Supporting Information

Novel Phosphorus (V) Tetrabenzotriazacorroles: Synthesis, Characterization, Optical, Electrochemical, and Femtosecond Nonlinear Optical Studies

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Methods and instrumentation

^{1}H-NMR spectra were recorded using either a 400 or 500 MHzINOVA spectrometer. A Thermo Nicolet Nexus 670 spectrometer was used to record the FTIR spectra using the KBr pellet technique. A Shimadzu Biotech Axima Performance2.9.3.20110624: Mode Linear, Power spectrometer was used to record Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra. Cyclicvoltammetric measurements were performed using a CHI instruments model CHI 620C potentiostat, as detailed in our previous reports [1]. The spectroelectrochemical studies were also carried out using the same instrument at 25 ^{0}C. Pt gauge was the working electrode and Pt wire was the counter electrode. UV-visible spectra were recorded with a Shimadzu spectrophotometer (Model UV-3600). The concentrations of the samples used for these measurements using 1 x 10^{-5} M. Steady-state fluorescence spectra were measured using a Fluorolog-3 spectrofluorometer (FluoroLog3 model, JobinYvon), as detailed in our previous reports. Fluorescence lifetime measurements were carried out using a picosecond time-correlated single-photon counting (TCSPC) setup (FluoroLog3-Triple Illuminator, IBH Horiba JobinYvon), employing a picosecond light-emitting diode laser (NanoLED, λ_{ex} = 405 nm) as the excitation source.

Ground state geometry optimization of the structures of the TBCs in the gas phase was carried out with DFT studies and the B3LYP method using the 6-31G(d,p) basis set by the Gaussian 09 software on a personal computer [2-4]. TD-DFT (time-dependent density functional theory) was employed for the estimation of ground state to excited state transitions using B3LYP and the 6-31G(d,p) basis set. The geometries were used to obtain the frontier molecular orbitals (FMOs) and were also subjected to single-point TDDFT studies to obtain the UV-Visible spectra of the sensitizers. The integral equation formalism polarizable continuum model (PCM) within the self-consistent reaction field (SCRF) theory was used in the TDDFT calculations to describe the solvation of the dyes in tetrahydrofuran [5,6]. The software GaussSum 2.2.5 was employed to simulate the major portions of the absorption spectra and to interpret the nature of transitions [7,8].

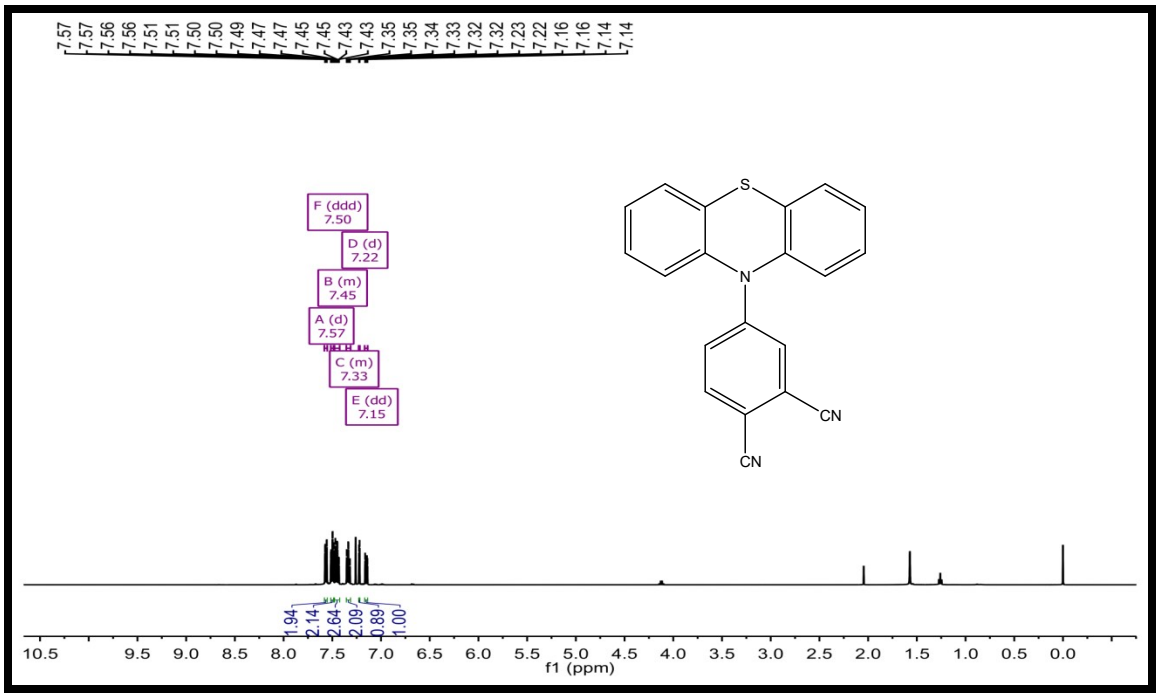

Fig. S1. ^{1}H NMR spectrum of 1in $CDCl_3$.

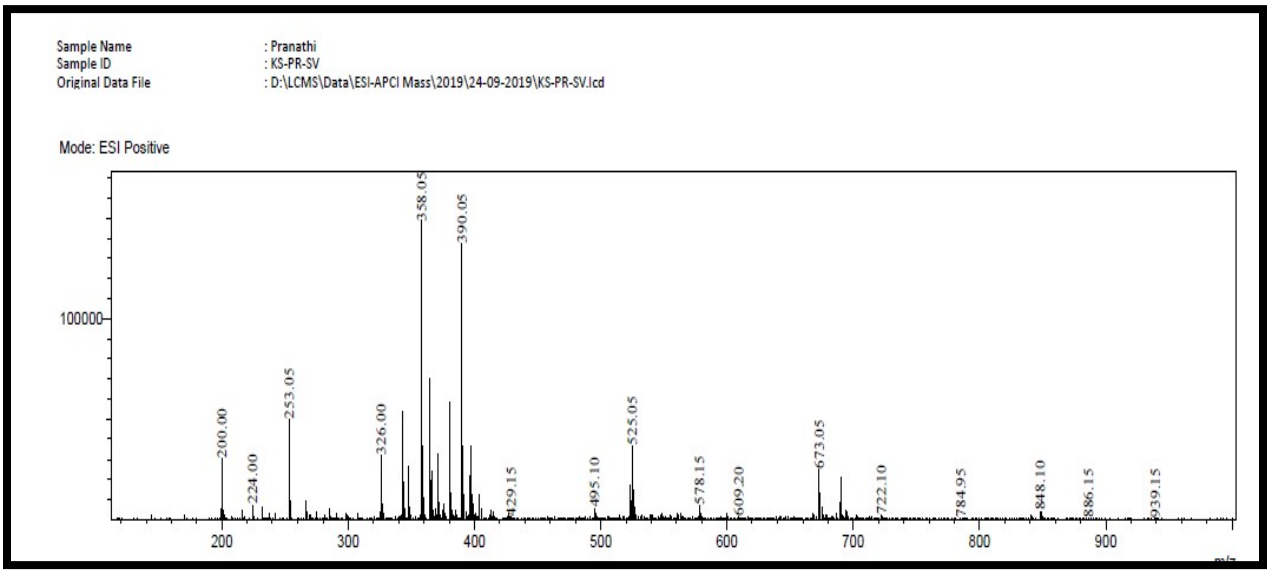

Fig. S2. ESI-MS spectrum of 1.

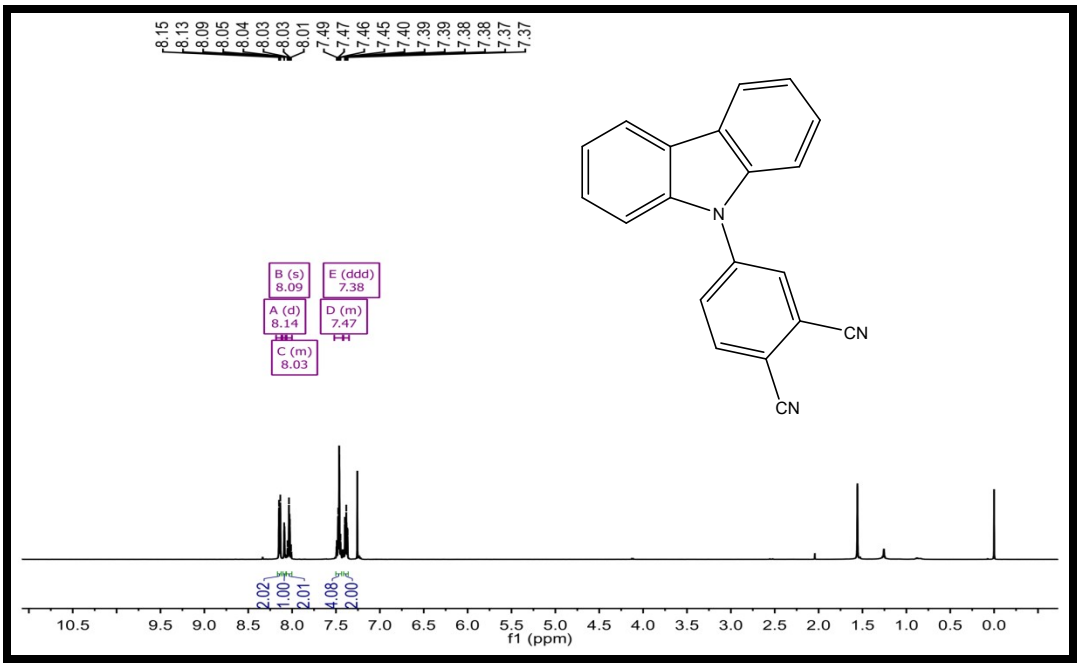

Fig. S3. ^{1}H NMR spectrum of 2 in $CDCl_3$.

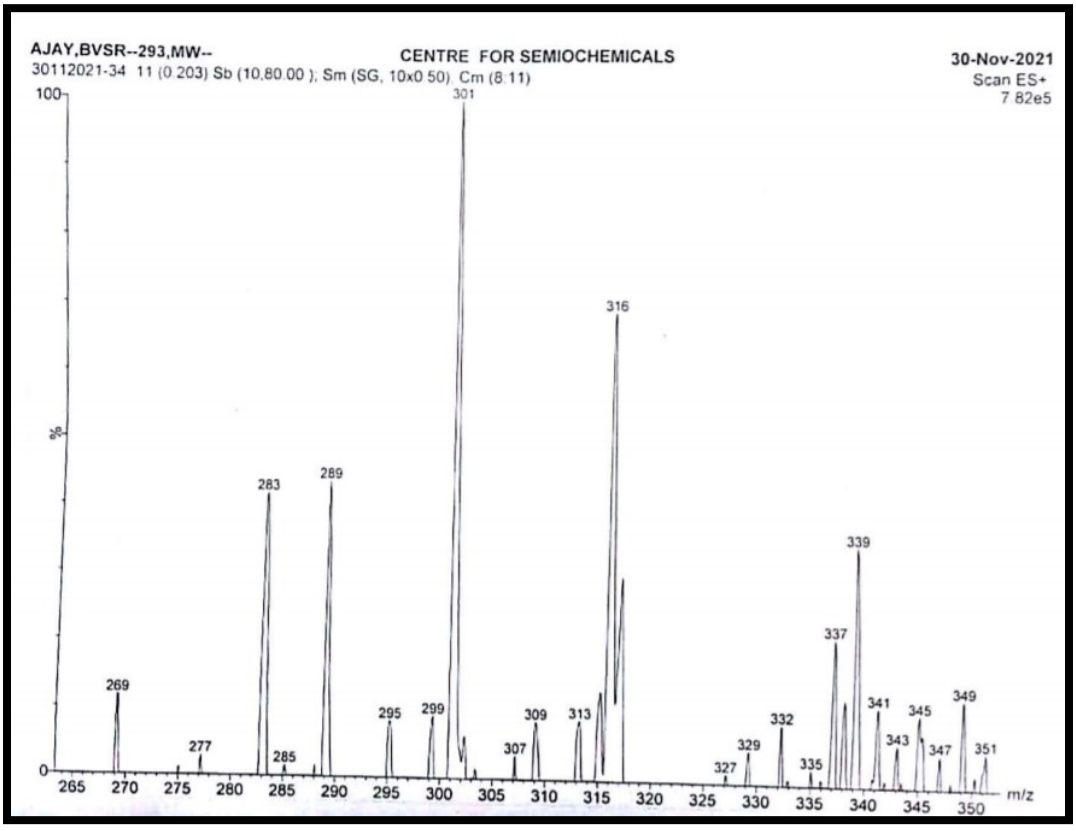

Fig. S4. ESI-MS spectrum of 2.

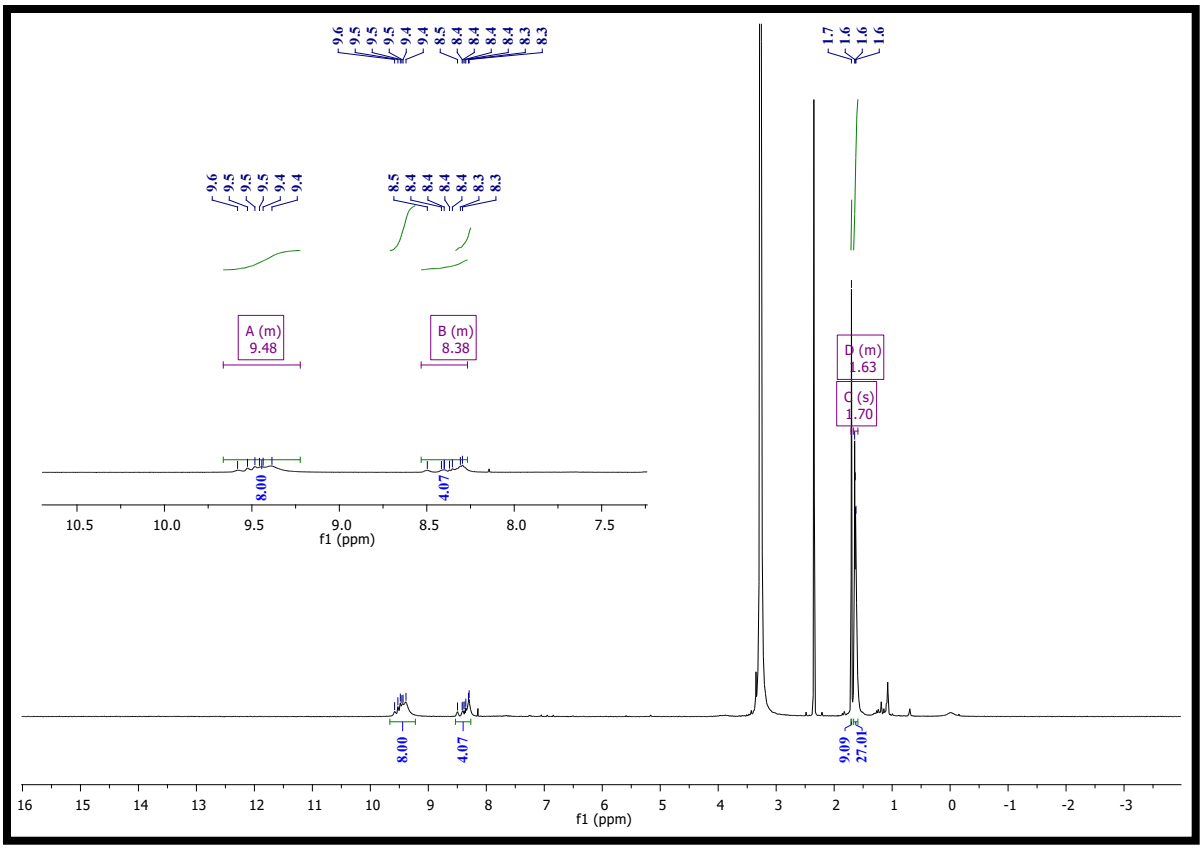

Fig. S5. ^{1}H NMR spectrum of **TBC-*tert*** in DMSO-d_6.

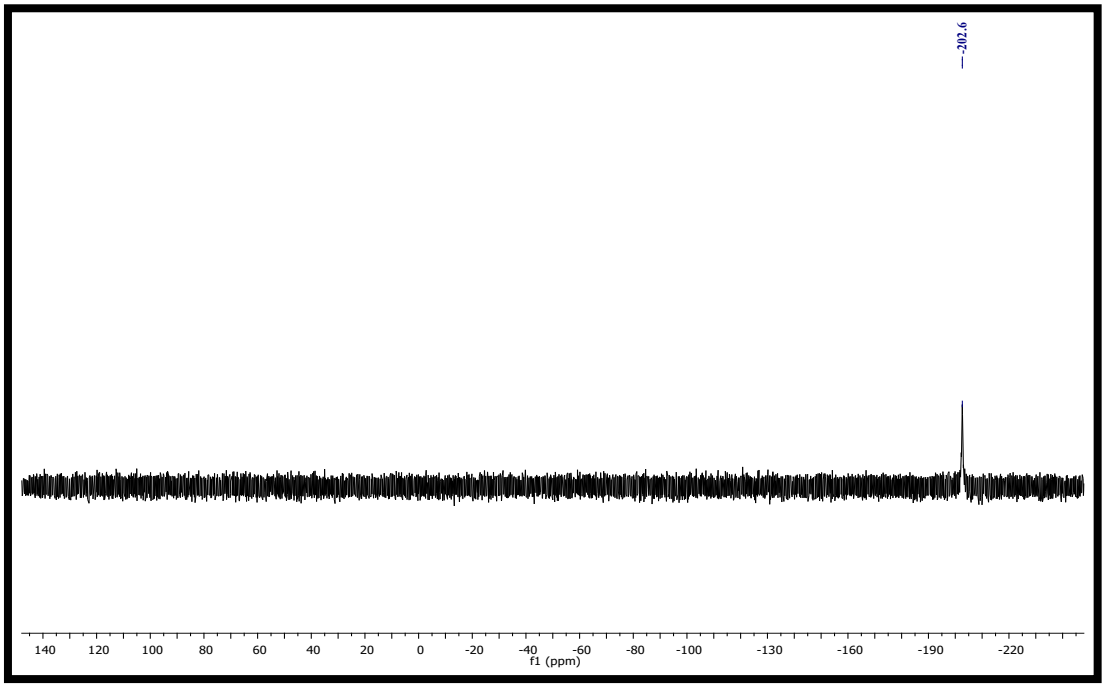

Fig. S6. ^{31}P NMR of **TBC-*tert*** in DMSO-d_6.

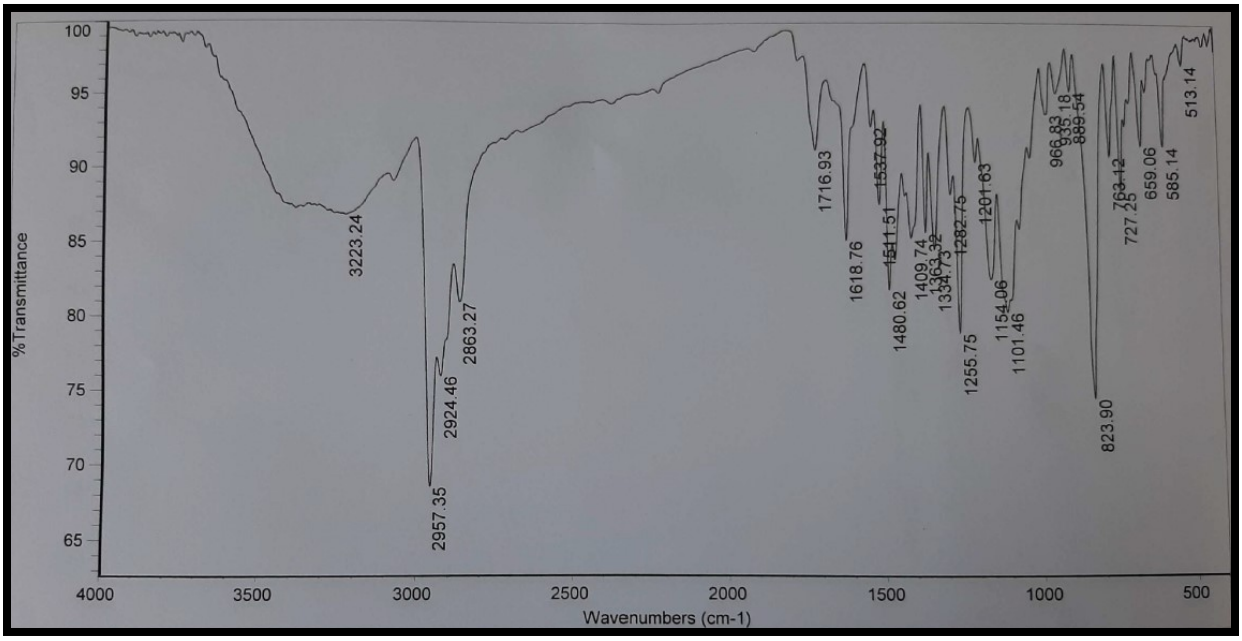

Fig. S7. IR spectrum of **TBC-*tert***.

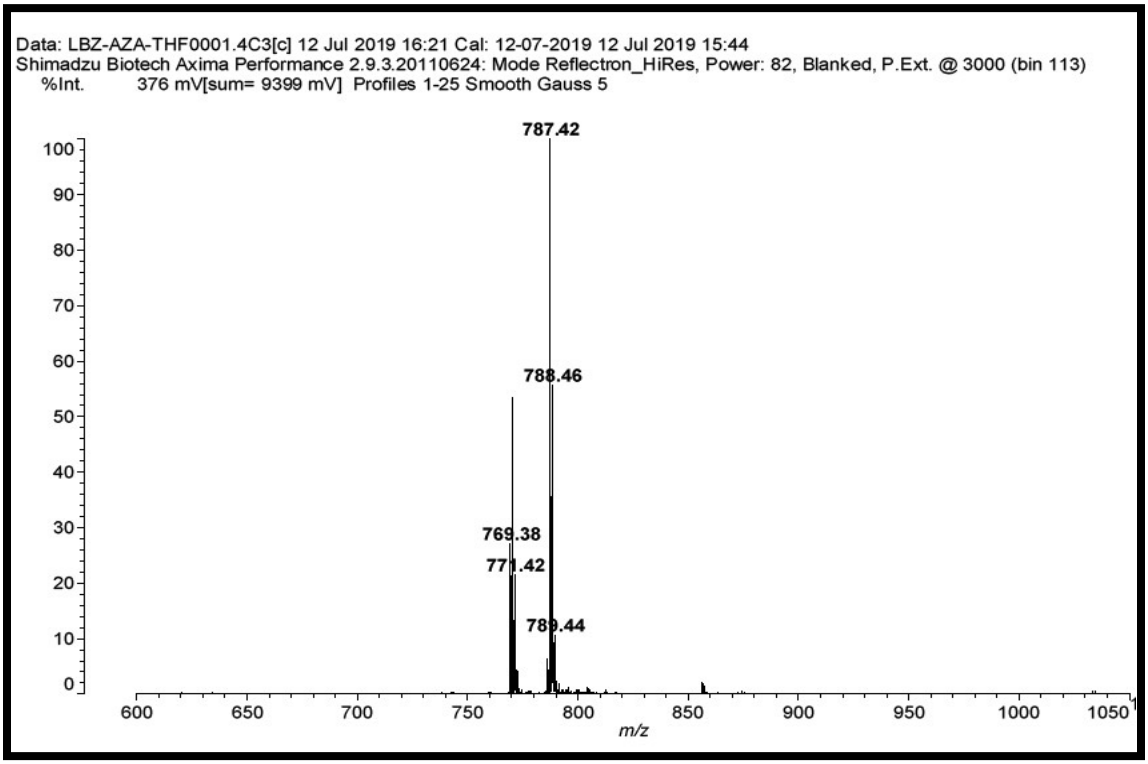

Fig. S8. MALDI-MS spectrum of **TBC-*tert***.

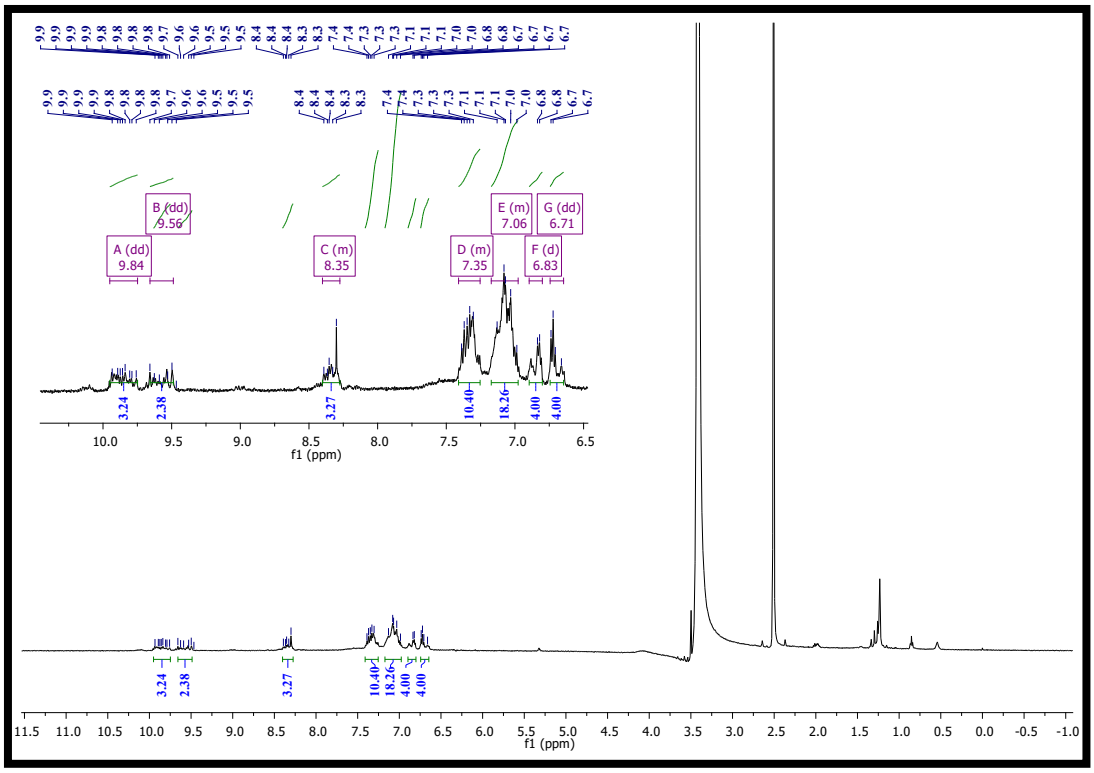

Fig. S9. ^{1}H NMR spectrum of **TBC-PTZ** in DMSO-d_6.

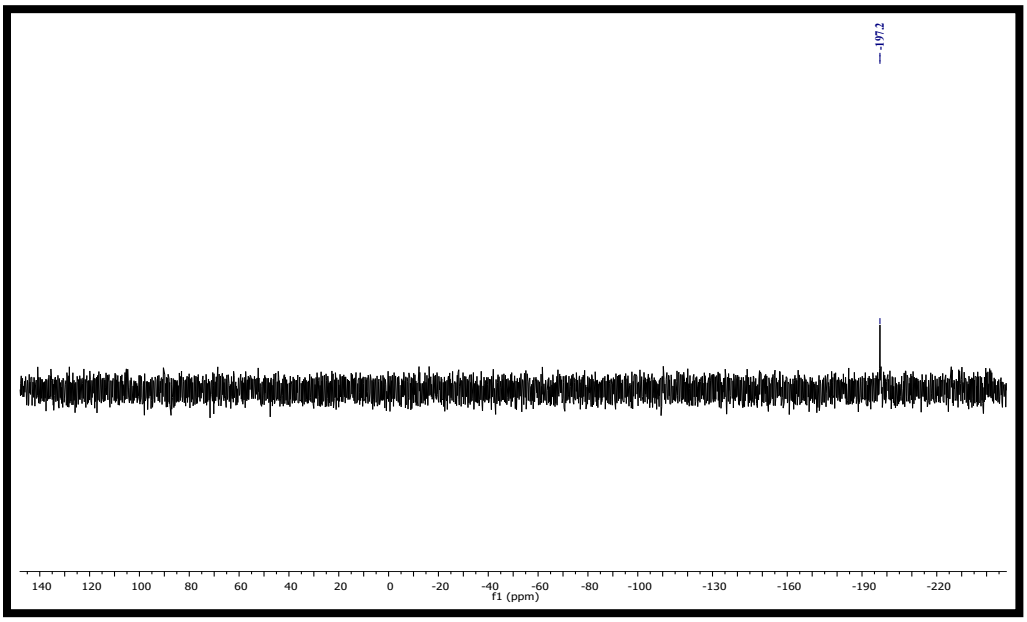

Fig. S10. ^{31}P NMR of **TBC-PTZ** in $CDCl_3$.

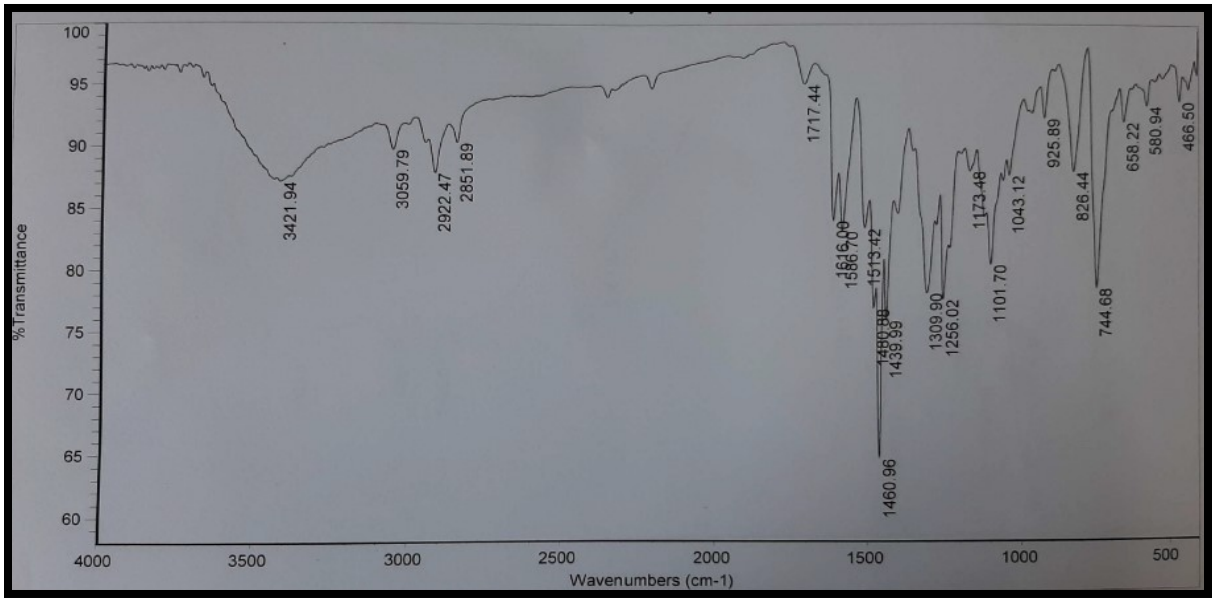

Fig. S11. IR spectrum of **TBC-PTZ**.

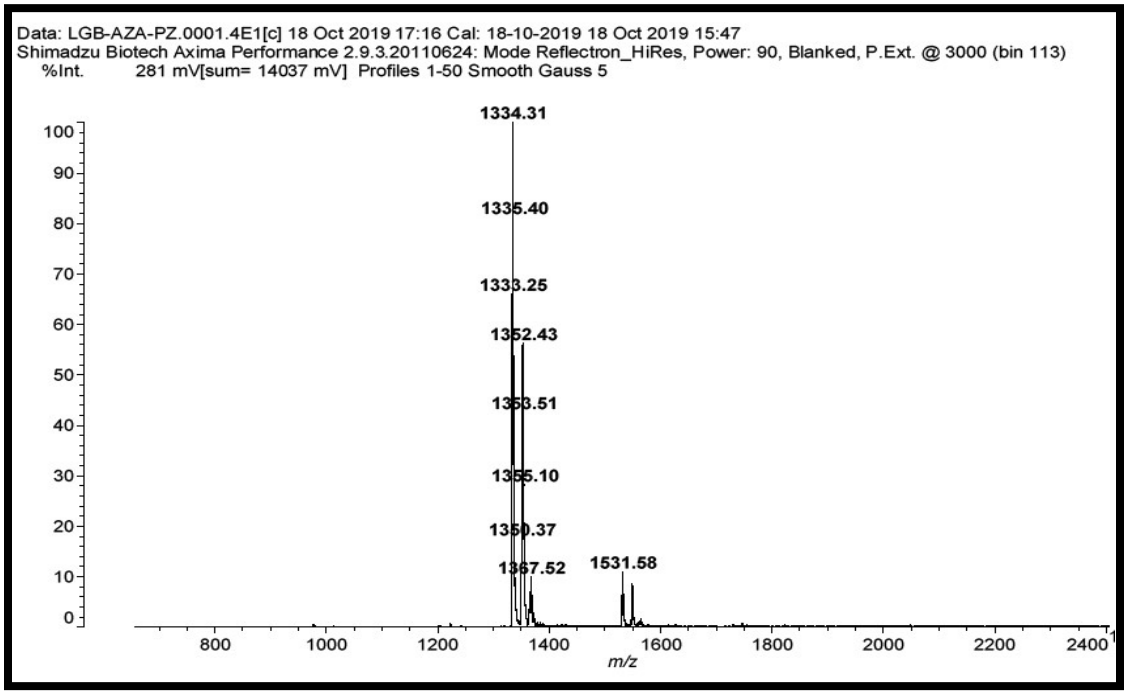

Fig. S12. MALDI-MS spectrum of **TBC-PTZ**.

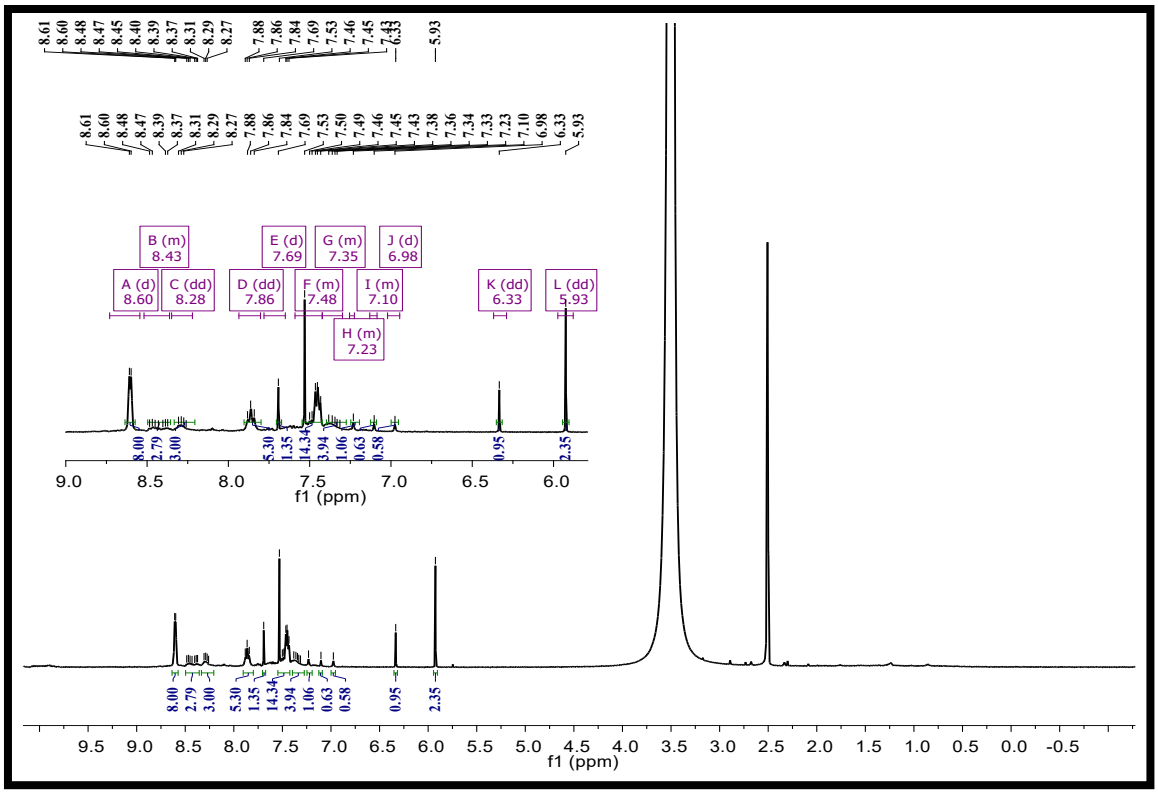

Fig. S13. ^{1}H NMR spectrum of **TBC-CBZ** in DMSO-d_6.

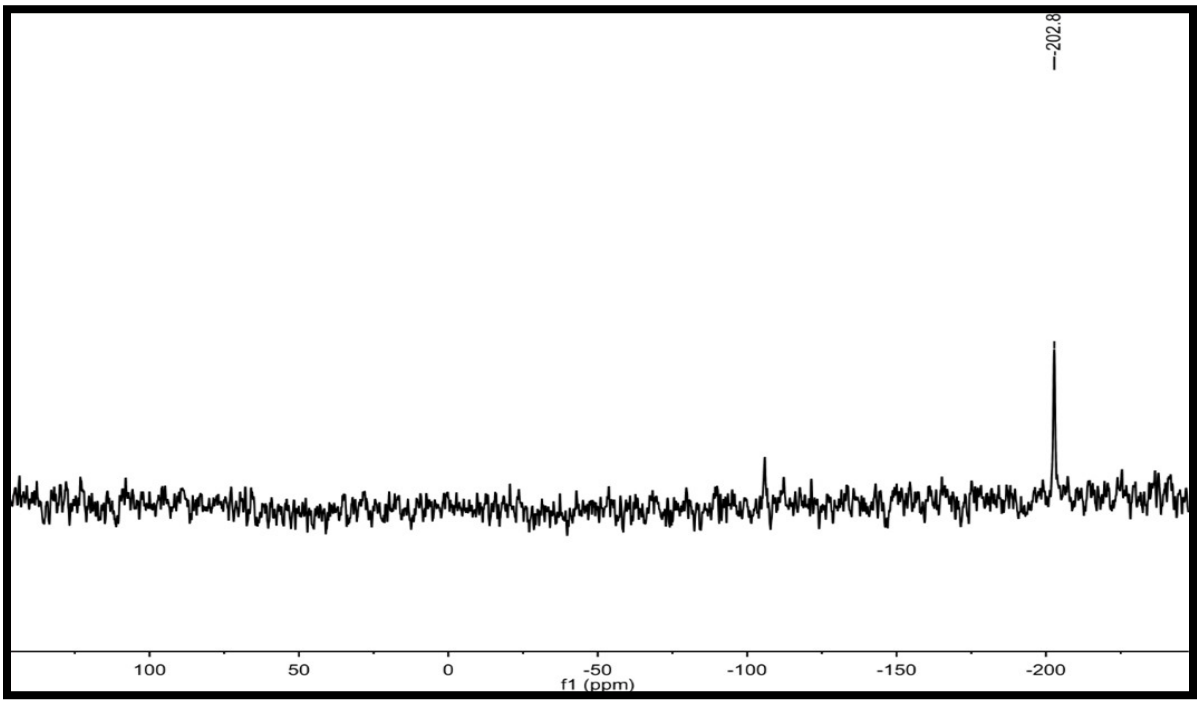

Fig. S14. ^{31}P NMR of **TBC-CBZ** in DMSO-d_6.

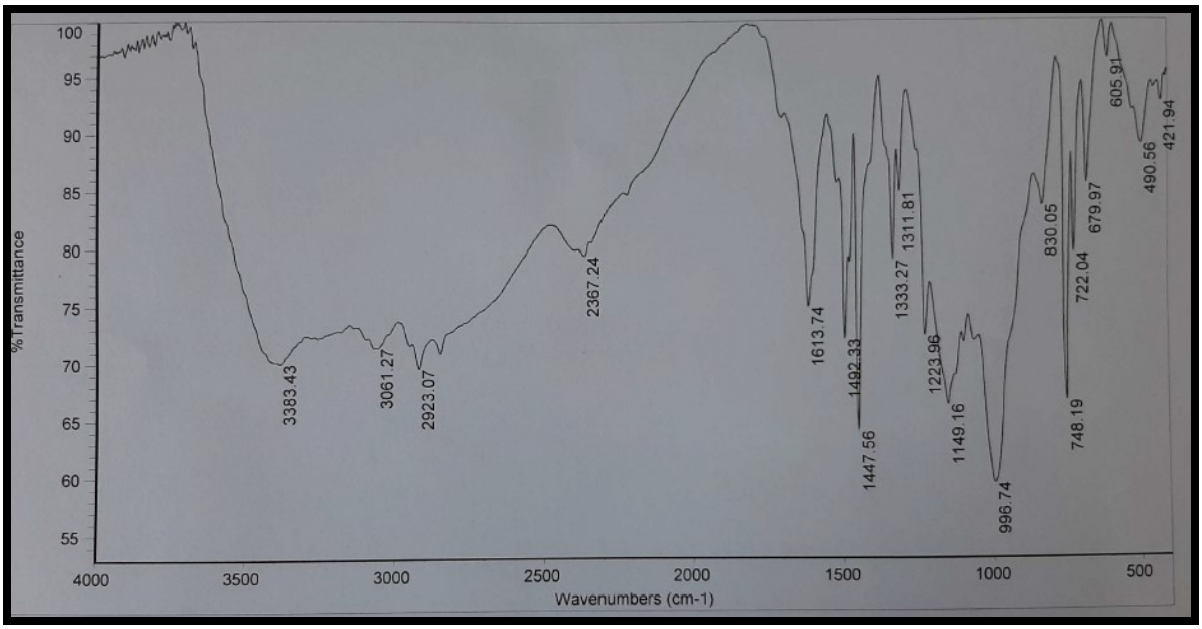

Fig. S15. IR spectrum of **TBC-CBZ**.

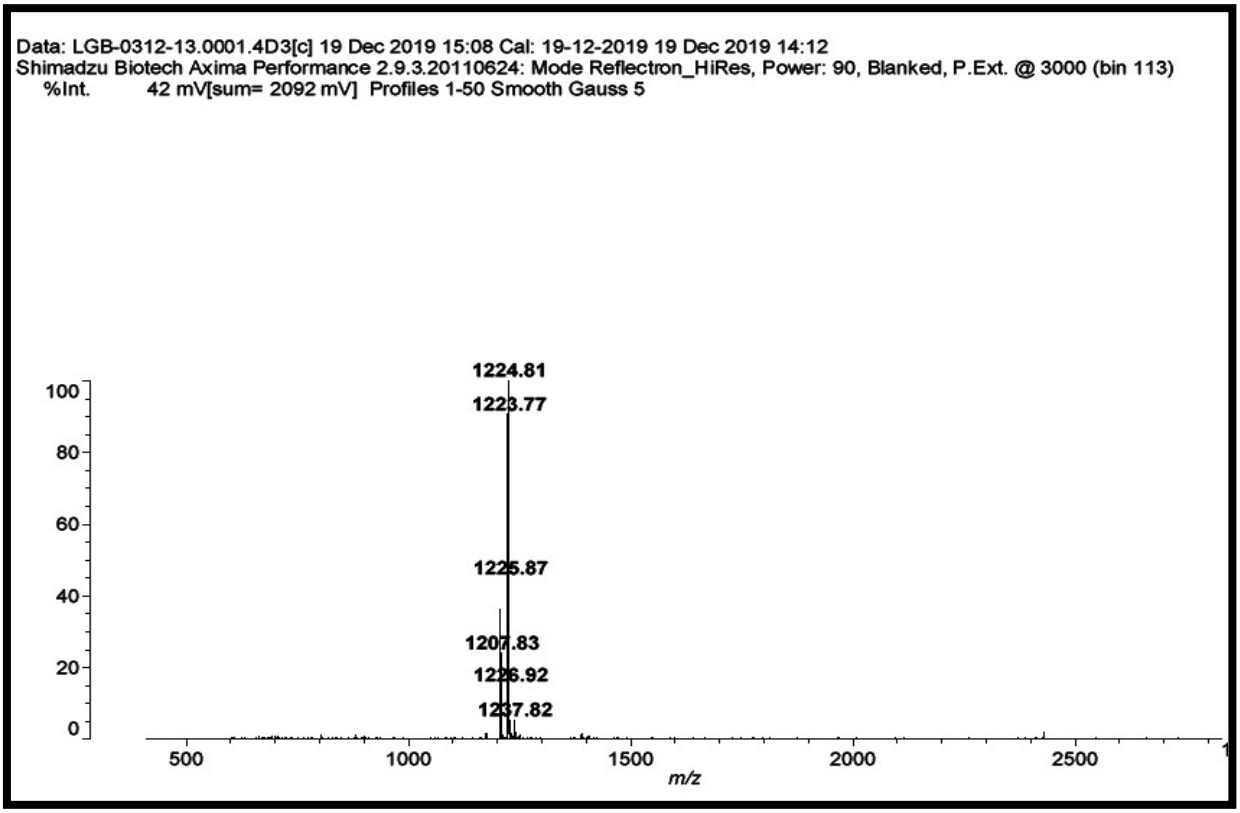

Fig. S16. MALDI-MS spectrum of **TBC-CBZ**.

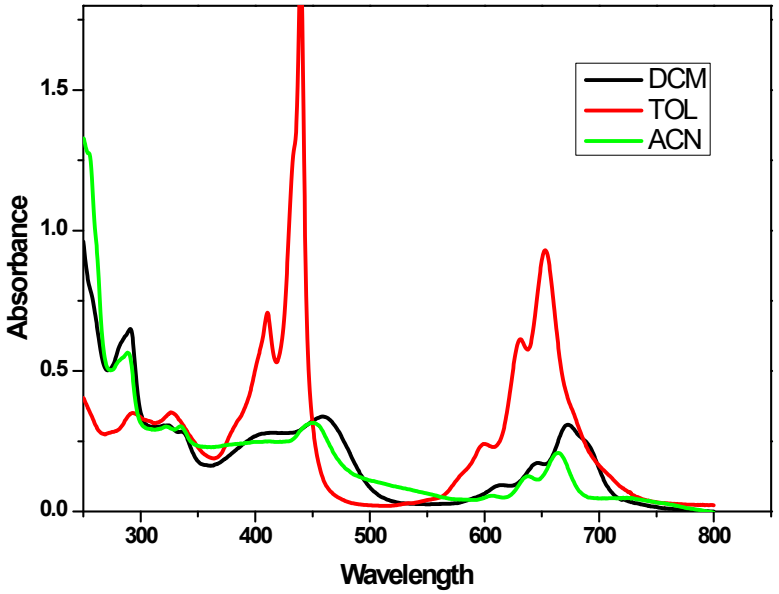

Fig. S17. Absorption spectra of **TBC-CBZ** in different solvents.

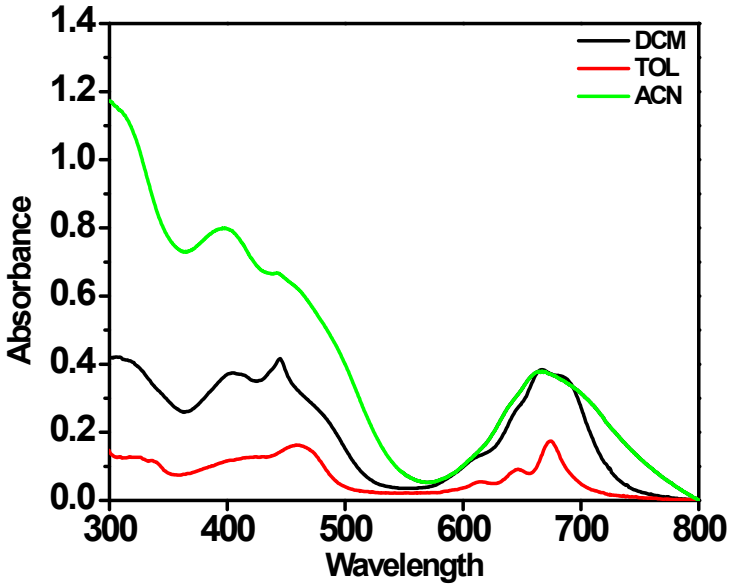

Fig. S18. Absorption spectra of **TBC-PTZ** in different solvents.

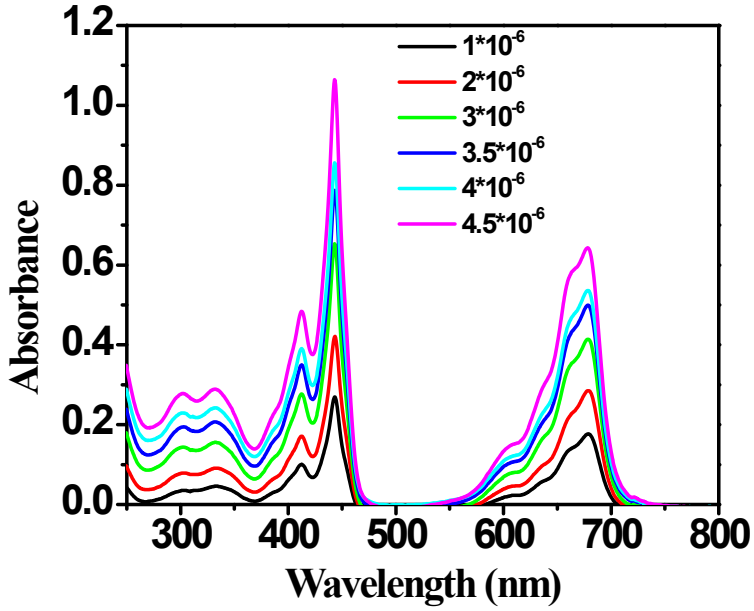

Fig. S19. Absorption spectra of **TBC-*tert*** in DCM at various concentrations.

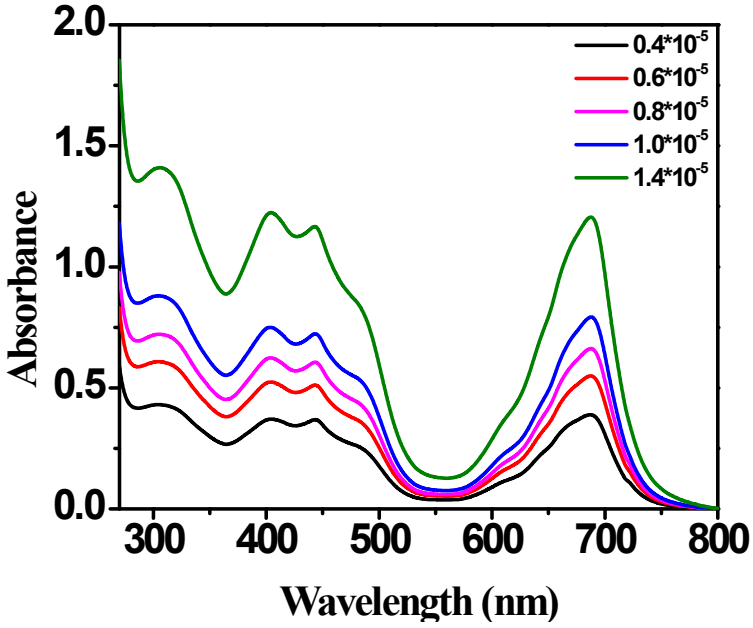

Fig. S20. Absorption spectra of **TBC-PTZ** in DCM at various concentrations.

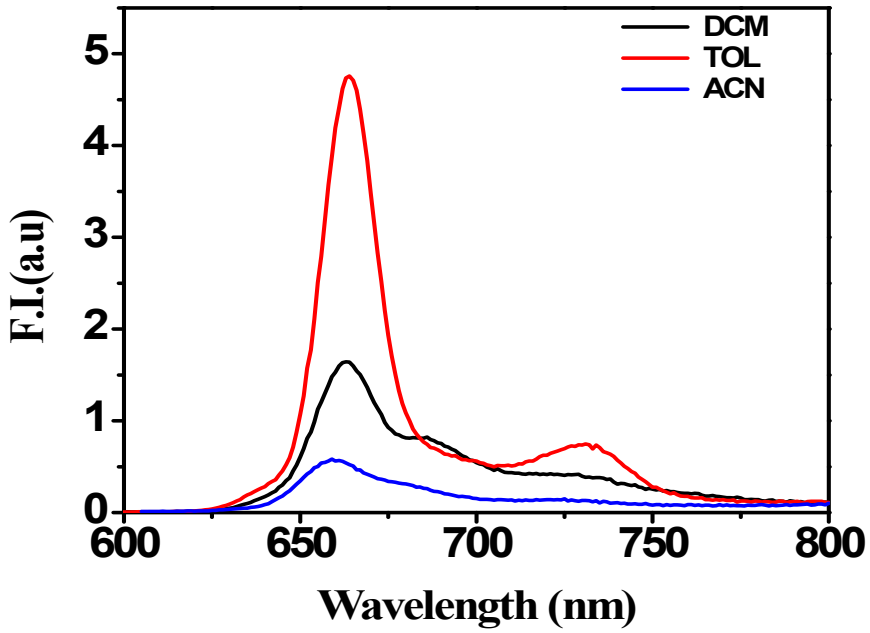

Fig. S21. Fluorescence spectra of **TBC-*tert*** in various solvents.

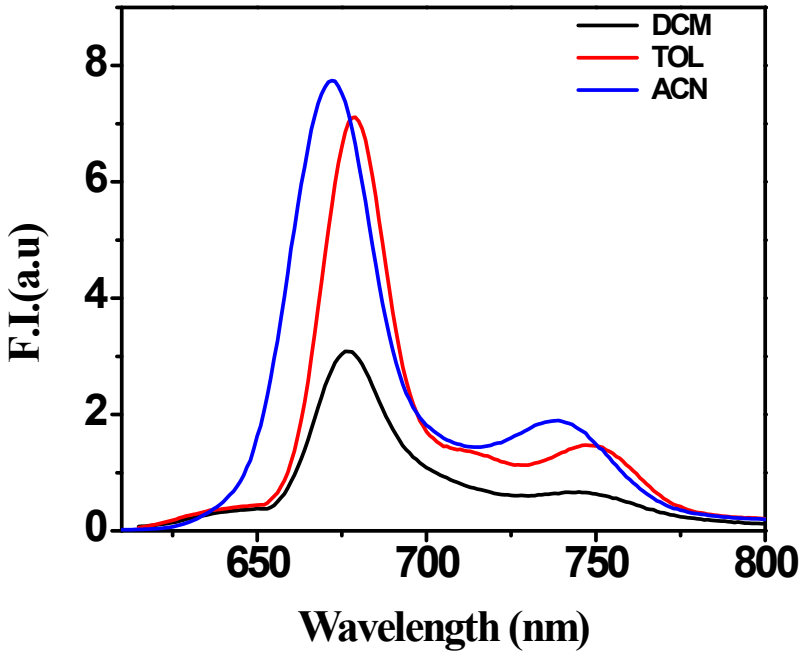

Fig. S22. Fluorescence spectra of **TBC-CBZ** in various solvents.

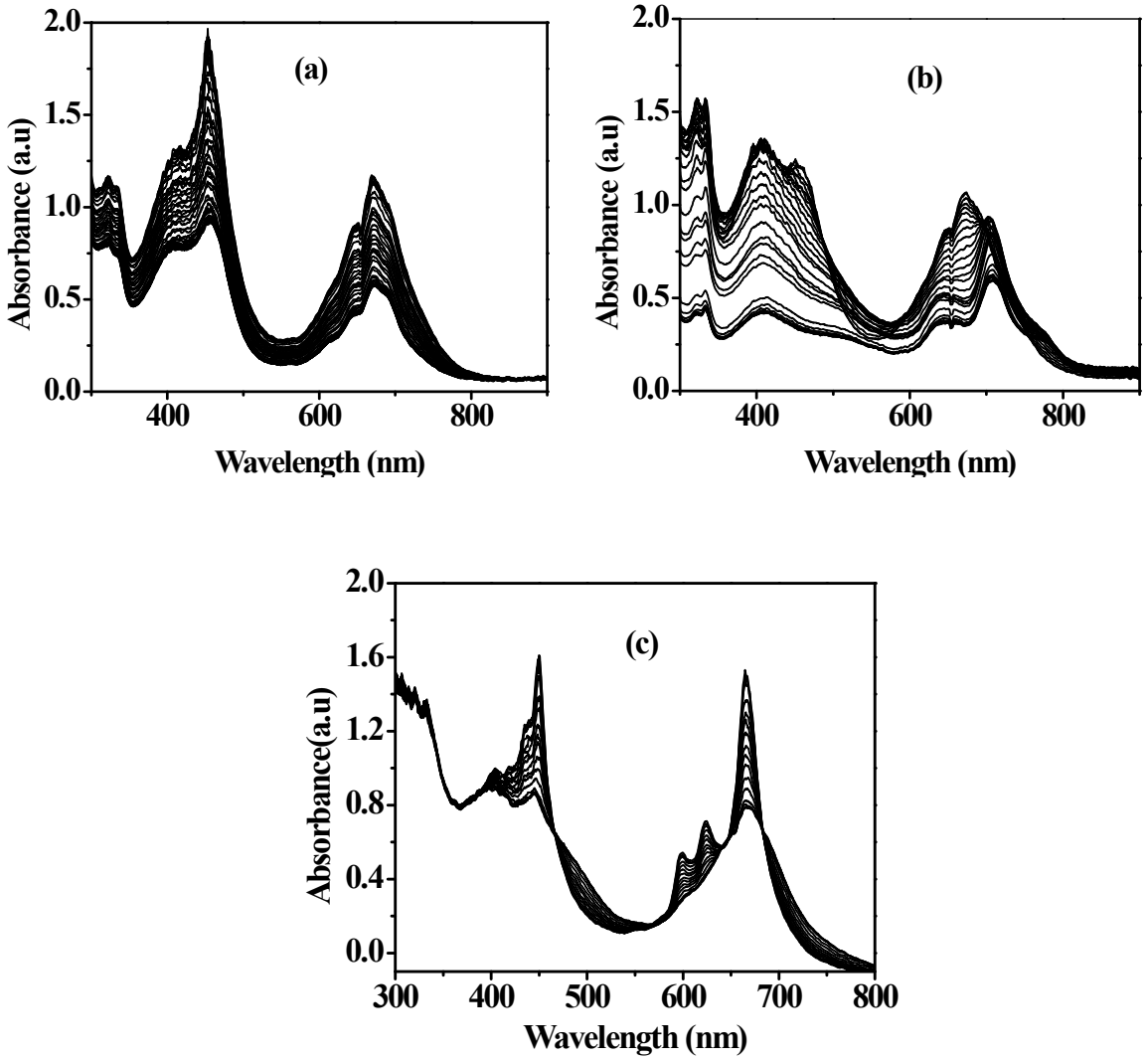

Fig. S23. *In-situ* UV-Vis spectro-electrochemical changes of **TBC-CBZ**. a) E_{app} = 0.90 V b) E_{app} = 1.60 V c) E_{app} = -1.30 V.

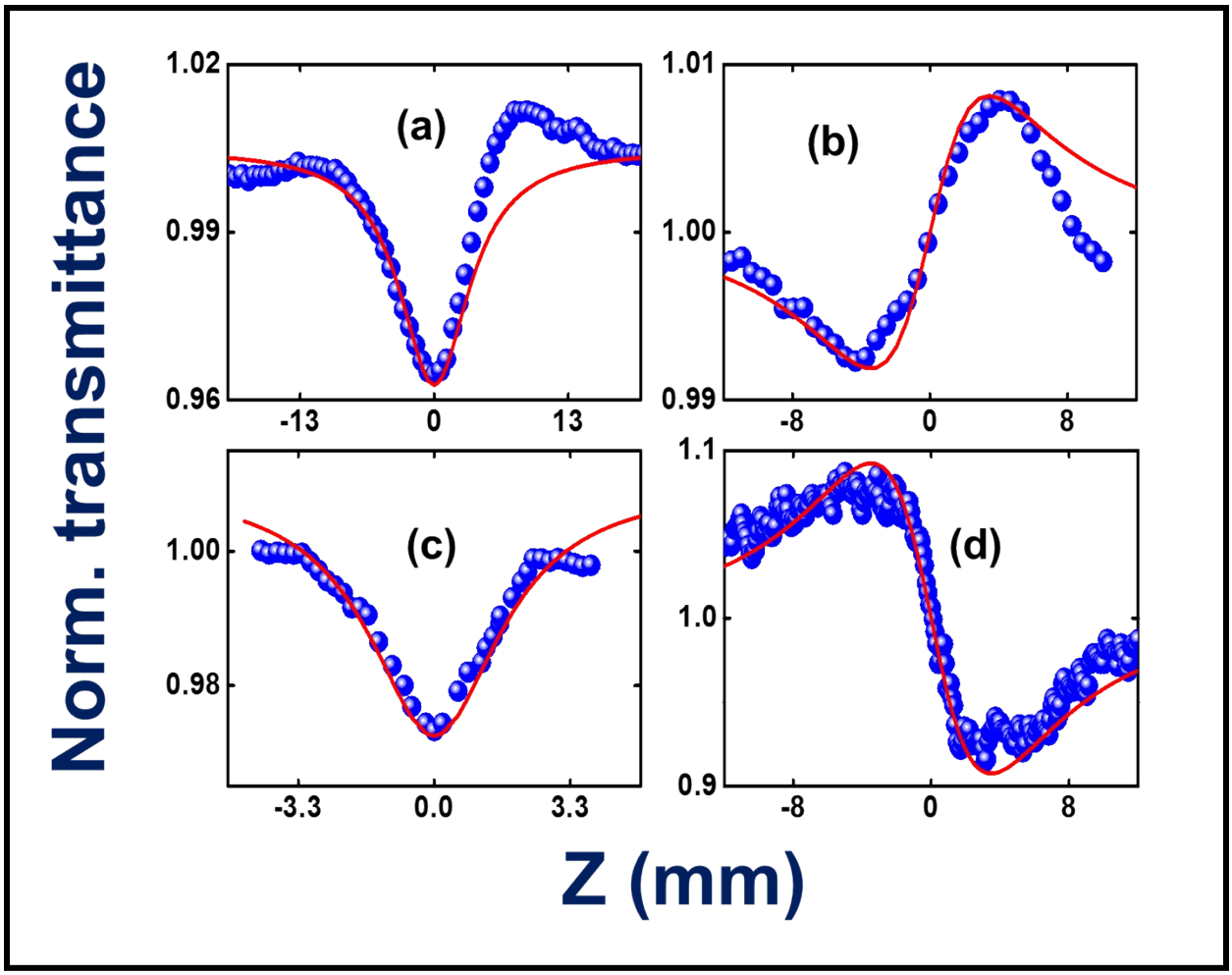

Fig. **S24 .** NLO optical data (a) OA (b) CA of DCM solvent under excitation of femtosecond1 kHz, 50 fs, 800 nm pulses. NLO optical data (c) OA (d) CA of DCM solvent under the excitation of femtosecond80 MHz, 150 fs, 800 nm pulses. 3D blue spheres and red continuous lines correspondingly represent experimental data and theoretically fitted curves.

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