

Supplementary Information for:

## Two-dimensional triphenylene cored hole-transporting materials for efficient perovskite solar cells

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### 1. Synthetic procedure and structural characterization

#### (1) **TPH-D** (*N*<sup>2</sup>,*N*<sup>2</sup>,*N*<sup>7</sup>,*N*<sup>7</sup>-tetrakis(4-methoxyphenyl)triphenylene-2,7-diamine)

**TPH-D** is prepared in a desired yield through the Buchwald-Hartwig amination reaction which is conducted using the palladium (II) catalytic system. An anhydrous toluene solution (10 mL) containing 2,7-Dibromotriphenylene (683 mg, 1.0 mmol) and 4,4'-Dimethoxydiphenylamine (573 mg, 2.5 mmol) was purged with Ar for 30 minutes. Afterward, the palladium (II) acetate (2.26 mg, 0.01 mmol), sodium *tert*-butoxide (240 mg, 2.5 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (3.9 mg, 0.013 mmol) were added in the solution; as a result, the solution was refluxed under Ar atmosphere for 24 h. After cooling down, the mixture was filtered to get the filtrate. Then, a mass of deionized water was added to the filtrate, afterwards the extraction was fulfilled by using ethyl acetate/CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layer was dried over anhydrous MgSO<sub>4</sub>. The dried solution was filtered again, and the superfluous solvent was evaporated. Using the column chromatography (PE/EA, 3:1, v/v), the purification of remaining crude product was executed to gain the final compound as a light yellow

powder (552 mg, yield 81%). <sup>1</sup>H NMR (400MHz, DMSO-d<sub>6</sub>), δ/ppm: 8.43-8.40 (d, 2H), 8.11 (s, 2H), 7.96 (s, 2H), 7.52 (s, 2H), 7.12-7.10 (m, 10H), 6.96-6.94 (m, 8H), 3.76 (s, 12H). <sup>13</sup>C NMR (400 MHz, DMSO-d<sub>6</sub>): δ/ppm: 156.22, 147.37, 140.65, 129.41, 124.62, 121.42, 115.51, 112.73, 55.71. MALDI-TOF-MS (m/z): calcd for [M-H] C<sub>46</sub>H<sub>38</sub>N<sub>2</sub>O<sub>4</sub>: 682.0817, found: 682.0845.

(2) **TPH-T** (*4,4'-(triphenylene-2,7-diyl)bis(N,N-bis(4-methoxyphenyl)aniline)*)

**TPH-T** is synthesized in a desired yield through the traditional Suzuki-Miyaura palladium (0) catalyzed cross-coupling reaction. An mixture tetrahydrofuran/ toluene solution (3/2, v/v) comprising 4-methoxy-*N*-(4-methoxyphenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (2.4 mmol, 1034 mg) and 2,7-Dibromotriphenylene (683 mg, 1.0 mmol) was deoxygenated with Ar for 30 minutes. In the second step, the 700 mg of potassium carbonate was dissolved in deionized water (2 mL); afterwards, the aqueous solution was added to the preceding mixture solution. Finally, tetrakis(triphenylphosphine)palladium (58 mg, 0.05 mmol) was added to the reacted system. The ultimate solution was stirred at the refluxed condition for 24 h. After the reacted system was cooling down, the mixture was filtered for three times, and the undissolved residue was removed thoroughly. The filtrate was extracted with ethyl acetate and water. The organic section was collected carefully and dried over anhydrous MgSO<sub>4</sub>. Then evaporating the chemical solvent under reduced pressure, the crude product was purified using column chromatography with a mixture of DCM/PE (1:5, v/v) as eluent. The desired product as light green solid was obtained for 367 mg with a yield of 44%. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>-d<sub>6</sub>), δ/ppm: 8.77 (s, 2H), 8.73 (d, 2H), 8.65-8.63 (d, 2H), 7.84-7.82 (d, 2H), 7.66-7.65 (d, 6H), 7.07 (m, 12H), 6.89-6.87 (d, 8H), 3.84 (s, 12H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ/ppm: 156.21, 139.24, 130.13, 129.89, 127.52, 127.24, 127.02, 126.06, 124.00, 123.74, 120.86, 114.50, 55.71. MALDI-TOF-MS (m/z): calcd for [M-H] C<sub>58</sub>H<sub>46</sub>N<sub>2</sub>O<sub>4</sub>: 834.3573, found: 834.3620.

## 2. Photophysical and electrochemical properties.

**Table S1** Optical and electrochemical data for **TPH-D**, **TPH-T** and *spiro*-OMeTAD.

HTMs	$\lambda_{\text{abs\_max}}$ [nm]	$E_{\text{g}}^{\text{opt(a)}}$ [eV]	$E_{\text{ox}}^0$ <sup>(b)</sup> [V]	$E_{\text{HOMO}}$ <sup>(c)</sup> [eV]	$E_{\text{LUMO}}$ <sup>(d)</sup> [eV]	$\mu$ <sup>(e)</sup> [cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ]	$E_{\text{R}}$ <sup>(f)</sup> [meV]
TPH-D	366	2.99	0.40	-5.47	-2.48	$8.55 \times 10^{-5}$	438
TPH-T	380	2.93	0.37	-5.44	-2.51	$1.83 \times 10^{-4}$	419
<i>spiro</i> - OMeTAD	388	3.10	0.13	-5.20	-2.10	$4.64 \times 10^{-5}$	490

<sup>a</sup> Estimated by the intersection of the absorption and emission spectra in DCM solution.

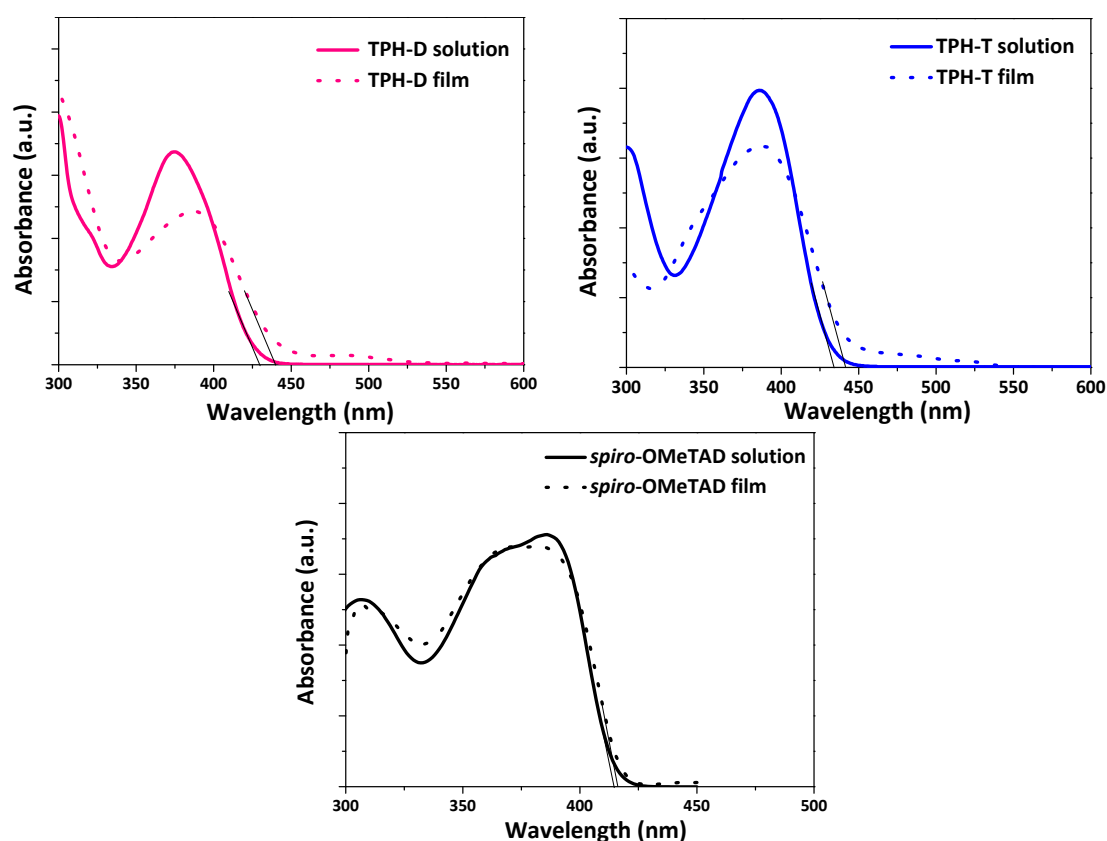
<sup>b</sup> Using Ag/AgCl as reference electrode, carbon as working electrode and Pt as counter electrode.

<sup>c</sup> Calculated from  $E_{\text{ox}}^0$  (V) versus Fc/Fc<sup>+</sup> + 0.63 versus NHE + 4.44 versus vacuum.

<sup>d</sup> Determined by the equation  $E_{\text{HOMO}} + E_{\text{g}}^{\text{opt}}$ .

<sup>e</sup> Displayed on the hole-only devices with the structure ITO/PEDOT:PSS/HTM/Au.

<sup>f</sup> Obtained according to the computational adiabatic potential energy surface data.



**Fig. S1** The electronic absorption spectra of TPH-D, TPH-T and *spiro*-OMeTAD in DCM solution and on glass films.

### 3. DSC results for TPH-D and TPH-T

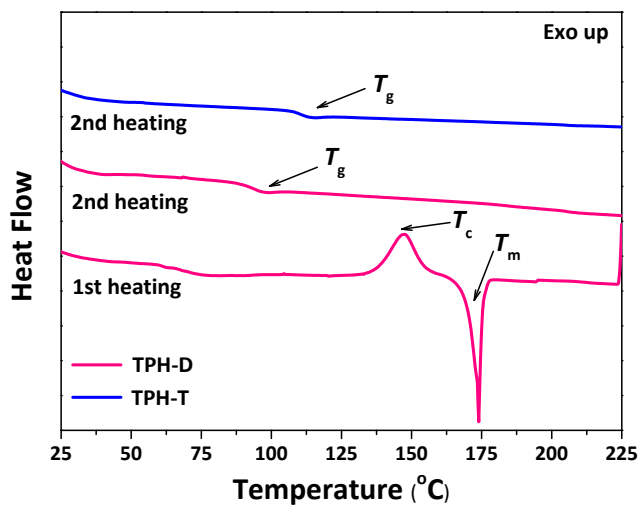


Fig. S2 DSC curves for TPH-D and TPH-T (heating rate 10 °C min<sup>-1</sup>).

### 4. DFT calculations of TPH-D and TPH-T

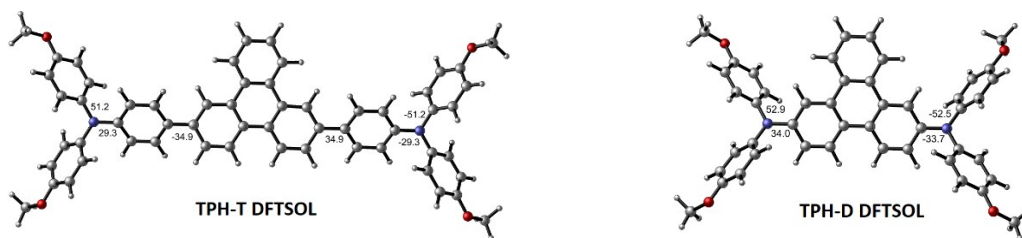


Fig. S3 DFT-optimized geometrical structure

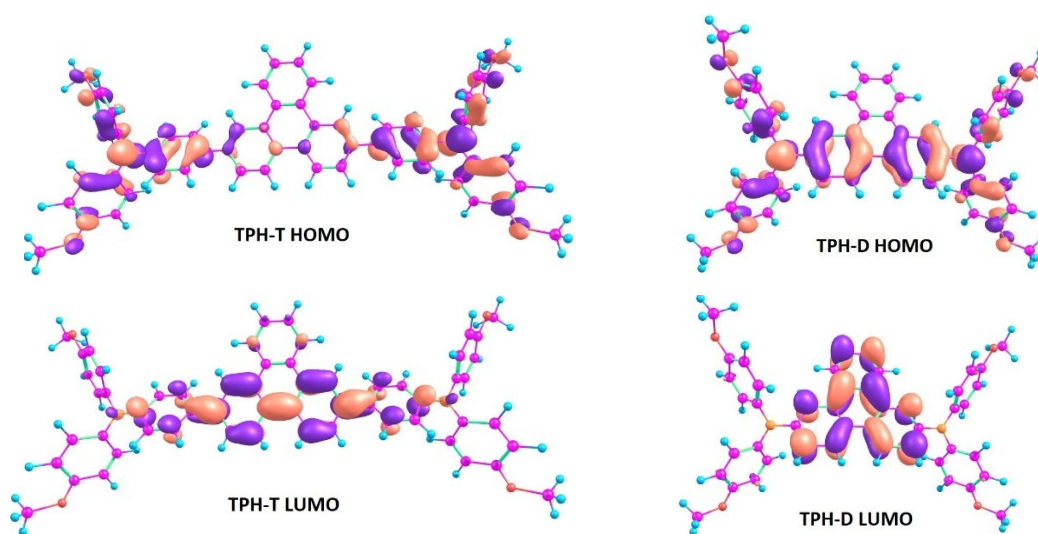
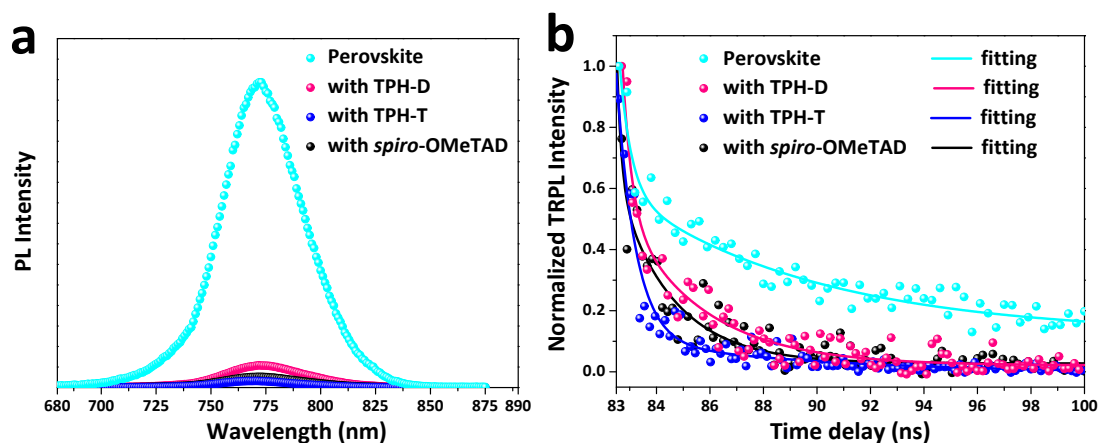


Fig. S4 Isodensity surface plots of HOMO and LUMO

## 5. PL/TRPL results



**Fig. S5** (a) Steady-state PL curves upon excitation at 475 nm. (b) Time-resolved PL decay spectra of the pristine perovskite, perovskite/**TPH-D**, perovskite/**TPH-T** and perovskite/*spiro*-OMeTAD.

The considerable hole extraction and collection abilities of HTM can significantly promote photo-generated charge separation and transfer processes, and prevent non-radiative trap-induced charge recombination at the same time. The hole extraction, collection abilities of these HTMs and interfacial charge transporting behaviors between HTM and perovskite layer are evaluated employing the steady-state and time-resolved photoluminescence decay (PL/TRPL) measurements. The PL curves of perovskite with or without HTM uplayer are shown in Fig. S5a. For the pristine perovskite sample, a strong and broad emission band is observed upon excitation at 475 nm. The corresponding results of **TPH-D**, **TPH-T** and *spiro*-OMeTAD/perovskite bilayers give apparent PL quenching, which can be attributed to the fruitful hole-extraction processes caused by the introduced HTM. Especially, **TPH-T** provides lower PL intensity than **TPH-D** and *spiro*-OMeTAD, which may result from the remarkable hole mobility. In Fig. S5b, the TRPL decays of pristine perovskite and perovskite/HTM bilayers can be well fitted with exponential time constant. Compared with the decay lifetime of perovskite-only film (35.4 ns), the **TPH-D**, **TPH-T** and *spiro*-OMeTAD coated perovskite films display shorter lifetime of 7.8, 1.5 and 3.2 ns, respectively. Moreover, the faster hole collection and interfacial charge transporting kinetics are achieved by **TPH-T** relative to **TPH-D** and *spiro*-OMeTAD.

## 6. Solar Cell Fabrication

The assembly processes of mixed-cation perovskite solar cells were implemented according to the preceding papers.[1, 2] FTO glass substrates were oscillated in the ultrasonic bath containing cleanser essence, and then rinsed following by deionized water and anhydrous ethanol. The TiO<sub>2</sub> compact layer was deposited on the etched FTO plates through spray pyrolysis method at 430 °C. The employed solution was a mixture containing 6 mL of anhydrous isopropanol and 0.6 mL of titanium diisopropoxide bis(acetylacetonate). The TiO<sub>2</sub> mesoporous layer was then deposited above the compact layer by spin-coating the diluted *Dyesol 18NR-T* TiO<sub>2</sub> paste (1:5, w/w, diluted with ethanol) at 5500 rpm for 30 s, following by sintered at 510 °C for 30 minutes. The mixed-cation perovskite film was also deposited by the one-step solvent engineering method. The perovskite precursor solution (1.1 M PbI<sub>2</sub>, 0.2 M PbBr<sub>2</sub>, 0.2 M MABr, and 1 M FAI in a DMF and DMSO mixture solution) was spin-coating on the mesoporous layer upwardly. In general, the first stage was executed at 1500 rpm for 10 s. The second one was performed at 5000 rpm for 30 s. During the second spin-coating step, 90 μL of CB was dripped on spinning substrates; as a result, the processed film was sintered at 100 °C for 90 minutes in time. After cooling down, the HTM, which was dissolved in anhydrous CB solution (TPH-D: 20 mg mL<sup>-1</sup>, TPH-T: 75 mg mL<sup>-1</sup>, *spiro*-OMeTAD: 75 mg mL<sup>-1</sup>, 5-20 μL of *t*BP, and 5-13 μL of Li-TFSI), was spin-coating above the (FAPbI<sub>3</sub>)<sub>0.85</sub>(MAPbI<sub>3</sub>)<sub>0.15</sub>/m-TiO<sub>2</sub>/c-TiO<sub>2</sub>/FTO substrate at 4000 rpm for 20 s. Finally, employing thermal evaporation technology, the Au counter electrode (~60 nm) was deposited on the top of device.

## 7. General measurements

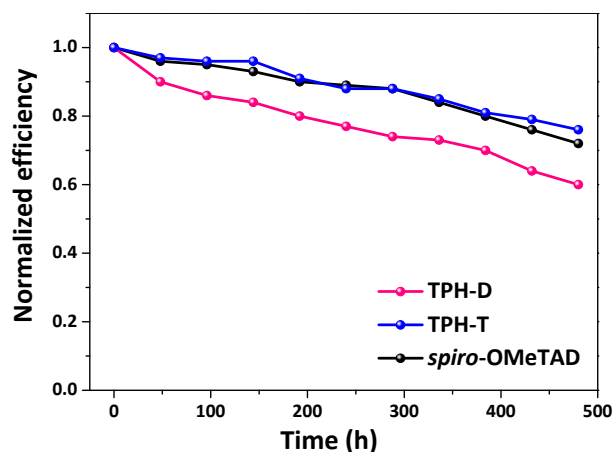
All the chemical solvent and regular reagents were purchased from Sinopharm Group, Sigma-Aldrich and Aladdin. The intermediate compounds 4-bromo-*N,N*-bis(4-methoxyphenyl)aniline, 4,4'-Dimethoxydiphenylamine and 4-methoxy-*N*-(4-methoxyphenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline were synthesized according to the published literature route.[3, 4] Both the target HTM molecules based on triphenylene core could be dissolved in most eluents and organic

solvents used in devices assembly engineering such as dichloromethane, ethyl acetate and chlorobenzene.

The identification for the final compounds was carefully displayed.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR were carried out on the Bruker Advance III spectrometer, and the chemical shifts ( $\delta$ ) are described in parts per million (ppm) calibrated against the internal standard tetramethylsilane (TMS). Matrix-assisted laser desorption/ionization mass spectra (MALDI-TOFMS) were collected on the Thermo Scientific Q Exactive HF Hybrid Quadrupole Orbitrap Spectrometer. The UV-Vis absorption behavior were investigated on the Thermo-Fisher Evolution 220 Spectrophotometers. The PL and TRPL data were recorded on the PTI QM400 fluorescence detector, which was equipped with a 450 W xenon CW lamp and a pulsed nitrogen laser. The CV properties were analyzed with Autolab PGSTAT analyzer using a formal three electrode electrochemical system (carbon electrode as working electrode, platinum wire as the counter electrode and Ag/AgCl as the reference electrode).

For the completed solar cell devices, the photovoltaic characteristics were measured employing a Newport AAA grade solar simulator. The actual light intensity was calibrated by a standard Si reference device before the cell performance measurement. The current density-voltage ( $J$ - $V$ ) characteristics of each cell were gained by exerting an external voltage bias while recording the current response with Keithley 2400/2604 digital source meter. The IPCE results were carried out with Newport QE/IPCE measurement kit.

## 8. Stability test



**Fig. S6** PCEs attenuation measured in ambient without encapsulation for PSCs employing *spiro*-OMeTAD, **TPH-D** and **TPH-T** as the HTMs.

## 9. Cost calculation

**Table S2** Materials, quantities and costs for the synthesis process of **TPH-T**.

<b>Chemical</b>	<b>Weight for Reagent (g/g)</b>	<b>Price (RMB/g)</b>	<b>Cost (RMB/g product)</b>
4-methoxy- <i>N</i> -(4-methoxyphenyl)- <i>N</i> -(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline	2.70	75.00	202.50
2,7-Dibromotriphenylene	1.80	62.30	112.10
Pd(PPh <sub>3</sub> ) <sub>4</sub>	0.12	58.00	7.00
K <sub>2</sub> CO <sub>3</sub>	1.10	0.040	0.04
Tetrahydrofuran	20.00	0.012	0.24
Toluene	20.00	0.010	0.20
MgSO <sub>4</sub>	5.00	0.030	0.15
CH <sub>2</sub> Cl <sub>2</sub>	300.00	0.015	4.50
PE	800.00	0.012	9.60
<b>Total Cost : TPH-T: 336.33 RMB/g or 47.93 \$/g</b>			

<b>HTM</b>	<b>Material cost (\$/g)</b>	<b>Commercial price (\$/g)</b>
TPH-T	47.93	-
<i>spiro</i> -OMeTAD	91.67 [5]	170-475 [5]



## 10. NMR and MS for TPH-D and TPH-T

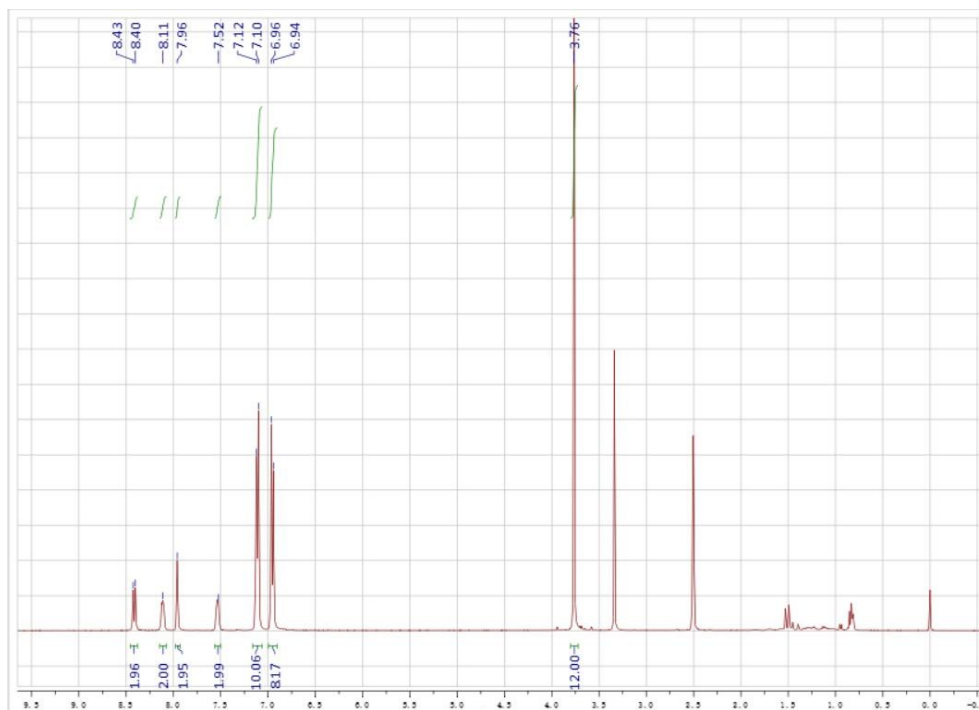


Fig. S7  $^1\text{H-NMR}$  of TPH-D.

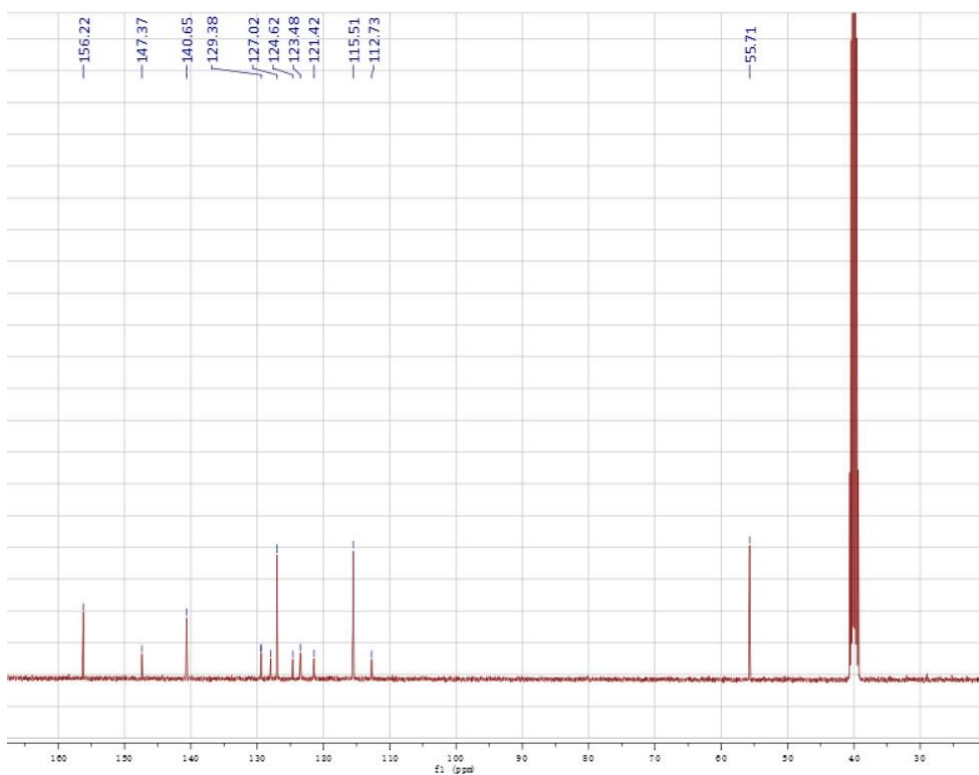
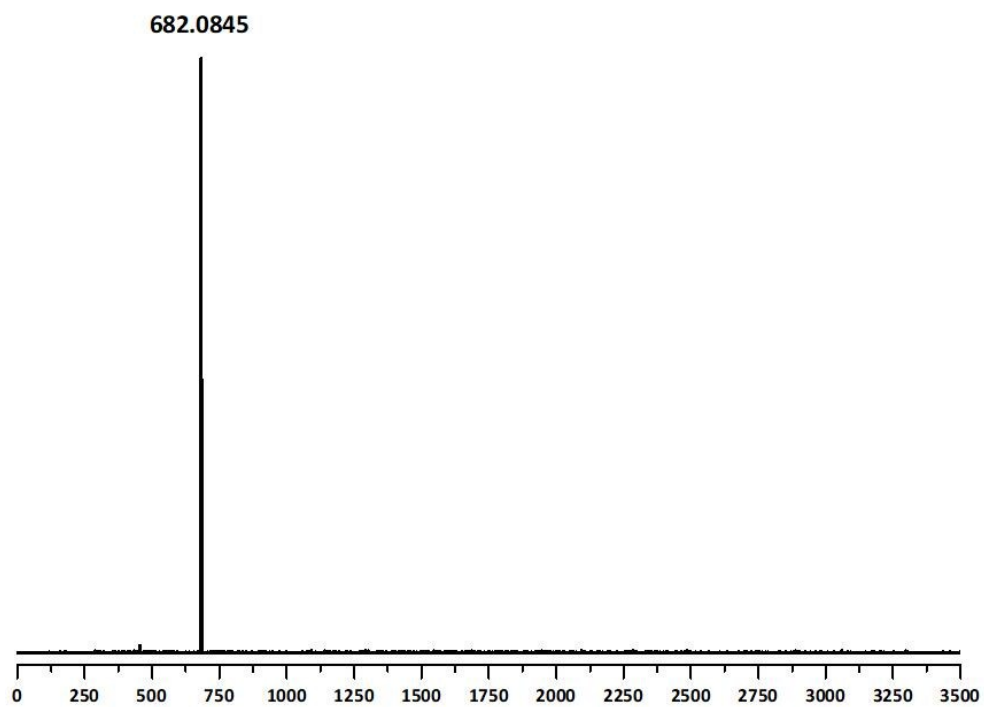
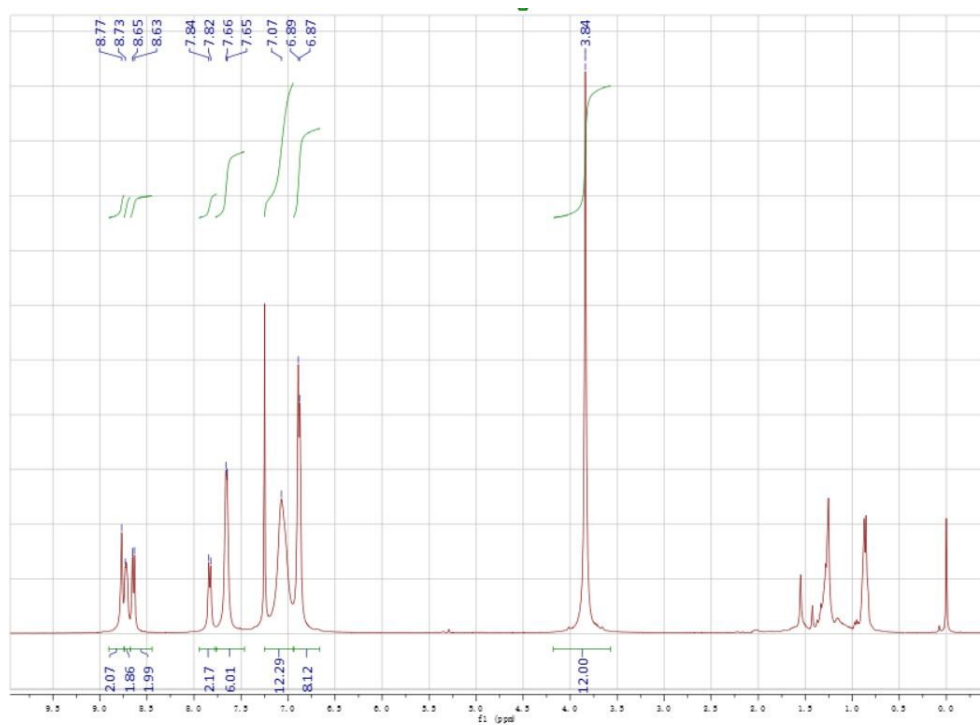


Fig. S8  $^{13}\text{C-NMR}$  of TPH-D.



**Fig. S9** MALDI-TOF-MS of TPH-D.



**Fig. S10** <sup>1</sup>H-NMR of TPH-T.

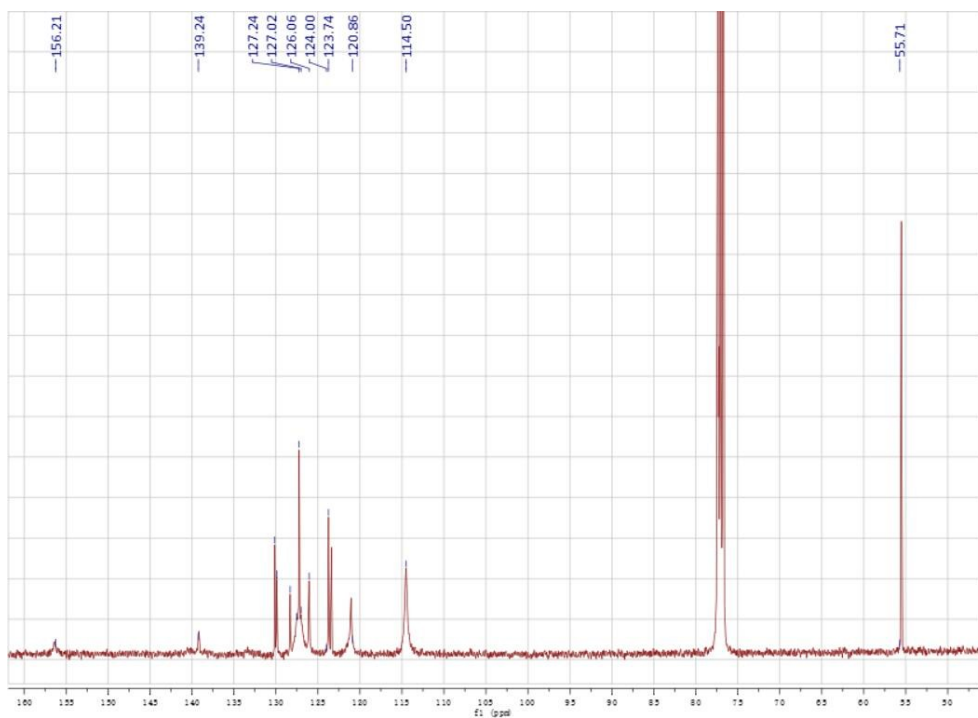


Fig. S11  $^{13}\text{C}$ -NMR of TPH-T.

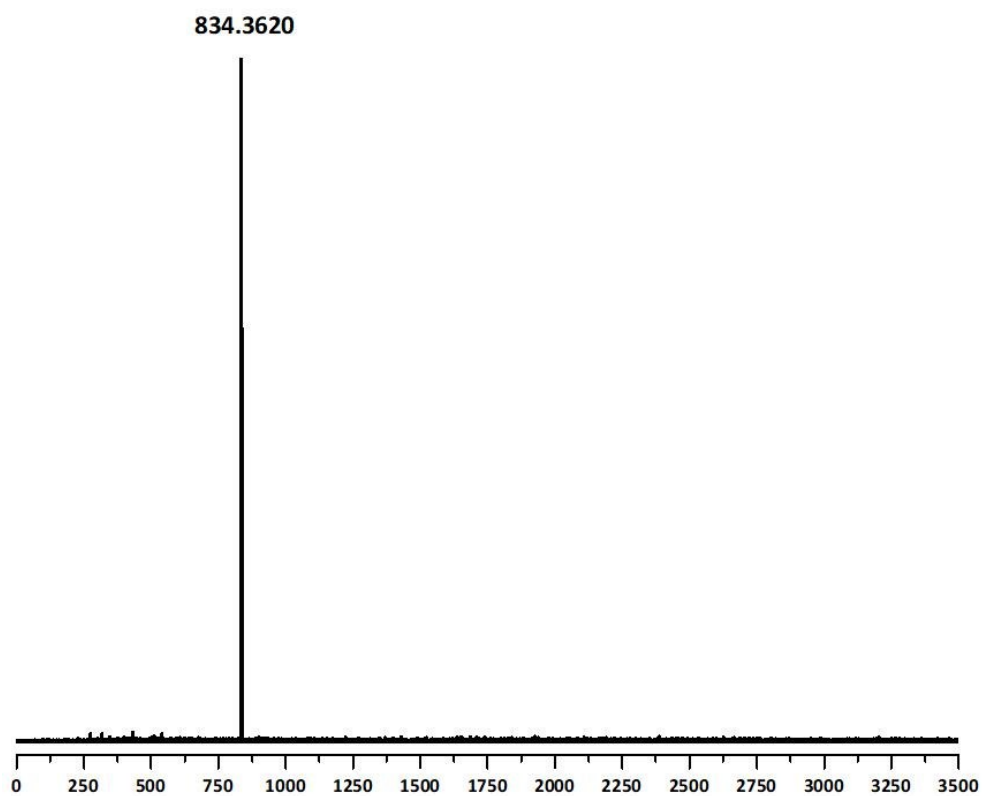


Fig. S12 MALDI-TOF-MS of TPH-T.

### References

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