Electronic Supplementary Information

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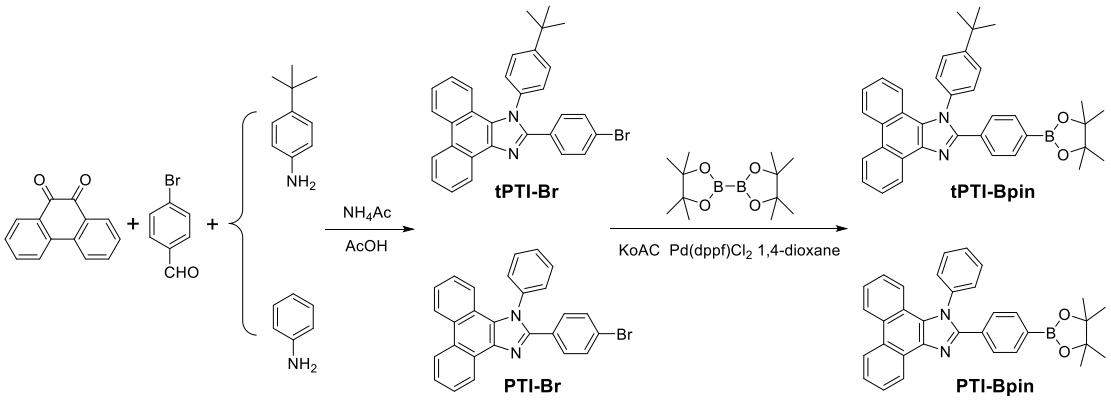
1. General experimental procedures

Characterization: ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz Varian Mercury, using CD_2Cl_2 or THF-d_8 as the solvent. High-resolution mass spectra were measured on an LTQ-Orbitrap Elite high-resolution mass spectrometer (Thermo-Fisher Scientific, Waltham, MA, USA) equipped with an electrospray ionization (ESI) source and a Dionex Ultimate 3000 UPLC system (Thermo-Fisher Scientific, Waltham, MA, USA). Mass spectra were measured on a ZAB 3F-HF mass spectrophotometer. Elemental analyses of carbon, hydrogen and nitrogen were performed on a Perkin-Elmer microanalyzer. PL spectra were recorded by a Hitachi F-4600 fluorescence spectrophotometer. The ML spectra were measured on a spectrometer of Acton SP2750 with CCD (SPEC-10, Princeton) as a power detector. Absolute photoluminescence quantum yield (PLQY) and fluorescence decay were recorded by an Edinburgh FLS980 spectrometer. The powder X-ray diffraction patterns were measured on Rigaku MiniFlex 600 at 25 ºC at 40 KV and 40 mA at a scan rate of 10º (2θ)/min (scan range: 5-60º). The single-crystal X-ray diffraction data were recorded by a Bruker Smart Apex II CCD diffractometer. The CCDC numbers of tPTI-B1, tPTI-B2 and PTI-B are 1948492, 1948484 and 1948485 respectively. Thermogravimetric analysis were carried out on TG 209 F1 of Thermogravimetric Analyzer under nitrogen at heating rate of 10°C min^{-1}. Differential scanning calorimetry were performed on NETZSCHDSC 200 PC instrument from room temperature to 250 ºC at a heating rate of 10 ºC/min under nitrogen. The Gaussian 09 program was utilized to perform the TD-DFT calculations. The ground state (S_0) geometry was obtained from the single crystal structure and no further geometry optimization was conducted in order to maintain the specific molecular configuration and corresponding intermolecular locations.

2. Synthesis



Scheme S1. The synthetic routes of tPTI-Bpin and PTI-Bpin.

tPTT-Br: To a round-bottom flask fitted with a reflux condenser, was added 9,10-phenanthrenedione (4.17 g, 20 mmol), 4-bromobenzaldehyde (1.90 g, 10 mmol), 4-tert-butylaniline (1.60 mL, 10 mmol), ammonium acetate (4.63 g, 60 mmol) and acetic acid (50 mL). The resultant solution was stirred under nitrogen atmosphere at refluxing temperature for 4 h. After the reaction completed, the mixture was cooled to room temperature and quenched with a large amount of water, after stirring for 30 mins, the

mixture was filtered and washed with a small amount of methanol to afford a crude product. The crude product was purified by column chromatography (eluent:petroleum ether/dichloromethane = 1/3) to give the pure compound of tPTI-Br as a light yellow solid (4.06 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.85-8.83 (d, *J* = 8 Hz 1H, Ar-H), 8.77-8.75 (d, *J* = 8 Hz, 1H, Ar-H), 8.71-8.69 (d, *J* = 8 Hz, 1H, Ar-H), 7.76-7.72 (m, 1H, Ar-H), 7.67-7.60 (m, 3H, Ar-H), 7.53-7.49 (m, 1H, Ar-H), 7.47-7.40 (m, 6H, Ar-H), 7.28-7.24 (m, 1H, Ar-H), 7.19-7.17 (d, *J* = 8 Hz, 1H, Ar-H), 1.45 (s, 9H, -tBu). MS (ESI), m/z: 504.01, calcd for $C_{20}H_{18}NO_2Br$: 504.12.

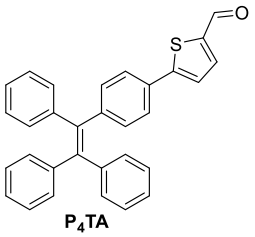
PTT-Br: To a round-bottom flask fitted with a reflux condenser, was added 9,10-phenanthrenedione (4.17 g, 20 mmol), 4-bromobenzaldehyde (1.90 g, 10 mmol), aniline (0.91 mL, 10 mmol), ammonium acetate (4.63 g, 60 mmol) and acetic acid (50 mL). The resultant solution was stirred under nitrogen atmosphere at refluxing temperature for 4 h. After the reaction completed, the mixture was cooled to room temperature and quenched with a large amount of water, after stirring for 30 mins, the mixture was filtered and washed with a small amount of methanol to afford a crude product. The crude product was purified by column chromatography (eluent:petroleum ether/dichloromethane = 1/3) to give the pure compound of PTI-Br as a light yellow solid (3.51 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.85-8.84 (d, *J* = 4 Hz 1H, Ar-H), 8.78-8.76 (d, *J* = 8 Hz, 1H, Ar-H), 8.71-8.70 (d, *J* = 4 Hz, 1H, Ar-H), 7.75-7.73 (m, 1H, Ar-H), 7.67-7.61 (m, 4H, Ar-H), 7.53-7.50 (m, 3H, Ar-H), 7.46-7.41 (m, 4H, Ar-H), 7.27-7.26 (m, 1H, Ar-H), 7.18-7.16 (d, *J* = 8 Hz, 1H, Ar-H). MS (ESI), m/z: 447.95, calcd for $C_{20}H_{18}NO_2Br$: 448.06.

tPTT-Bpin: tPTI-Br (4.50 g, 9 mmol), bis(pinacolato)diboron (3.93 g, 13.5 mmol), potassium acetate (3.10 g, 31.5 mmol), and $Pd(dppf)_2Cl_2$ (0.33 g, 0.45 mmol) in anaerobic 1,4-dioxane (80 mL) were refluxed under nitrogen for 12 h. After the reaction completed, the mixture was cooled to room temperature and then water (100 mL) was added, and extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography (eluent:petroleum ether/dichloromethane = 1/4) to give the pure compound of tPTI-Bpin as a white solid (1.91 g, 39%). ^{1}H NMR (400 MHz, CD_2Cl_2, δ): 8.85-8.83 (d, *J* = 8 Hz 1H, Ar-H), 8.78-8.76 (d, *J* = 8 Hz, 1H, Ar-H), 8.73-8.71 (d, *J* = 8 Hz, 1H, Ar-H), 7.78-7.71 (m, 3H, Ar-H), 7.69-7.63 (m, 5H, Ar-H), 7.53-7.49 (m, 1H, Ar-H), 7.46-7.44 (d, *J* = 8 Hz, 2H, Ar-H), 7.30-7.27 (m, 1H, Ar-H), 7.22-7.20 (d, *J* = 8 Hz, 1H, Ar-H), 1.47 (s, 9H, -tBu), 1.35 (s, 12H, $-CH_3$). ^{13}C NMR (100 MHz, CD_2Cl_2, δ): 153.87, 150.88, 137.69, 136.32, 134.68, 133.58, 129.47, 128.88, 128.80, 128.73, 128.54, 127.68, 127.65, 127.48, 126.68, 125.90, 125.28, 124.36, 123.55, 122.86, 121.38, 84.33, 35.30, 31.53, 25.07. MS (ESI), m/z: 552.17, calcd for $C_{37}H_{37}BN_2O_2$: 552.29. HRMS (ESI), m/z: [M^+] 553.3006, calcd for $C_{37}H_{37}BN_2O_2$: 553.3027. Elemental analyses for $C_{37}H_{37}BN_2O_2$: C, 80.43; H, 6.75; N, 5.07. Found: C, 79.95; H, 6.98; N, 4.98. [CCDC 1948492, 1948484]

PTT-Bpin: PTI-Br (5.40 g, 12 mmol), bis(pinacolato)diboron (3.66 g, 14.4 mmol), potassium acetate (4.10 g, 42 mmol), and $Pd(dppf)_2Cl_2$ (0.44 g, 0.60 mmol) in anaerobic 1,4-dioxane (100 mL) were

refluxed under nitrogen for 12 h. After the reaction completed, the mixture was cooled to room temperature and then water (150 mL) was added, and extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography (eluent:petroleum ether/dichloromethane = 1/4) to give the pure compound of tPTI-Bpin as a white solid (2.80 g, 47%). ^{1}H NMR (400 MHz, CD_2Cl_2, δ): 8.88-8.86 (d, J = 8 Hz 1H, Ar-H), 8.77-8.75 (d, J = 8 Hz, 1H, Ar-H), 8.72-8.70 (d, J = 8 Hz, 1H, Ar-H), 7.77-7.74 (m, 3H, Ar-H), 7.66-7.60 (m, 6H, Ar-H), 7.53-7.51 (m, 3H, Ar-H), 7.28-7.24 (m, 2H, Ar-H), 1.36 (s,12H, -CH_3). ^{13}C NMR (100 MHz, CD_2Cl_2, δ): 150.94, 139.08, 137.77, 134.69, 133.48, 130.51, 130.20, 129.48, 129.45, 128.85, 128.72, 128.56, 127.67, 127.66, 126.70, 125.95, 125.33, 124.40, 123.56, 123.41, 122.88, 121.29, 84.32, 25.08. MS (ESI), m/z: 496.12, calcd for $C_{33}H_{29}BN_2O_2$: 496.23. HRMS (ESI), m/z: [M^+] 497.2383, calcd for $C_{33}H_{29}BN_2O_2$: 497.2401. Elemental analyses for $C_{33}H_{29}BN_2O_2$: C, 79.84; H, 5.89; N, 5.64. Found: C, 79.70; H, 6.04; N, 5.86. [CCDC 1948485]

3. Figures and Tables

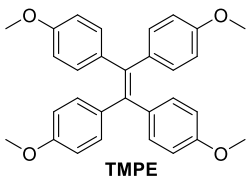


P_4TA

Chem. Sci., 2015, **6**, 3236-3241

SC_g: λ_{em} = 498 nm, PLQY = 52%, λ_{ML} = 517 nm
P2(1), Monoclinic, Noncentrosymmetric

SC_b: λ_{em} = 476 nm, PLQY = 36%
P2(1), Monoclinic, Noncentrosymmetric

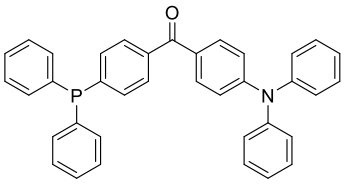


TMPE

Mater. Horiz., 2016, **3**, 220-225

C_p: λ_{em} = 429 nm, PLQY = 69.9%, λ_{ML} = 460 nm
P21(c), Monoclinic, Centrosymmetric

C_c: λ_{em} = 420 nm, PLQY = 67.4%
C2, Monoclinic, Noncentrosymmetric

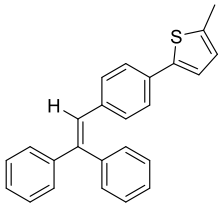


CDpP

Chem. Sci., 2018, **9**, 5787-5794

CDpP-B: λ_{em} = 473 nm, PLQY = 31%, λ_{ML} = 473 nm
P21/n, Monoclinic, Centrosymmetric

CDpP-G: λ_{em} = 504 nm, PLQY = 26%, λ_{ML} = 504 nm
Cc, Monoclinic, Noncentrosymmetric



tPE-5-MeTh

Mater. Chem. Front., 2019,**3**, 32-38

P1: λ_{em} = 440 nm, PLQY = 33.3%, λ_{ML} = 453 nm
P1, Triclinic, Noncentrosymmetric

P2: λ_{em} = 473 nm, PLQY = 25.5%,
P212121, Orthorhombic, Centrosymmetric

Chart S1. Molecular structures of previously reported ML-active polymorphs.

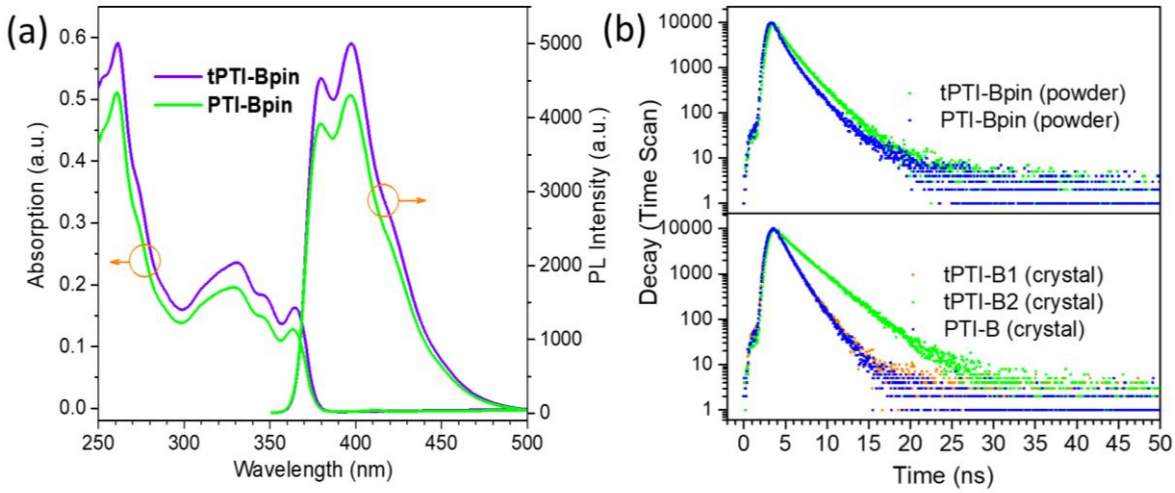


Fig. S1 (a) UV and PL spectra of tPTI-Bpin and PTI-Bpin in THF solution. (c = 10^{-5} M) (b) Fluorescence decay of tPTI-Bpin and PTI-Bpin in different states.

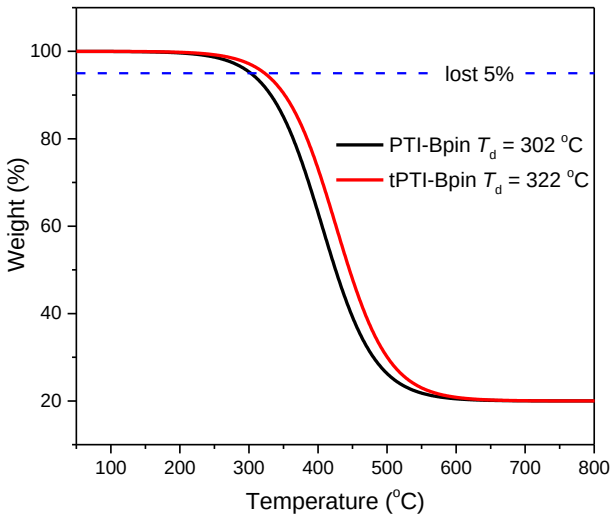


Fig. S2 The TGA (Thermogravimetric Analysis) curves of PTI-Bpin and tPTI-Bpin.

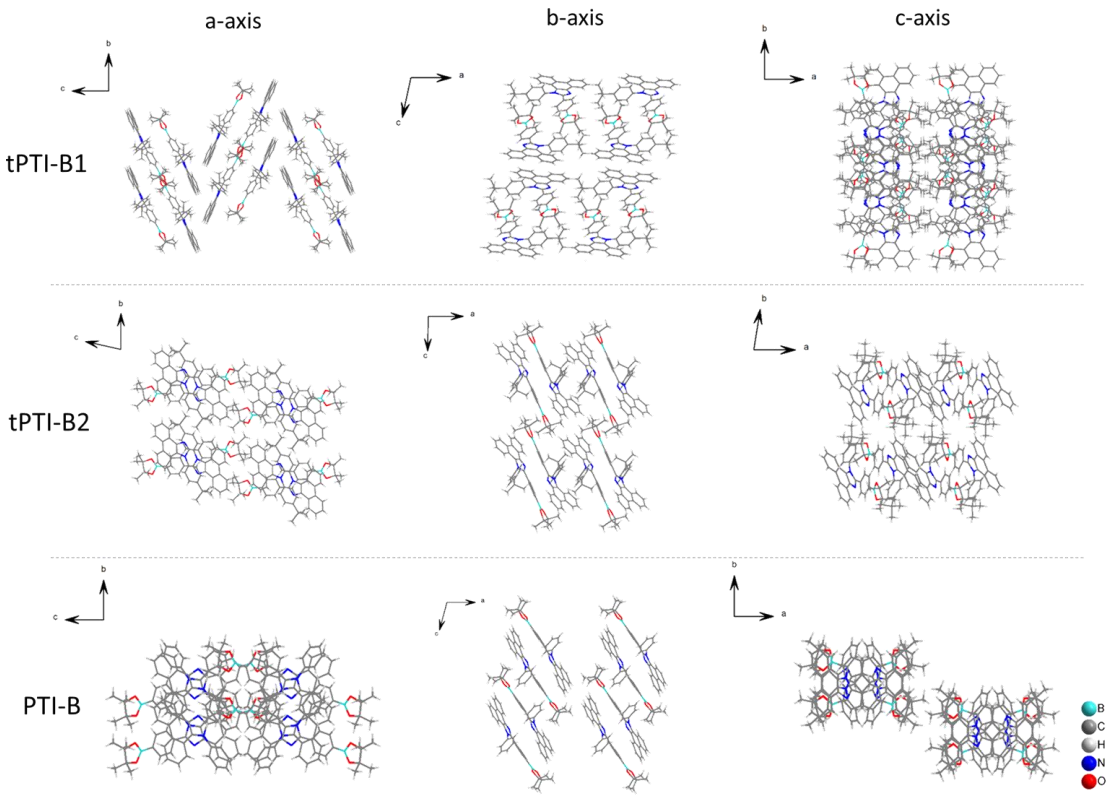


Fig. S3 Crystal molecular packing of tPTI-B1, tPTI-B2 and PTI-B.

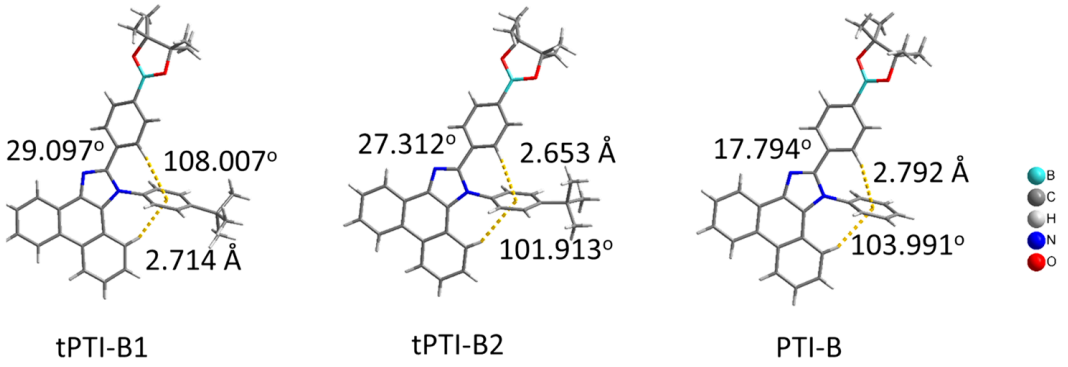


Fig. S4 Single molecule conformations of tPTI-B1, tPTI-B2 and PTI-B in the crystals.

Table S1. Summarization of the torsion angles and intramolecular interactions in single molecules of tPTI-B1, tPTI-B2 and PTI-B.

	Torsion angle 1	Torsion angle 2	C-H...π interaction 1	C-H...π interaction 2
tPTI-B1	29.097°	108.007°	3.042 Å	2.714 Å
tPTI-B2	27.312 °	101.913°	2.653 Å	3.105 Å
PTI-B	17.794 °	103.991°	2.792 Å	2.863 Å

Table S2. Summarization of intermolecular interactions in different molecular dimers derived from the unit cell of tPTI-B1.

Dimer-1	Orientation of Interaction		d /Å [a]	Number(4)
	1	C-H…π	3.593	2
	2	C-H…π	3.633	2
	Orientation of Interaction		d /Å [a]	Number(8)
	1	C-H…O	2.663	2
	2	C-H…O	3.029	2
	3	C-H…O	3.709	2
	4	C-H…O	3.987	2
Dimer -2	Orientation of Interaction		d /Å [a]	Number(7)
	1	C-H…π	2.693	1
	2	C-H…π	3.312	1
	3	C-H…π	3.420	1
	4	C-H…π	3.425	1
	5	C-H…π	3.533	1
	6	C-H…π	3.780	1
	7	C-H…π	3.971	1
	Orientation of Interaction		d /Å [a]	Number(7)
	1	C-H…N	2.746	1
	2	C-H…N	2.916	1
	3	C-H…N	2.979	1
	4	C-H…N	3.543	1
	5	C-H…N	3.594	1
	6	C-H…N	3.623	1
	7	C-H…N	3.975	1
Dimer -3	Orientation of Interaction		d /Å [a]	Number(11)
	1	C-H…π	3.136	1
	2	C-H…π	3.300	1
	3	C-H…π	3.394	1
	4	C-H…π	3.404	1
	5	C-H…π	3.445	1
	6	C-H…π	3.502	1
	7	C-H…π	3.525	1
	8	C-H…π	3.539	1
	9	C-H…π	3.802	1
	10	C-H…π	3.839	1
	11	C-H…π	3.932	1
	Orientation of Interaction		d /Å [a]	Number(4)
	1	C-H…N	3.207	1
	2	C-H…N	3.451	1
	3	C-H…N	3.818	1
	4	C-H…N	3.900	1

Table S3. Summarization of intermolecular interactions in different molecular dimers derived from the unit cell of tPTI-B2.

Dimer-1	Orientation of Interaction		d /Å [a]	Number(16)
	1	C-H…π	2.686	1
	2	C-H…π	2.699	1
	3	C-H…π	2.998	2
	4	C-H…π	3.284	2
	5	C-H…π	3.510	2
	6	C-H…π	3.770	2
	7	C-H…π	3.863	1
	8	C-H…π	3.879	1
	9	C-H…π	3.903	2
	10	C-H…π	3.996	2
	Orientation of Interaction		d /Å [a]	Number(10)
	1	C-H…N	3.326	2
	2	C-H…N	3.417	2
	3	C-H…N	3.560	2
	4	C-H…N	3.649	2
	5	C-H…N	3.692	2
Dimer-2	Orientation of Interaction		d /Å [a]	Number(18)
	1	C-H…π	2.925	1
	2	C-H…π	2.944	1
	3	C-H…π	3.157	2
	4	C-H…π	3.175	2
	5	C-H…π	3.228	1
	6	C-H…π	3.264	1
	7	C-H…π	3.311	2
	8	C-H…π	3.441	2
	9	C-H…π	3.656	2
	10	C-H…π	3.822	2
	11	C-H…π	3.953	2
	Orientation of Interaction		d /Å [a]	Number(2)
	1	C-H…N	3.359	2

Table S4. Summarization of intermolecular interactions in different molecular dimers derived from the unit cell of PTI-B.

Dimer-1	Orientation of Interaction		d /Å [a]	Number(2)
	1	π…π	3.793	2
	Orientation of Interaction		d /Å [a]	Number(12)
	1	C-H…π	3.206	2
	2	C-H…π	3.434	2
	3	C-H…π	3.504	2
	4	C-H…π	3.576	2
	5	C-H…π	3.703	2
	6	C-H…π	3.817	2
	Orientation of Interaction		d /Å [a]	Number(4)
	1	C-H…O	3.190	2
	2	C-H…O	3.253	2
	Orientation of Interaction		d /Å [a]	Number(4)
	1	C-H…N	2.556	2
	2	C-H…N	3.722	2
Dimer-2	Orientation of Interaction		d /Å [a]	Number(6)
	1	C-H…π	3.285	2
	2	C-H…π	3.691	2
	3	C-H…π	3.704	2
	Orientation of Interaction		d /Å [a]	Number(4)
	1	C-H…O	3.012	2
	2	C-H…O	3.709	2
	Orientation of Interaction		d /Å [a]	Number(8)
	1	C-H…N	2.750	2
	2	C-H…N	3.070	2
	3	C-H…N	3.093	2
	4	C-H…N	3.615	2

Table S5. Structure data of crystals tPTI-B1, tPTI-B2 and PTI-B.

Name	tPTI-B1	tPTI-B2	PTI-B
Empirical formula	$C_{37}H_{37}BN_2O_2$	$C_{37}H_{37}BN_2O_2$	$C_{33}H_{29}BN_2O_2$
Wavelength (Å)	0.71073	0.71073	1.54184
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$ (14)	P-1 (2)	$C2/c$ (15)
Unit cell angles (°)	α = 90 β = 102.12(1) γ = 90	α = 77.44(0) β = 89.44(0) γ = 80.78(0)	α = 90 β = 104.84(0) γ = 90
Unit cell length (Å)	a = 12.265(4) b = 9.760(3) c = 26.828(9)	a = 10.253(19) b = 10.807(2) c = 14.406(3)	a = 28.078(7) b = 9.992(2) c = 20.671(4)
Unit cell volume ($Å^3$)	3139.91(441)	1537.39(141)	5606.41(298)
Z	4	2	8
Density (g/cm^3)	1.168	1.193	1.214
F(000)	1176.0	588.0	2160.0
CCDC number	1948492	1948484	1948485

4. Structure Information

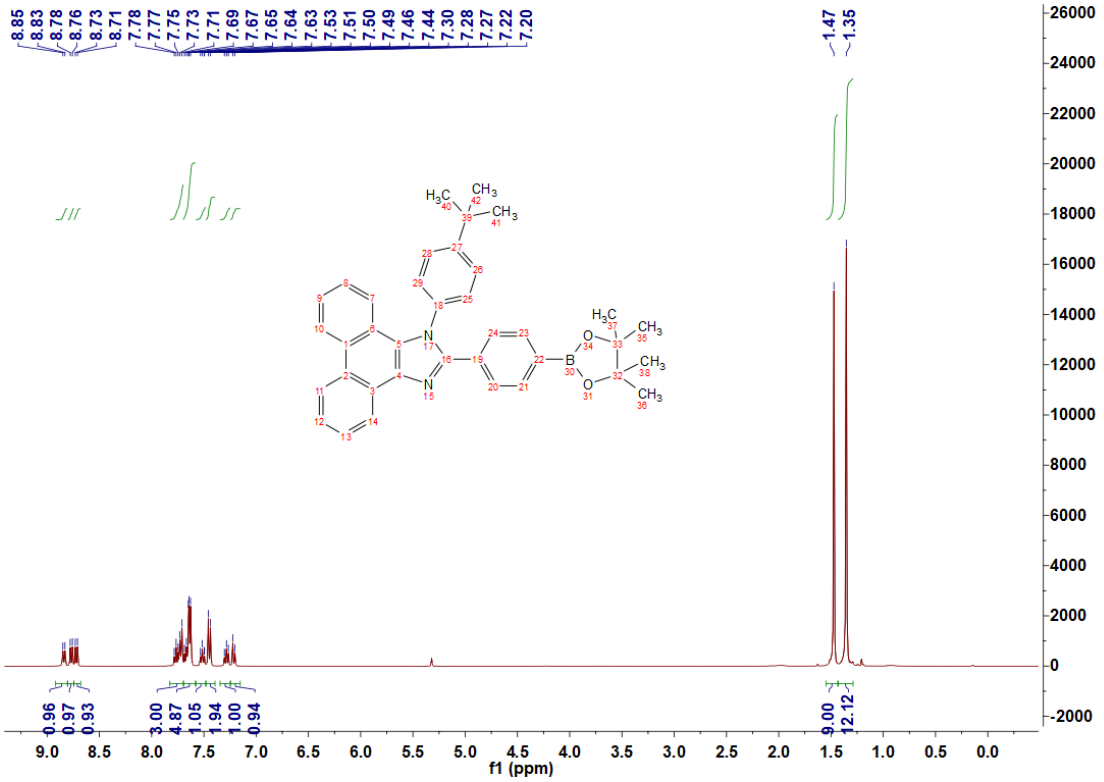


Fig. S5 ^{1}H NMR spectrum of tPTI-Bpin conducted in CD_2Cl_2.

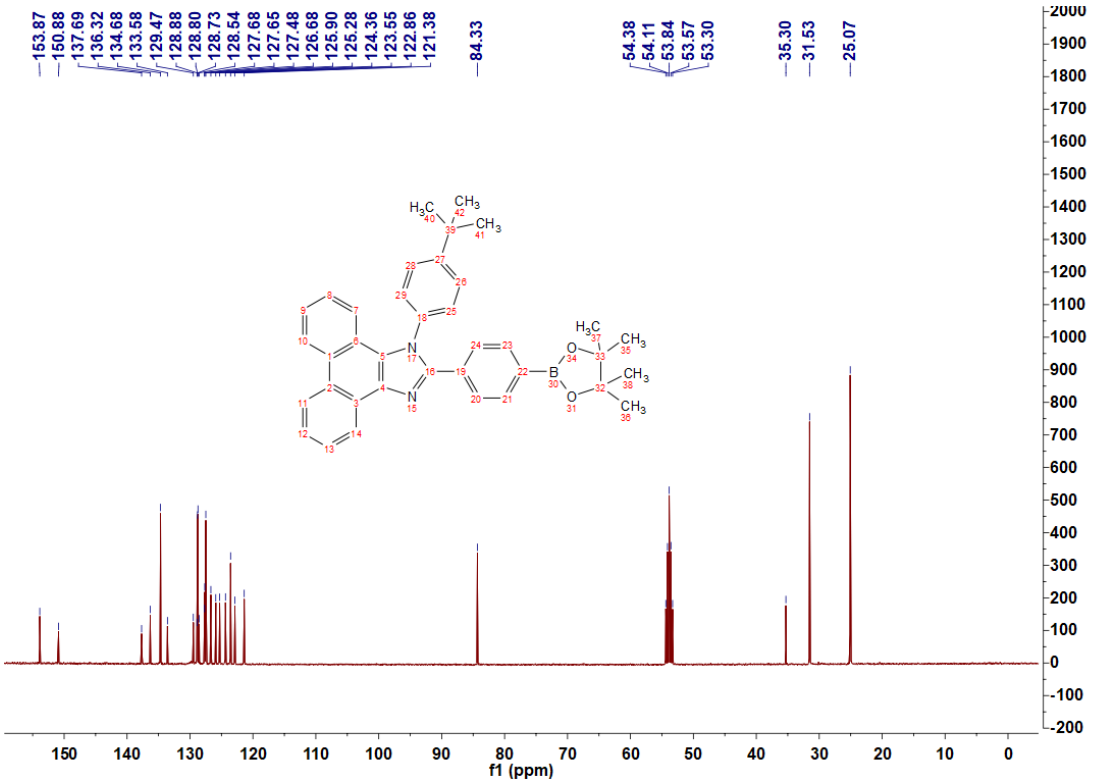


Fig. S6 ^{13}C NMR spectrum of tPTI-Bpin conducted in CD_2Cl_2.

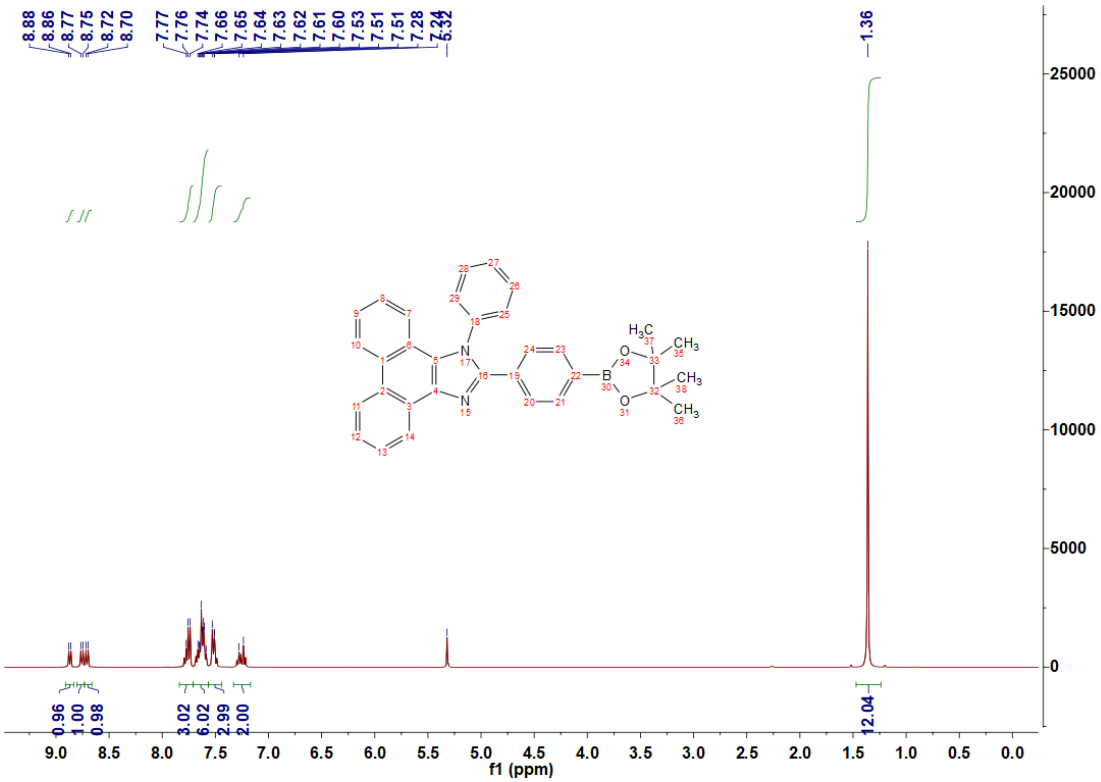


Fig. S7 ^{1}H NMR spectrum of PTI-Bpin conducted in CD_2Cl_2.

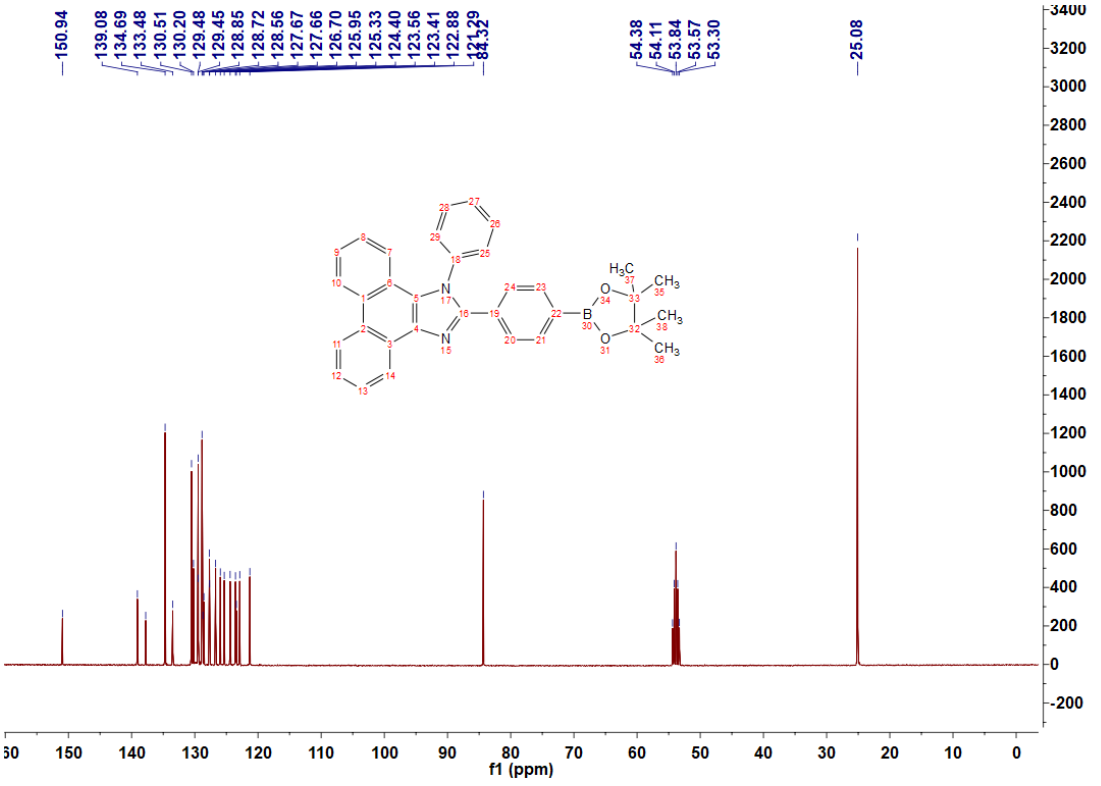


Fig. S8 ^{13}C NMR spectrum of tPTI-Bpin conducted in CD_2Cl_2.

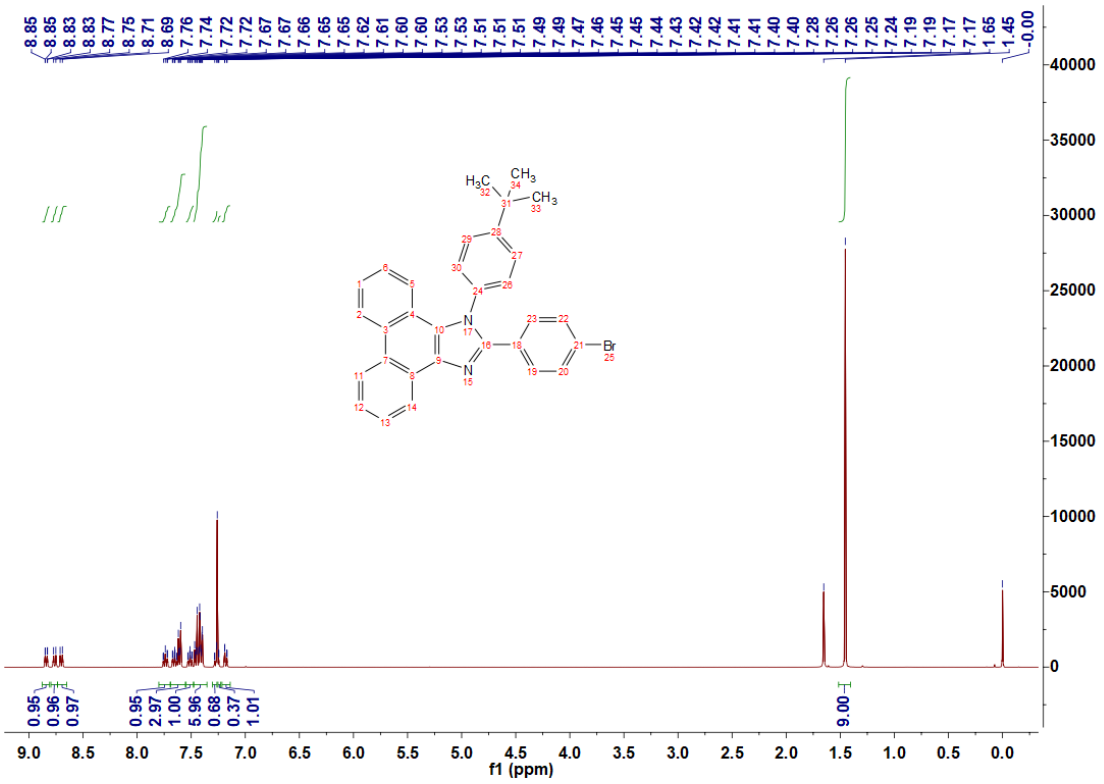


Fig. S9 ^{1}H NMR spectrum of tPTI-Br conducted in $CDCl_3$.

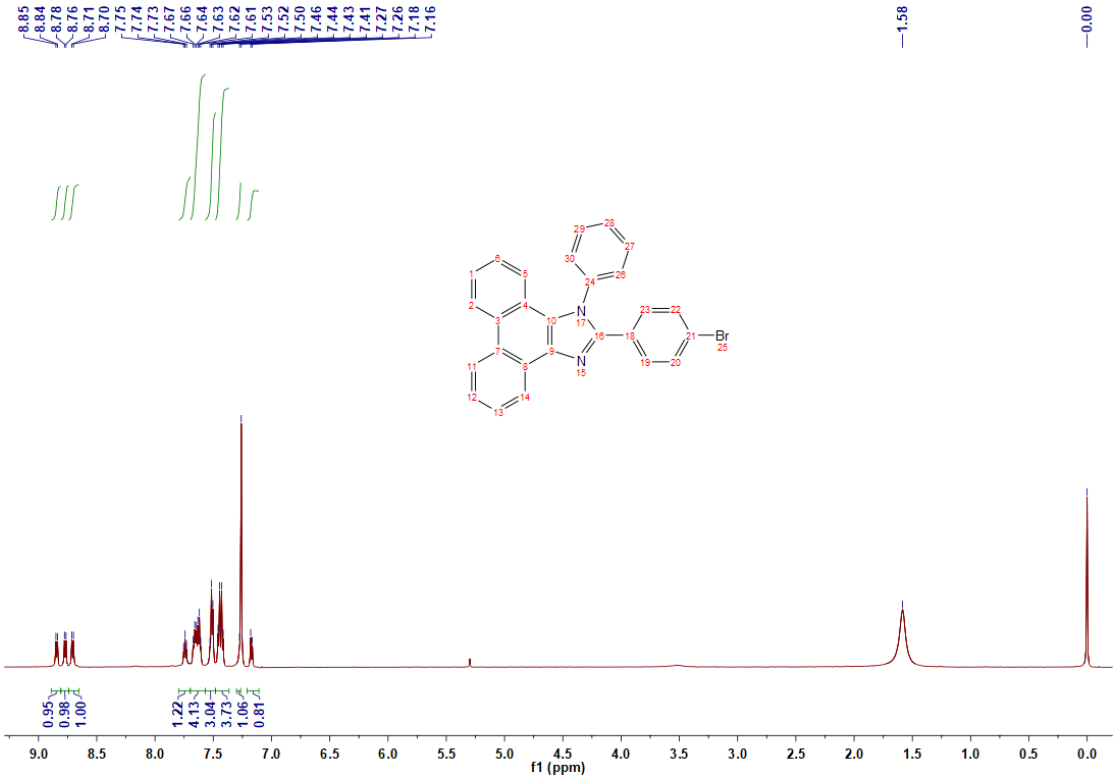


Fig. S10 ^{1}H NMR spectrum of PTI-Br conducted in $CDCl_3$.

Compound Spectrum SmartFormula Report

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Comment			

Acquisition Parameter

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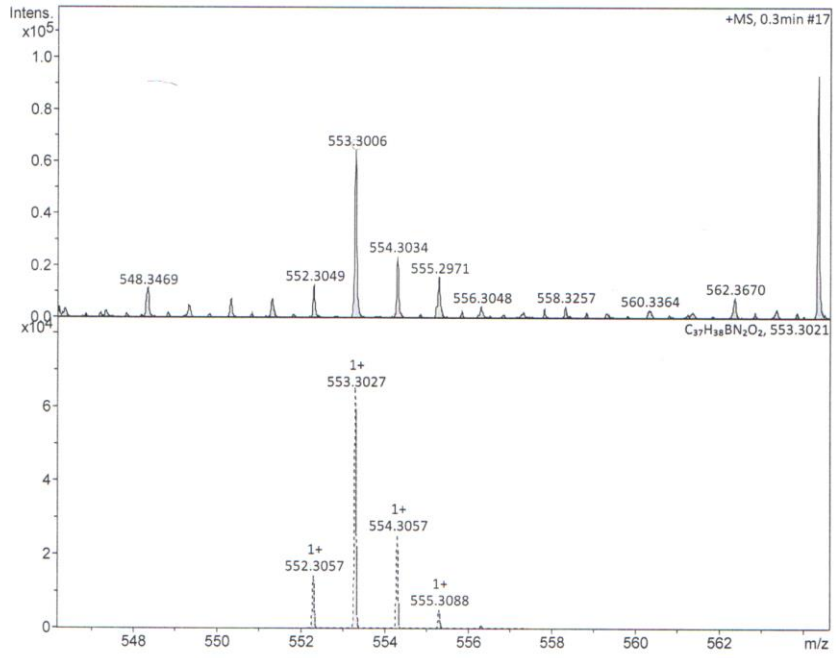

Meas. m/z	#	Ion Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule	Adduct
553.300649	1	C37H38BN2O2	100.00	553.302085	2.1	3.8	78.2	20.5	even	ok	M+H

YY-1_RA1_01_19900.d

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Fig. S11 HRMS spectrum of tPTI-Bpin.

Compound Spectrum SmartFormula Report

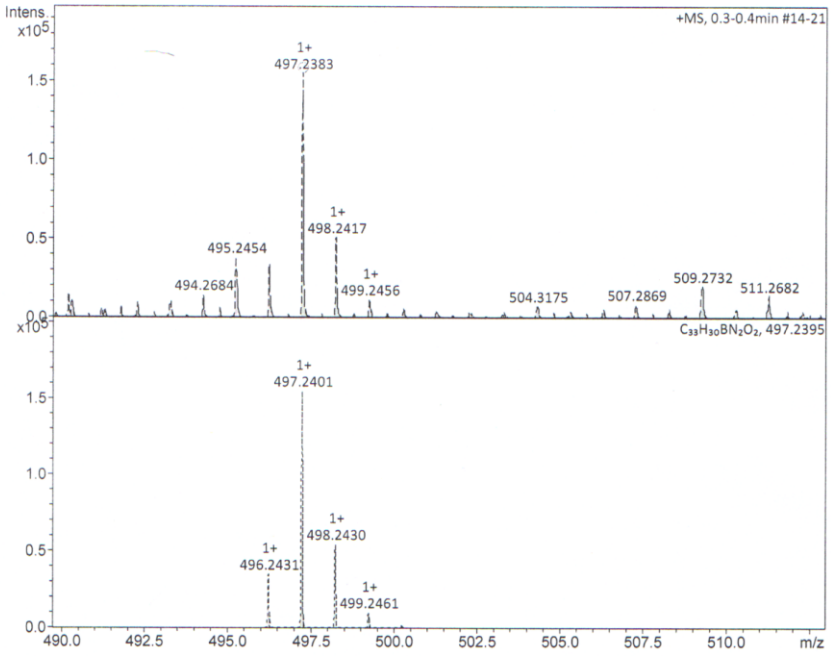
Analysis Info

Analysis Name	D:\Data\other groups\lizhen\YY-2_RA2_01_19901.d	Acquisition Date	10/5/2019 3:34:27 PM
Method	MS_no column_pos_std.m	Operator	BDAL@DE
Sample Name	YY-2	Instrument	compact 8255754.20129
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	8.0 l/min
Scan End	1500 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C

+MS, 0.3-0.4min #14-21



Meas. m/z	#	Ion Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule	Adduct
497.238275	1	C33H30BN2O2	100.00	497.239485	1.8	3.6	12.6	20.5	even	ok	M+H

YY-2_RA2_01_19901.d
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Fig. S12 HRMS spectrum of PTI-Bpin.