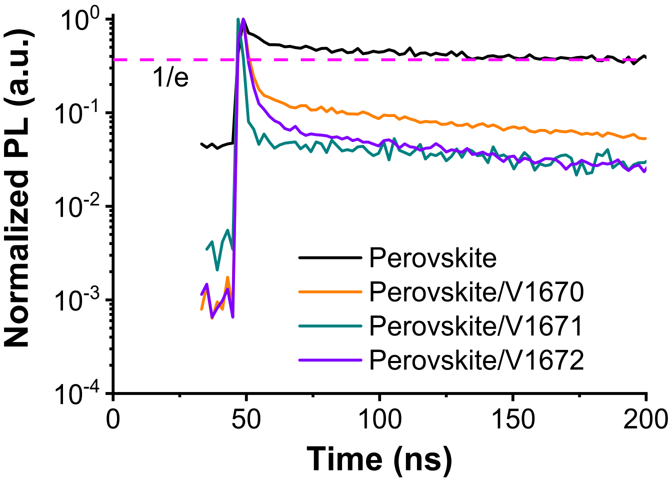
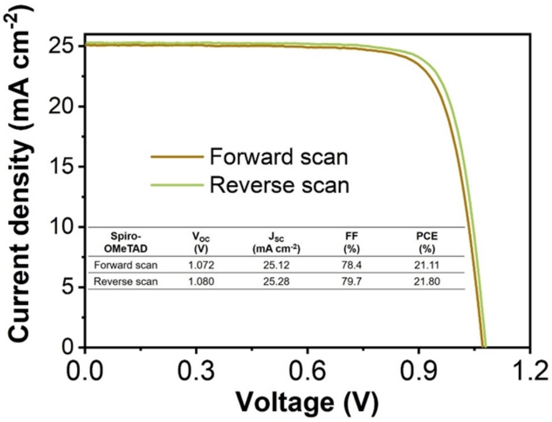


Figure S15. TRPL spectra of perovskite, perovskite/**V1670**, perovskite/**V1671**, and perovskite/**V1672** films.



Spiro-OMeTAD	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
Forward scan	1.072	25.12	78.4	21.11
Reverse scan	1.080	25.28	79.7	21.80

Figure S16. The *J-V* curves of the Spiro-OMeTAD-based PSC under reverse and forward scan modes. The hysteresis index (HI) of the Spiro-OMeTAD-based PSC is 3.2%.

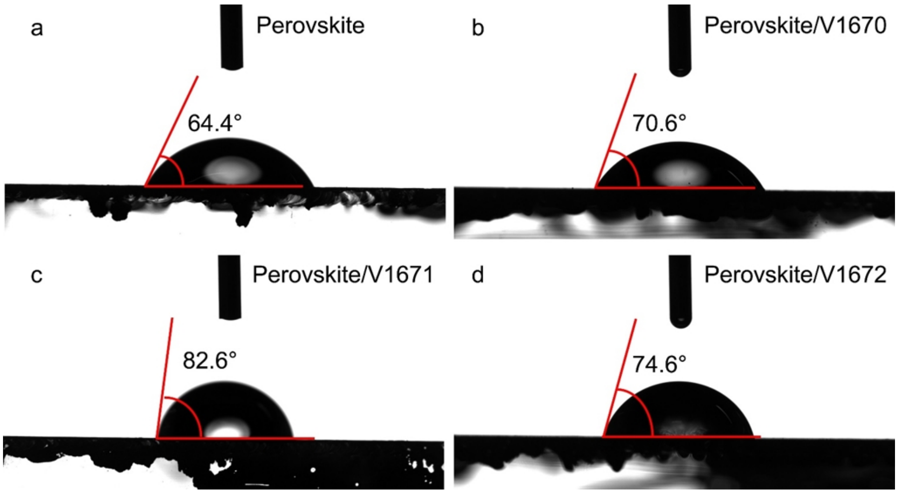


Figure S17. Contact angles of (a) perovskite, (b) perovskite/**V1670**, (c) perovskite/**V1671** and (d) perovskite/**V1672** on the FTO/SnO_2 substrates.

Table S1. Average photovoltaic parameters of the PSCs based on **V1671** with different concentrations.

Device \ **Average**	V_{OC} (V)	J_{SC} (mA·cm^{-2})	FF (%)	PCE (%)
20 mg/mL	0.9506	24.07	70.6	16.21
25 mg/mL	1.006	24.91	73.8	18.54
30 mg/mL	0.9929	24.32	68.4	16.51
35 mg/mL	0.9109	19.96	58.0	10.45

References

1 S. Tian, X. Gao, D. Reyes, O. A. Syzgantseva, M. M. Baytemirov, N. Shibayama, H. Kanda, P. A. Schouwink, Z. Fei, L. Zhong, F. F. Tiranito, Y. Fang, P. J. Dyson and M. K. Nazeeruddin, *Small*, 2024, **20**, 2406929.

2 J. J. Yoo, G. Seo, M. R. Chua, T. G. Park, Y. Lu, F. Rotermund, Y.-K. Kim, C. S. Moon, N. J. Jeon, J.-P. Correa-Baena, V. Bulović, S. S. Shin, M. G. Bawendi and J. Seo, *Nature*, 2021, **590**, 587–593.

3 M. Abuhelaiqa, S. Paek, Y. Lee, K. T. Cho, S. Heo, E. Oveisi, A. J. Huckaba, H. Kanda, H. Kim, Y. Zhang, R. Humphry-Baker, S. Kinge, A. M. Asiri and M. K. Nazeeruddin, *Energy Environ Sci*, 2019, **12**, 1910–1917.