Supporting Information

Novel phosphorescent triptycene-based Ir(III) complexes for organic light-emitting diodes

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1. General descriptions

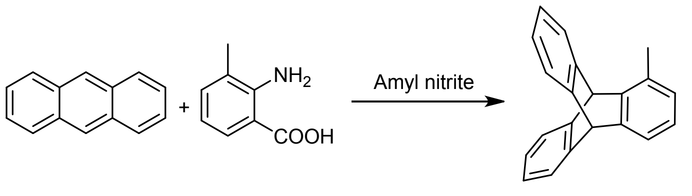
1.1. General methods and requirements

Unless otherwise indicated, all reagents with commercial availability were used without purification. An Aglilent 6460 mass spectrometer was used to record ESI mass spectra. A Bruker AV400 spectrometer was employed to measure NMR spectra. X-ray crystallography diffraction data were acquired by the ω scan mode of a Bruker SMART Apex CCD diffractometer with Mo$K\alpha$ radiation at 296 K. Thermogravimetric analysis (TGA) was carried out on a Shimadzu DTG-60H thermogravimetric analyses under nitrogen flux at a heating rate of 10 ^{o}C min^{-1}. A Purkinje General TU-1901 spectrophotometer recorded UV/Vis absorption spectra, and a PerkinElmer LS-55 fluorescence spectrophotometer was used to measure photoluminescence (PL) spectra. An Edinburgh FL920 time-correlated pulsed single-photon-counting instrument was employed to determine quantum efficiency and luminescence lifetime. Cyclic voltammetry (CV) were investigated on a CHI1140B Electrochemical Analyzer in a three-electrode configuration with a glassy carbon disk as the working electrode, platinum wire as the counter electrode, and Ag/AgCl reference electrode with 0.1 M tetrabutylammonium hexafluorophosphate as the electrolyte.

1.2. OLED fabrication and measurement

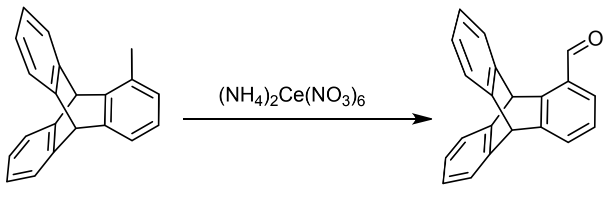
In a general procedure, indium tin oxide (ITO)-coated glass substrates were etched, patterned, and washed with detergent, deionized water, acetone, and ethanol in turn. For vacuum-deposited OLEDs, the ITO substrate was loaded in a deposition chamber and conducted with the treatment of ultraviolet ozone. Vacuum chambers were employed to deposit metal layer and organic layer, and the base pressure was higher than 8×10^{-5} Pa. For spin-coating OLEDs, PEDOT:PSS was spin-coated to smooth the ITO surface and to promote hole injection, and then the emissive layer was spin-coated from a chlorobenzene solution, on which an electron-transporting/hole-blocking layer and metal layer were deposited in a vacuum chamber at a pressure of 8 × 10^{-5} Pa. EL spectra were collected on a Spectra Scan PR655 photometer. Current density–voltage–luminance (J-V-L) measurements were recorded simultaneously using a Keithley 4200 semiconductor parameter analyzer coupled with a Newport Multi-Function 2835-C optical meter, which measured luminance in the forward direction. All device characterizations were carried out under ambient laboratory conditions at room temperature without encapsulation.

1.3. Preparation and structure determination of intermediates



1-methyltriptycene

Under N_2, a solution of 3-methylanthranilic acid (7.0 g, 46.4 mmol) in THF (50 mL) and a solution of amyl nitrite (12 mL, 89.1 mmol) in dichloroethane (30 mL) were concurrently added during 4 h to a refluxing mixture of anthracene (4.1 g, 23.0 mmol) in dichloroethane (50 mL). The resulting mixture was refluxed for 6 h. Then the solvents were removed by distillation and replaced by toluene (20 mL). Maleic anhydride (5.0 g) was added and the mixture solution refluxed 15 min. Then EtOAc (20 mL) was added and followed by a 10% aqueous Na_2CO_3 (40 mL). The mixture was extracted by EtOAc (3 × 20 mL). The combined organic extracts were washed with brine (50 mL), dried over Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/dichloromethane (3:1, v:v) as the eluent to afford the white 1-methyltriptycene in 64% yield (3.9 g). ^1H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H), 5.33 (s, 1H), 5.58 (s, 1H), 6.74-6.82 (m, 2H), 6.86-6.95 (m, 4H), 7.16 (d, J = 7.2 Hz, 1H), 7.27-7.33 (m, 4H). HRMS ((+)-ESI): m/z = 269.1317 (calcd. 269.1252 for $[C_{21}H_{16}]$ $[M+H]^+$).



1-formyltriptycene

To a 100 °C mixture of 1-methyltriptycene (2.7 g, 10.0 mmol) and of HOAc (5 mL) was added a solution of $(NH_4)_2Ce(NO_3)_6$ (27.4 g, 50.0 mmol) in 80 mL of 50% aqueous HOAc over a 2-h period. The mixture was stirred 15 min, cooled, poured onto ice and extracted with EtOAc (3 × 20 mL). The combined organic extracts were washed with brine (50 mL), dried over Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/dichloromethane (1:1, v:v) as the eluent to afford the light yellow solid of 1-formyltriptycene in 70% yield (1.9 g). ^1H NMR (400 MHz, $CDCl_3$) δ: 5.54 (s, 1H), 6.90 (s, 1H), 7.03-7.07 (m, 4H), 7.19 (t, J = 7. 6 Hz, 1H), 7.42-7.46 (m, 3H), 7.49-7.53 (m, 2H), 7.63 (d, J = 6.4 Hz, 1H), 10.32 (s, 1H). HRMS ((+)-ESI): m/z = 305.1118 (calcd. 305.0942 for $[C_{21}H_{14}ONa]$ $[M+Na]^+$).

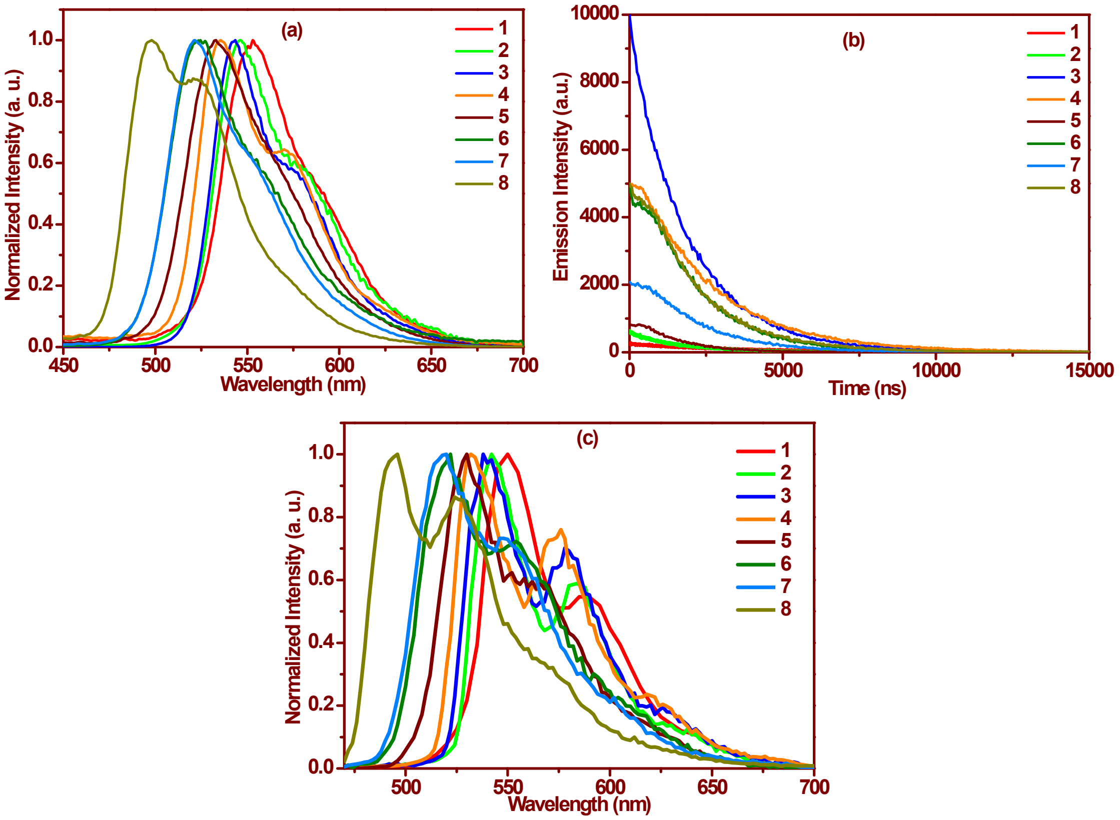
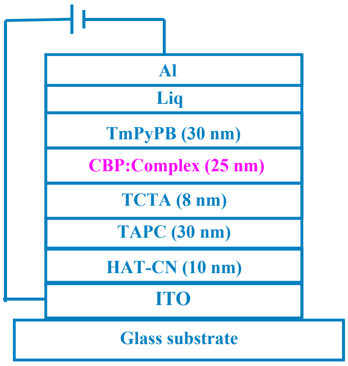
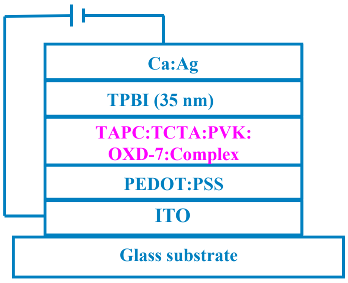


Fig. S1 The PL spectra ((a), r.t.; (c), 77K) and emission decay curves ((b), r.t.) of complexes **1**-**8** in PMMA films at a conc. of 1 wt%.



Vacuum-deposited OLEDs structure



Spin-coating OLEDs structure

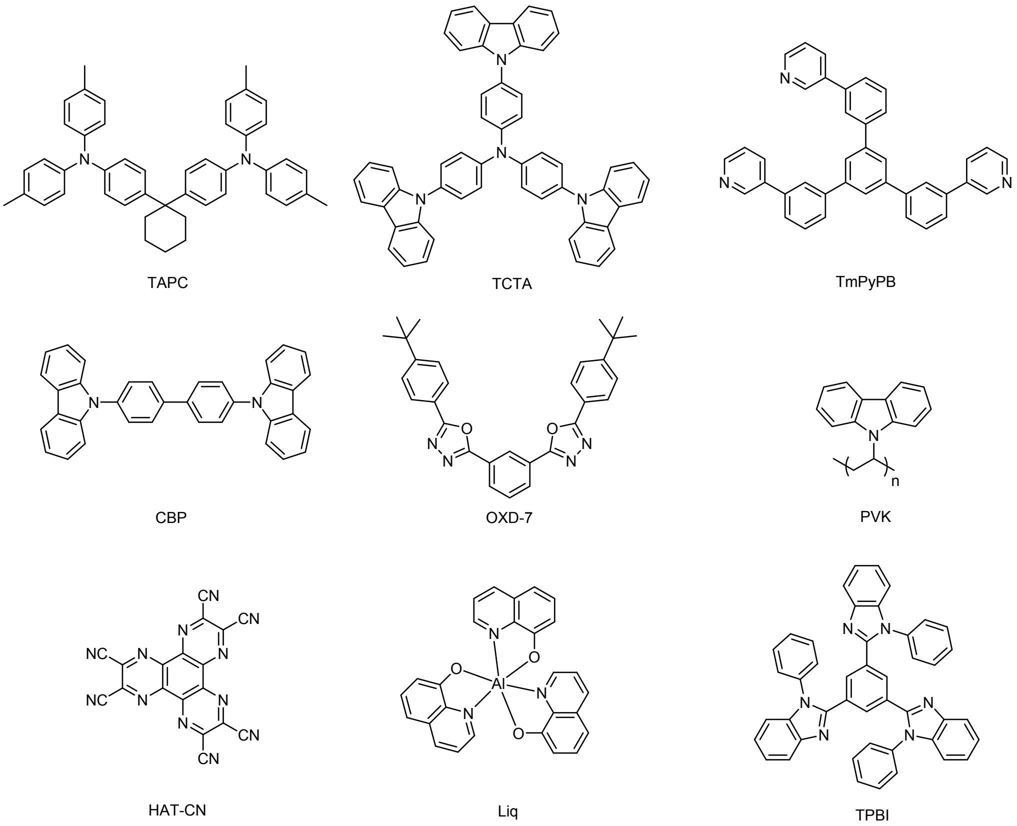


Fig. S2 The device configurations and chemical structures of the materials used.

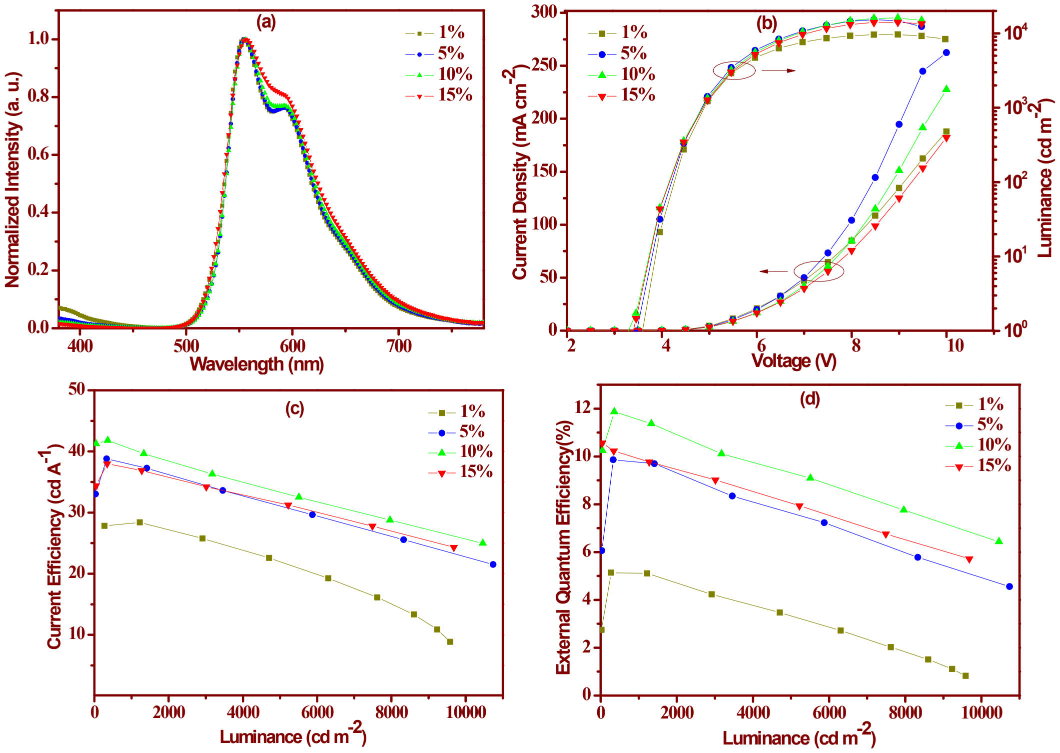


Fig. S3 (a) EL spectra at 7V. (b) Current density and luminance as a function of applied voltage. (c) Luminance efficiencies, and (d) EQE of devices based on complex **2**.

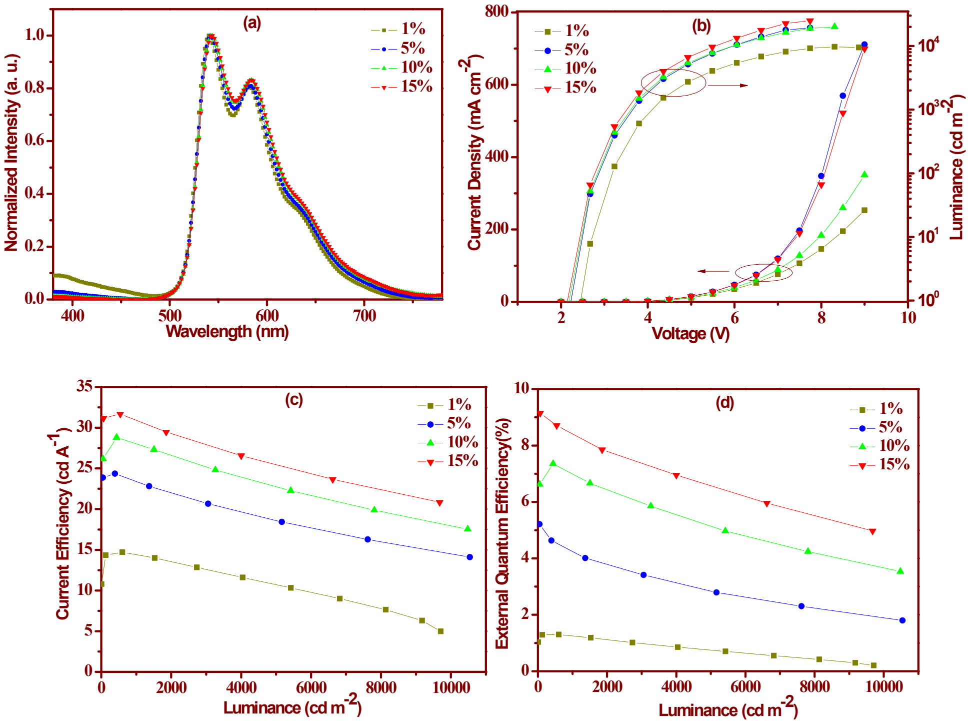


Fig. S4 (a) EL spectra at 7V. (b) Current density and luminance as a function of applied voltage. (c) Luminance efficiencies, and (d) EQE of devices based on complex **4**.

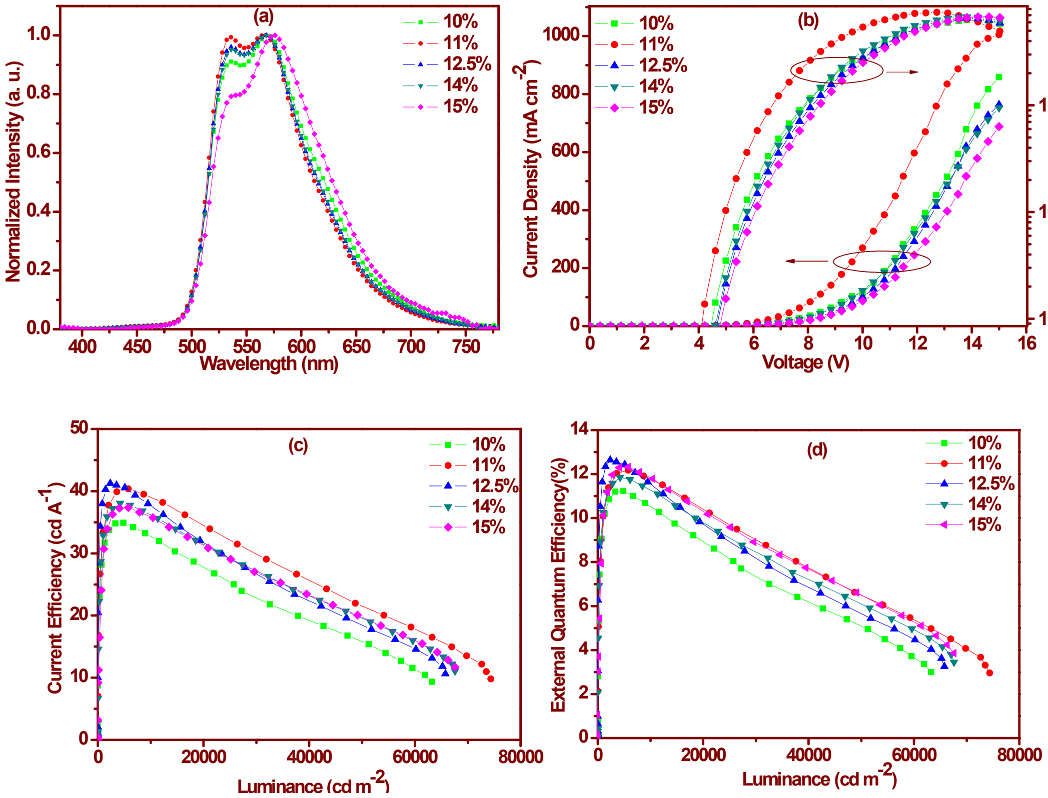


Fig. S5 (a) EL spectra at 7V. (b) Current density and luminance as a function of applied voltage. (c) Luminance efficiencies, and (d) EQE of devices based on complex **6**.

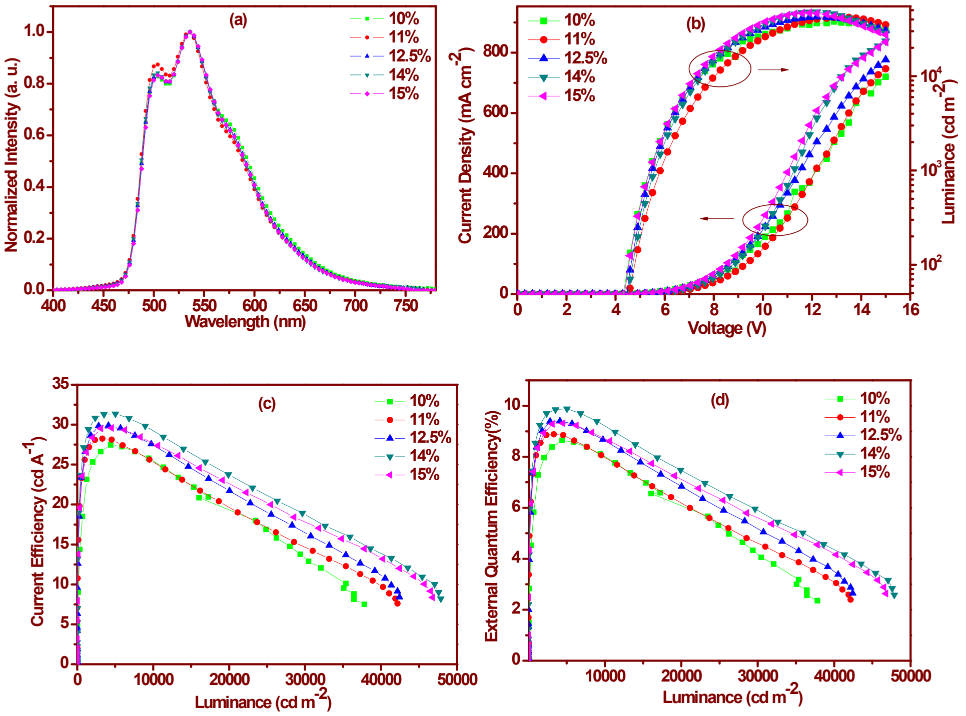


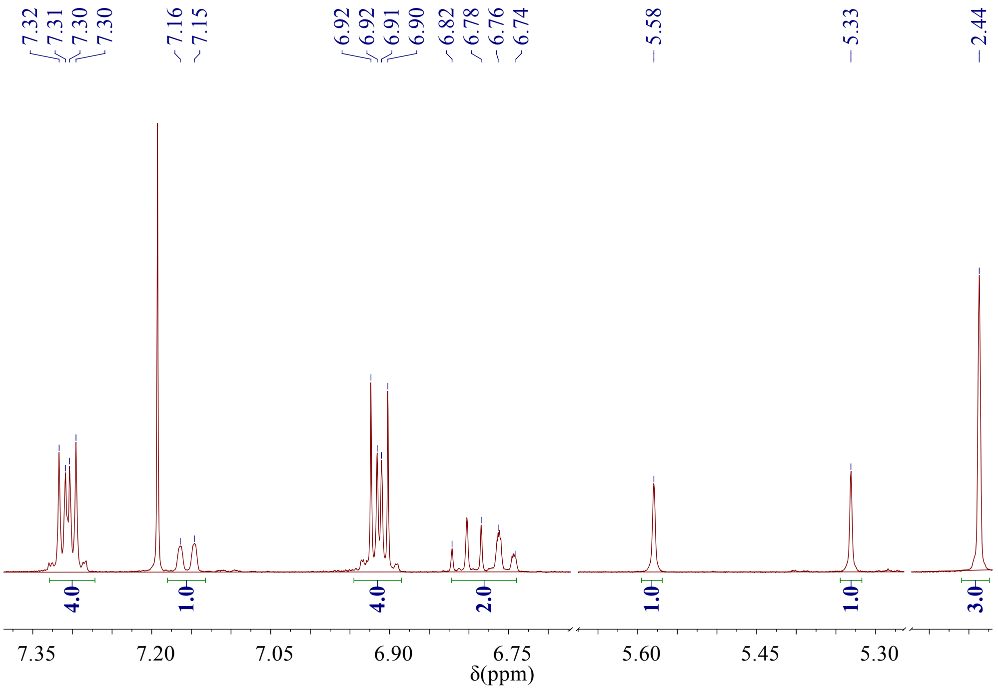
Fig. S6 (a) EL spectra at 7V. (b) Current density and luminance as a function of applied voltage. (c) Luminance efficiencies, and (d) EQE of devices based on complex **8**.

Table S1 Performance of the devices based on new complexes

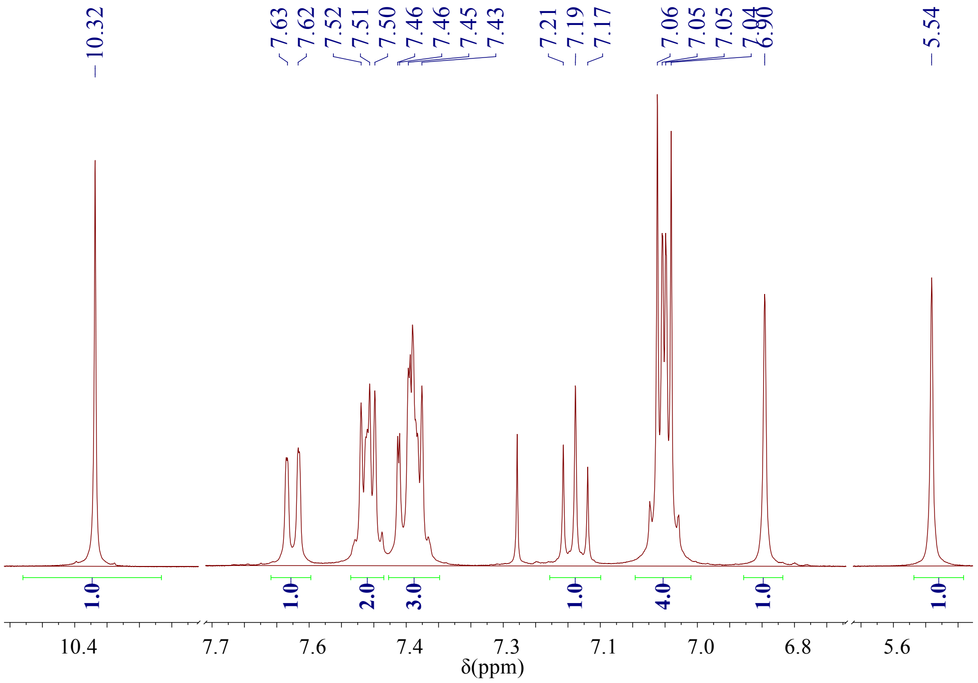
Device (dopant)	$\lambda_{EL,max}$ (nm)	V_{on} (V)	Brightness (cd m^{-2})	η_c (cd A^{-1})	η_{EQE} (%)	CIE$_{x,y}$ coordinates
2, 1%	554, 592 (s)	4.0	9616	25.7	5.1	0.47, 0.51
2, 5%	554, 592 (s)	4.0	15270	38.8	9.9	0.48, 0.51
2, 10%	556, 592 (s)	3.5	16070	41.7	11.9	0.48, 0.51
2, 15%	556, 592 (s)	3.5	14120	38.0	10.6	0.48, 0.51
4, 1%	540, 582 (s)	3.5	9710	14.7	1.3	0.43, 0.51
4, 5%	542, 582 (s)	3.5	19360	24.4	5.2	0.45, 0.52
4, 10%	542, 584 (s)	3.5	20030	28.8	7.3	0.46, 0.53
4, 15%	544, 584 (s)	3.5	25070	31.7	9.1	0.46, 0.53
6, 10%	536 (s), 568	3.9	63279	34.9	11.2	0.44, 0.54
6, 11%	536 (s), 568	3.5	74385	40.4	12.2	0.42, 0.55
6, 12.5%	536 (s), 568	3.9	65800	41.2	12.6	0.43, 0.55
6, 14%	536 (s), 568	3.9	67620	38.0	11.9	0.43, 0.55
6, 15%	536 (s), 576	3.9	67600	37.4	12.3	0.46, 0.52
8, 10%	504 (s), 536	3.7	37808	27.4	8.6	0.35, 0.56
8, 11%	504 (s), 536	4.0	42160	28.2	8.9	0.34, 0.57
8, 12.5%	504 (s), 536	3.7	42432	29.9	9.4	0.34, 0.57
8, 14%	504 (s), 536	4.0	47872	31.4	9.9	0.34, 0.57
8, 15%	504 (s), 536	4.0	46784	29.6	9.3	0.34, 0.57

^{1}H- and ^{19}F-NMR Spectra.

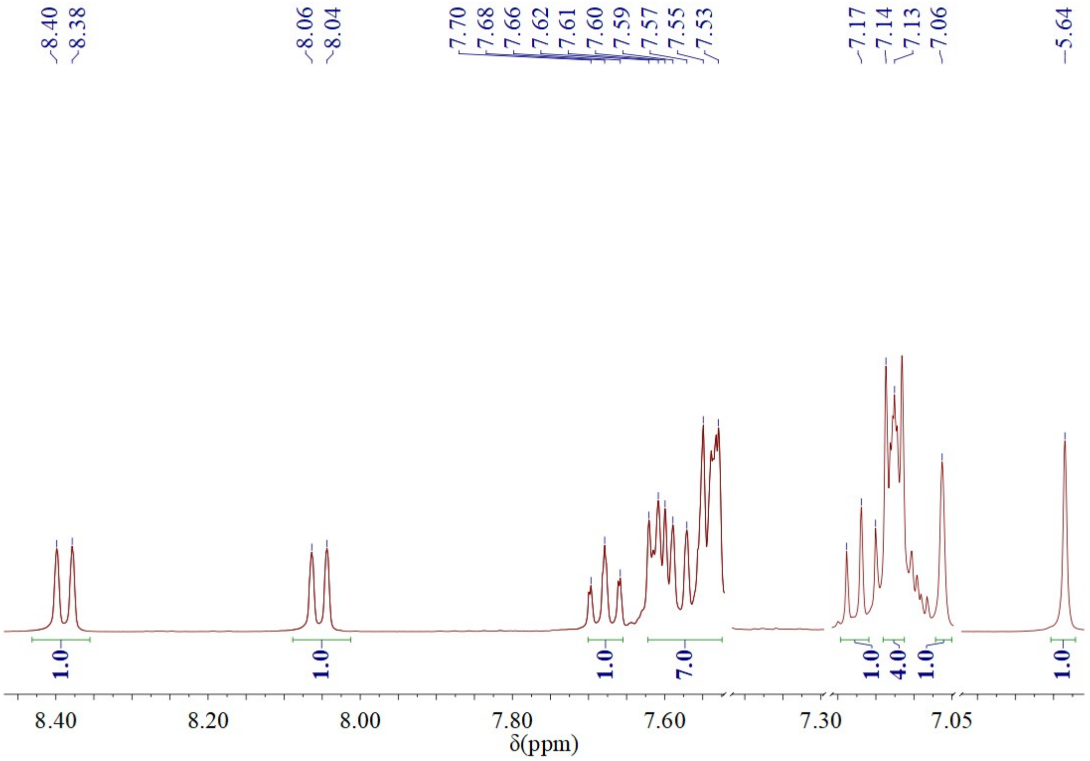
^{1}H-NMR Spectrum of **1-methyltriptycene** in C*D*Cl$_3$ (400 MHz):



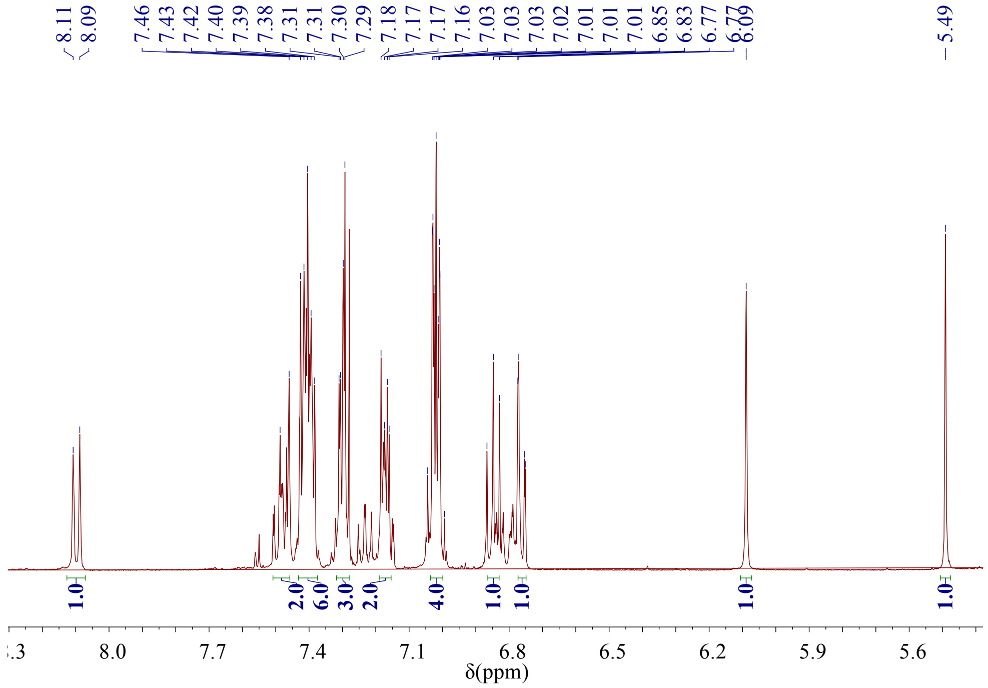
^{1}H-NMR Spectrum of **1-formyltriptycene** in C*D*Cl$_3$ (400 MHz):



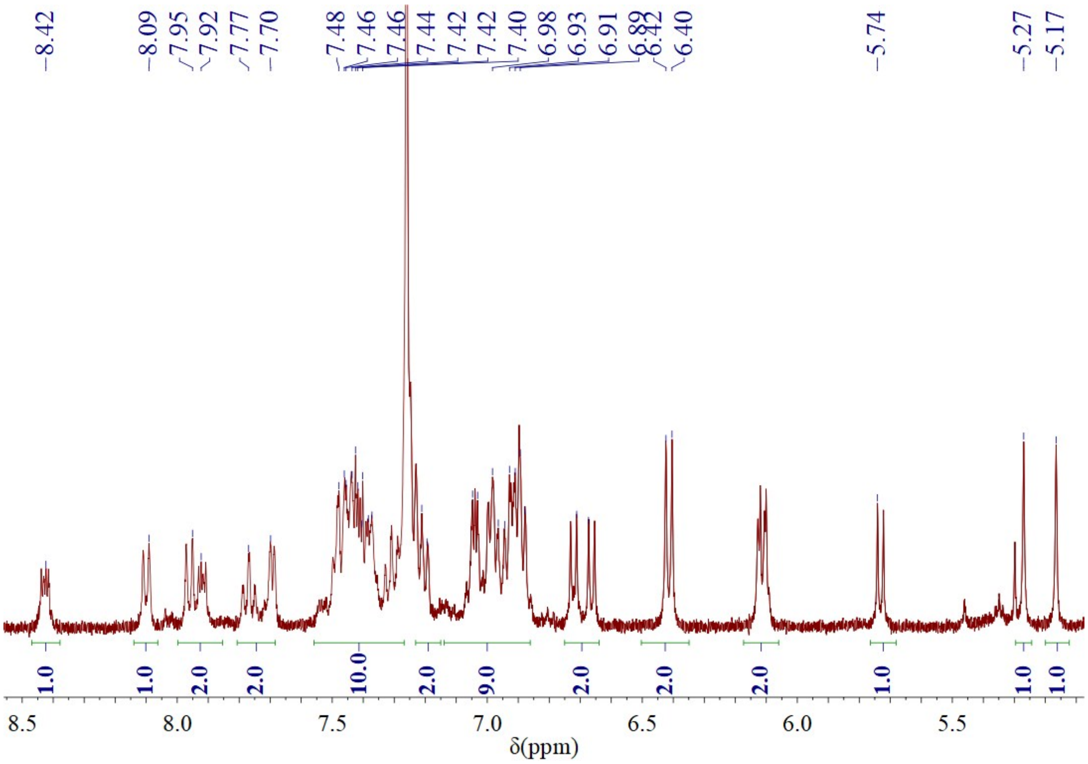
^{1}H-NMR Spectrum of **tbtH** in C*D*Cl$_3$ (400 MHz):



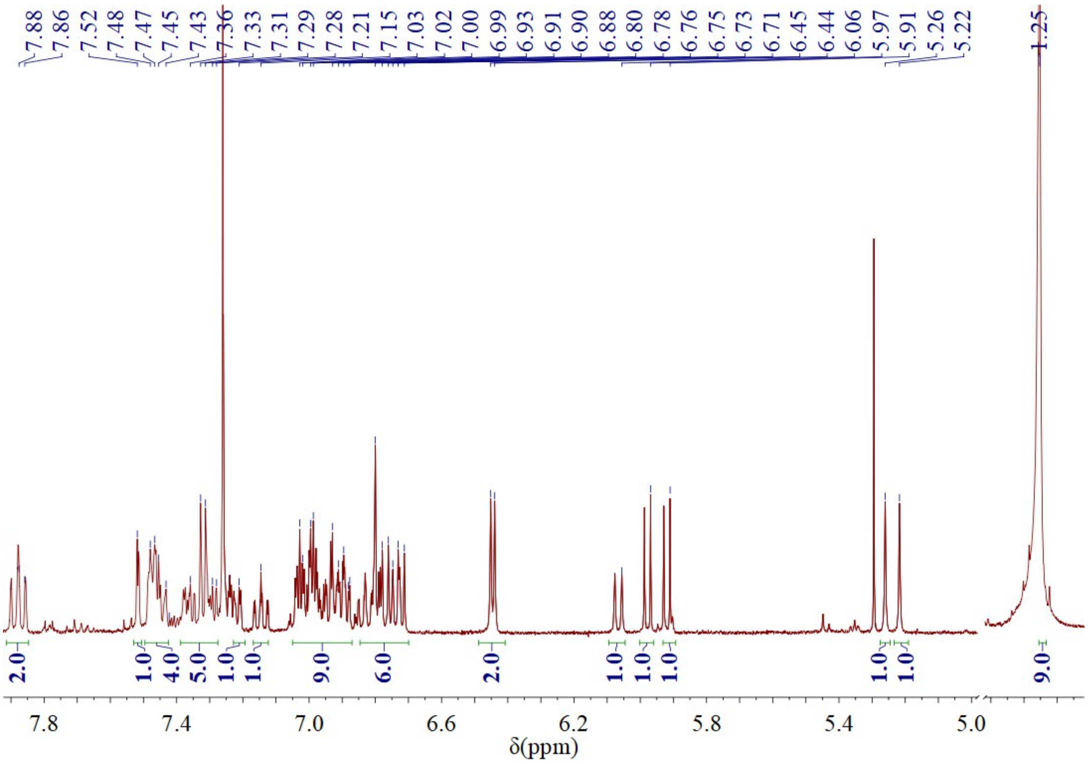
^{1}H-NMR Spectrum of **tpbiH** in C*D*Cl$_3$ (400 MHz):



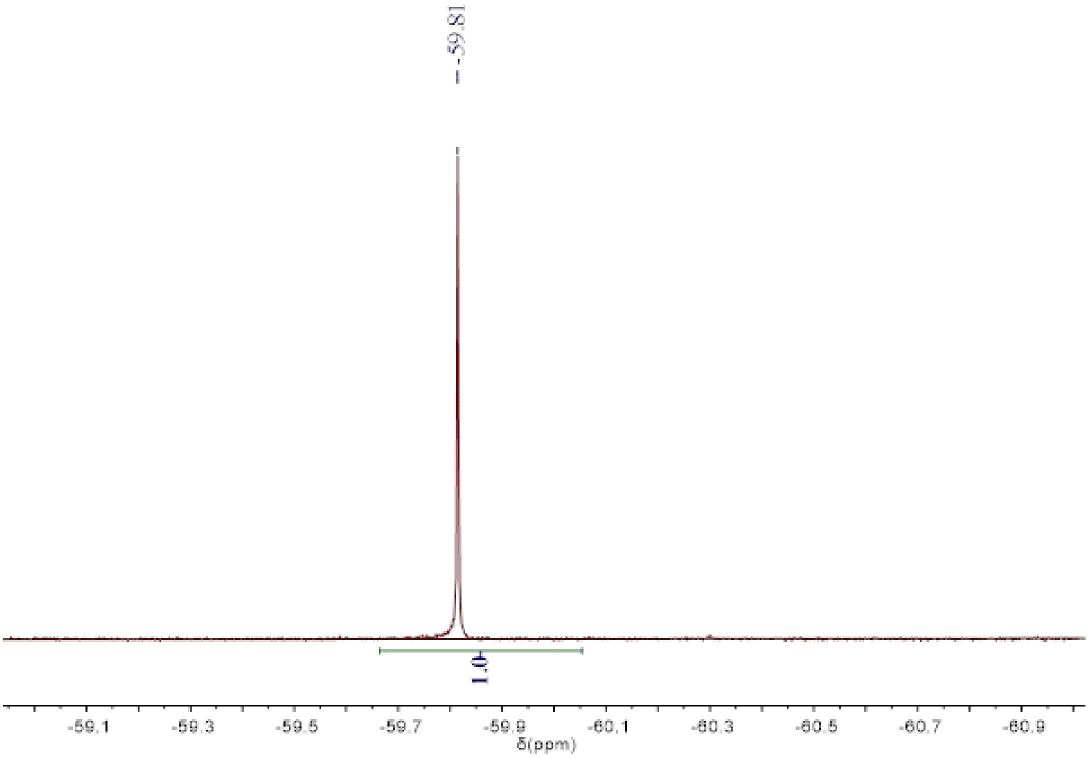
^{1}H-NMR Spectrum of **Ir(tbt)$_2$(pic) (1)** in C*D*Cl$_3$ (400 MHz):



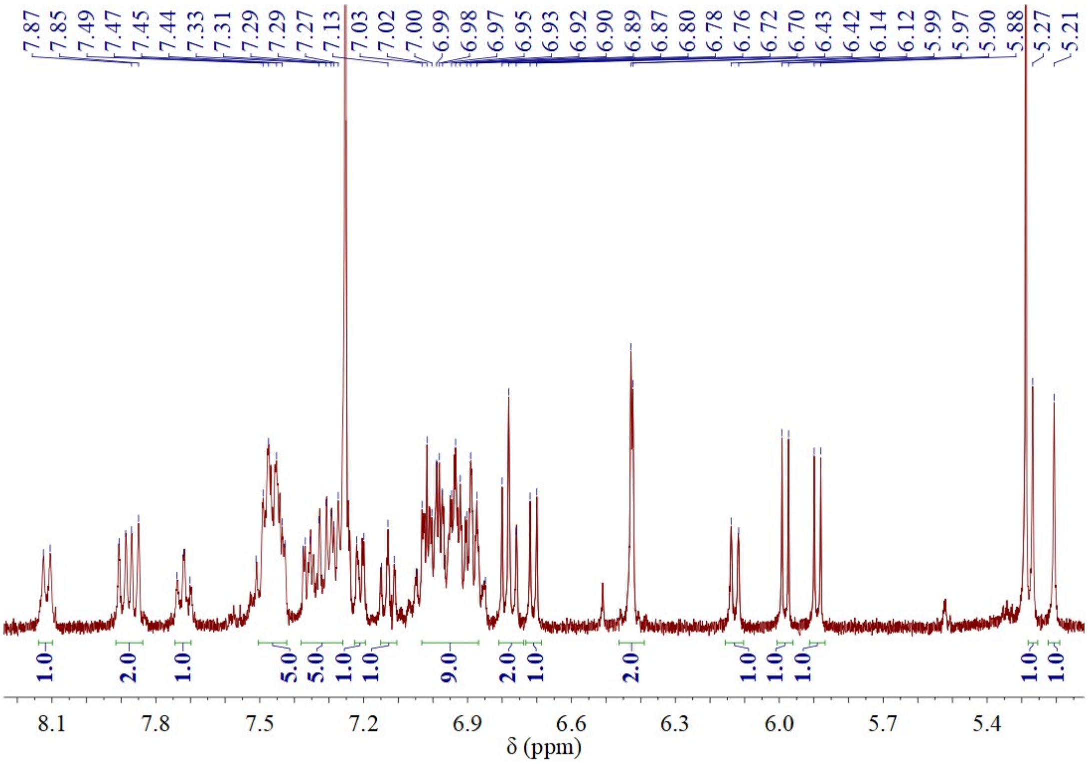
^{1}H-NMR Spectrum of **Ir(tbt)$_2$(bfppz) (2)** in C*D*Cl$_3$ (400 MHz):



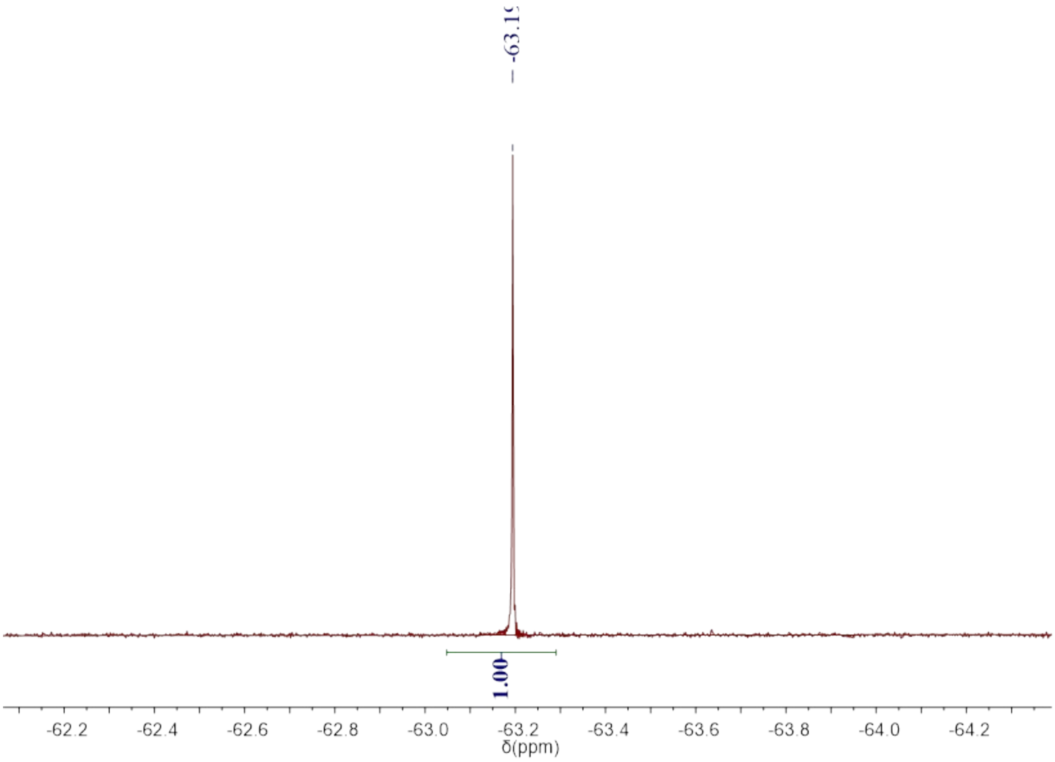
^{19}F-NMR Spectrum of **Ir(tbt)$_2$(bfppz) (2)** in C*D*Cl$_3$ (376 MHz):



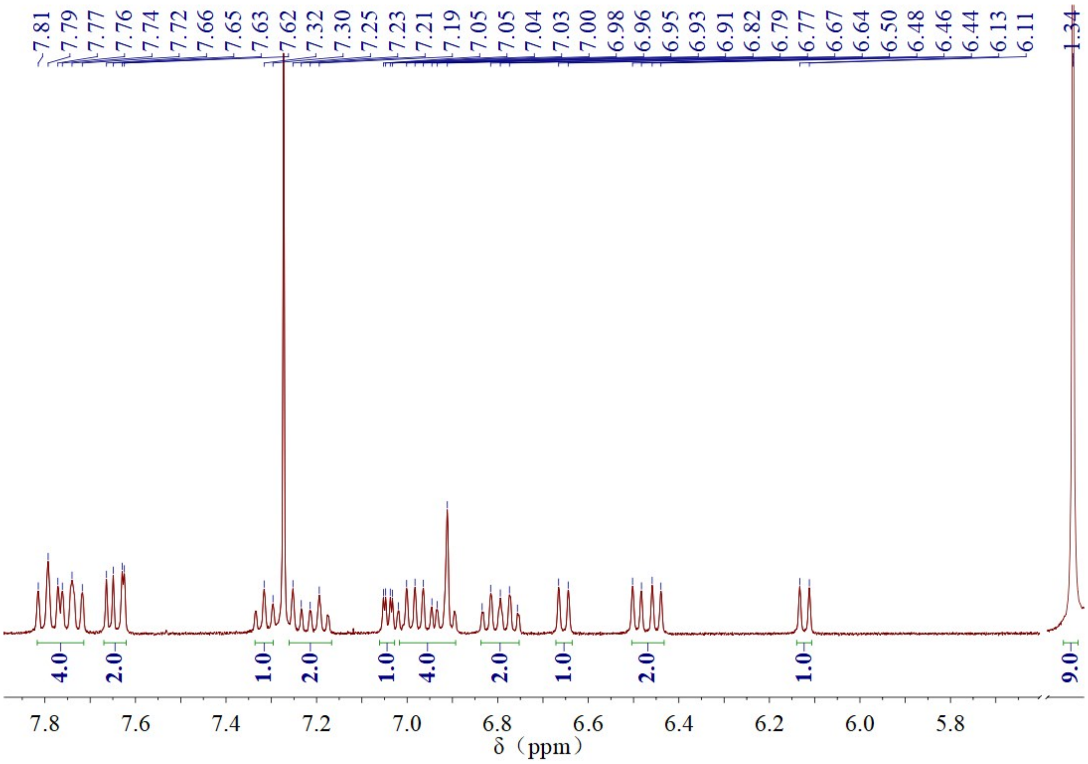
^{1}H-NMR Spectrum of **Ir(tbt)$_2$(taz) (3)** in C*D*Cl$_3$ (400 MHz):



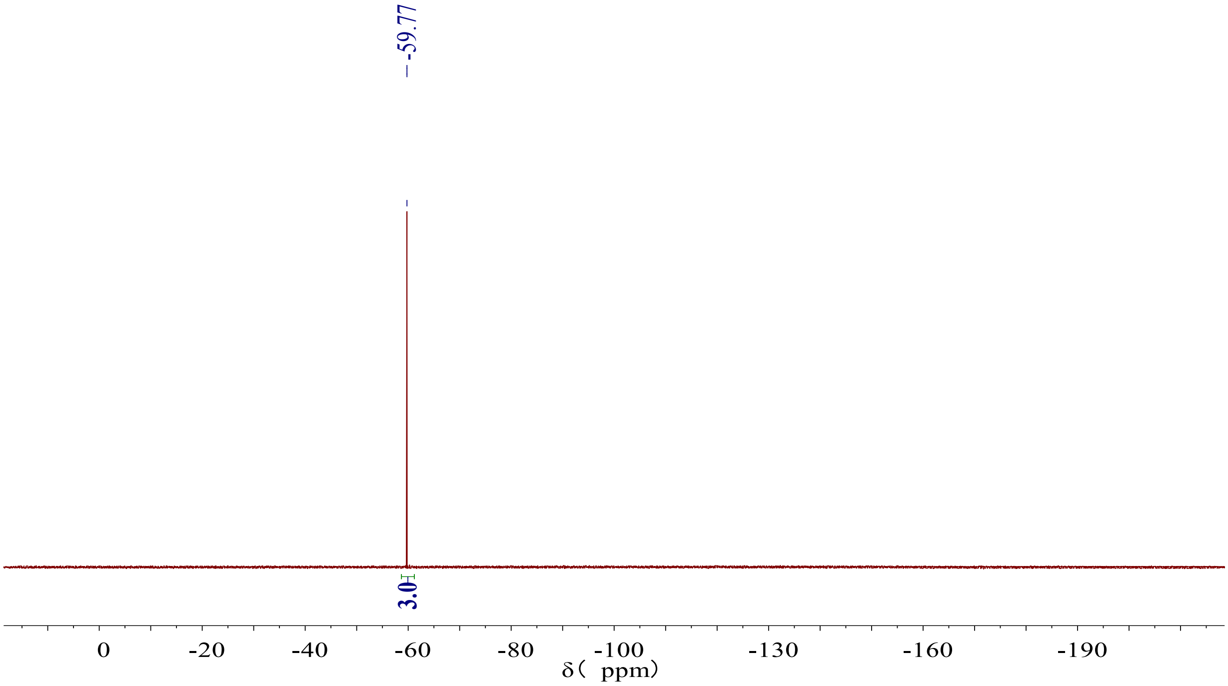
^{19}F-NMR Spectrum of **Ir(tbt)$_2$(taz) (3)** in C*D*Cl$_3$ (376 MHz):



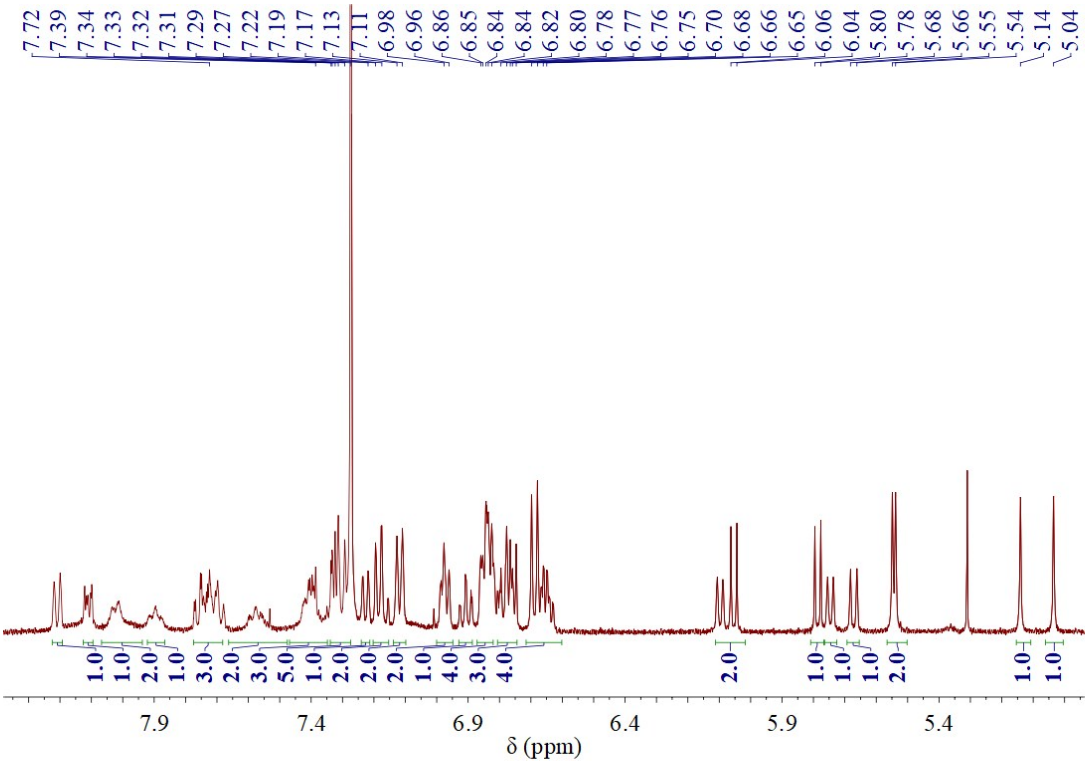
^{1}H-NMR Spectrum of **Ir(bt)$_2$(bfppz) (4)** in C*D*Cl$_3$ (400 MHz):



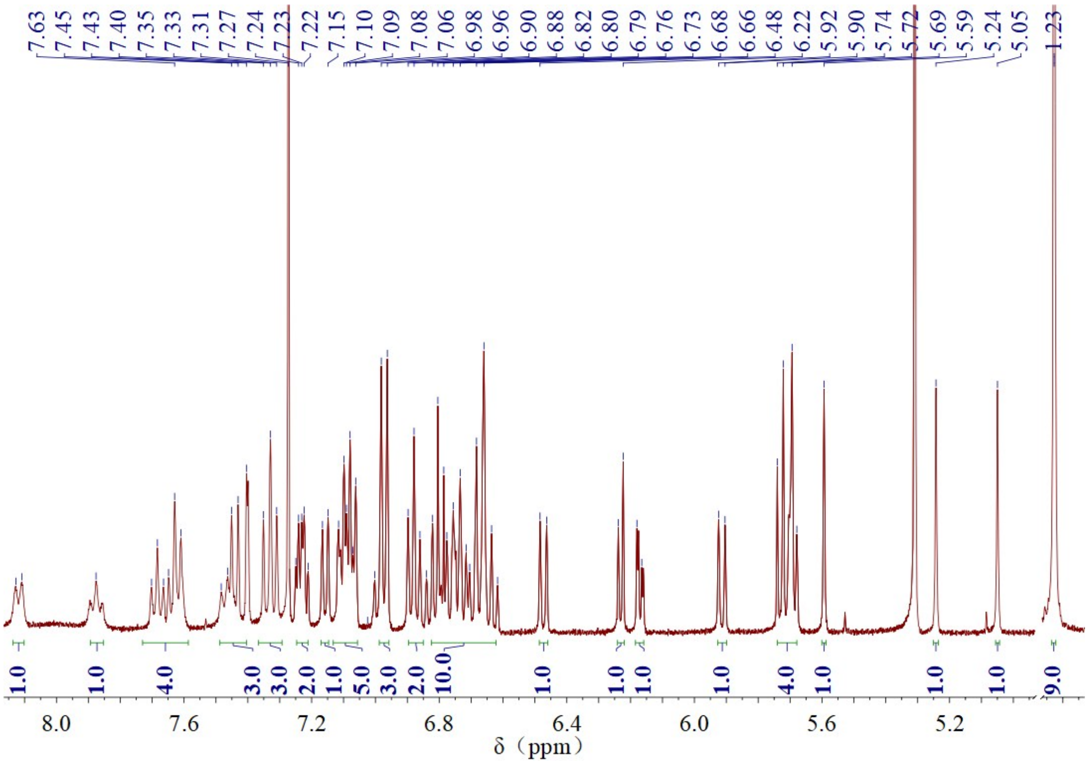
^{19}F-NMR Spectrum of **Ir(bt)$_2$(bfppz) (4)** in C*D*Cl$_3$ (376 MHz):



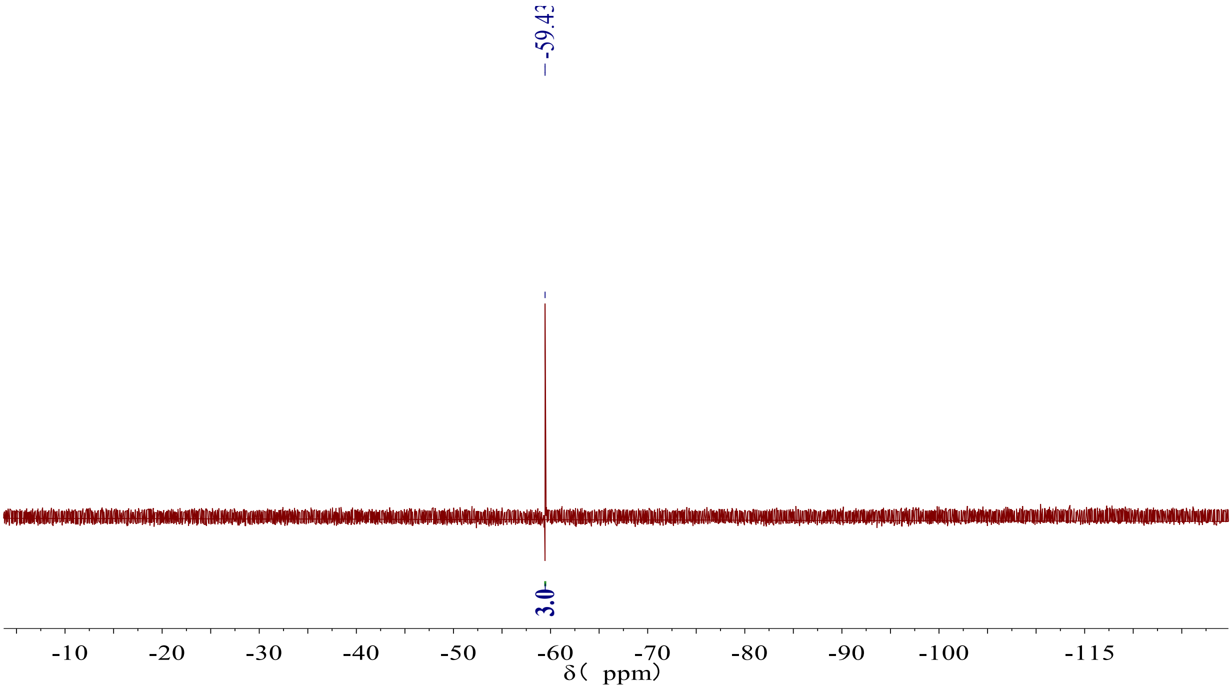
^{1}H-NMR Spectrum of **Ir(tpbi)$_2$(pic) (5)** in C*D*Cl$_3$ (400 MHz):



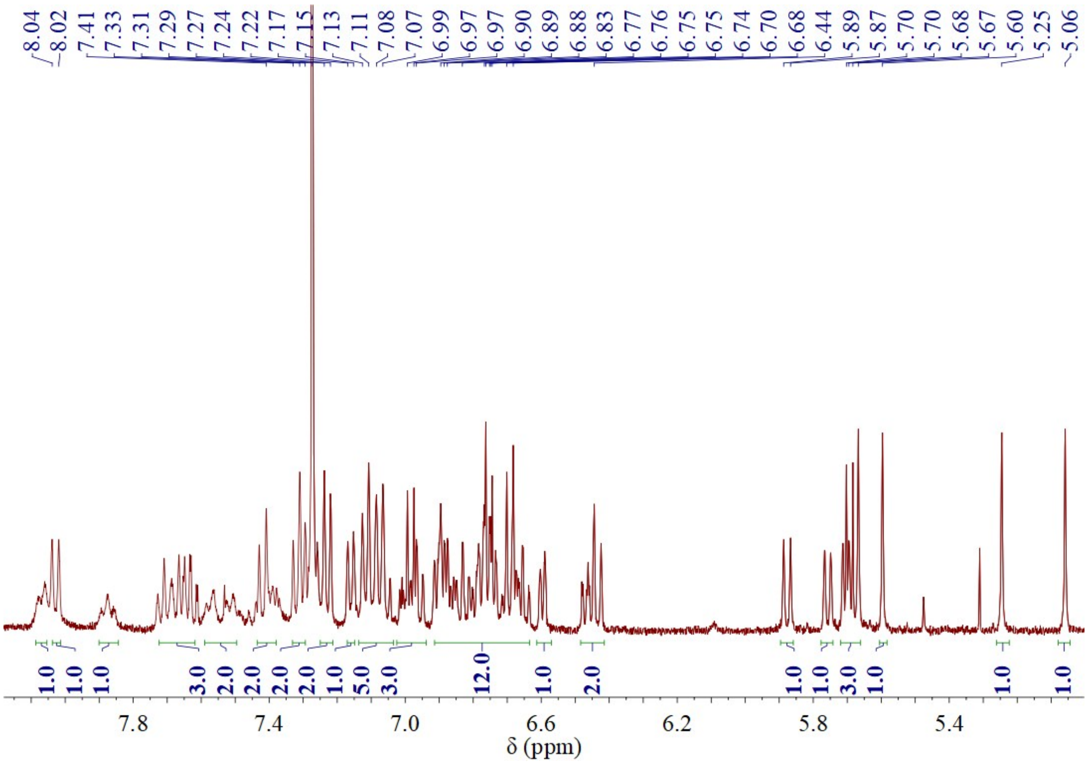
^{1}H-NMR Spectrum of **Ir(tpbi)$_2$(bfppz) (6)** in C*D*Cl$_3$ (400 MHz):



^{19}F-NMR Spectrum of **Ir(tpbi)$_2$(bfppz) (6)** in C*D*Cl$_3$ (376 MHz):



^{1}H-NMR Spectrum of **Ir(tpbi)$_2$(taz) (7)** in C*D*Cl$_3$ (400 MHz):



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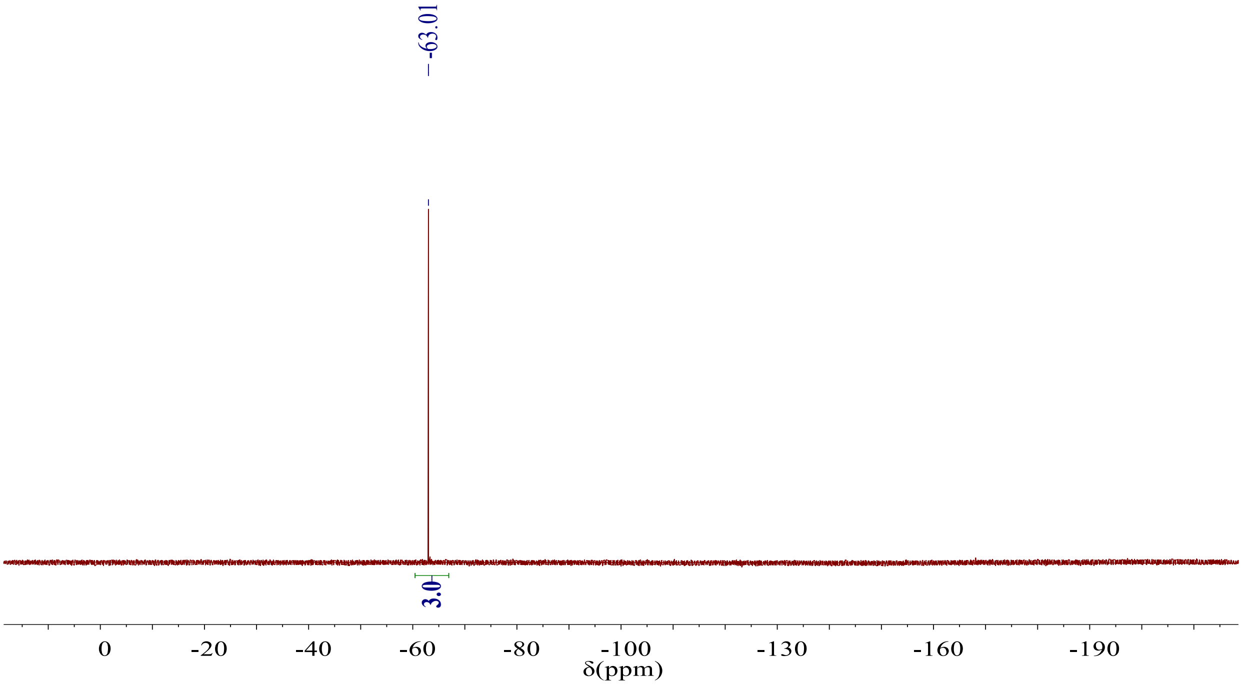
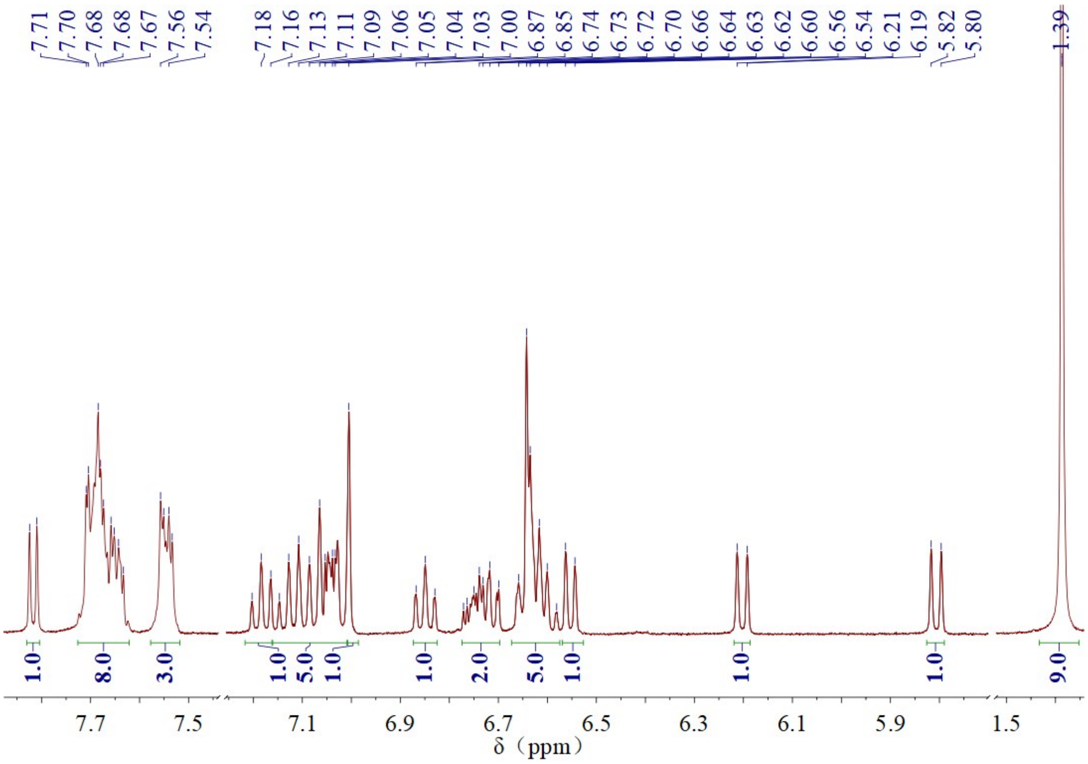
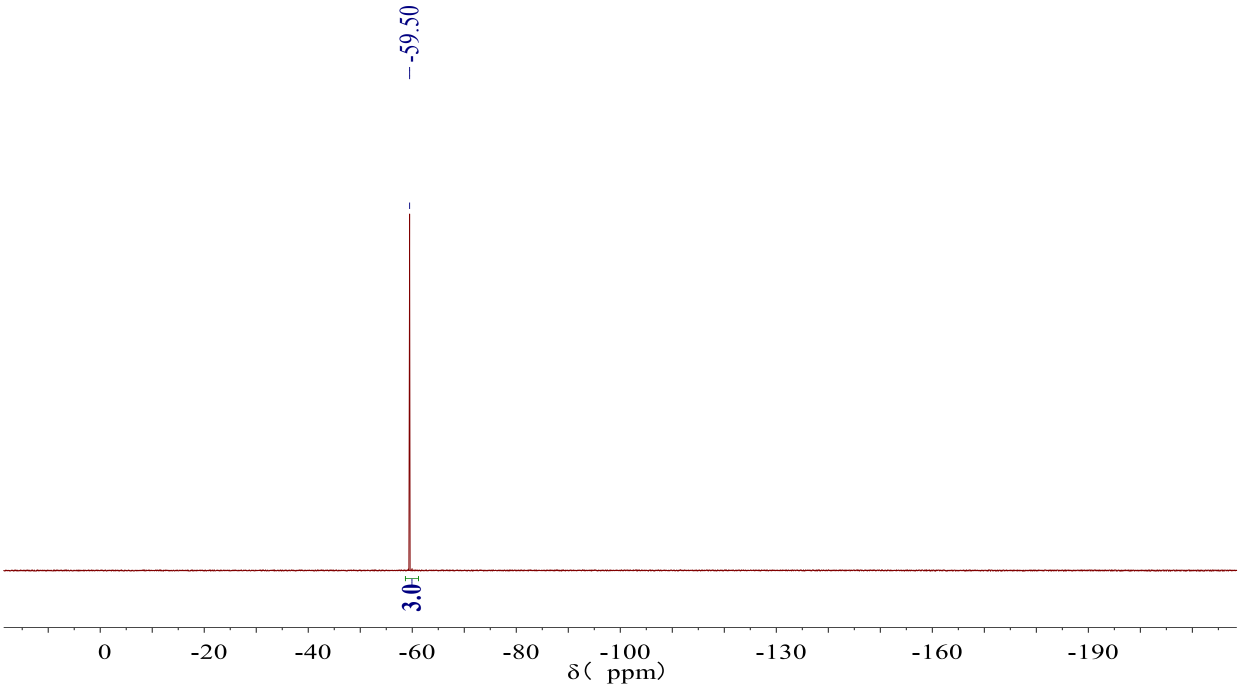


^{1}H-NMR Spectrum of **Ir(pbi)$_2$(bfppz) (8)** in C*D*Cl$_3$ (400 MHz):

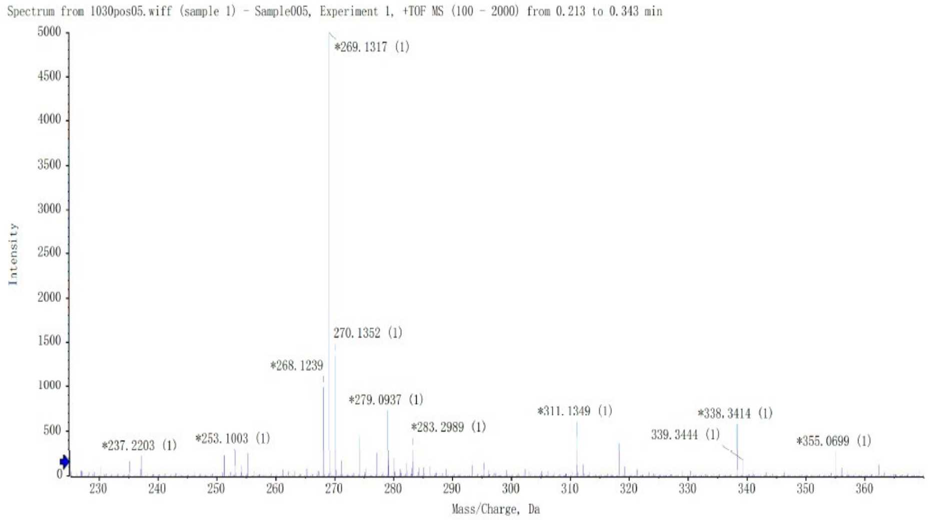


^{19}F-NMR Spectrum of **Ir(pbi)$_2$(bfppz) (8)** in C*D*Cl$_3$ (376 MHz):

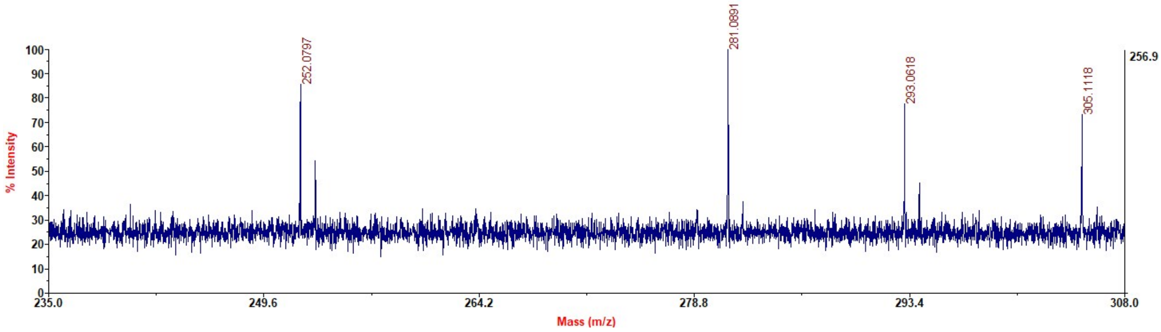


High resolution mass spectrometers (HRMS)

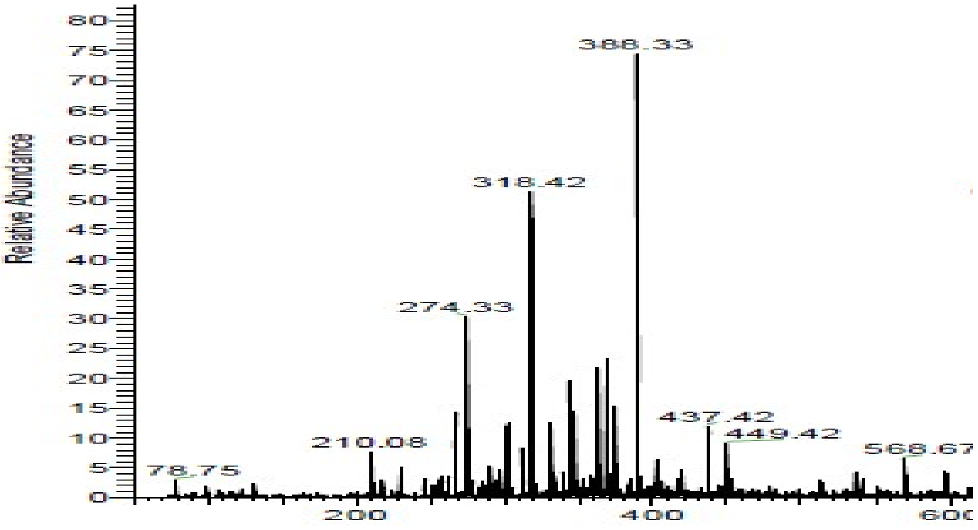
HRMS Spectrum of **1-methyltriptycene**:



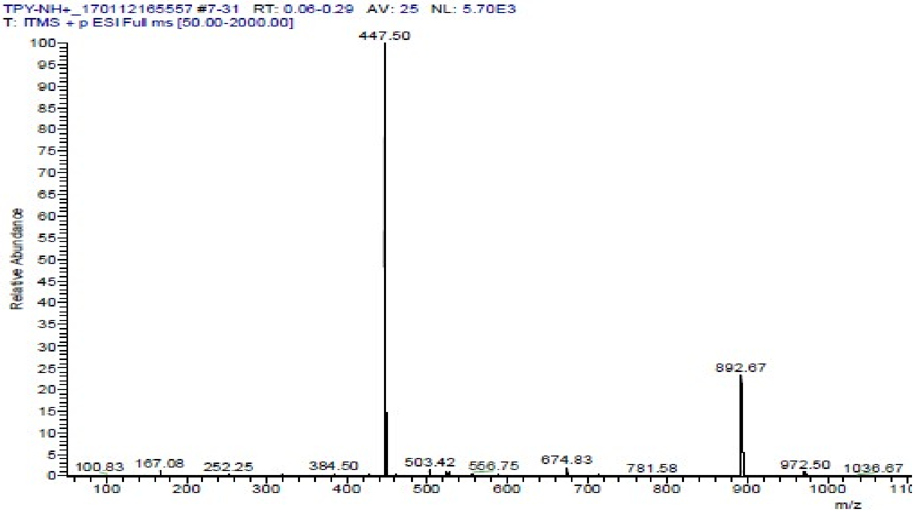
HRMS Spectrum of **1-formyltriptycene**:



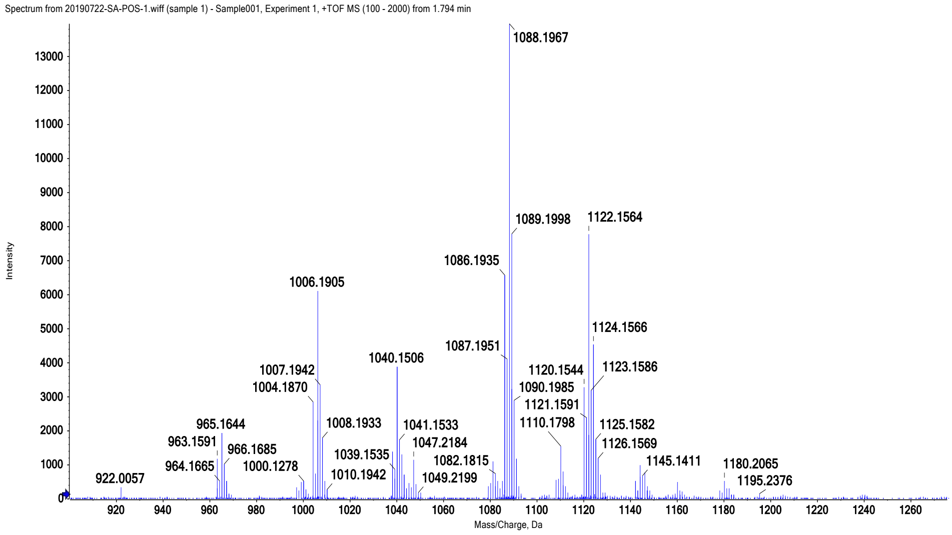
MS Spectrum of **tbtH**:



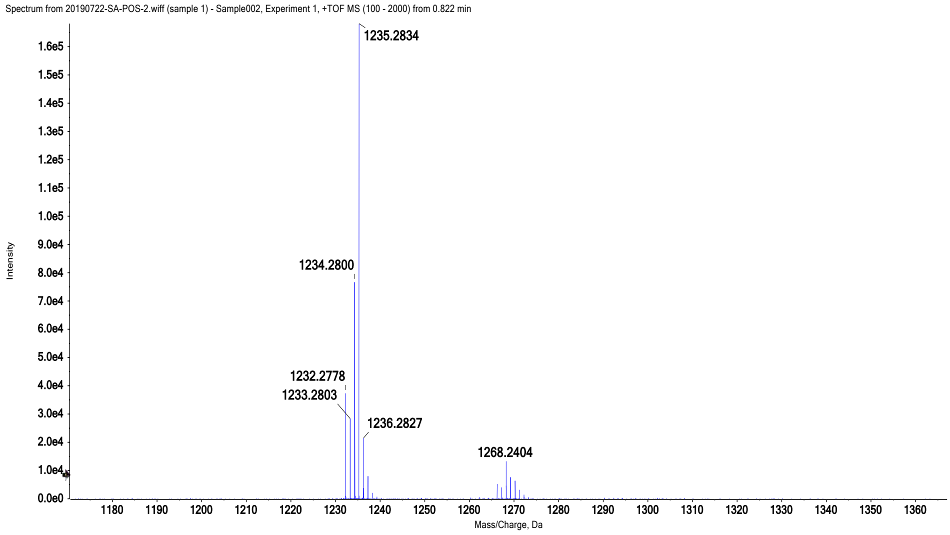
MS Spectrum of **tpbiH**:



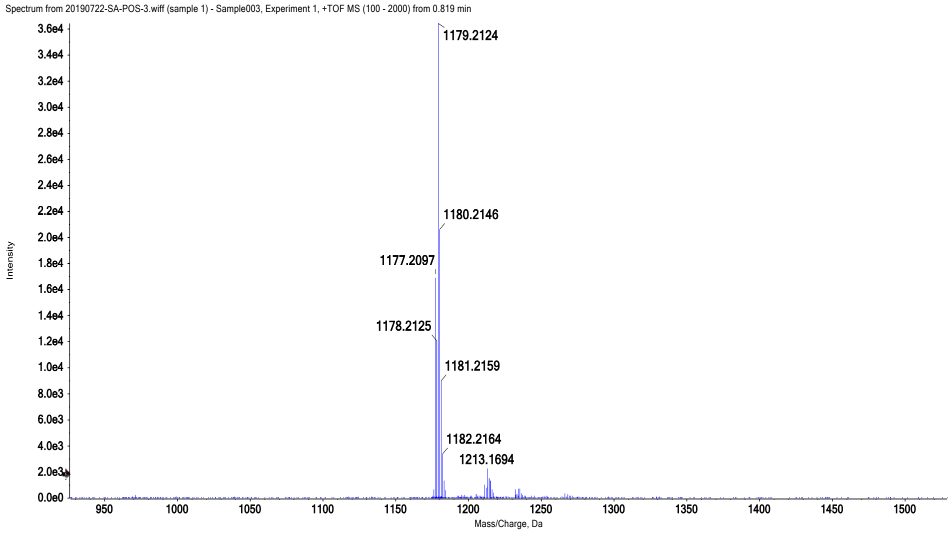
HRMS Spectrum of **1**:



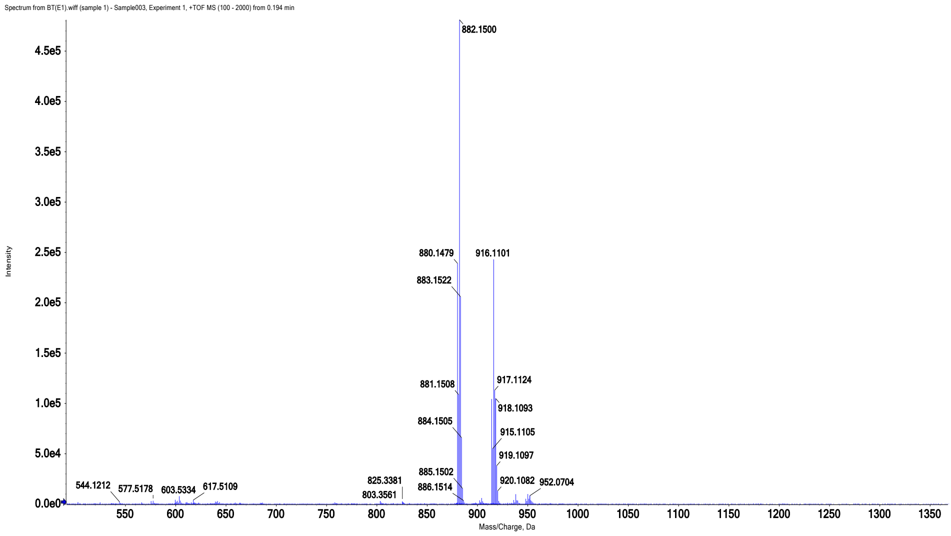
HRMS Spectrum of **2**:



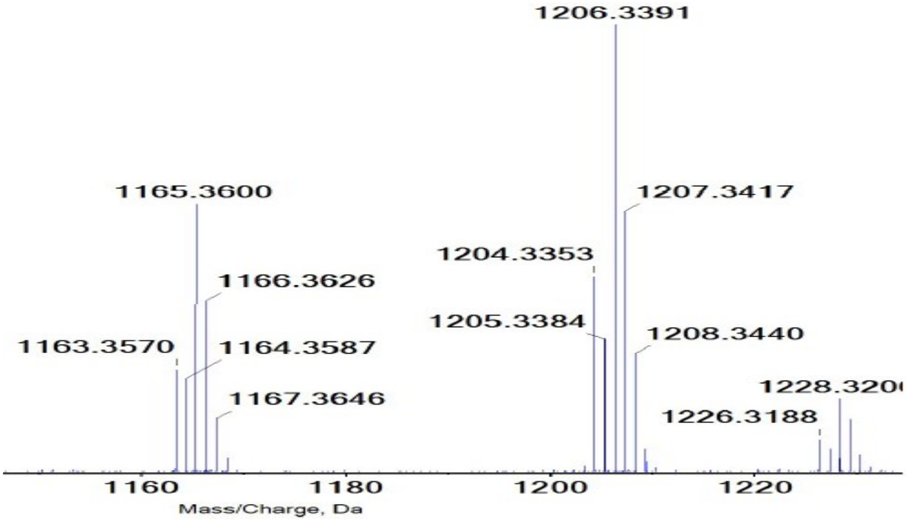
HRMS Spectrum of **3**:



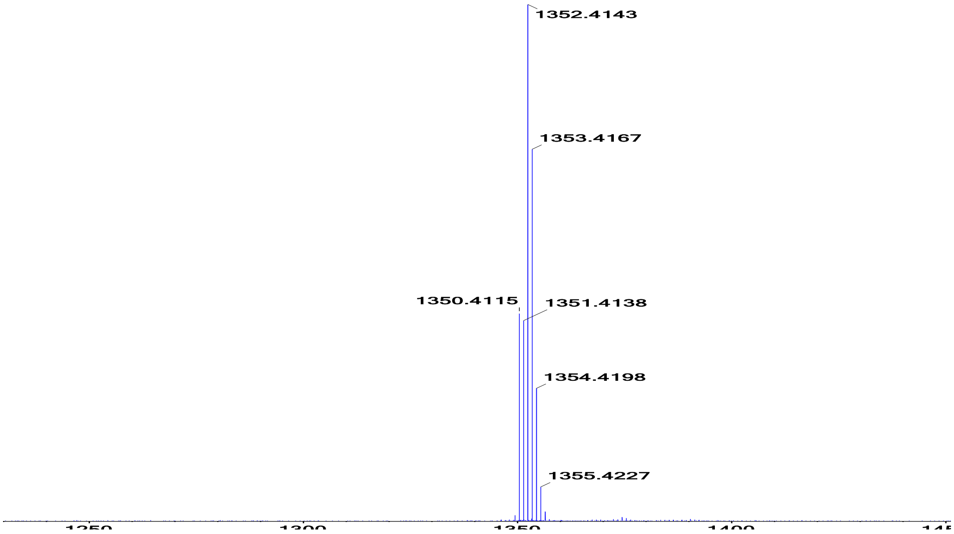
HRMS Spectrum of **4**:



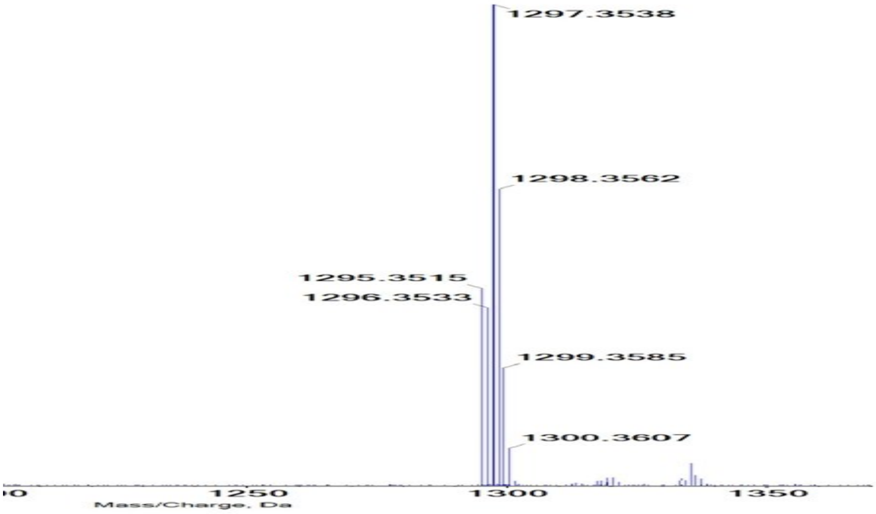
HRMS Spectrum of **5**:



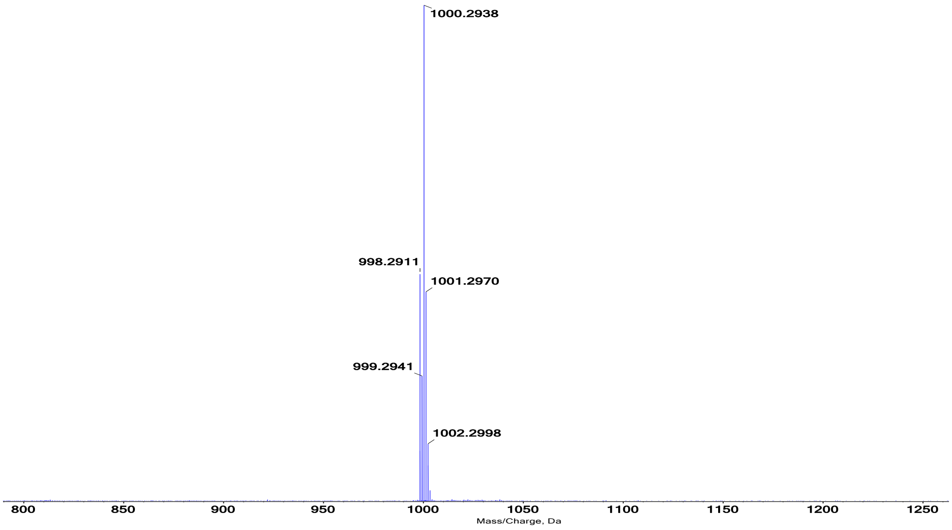
HRMS Spectrum of **6**:



HRMS Spectrum of **7**:



HRMS Spectrum of **8**: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Mass/Charge, Da