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Supplementary Information (SI)

Benzoate-based thermally activated delayed fluorescence materials

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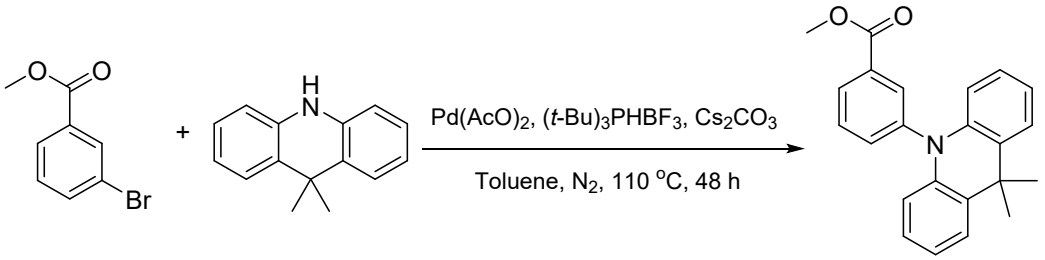
1. General information

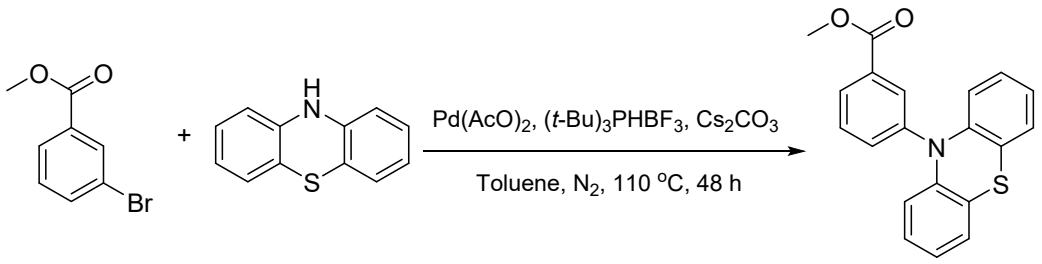
All reagents were obtained from commercial sources without further purification, and solvents were used as received except specifically mentioned. NMR spectra were recorded on AVIII 300-500 MHz NMR spectrometers. Mass spectra and high resolution mass spectra were recorded with Thermo Fisher® Exactive highresolution LC-MS spectrometer. Ultraviolet spectra were measured on a PerkinElmer® UV/Vis/NIR spectrometer (Lambda 950). The steady fluorescence spectra and lifetimes were recorded on Edinburgh Instruments FLS 980 spectrometer. The values of lifetime were calculated by exponential function fitting with luminescence spectrometer software F900. Theoretical calculations were carried out using the Gaussian 09 program.

2. Synthesis and characterization



DMAC-MBZ: A mixture of $Pd(OAc)_2$ (44 mg, 0.2 mmol), Cs_2CO_3 (977 mg, 3.0 mmol), (t-Bu)$_3$PHBF$_4$ (88 mg, 0.3 mmol), methyl 3-bromobenzoate (677 mg, 2.7 mmol) and 9,9-dimethyl-9,10-dihydroacridine (523 mg, 2.5 mmol) in toluene (20 mL) was refluxed under N_2 for 48 h. After cooling to room temperature, the reaction mixture was filtered, and the residue was purified by column chromatography on silica gel to give a white powder (686 mg, yield 80 %). Mp: 78-79 °C. 1H NMR (400 MHz, CDCl3) δ 8.28–8.13 (m, 1H), 8.04 (s, 1H), 7.86–7.65 (m, 1H), 7.56 (d, J = 6.3 Hz, 1H), 7.47 (m, J = 4.7, 2.0 Hz, 2H), 6.95 (d, J = 1.4 Hz, 4H), 6.20 (m, J = 5.2, 1.6 Hz, 2H), 3.92 (d, J = 3.9 Hz, 3H), 1.70 (s, 6H).

13C NMR (101 MHz, CDCl3) δ 166.29 (s), 141.52 (s), 140.67 (s), 136.41 (s), 133.25 (s), 132.83 (s), 131.02 (s), 130.15 (s), 129.48 (s), 126.43 (s), 125.35 (s), 120.84 (s), 113.95 (s), 77.38 (s), 77.06 (s), 76.74 (s), 52.37 (s), 36.02 (s), 31.25 (s). HRMS (APCI) *m/z*: $[M + H]^+$ calcd for $C_{23}H_{21}NO_2$, 344.1572; found, 344.1632. Elemental Analysis: calcd. for $C_{23}H_{21}NO_2$: C,80.44; H, 6.16; N, 4.08. Found: C,80.34; H, 6.10; N, 4.12.



PTZ-MBZ: A mixture of $Pd(OAc)_2$ (44 mg, 0.2 mmol), Cs_2CO_3 (977 mg, 3.0 mmol), (*t*-Bu)$_3$PHBF$_4$ (88 mg, 0.3 mmol), methyl 3-bromobenzoate (677 mg, 2.7 mmol) and 10H-phenothiazine (497 mg, 2.5 mmol) in toluene (20 mL) was refluxed under N_2 for 48 h. After cooling to room temperature, the reaction mixture was filtered, and the residue was purified by column chromatography on silica gel to give a yellowish powder (732 mg, yield 83 %). Mp: 99-100 °C. 1H NMR (400 MHz, CDCl3) δ 8.12 (m, J = 11.6, 10.6 Hz, 2H), 7.73 – 7.50 (m, 2H), 7.05 (d, J = 6.9 Hz, 2H), 6.85 (m, J = 10.1, 4.4 Hz, 4H), 6.21 (d, J = 7.4 Hz, 2H), 3.92 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 166.25 (s), 143.85 (s), 141.60 (s), 134.98 (s), 132.97 (s), 131.48 (s), 130.85 (s), 129.03 (s), 126.99 (d, J = 5.7 Hz), 122.96 (s), 121.31 (s), 116.69 (s), 77.43 (s), 77.11 (s), 76.80 (s), 52.42 (s). HRMS (APCI) m/z: [M + H]+ calcd for $C_{20}H_{15}NO_2S$, 334.0823; found, 334.0885. Elemental Analysis: calcd. for $C_{20}H_{15}NO_2S$: C,72.05; H, 4.54; N, 4.20; S, 9.62. Found: C,72.01; H, 4.48; N, 4.24; S, 9.68.

3. Symbolic Z-matrix

PTZ-MBZ (B3LYP-D3BJ/def2-SV(P) optimized geometry):

Charge = 0 Multiplicity = 1

C	2.08398	14.736	4.21212
C	2.65499	13.451	4.83187
C	4.16077	13.3388	5.14082
C	5.11631	14.5075	4.81009
C	4.52157	15.8091	4.2276
C	3.01818	15.9183	3.91639
H	0.97033	14.8143	3.98055
H	1.96073	12.5783	5.06875
S	4.77077	11.8354	5.92118
N	6.61691	14.4481	5.0846
H	5.19515	16.7063	4.03837
H	2.59695	16.88	3.47166
C	7.3065	13.2591	5.74676
C	6.5378	12.0035	6.21528
C	8.84062	13.2958	5.91861

C	9.58072	12.1449	6.62295
C	8.79834	10.9271	7.1364
C	7.27914	10.8529	6.922
H	9.43671	14.1765	5.51414
H	10.7113	12.1946	6.76008
H	9.34408	10.0769	7.66487
H	6.69898	9.93941	7.28087
C	7.465	15.6452	4.69483
C	7.03911	16.5487	3.52116
C	7.88473	17.7778	3.13916
C	9.15587	18.1157	3.93805
C	9.58442	17.2165	5.11112
C	8.74754	15.9787	5.48097
C	10.8409	17.5636	5.92899
O	11.6504	18.7889	5.58206
C	11.1202	19.9647	6.36655
O	11.2744	16.6671	7.06433
H	6.09571	16.3046	2.93001
H	7.56629	18.44	2.26771
H	9.77605	19.0324	3.66481

H	11.7283	20.8948	6.11258
H	11.2071	19.7465	7.4821
H	10.0264	20.1392	6.09706
H	9.06603	15.3209	6.35534
H	15.1803	17.2574	5.0669

DMAC-MBZ (B3LYP-D3BJ/def2-SV(P) optimized geometry):

Charge = 0 Multiplicity = 1

C	2.51422	15.4361	5.7566
C	2.93202	13.957	5.69124
C	4.42256	13.5723	5.62752
C	5.5029	14.6736	5.60962
C	5.07972	16.1523	5.74059
C	3.58953	16.5339	5.79516
H	1.40978	15.7169	5.78932
H	2.13549	13.1414	5.69129
C	4.80023	12.0791	5.60829
N	6.96884	14.3068	5.50392
H	5.87054	16.9678	5.8116
H	3.28365	17.6296	5.86929
C	7.37439	12.8482	5.5721

C	6.29984	11.7535	5.73226
C	4.05624	11.3836	6.76193
C	8.85668	12.4356	5.461
C	9.27432	10.9751	5.71177
C	8.20676	9.9121	6.02055
C	6.71868	10.2985	6.00918
H	9.64655	13.2061	5.18435
H	10.3749	10.6814	5.66777
C	4.30023	11.4838	4.2801
H	4.26787	10.2635	6.73714
H	2.93612	11.5649	6.65054
H	4.41626	11.8184	7.75208
H	8.51612	8.83601	6.23478
H	5.92249	9.50321	6.19145
H	3.17855	11.6644	4.18564
H	4.51146	10.3636	4.25598
H	4.8432	11.9937	3.41714
C	8.01282	15.4008	5.34954
C	7.58955	16.8015	4.86372
C	8.63078	17.9268	4.72645

C	10.1135	17.6418	5.0155
C	10.5499	16.2348	5.4573
C	9.49729	15.131	5.67268
C	12.0436	15.9325	5.67496
O	13.0664	17.0295	5.50254
C	14.4126	16.4237	5.18971
O	12.4917	14.5317	6.01303
H	6.50234	17.0045	4.59191
H	8.30472	18.9673	4.39393
H	10.8895	18.4676	4.89003
H	9.81763	14.1223	6.09171
H	14.3455	15.8234	4.22302
H	14.7308	15.7365	6.04181
H	15.1803	17.2574	5.0669

4. ^{1}H NMR and ^{13}C NMR spectra

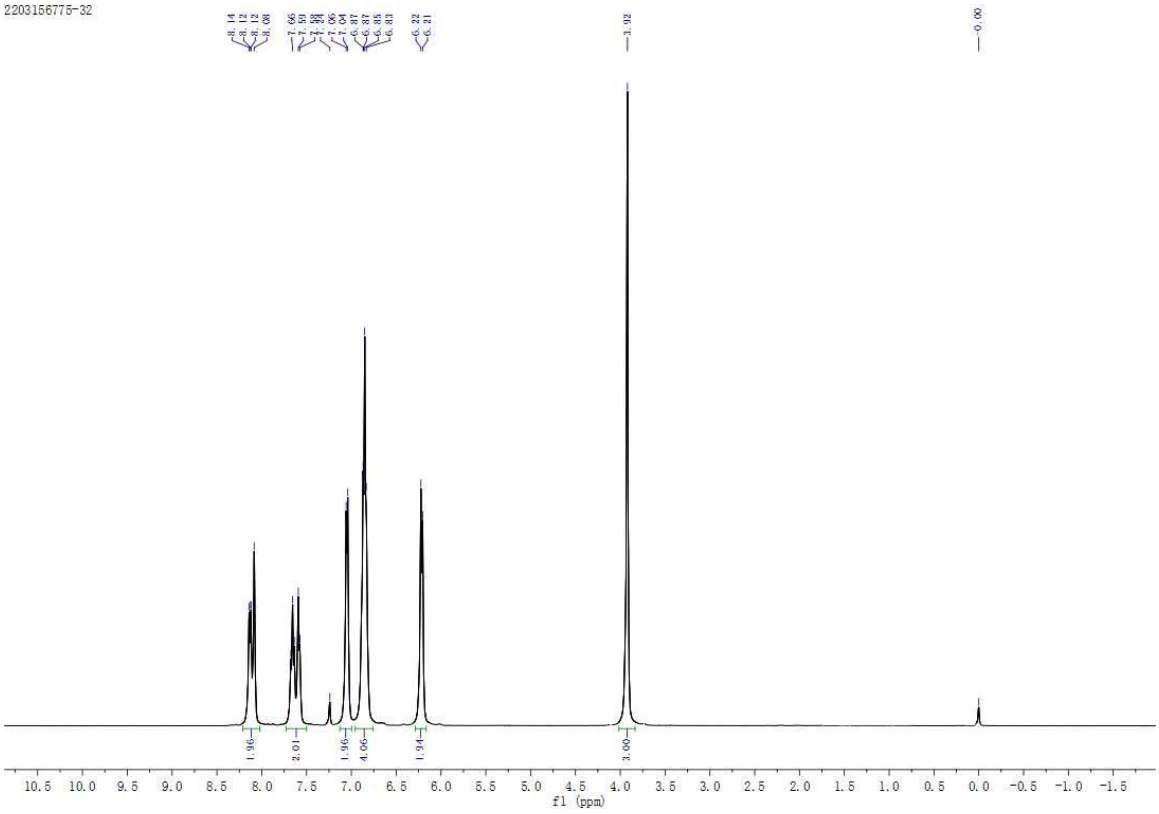


Fig. S1 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **PTZ-MBZ**.

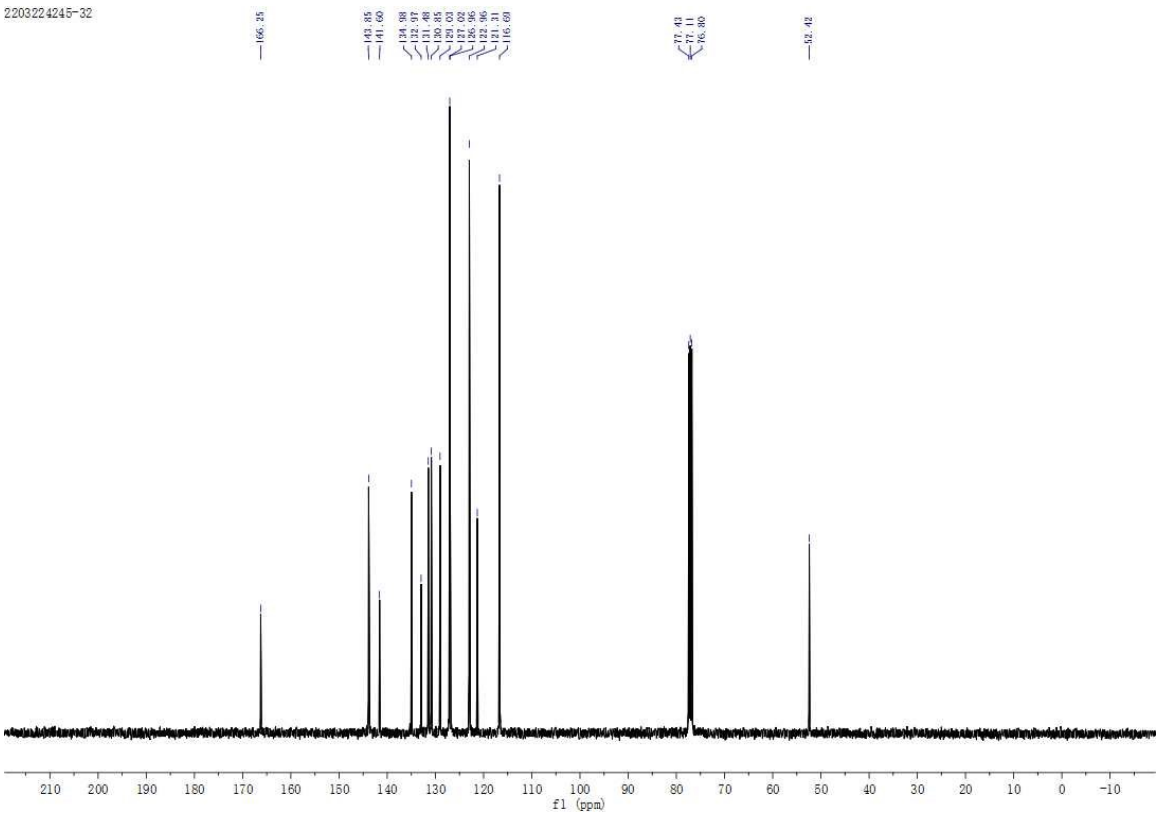


Fig. S2 ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **PTZ-MBZ**.

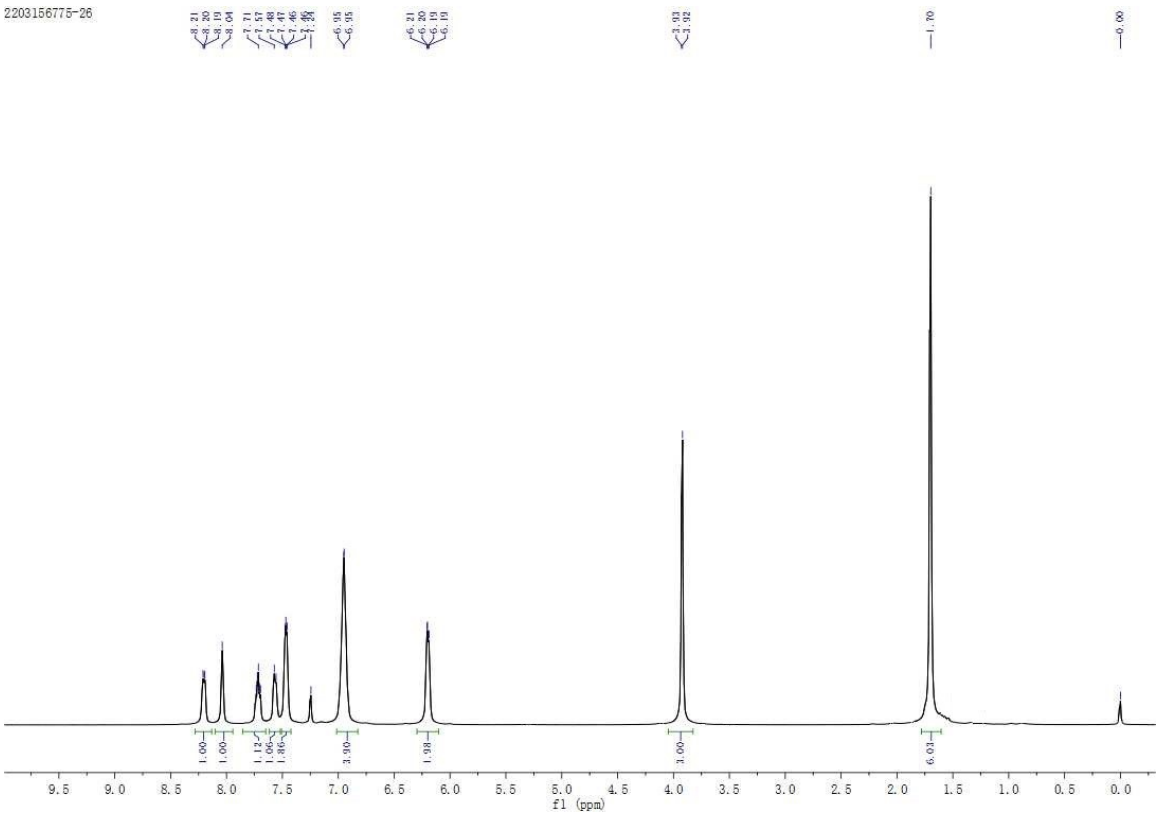


Fig. S3 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **DMAC-MBZ**.

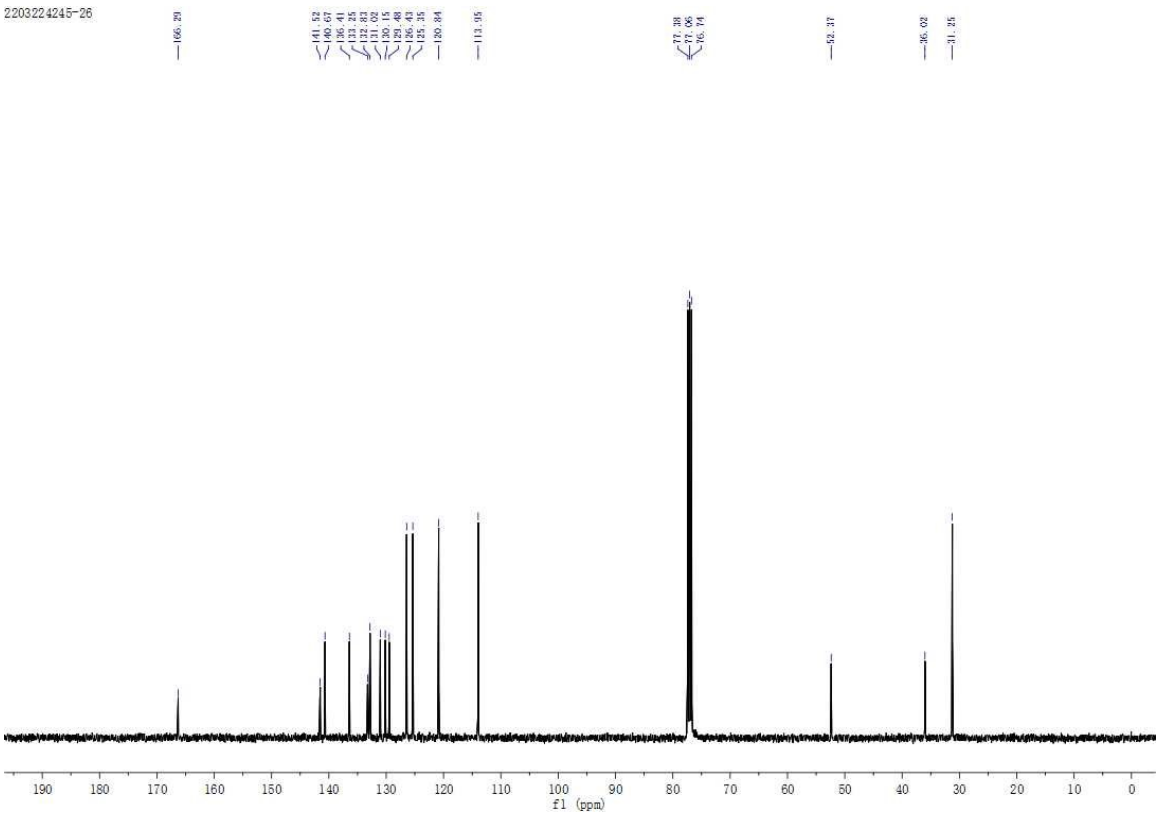


Fig. S4 ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **DMAC-MBZ**.

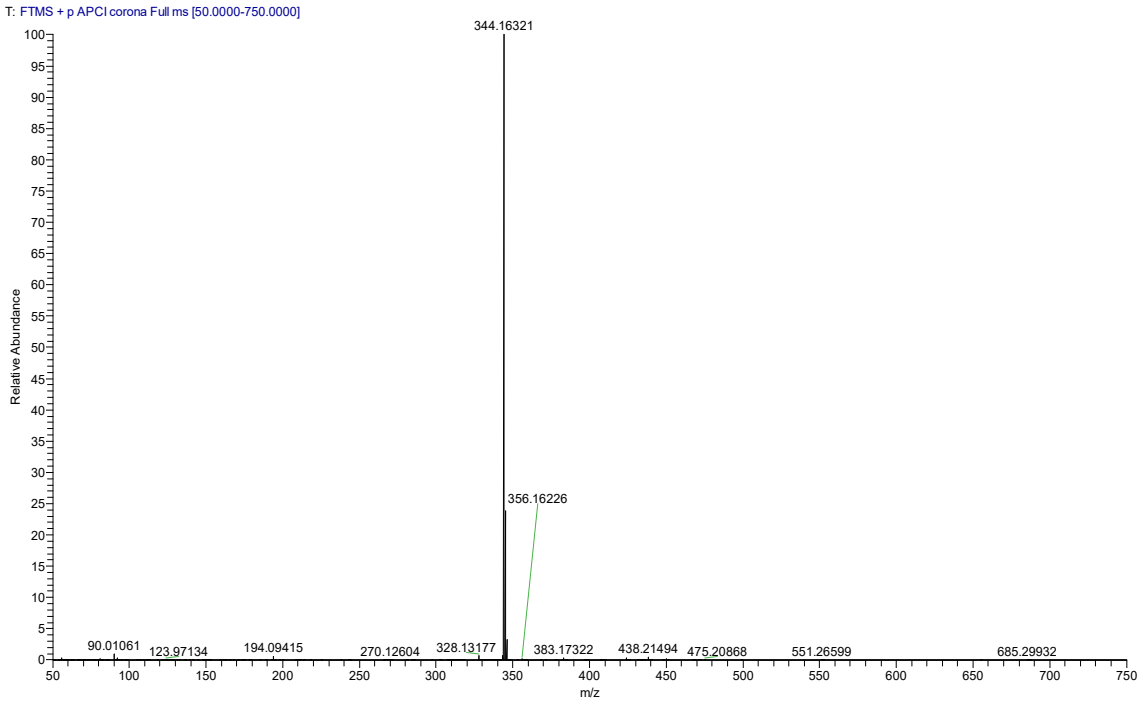


Fig. S5 HRMS spectra of **DMAC-MBZ**.

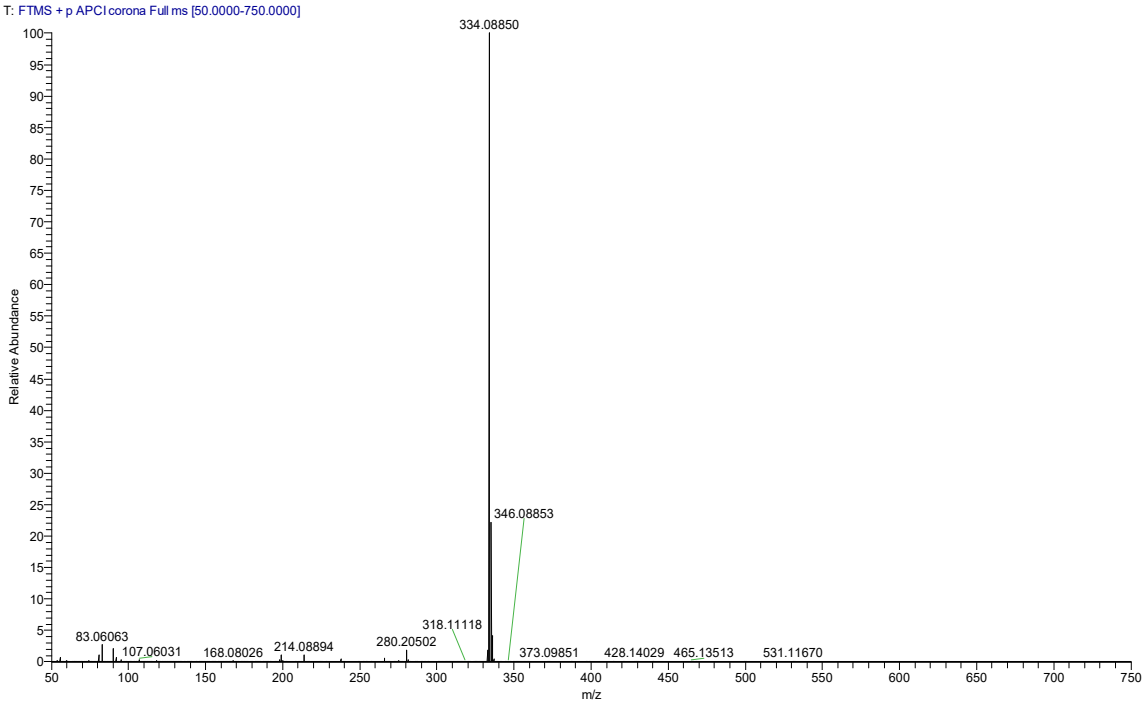


Fig. S6 HRMS spectra of **PTZ-MBZ**.