Synthesis of efficient bi-anchoring bifuran/biphenyl derivatives for dye-sensitized solar cell applications.

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Supplementary Material

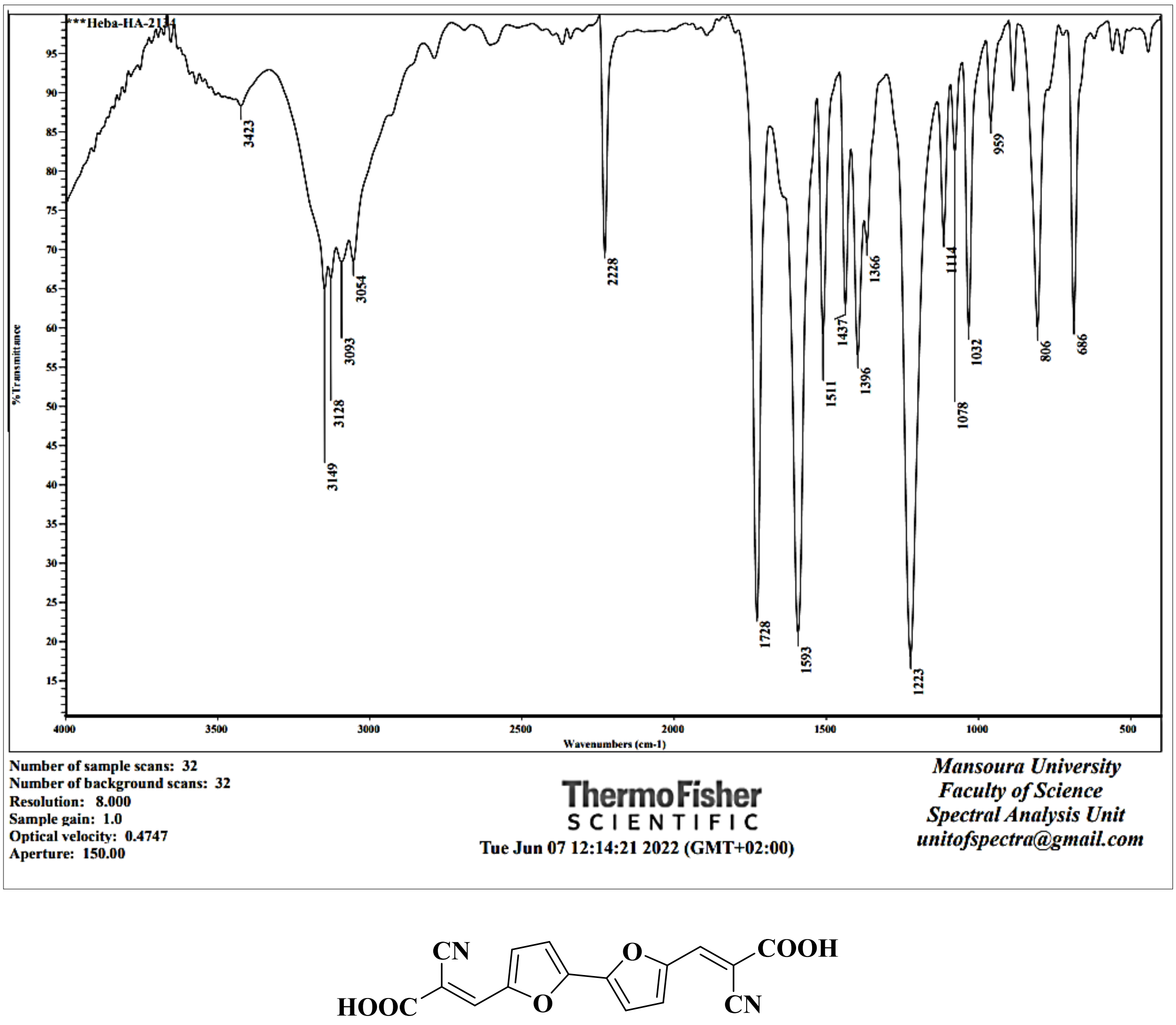
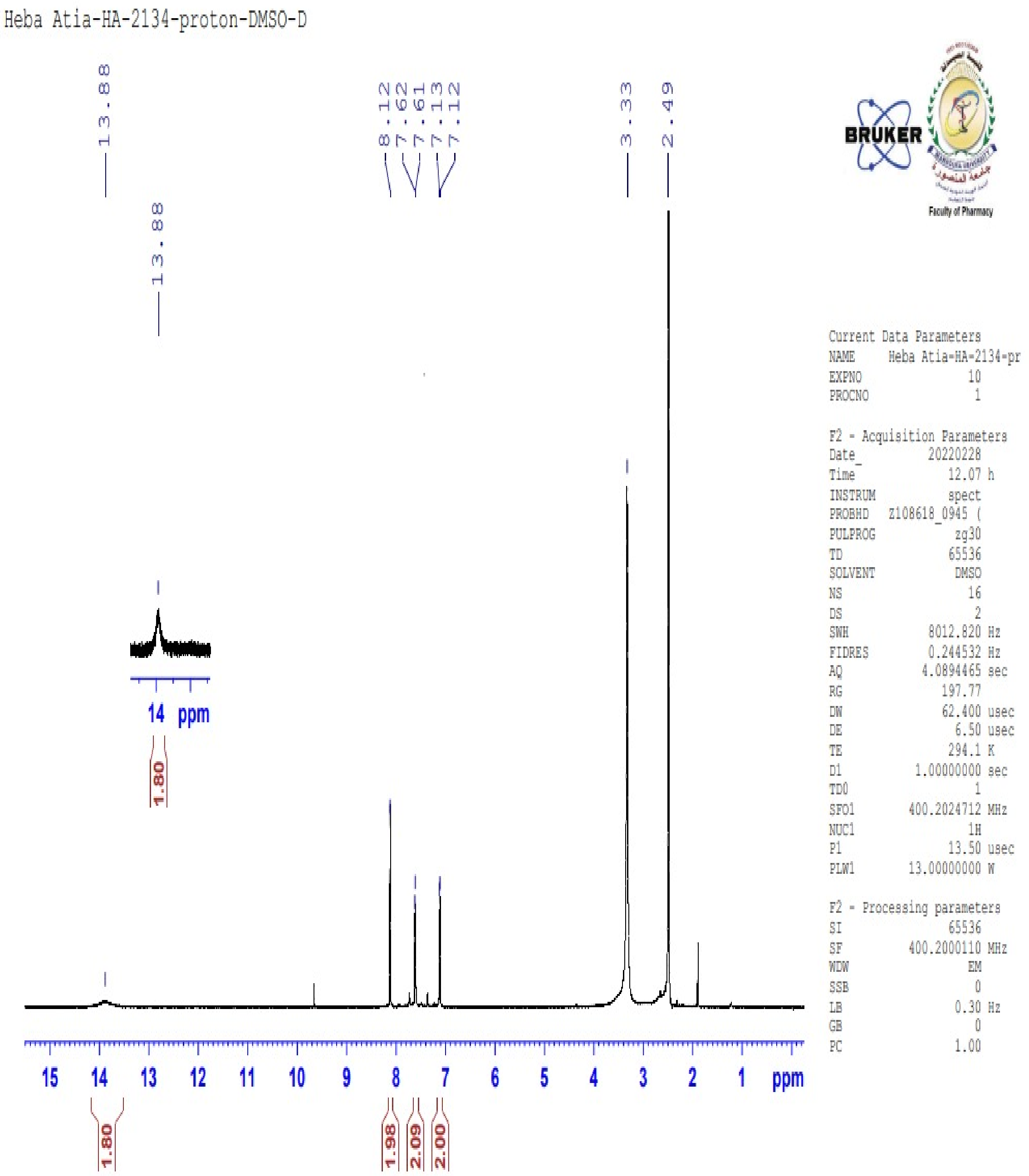


Figure S1: Compound HB-1 Infrared (IR) spectra



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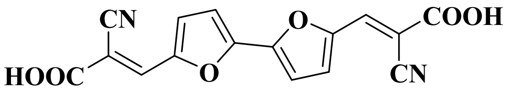

Figure S2: Compound HB-1 ^{1}H-NMR (DMSO-d_6)/Bruker 400 MHz

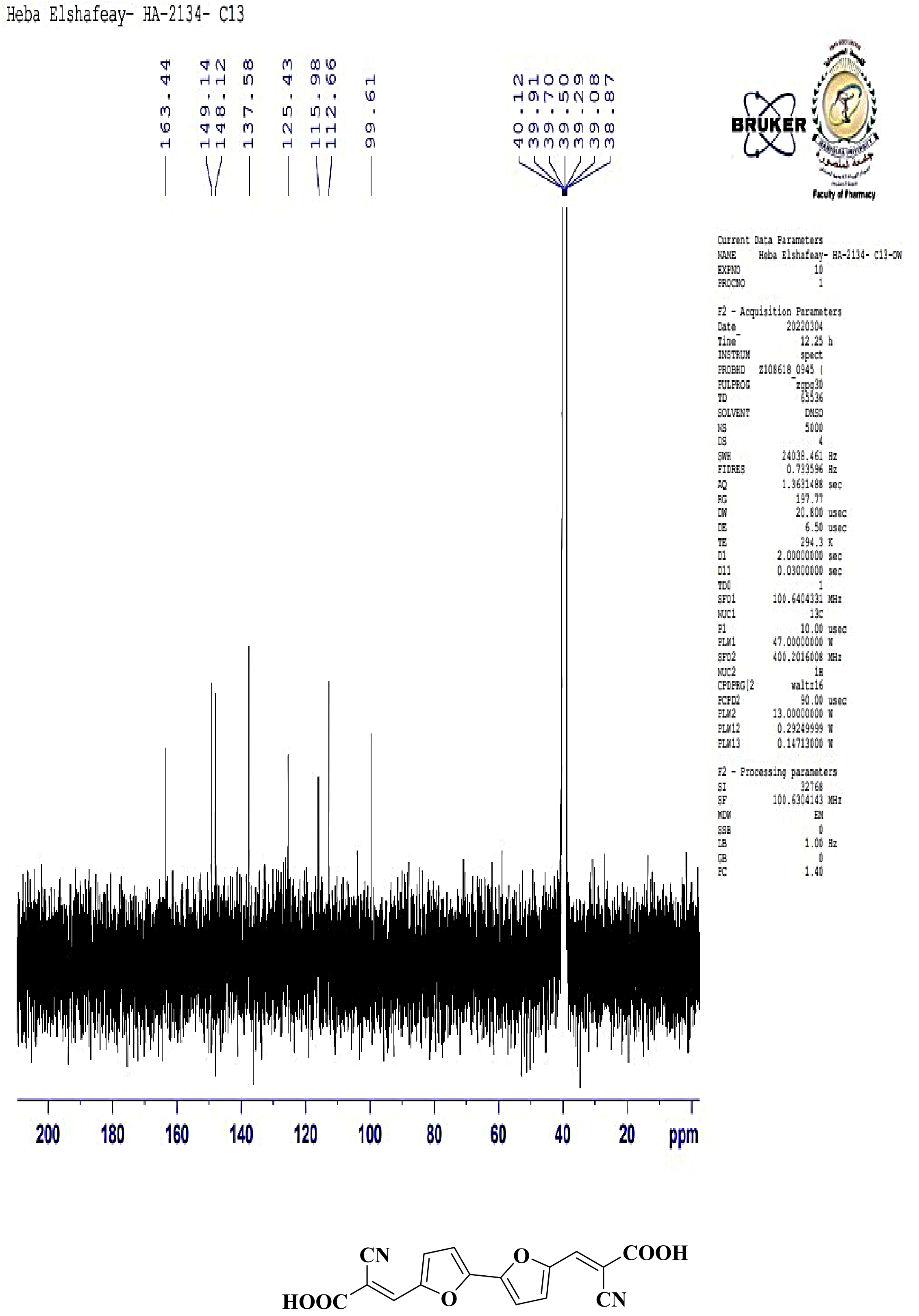

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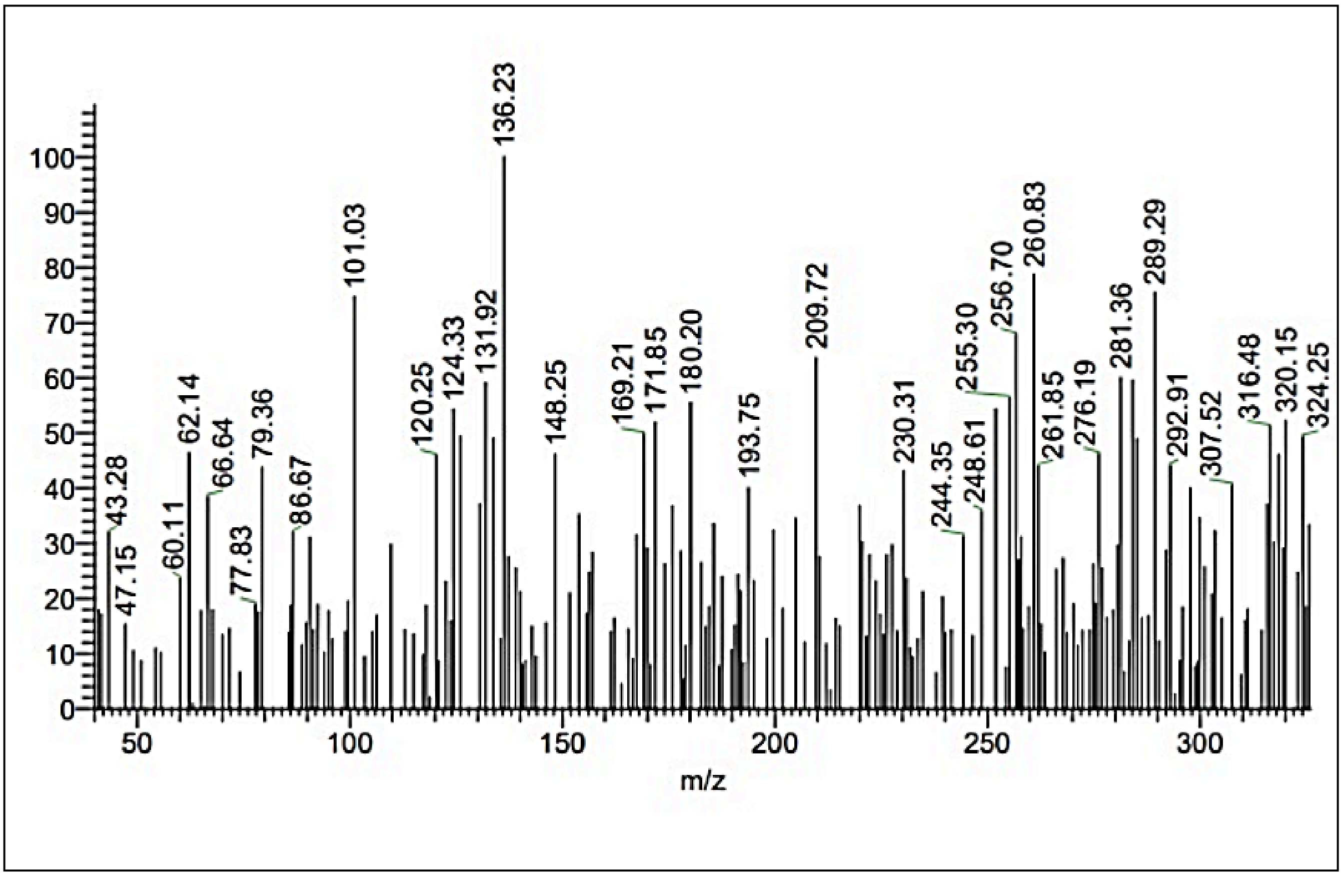
Figure S3: Compound HB-1 ^{13}C-NMR (DMSO-d_6)/Bruker 100 MHz



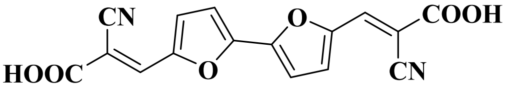
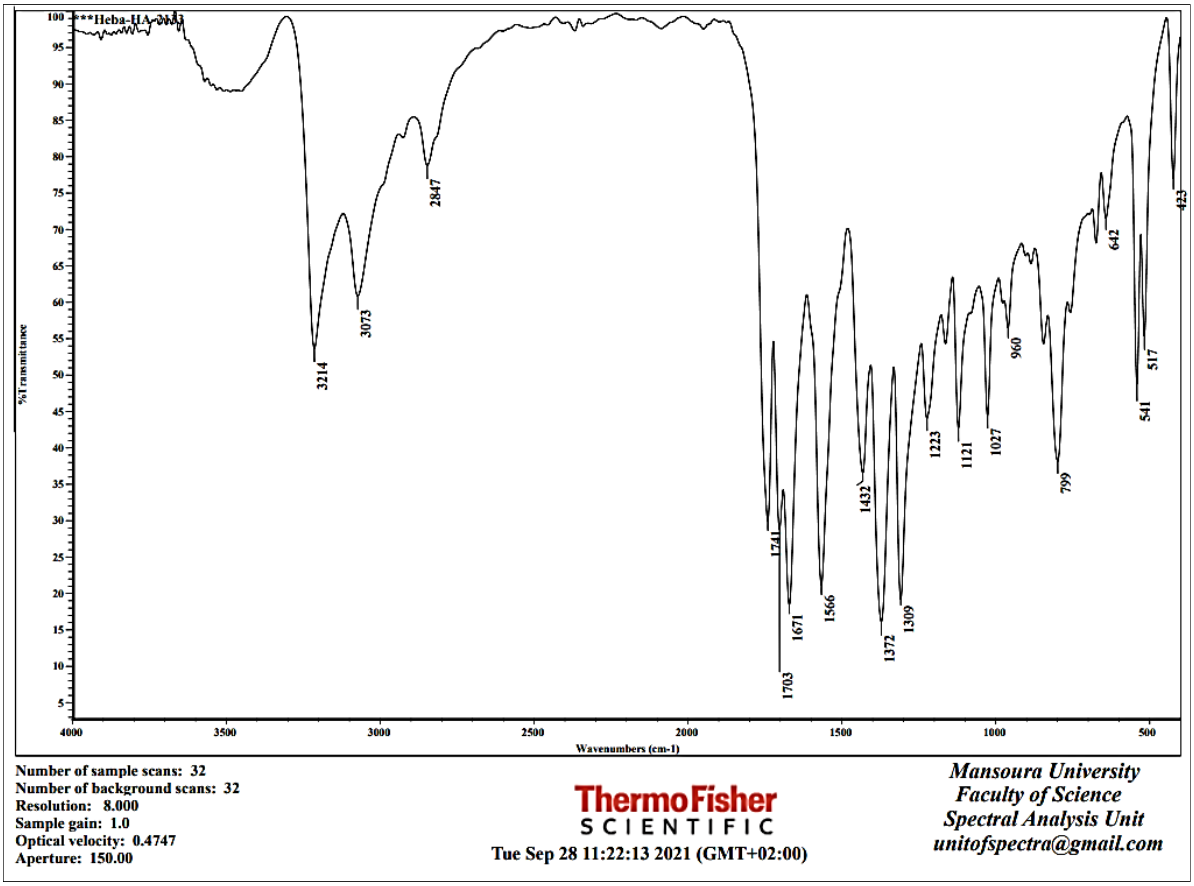


Figure S4: Compound HB-1Mass spectrum.



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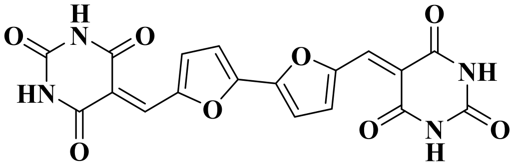

Figure S5: Compound HB-2 Infrared (IR) spectra

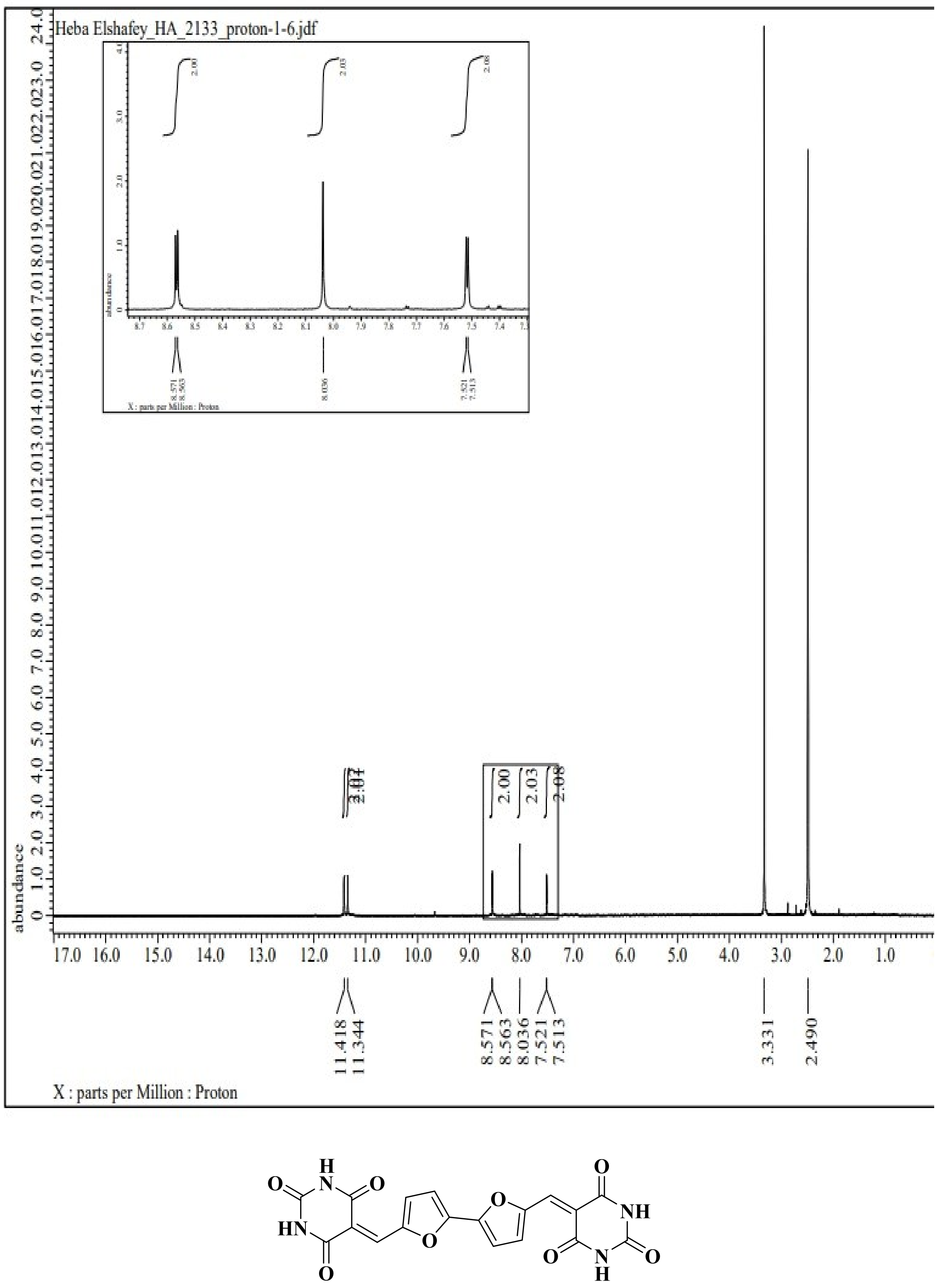

Figure S6: Compound HB-2 ^{1}H-NMR (DMSO-d_6)/JEOL 500 MHz

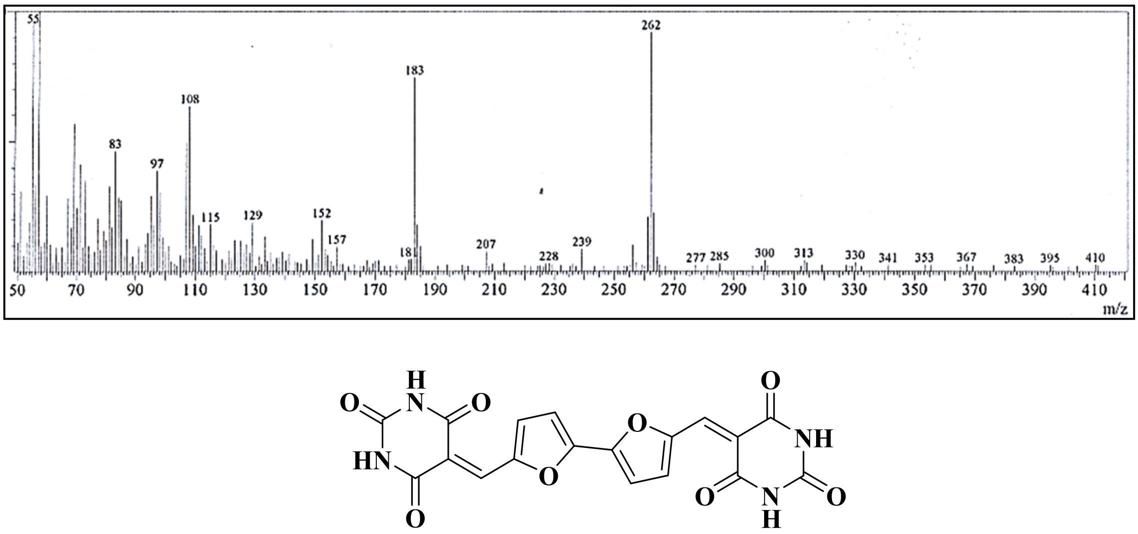

Figure S7: Compound HB-2 Mass spectrum.

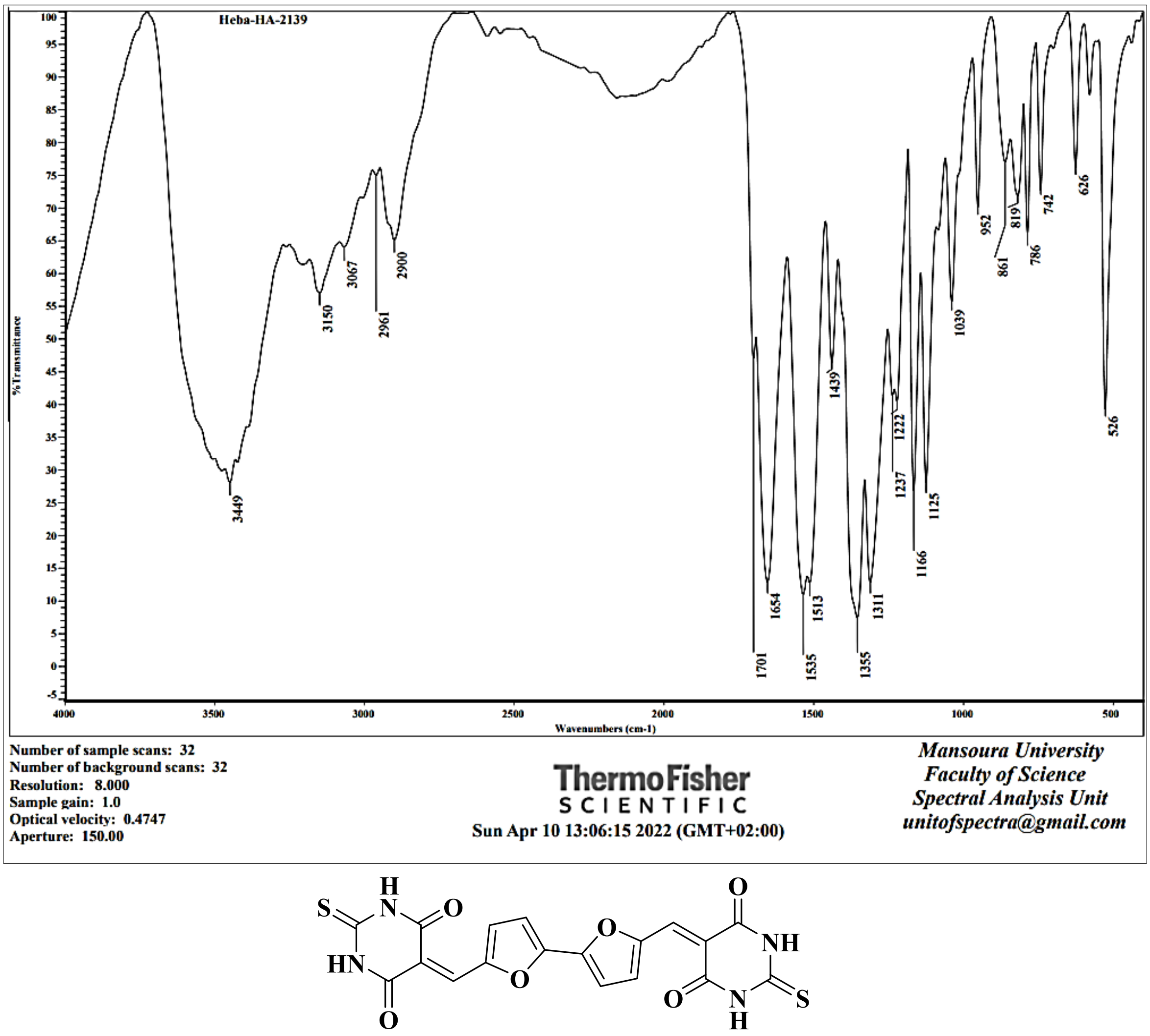

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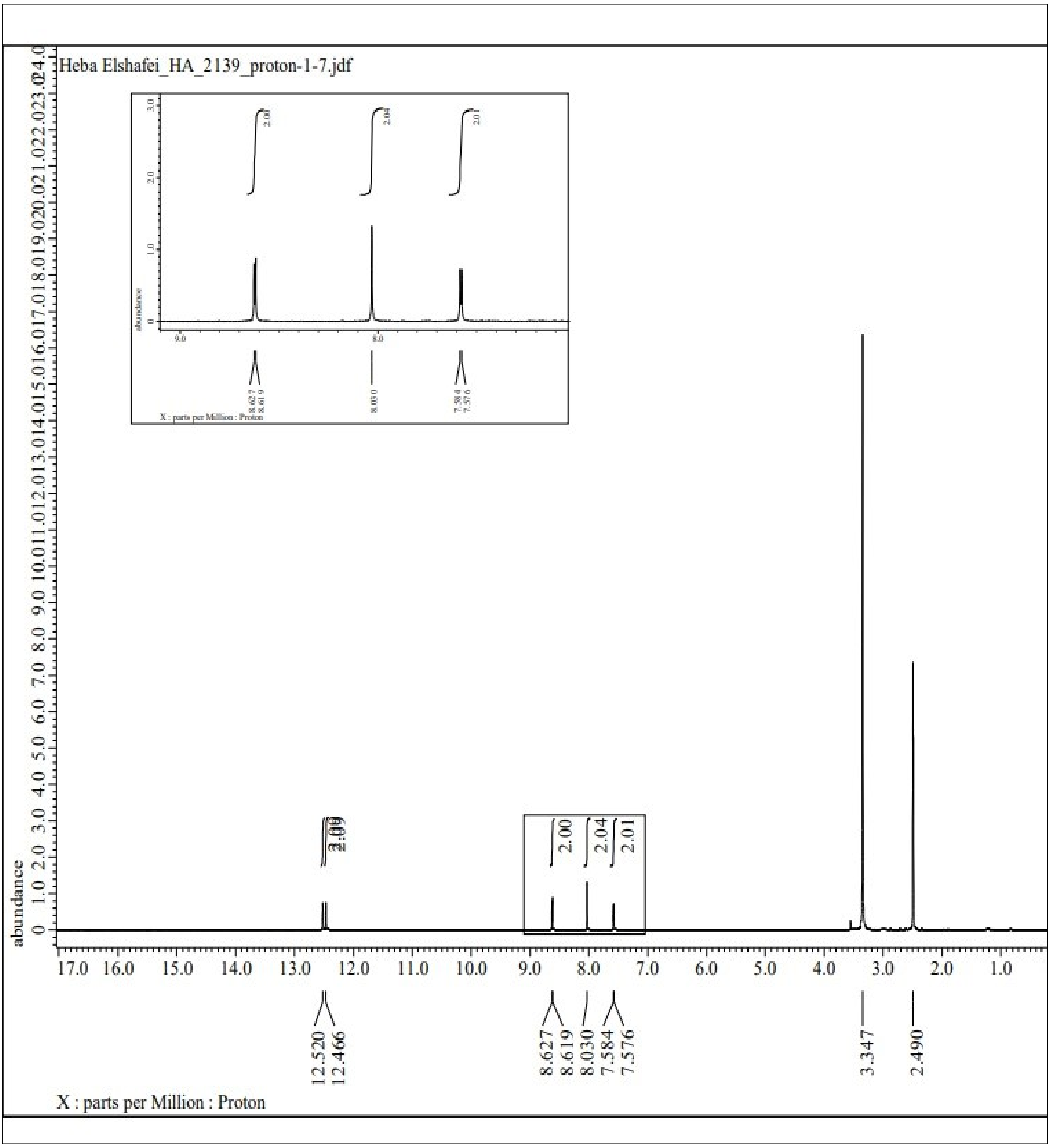
Figure S8: Compound HB-3 Infrared (IR) spectra



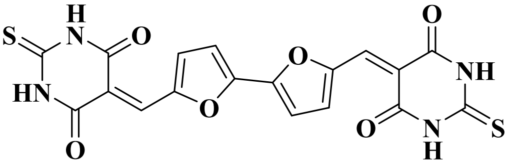
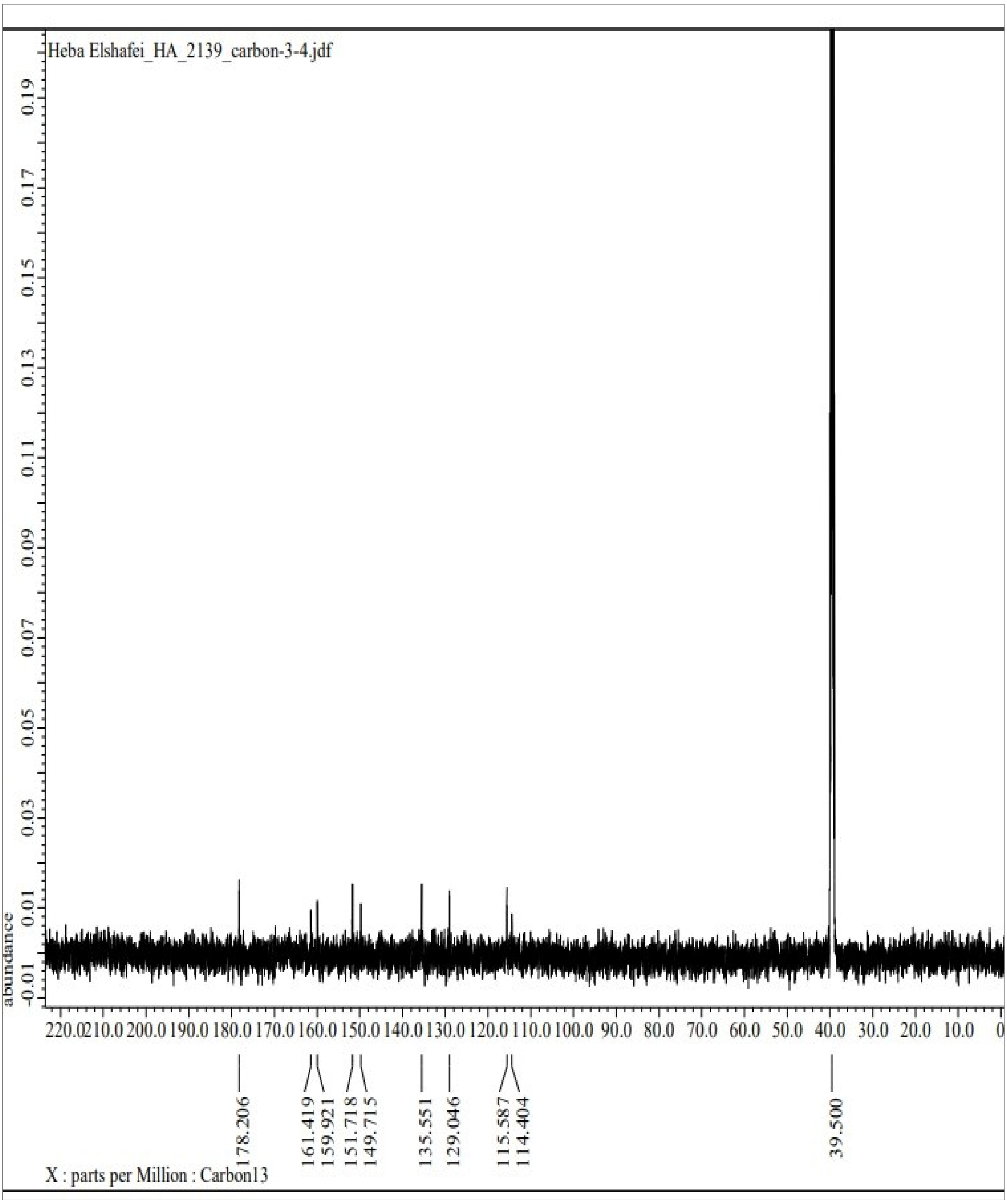


Figure S9: Compound HB-3 ^{1}H-NMR (DMSO-d_6)/JEOL 500 MHz



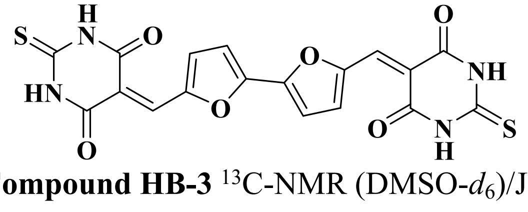


Figure S10: Compound HB-3 ^{13}C-NMR (DMSO-d_6)/JEOL 125 MHz

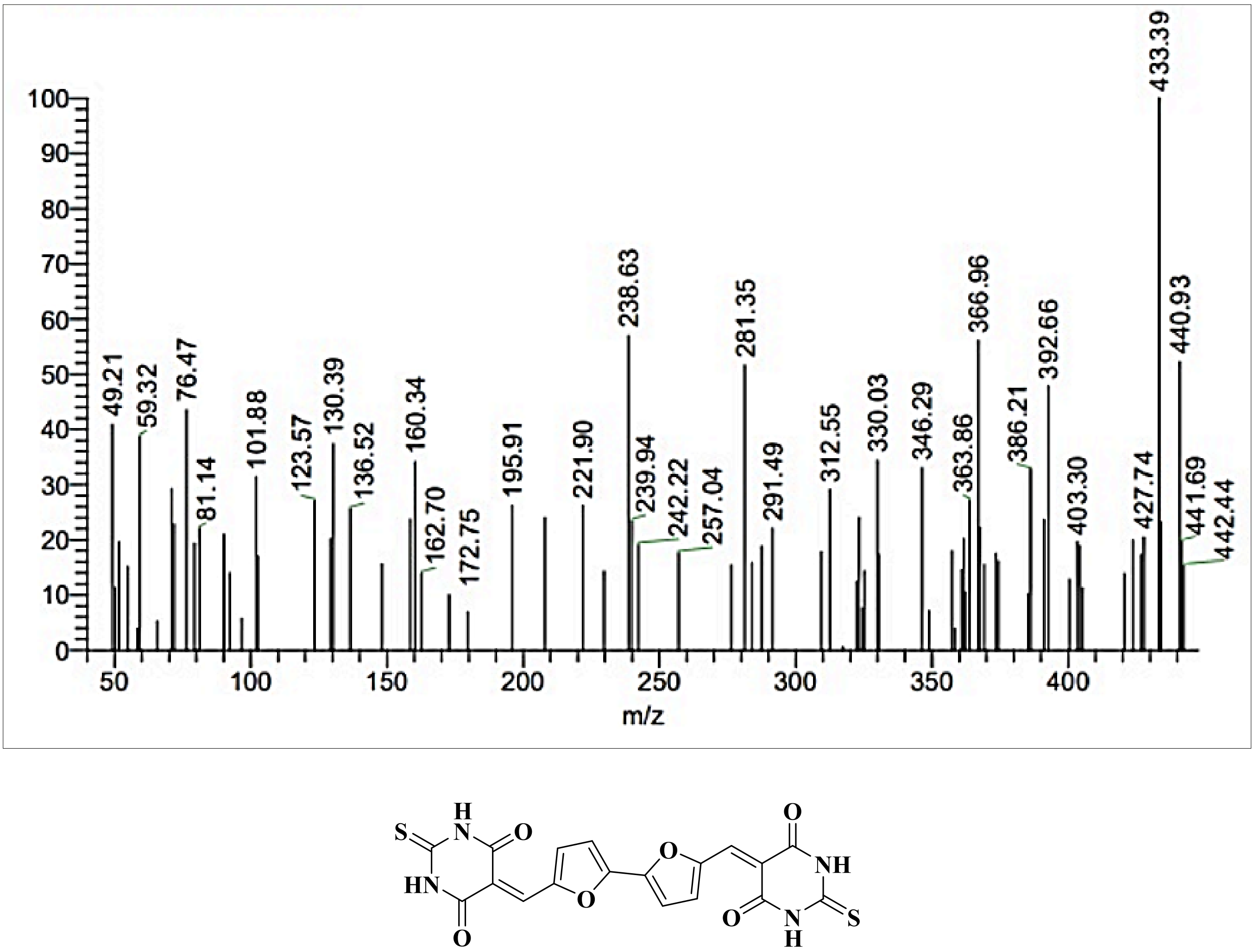
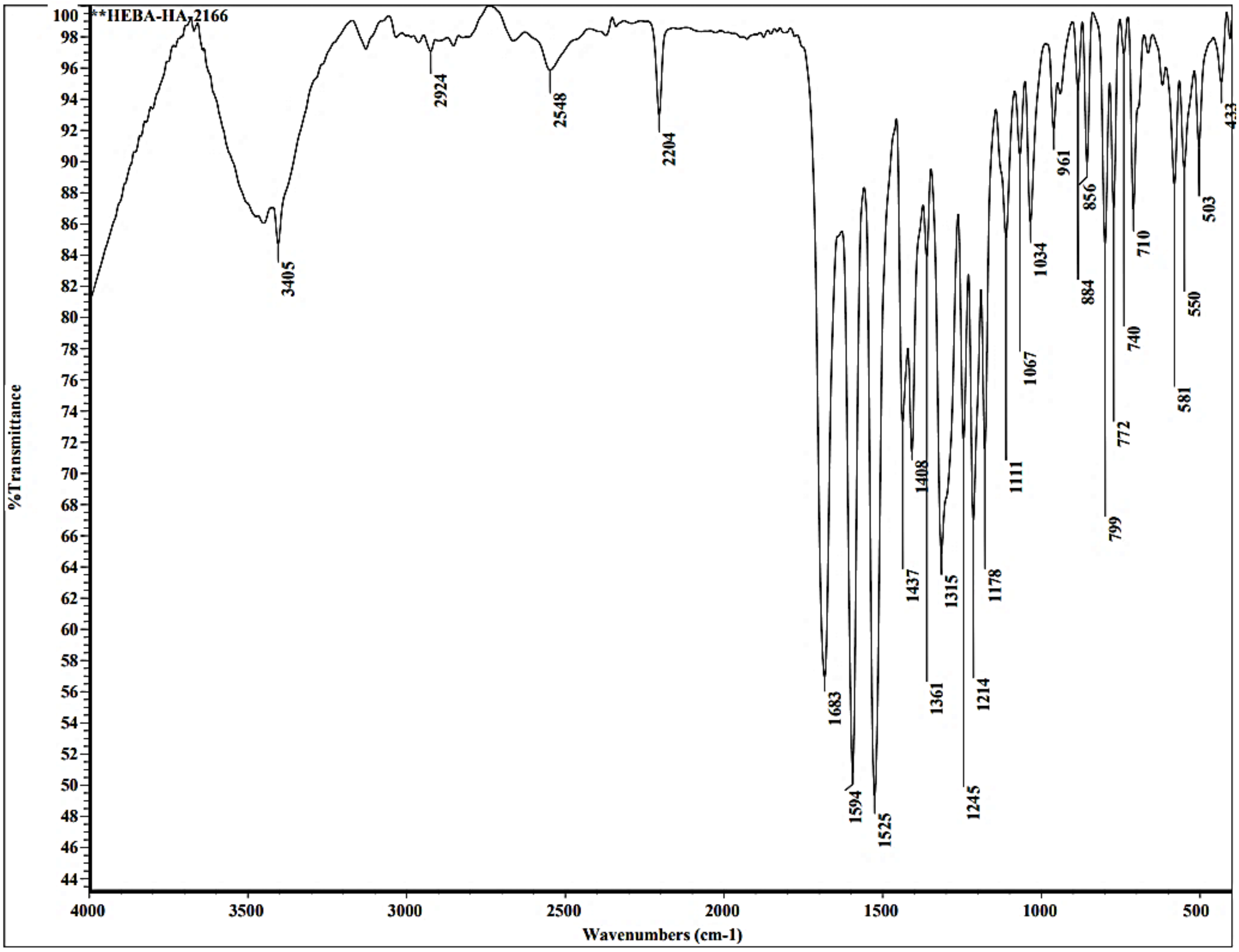


Figure S11: Compound HB-3 Mass Spectrum



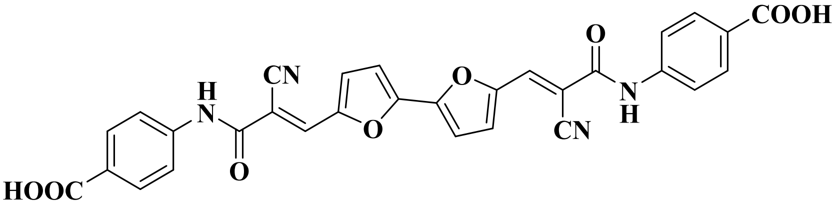
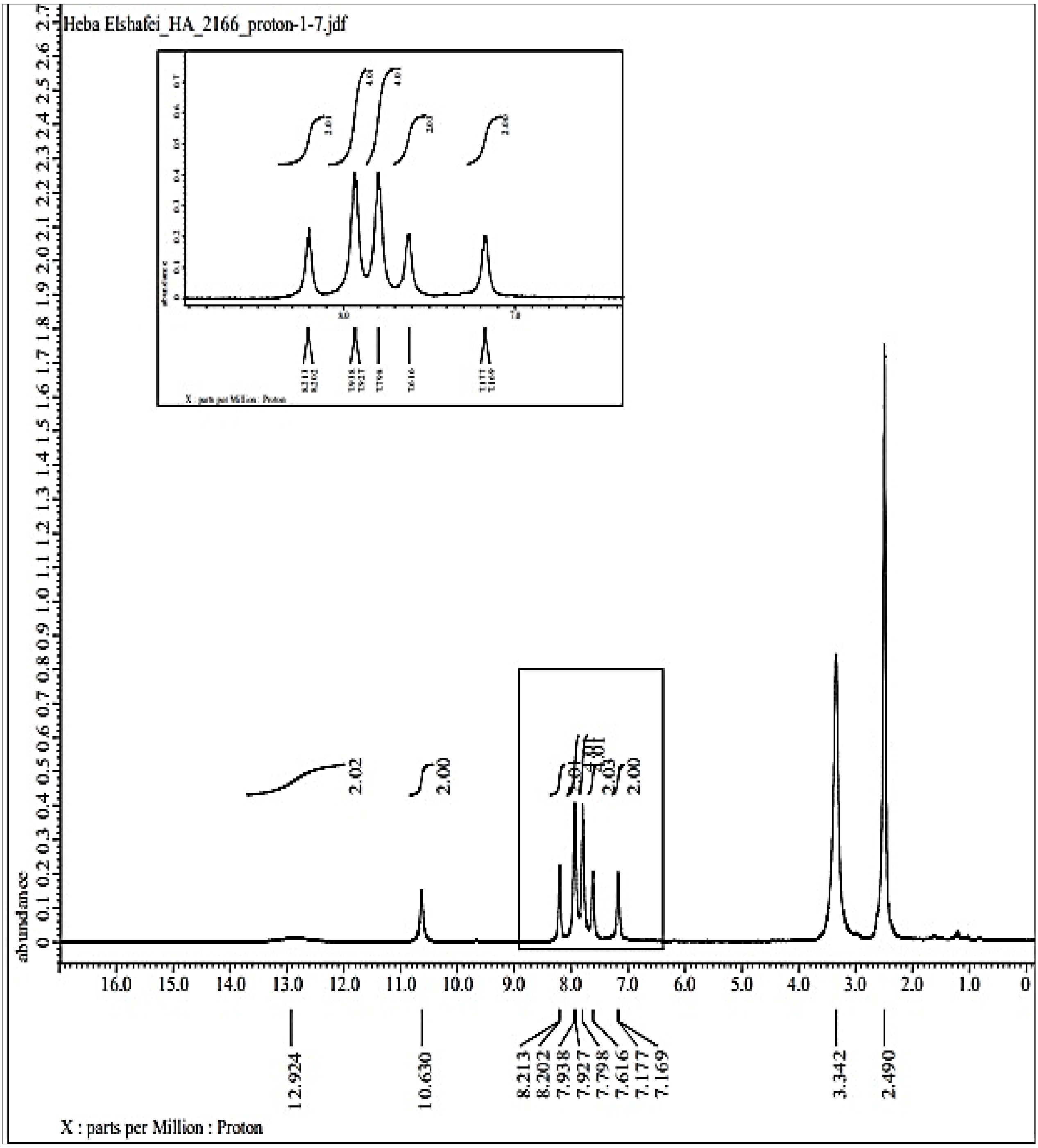


Figure S12: Compound HB-4 infrared (IR) spectra.



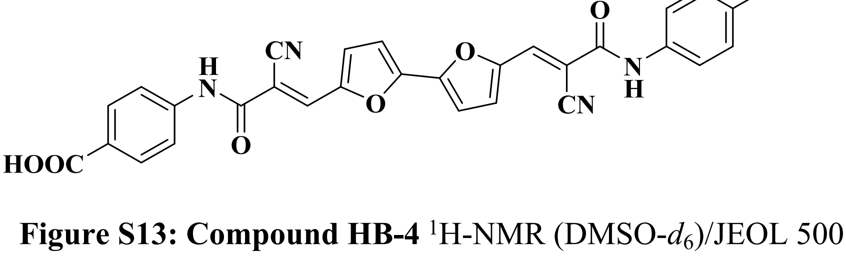


Figure S13: Compound HB-4 ^{1}H-NMR (DMSO-d_6)/JEOL 500 MHz

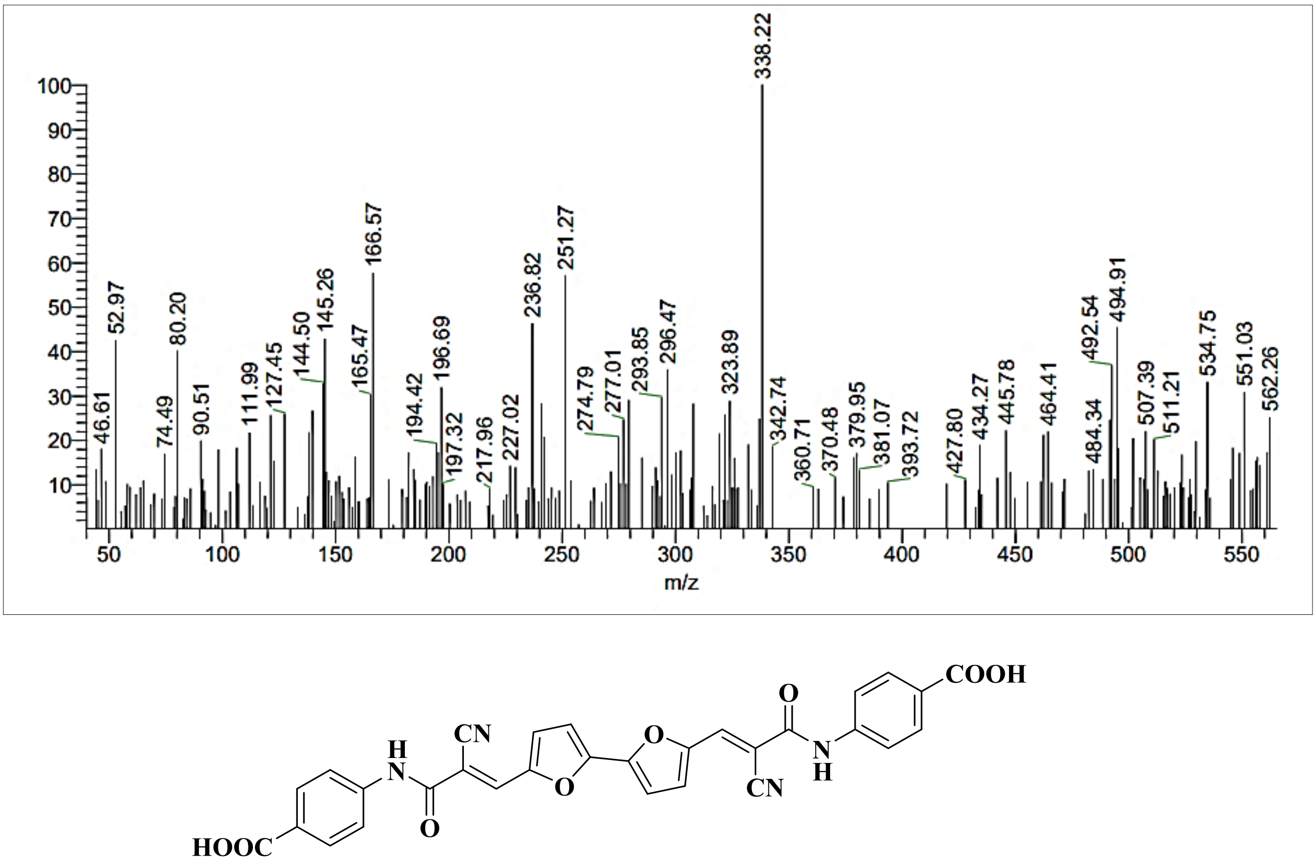


Figure S14: Compound HB-4 Mass Spectrum

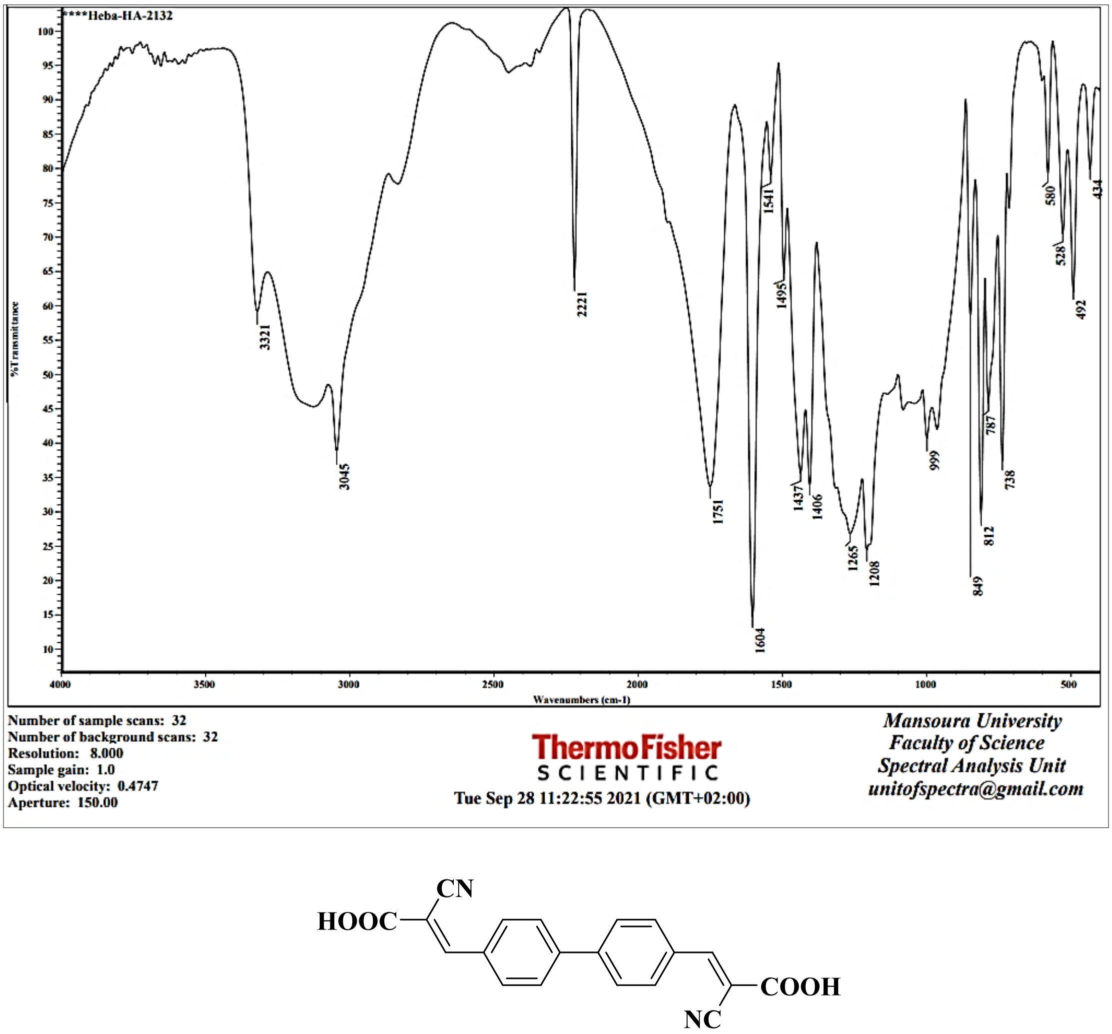


Figure S15: Compound HB-5 Infrared (IR) spectra

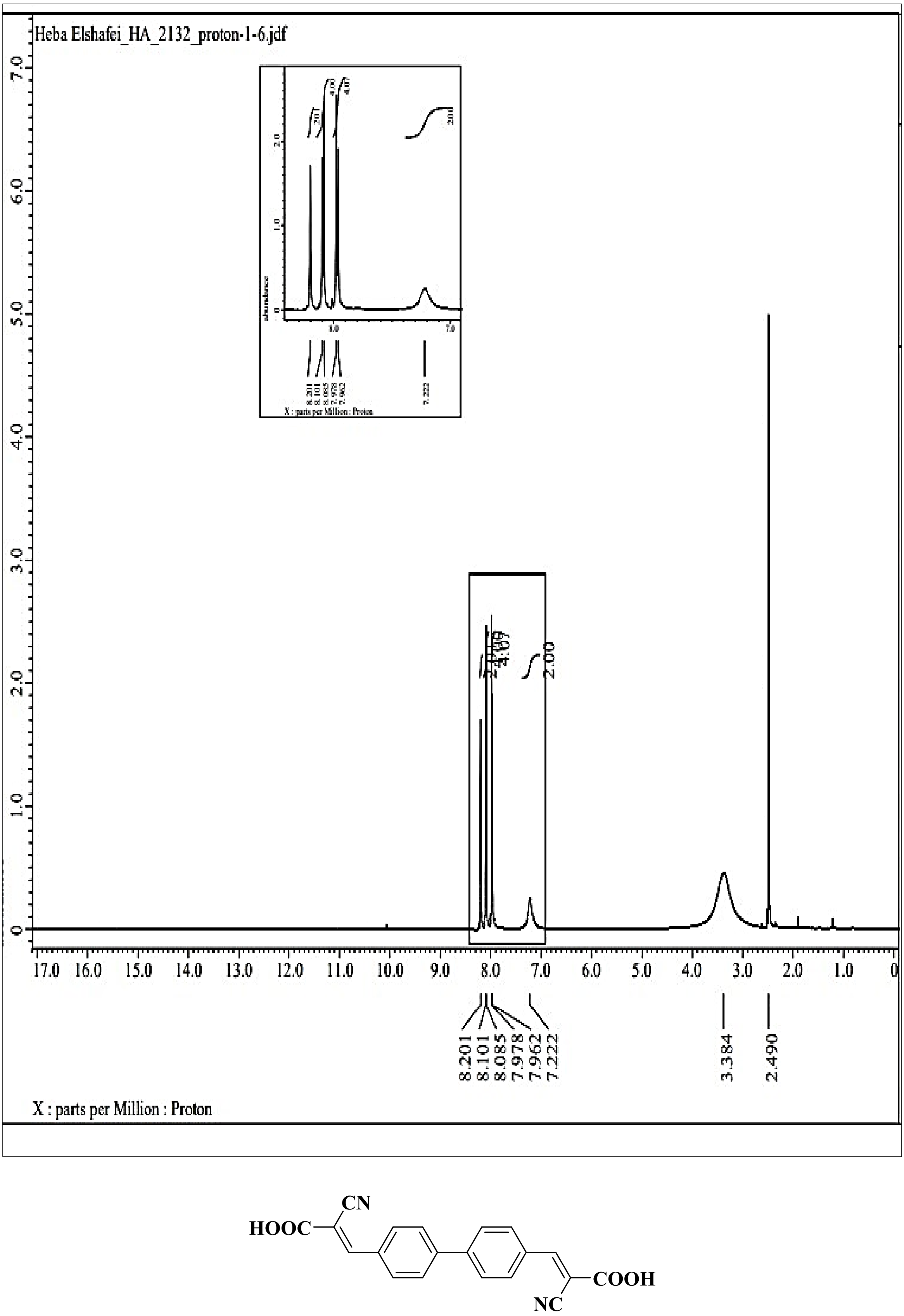
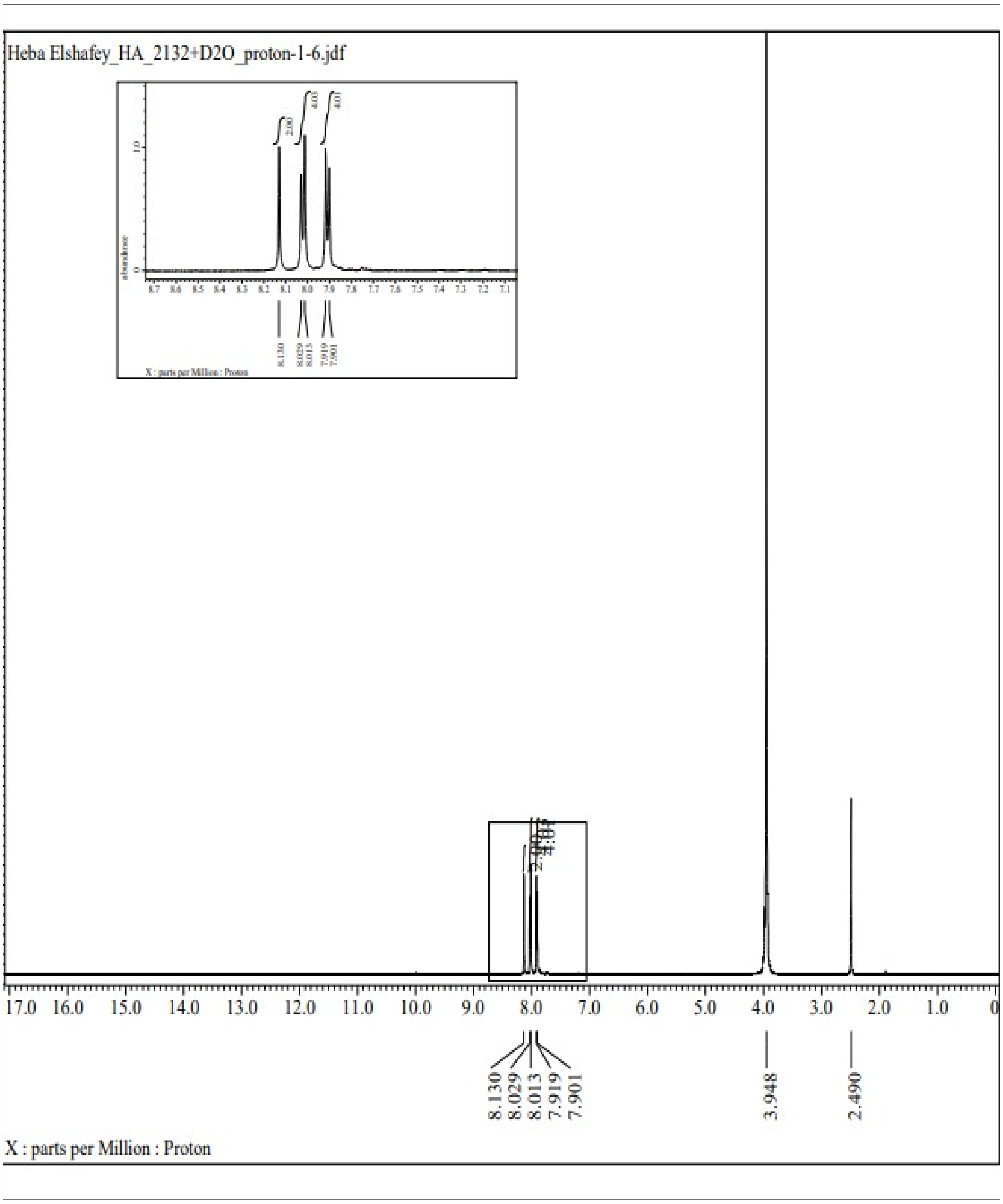


Figure S16: Compound HB-5 ^{1}H-NMR (DMSO-d_6)/JEOL 500 MHz



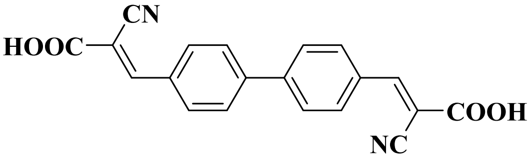


Figure S17: Compound HB-5 ^{1}H-NMR (D_2O/DMSO-d_6)/JEOL 500 MHz

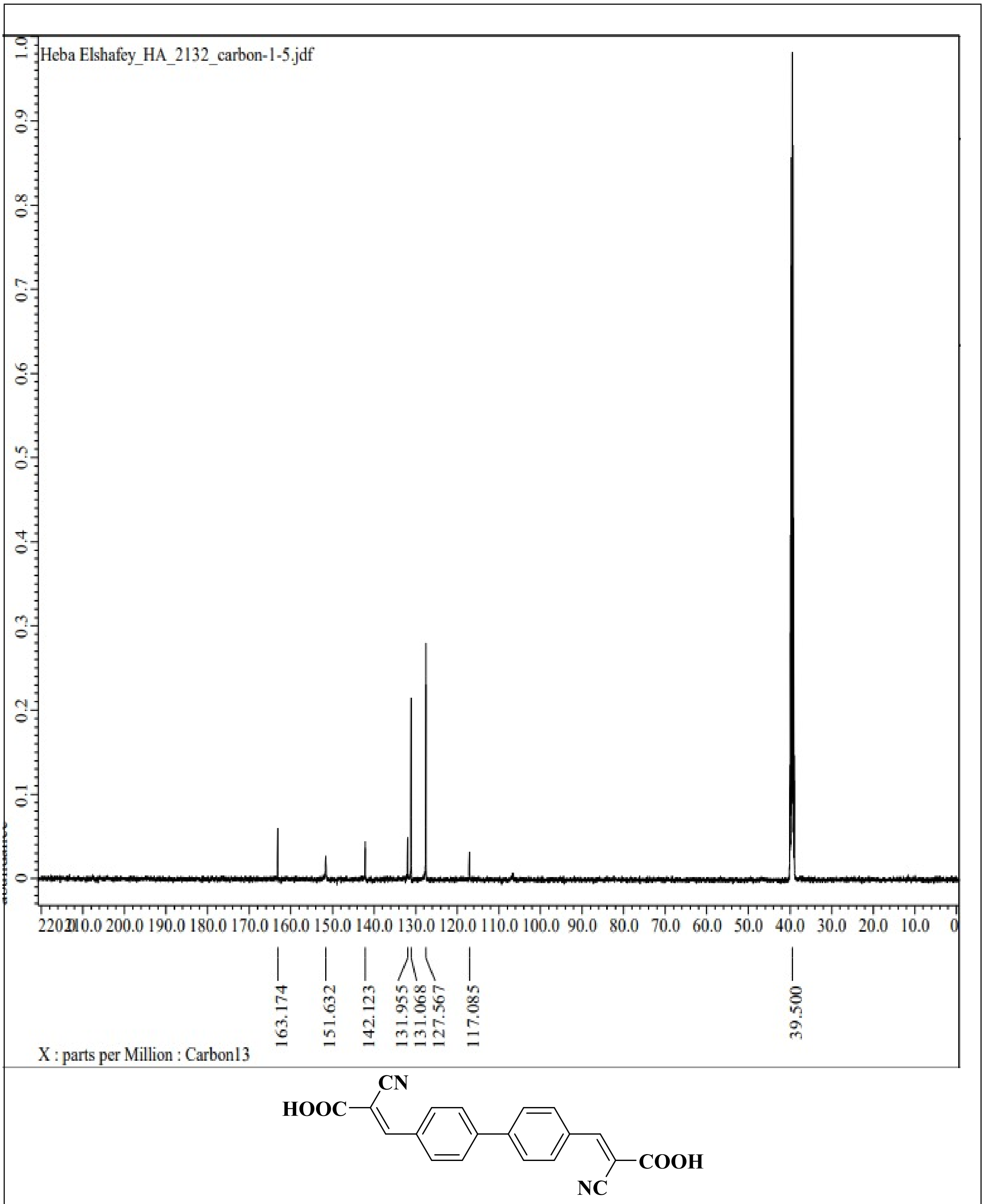


Figure S18: Compound HB-5 ^{13}C-NMR (DMSO-d_6)/JEOL 125 MHz

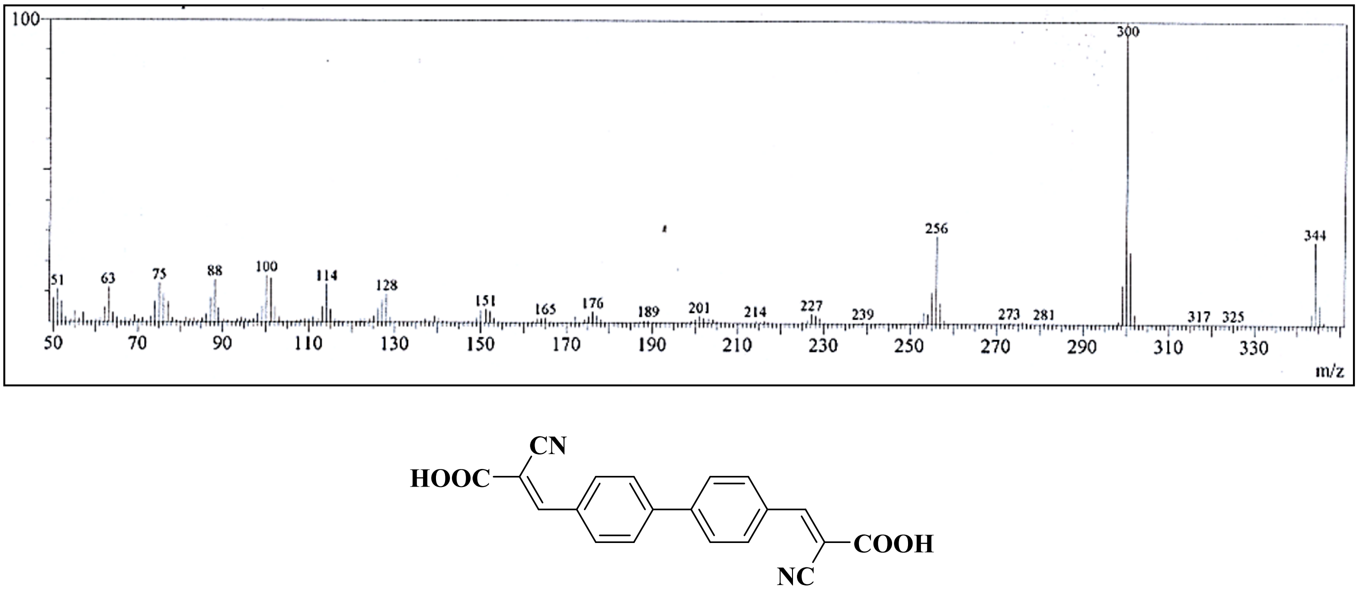


Figure S19: *Compound* HB-5 Mass Spectrum.

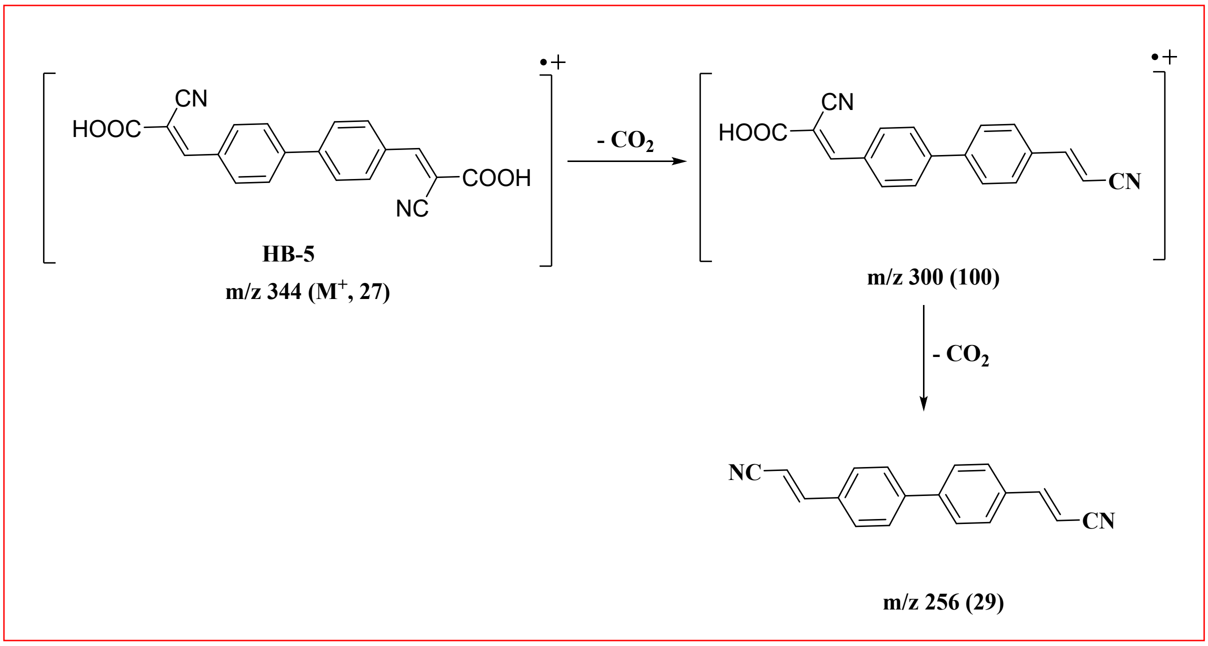
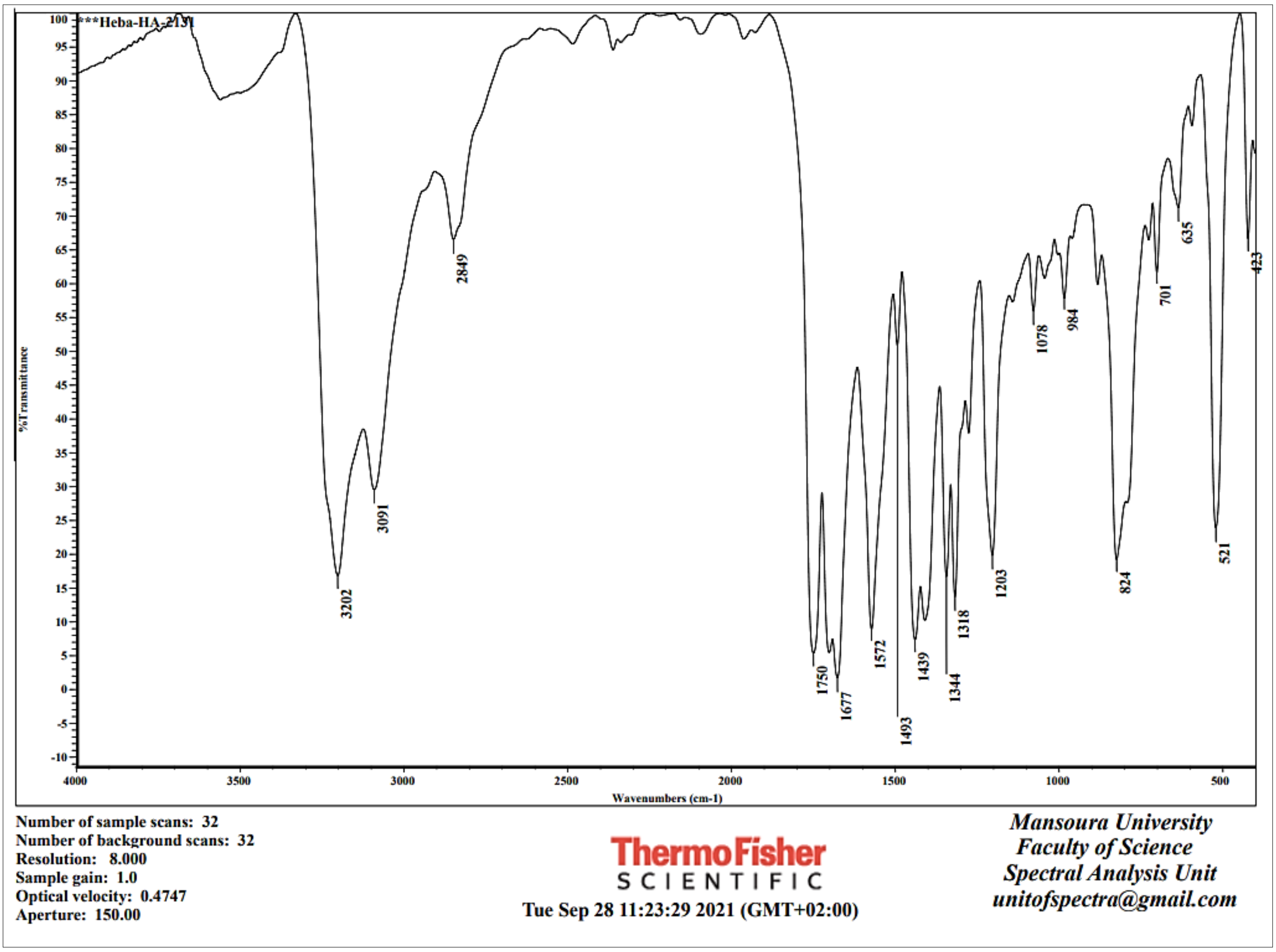


Figure S20: Mass fragmentation pattern of biphenyl dye **HB-5.**



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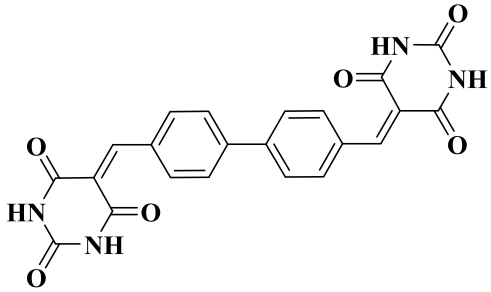


Figure S21: Compound HB-6 Infrared (IR) spectra

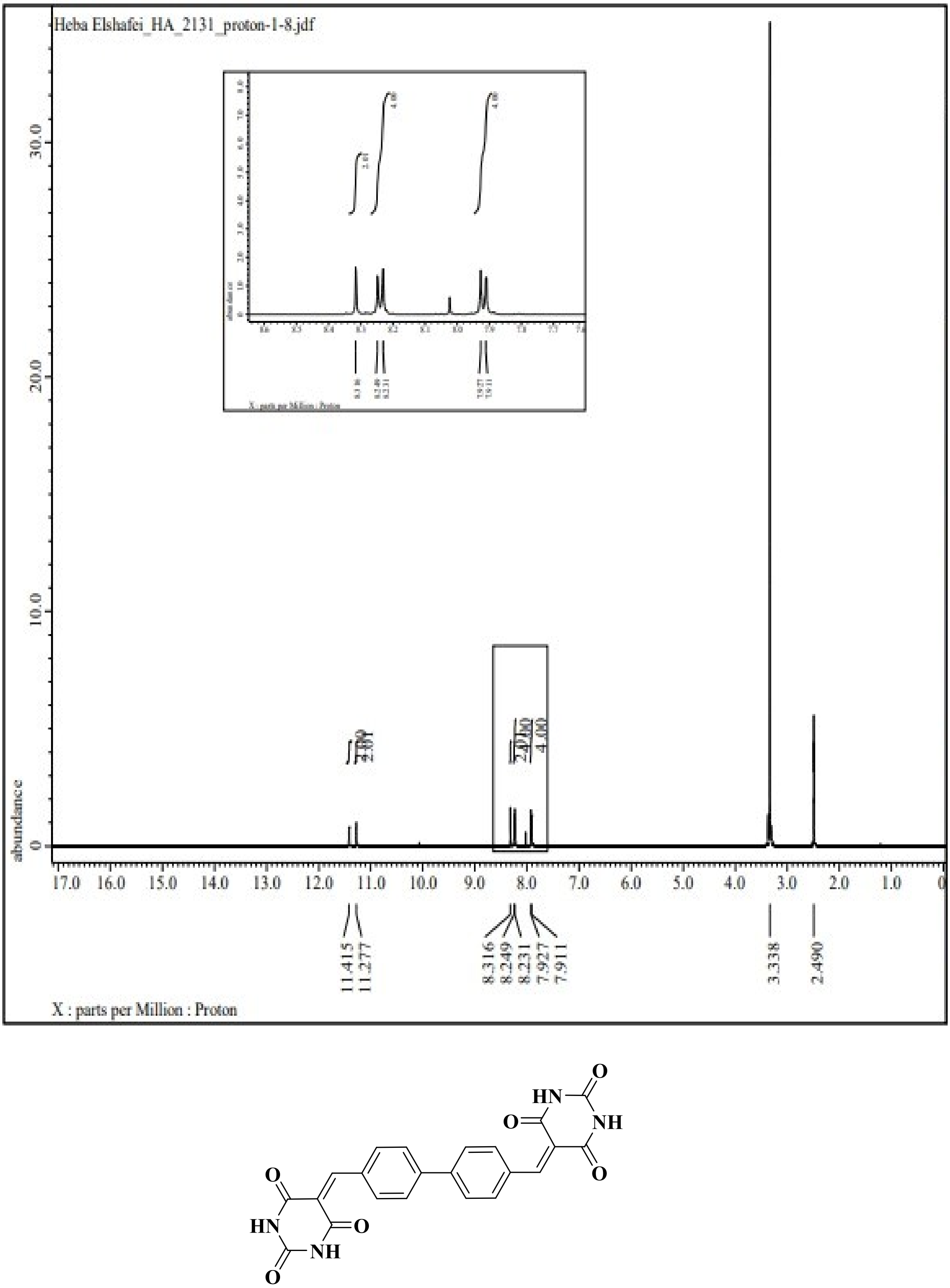


Figure S22: Compound HB-6 ^{1}H-NMR (DMSO-d_6)/JEOL 500 MHz

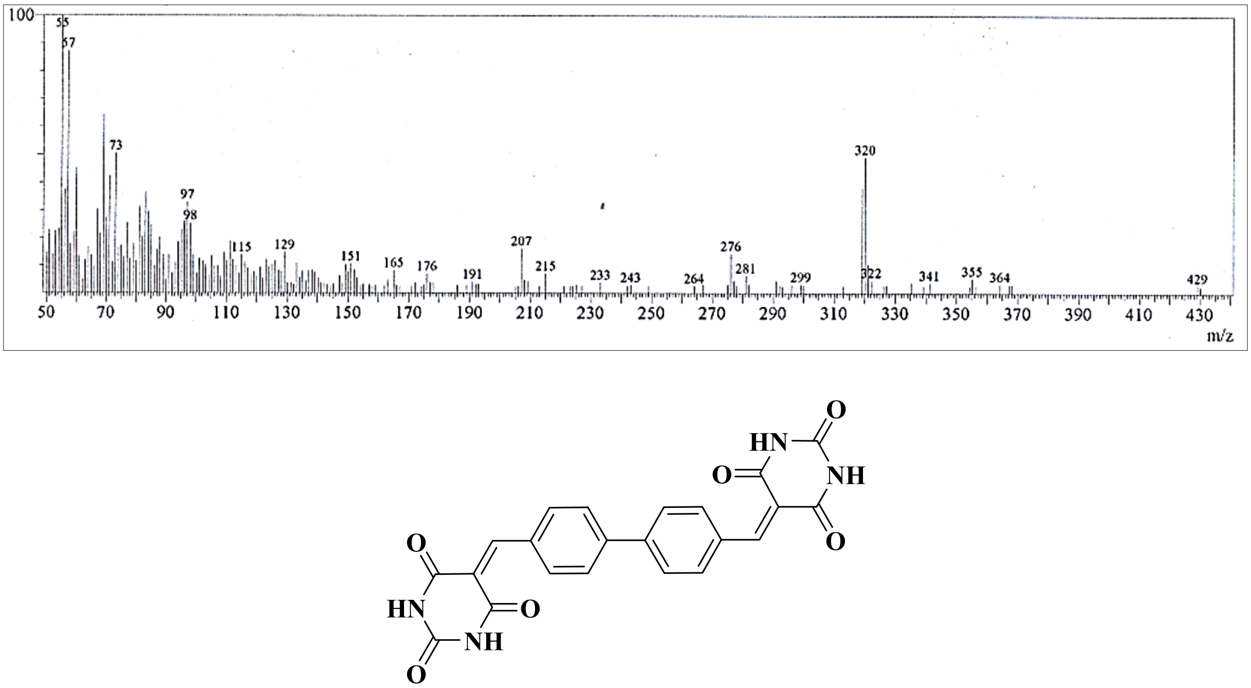
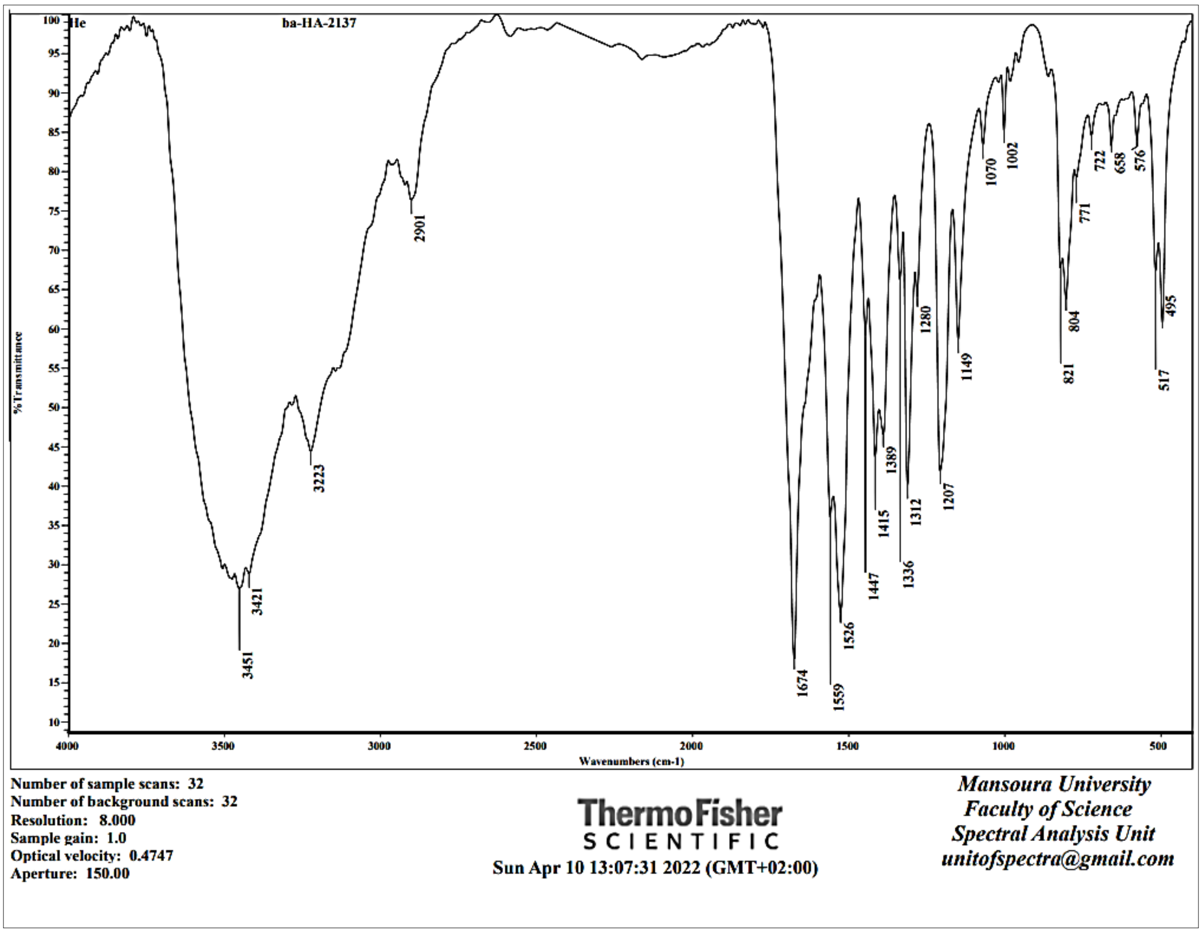


Figure S23: Compound HB-6 Mass Spectrum.



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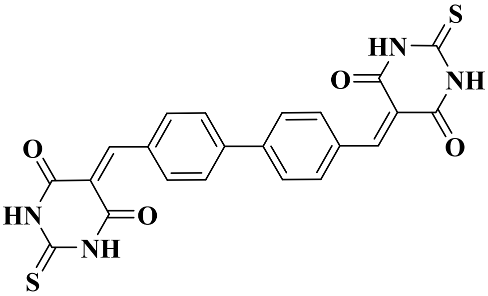

Figure S24: Compound HB-7 Infrared (IR) spectra.

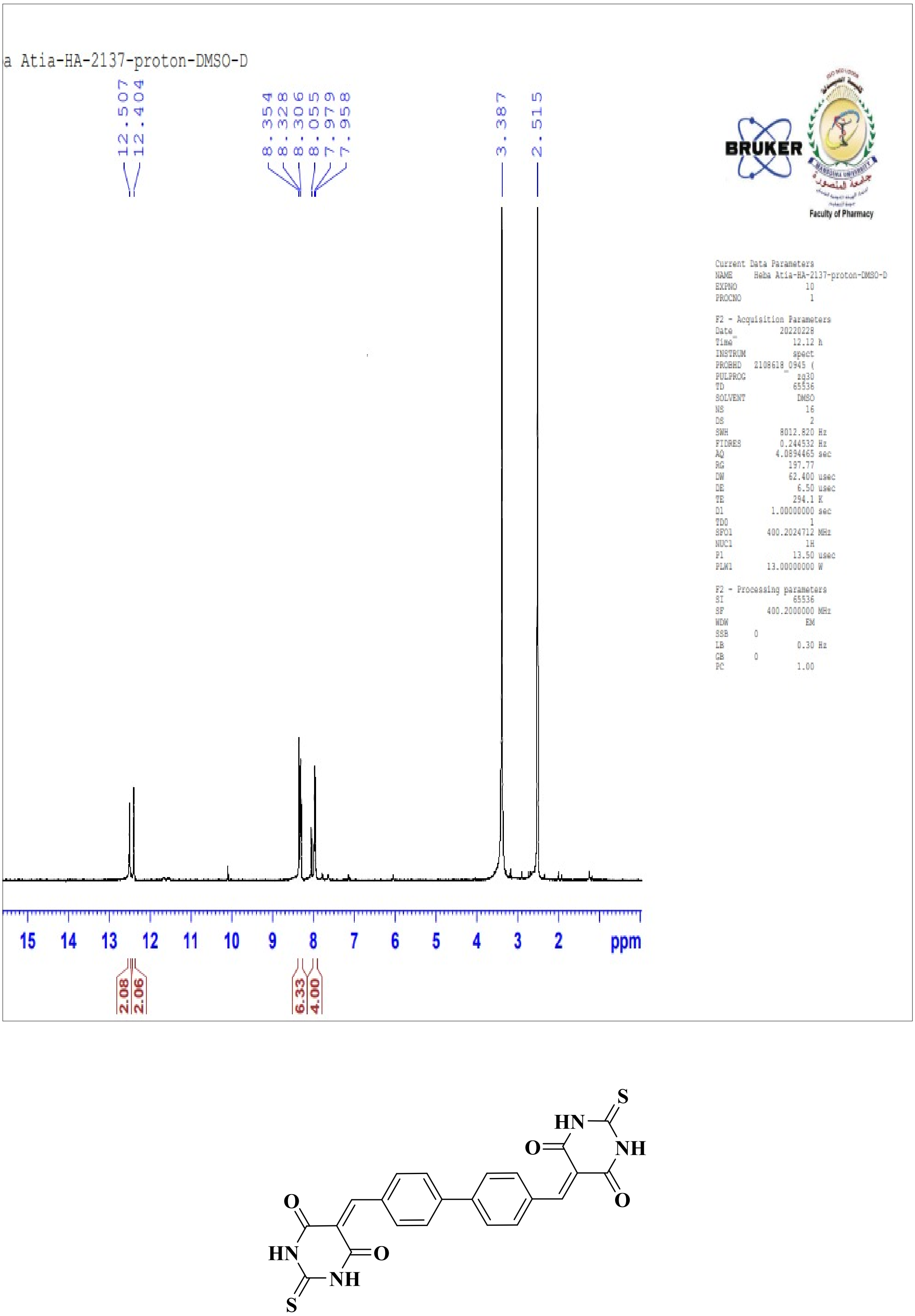

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Figure S25: Compound HB-7 ^{1}H-NMR (DMSO-d_6)/Bruker 400 MHz

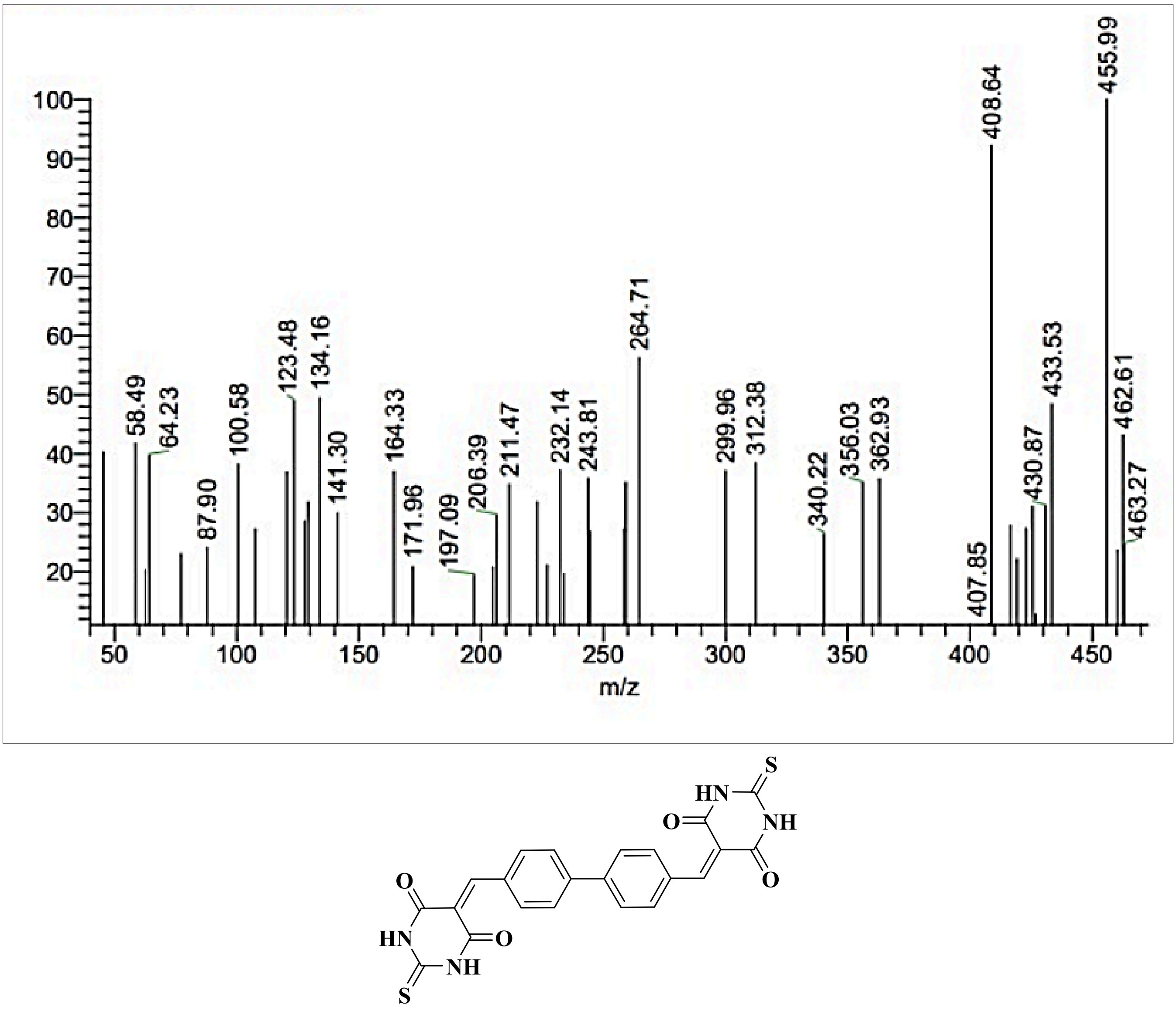
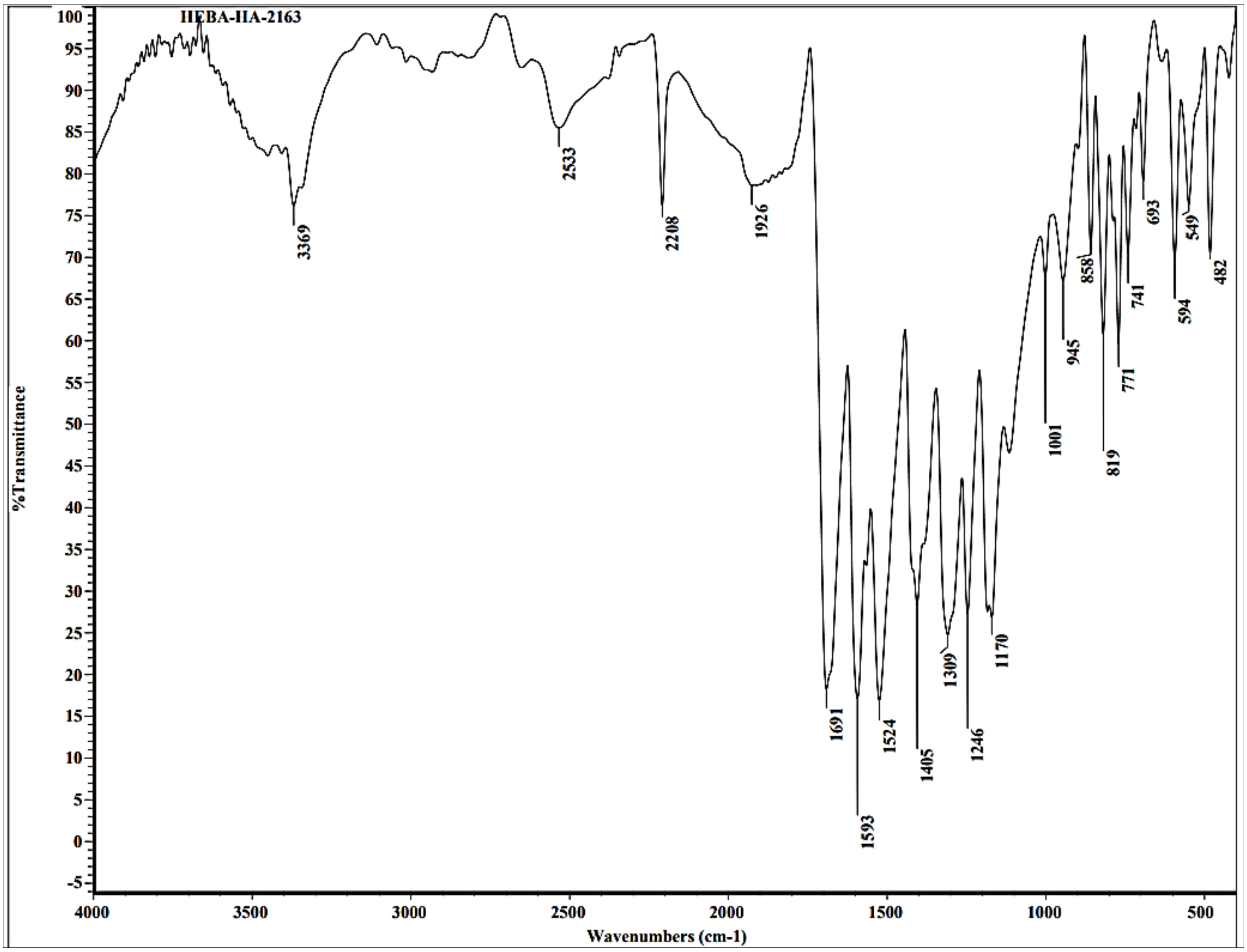


Figure S26: Compound HB-7 Mass Spectrum.



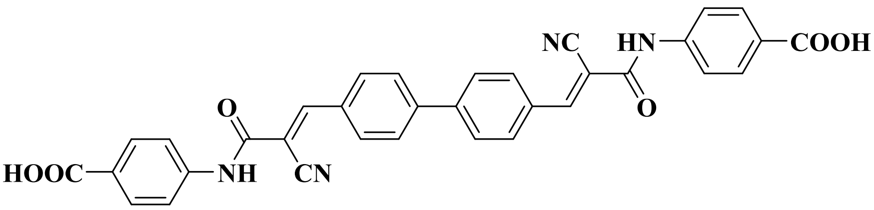
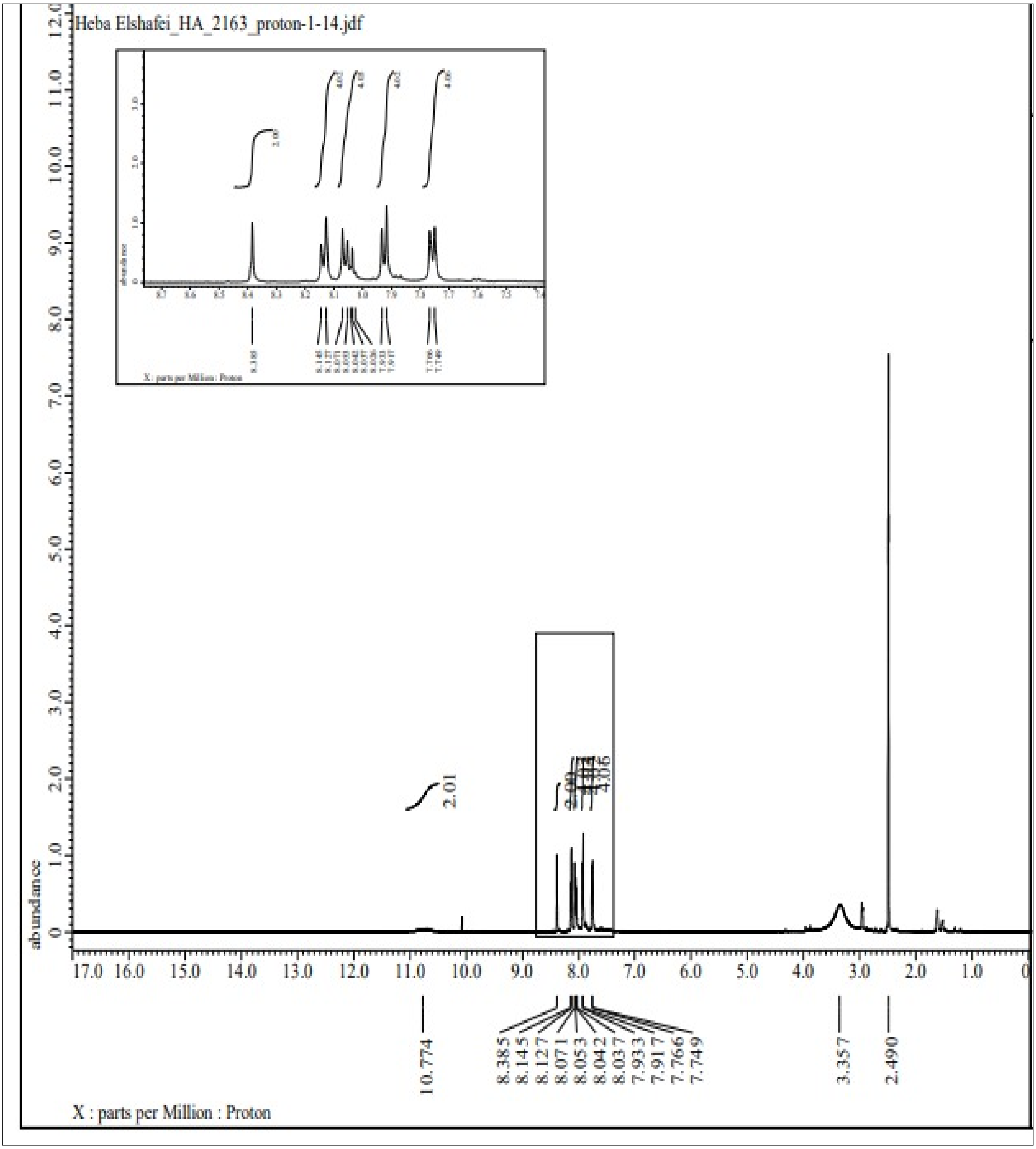


Figure S27: Compound HB-8 Infrared (IR) spectra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4.18
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4.06
10.774
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8.145
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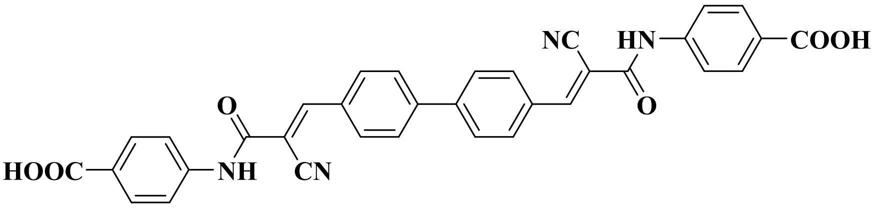
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O
HOOC
NH
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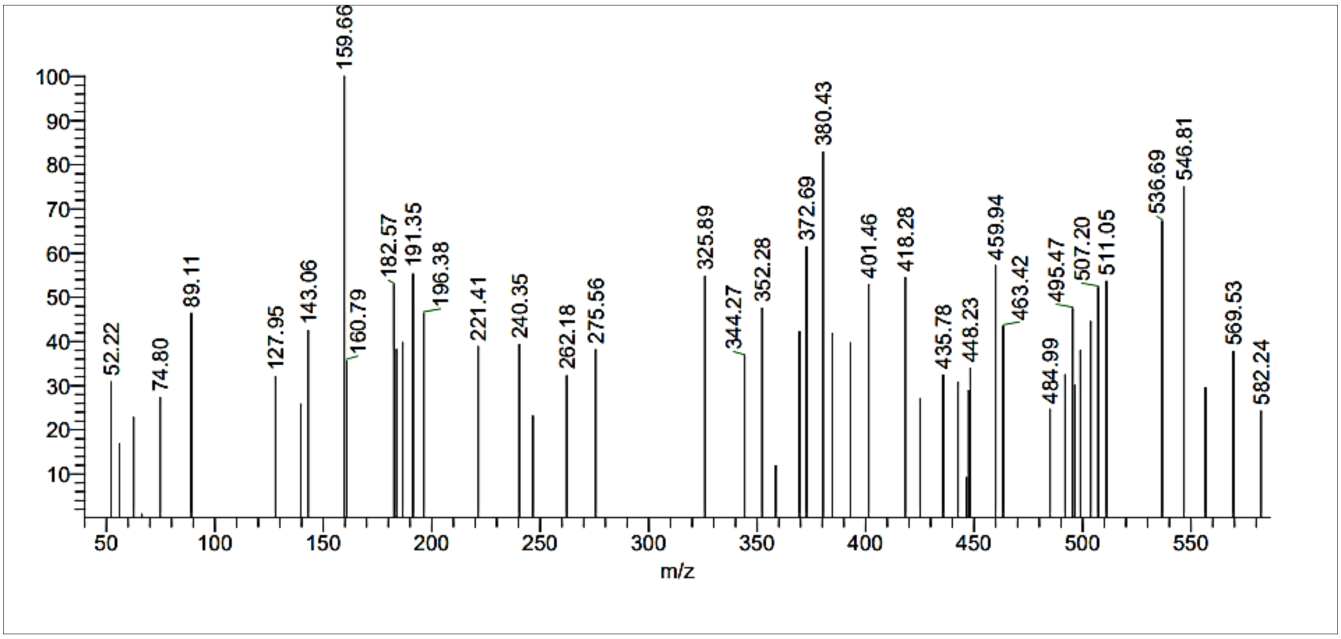
Figure S28: Compound HB-8 ^{1}H-NMR (DMSO-d_6)/ JEOL 500 MHz



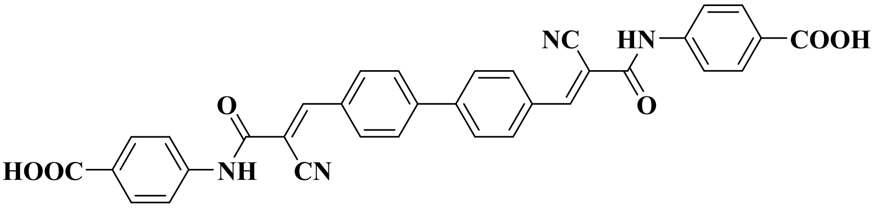


Figure S29: Compound HB-8 Mass Spectrum.

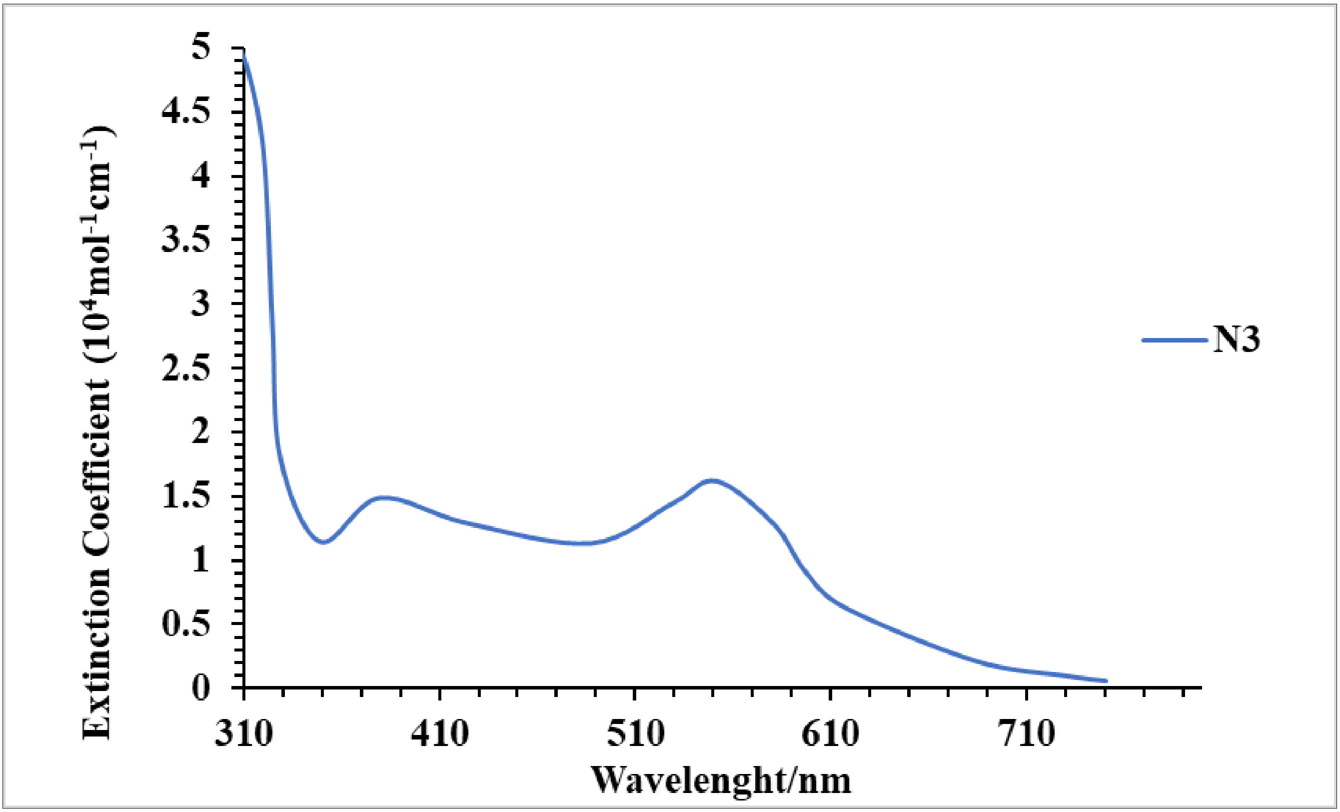


Fig. (S30): UV-Vis. absorption of N3.

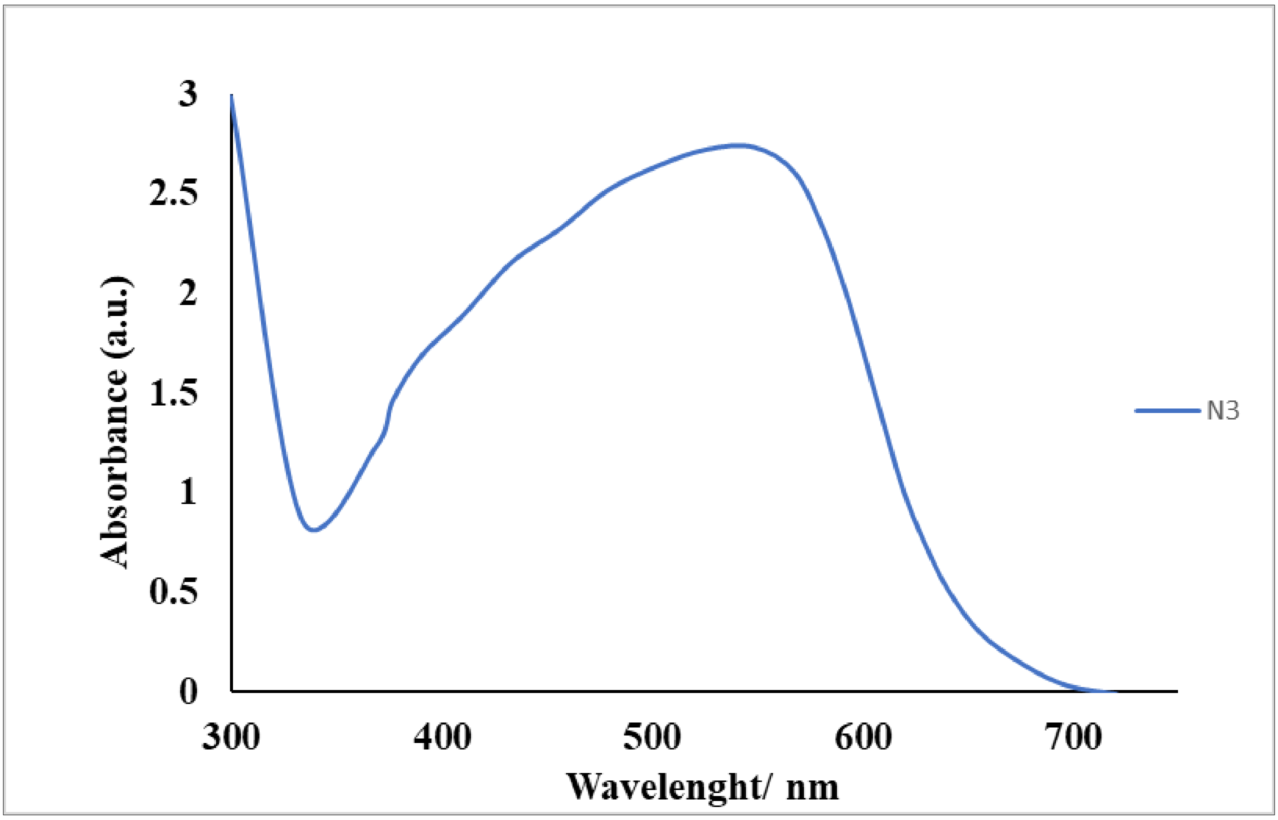


Fig. (S31): UV-Vis. absorption of N3 on TiO_2.

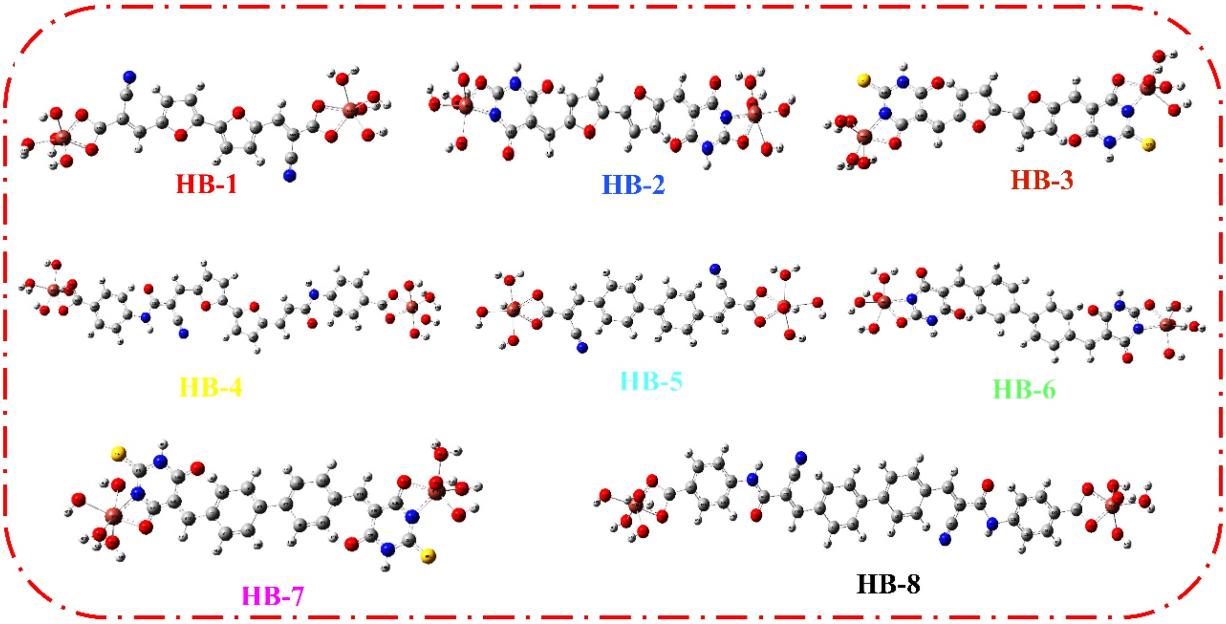


Fig. (S32): binding modes of HB-1-8 on TiO_2.

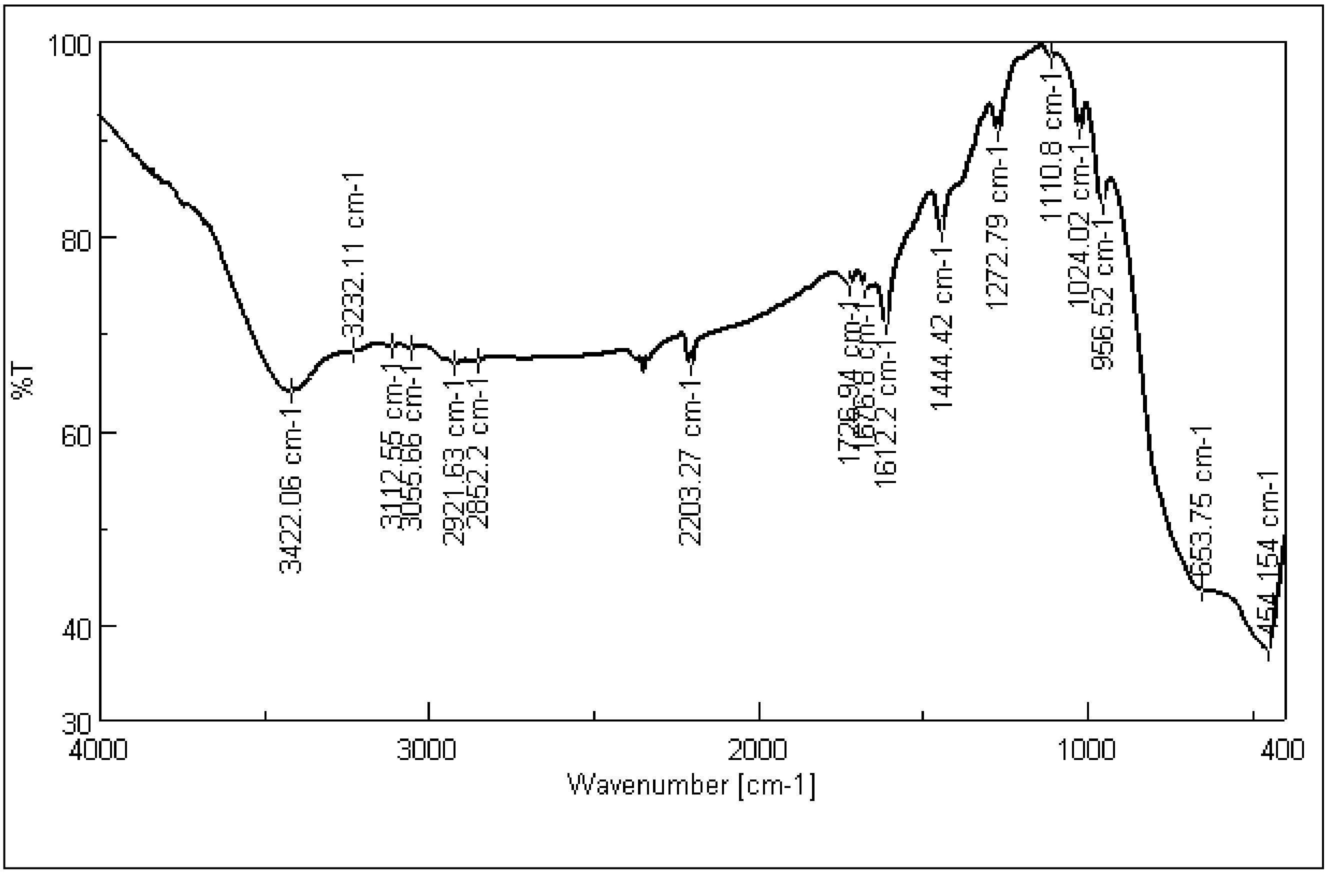


Figure S33: FTIR spectrum of compound HB-1 over TiO_2.

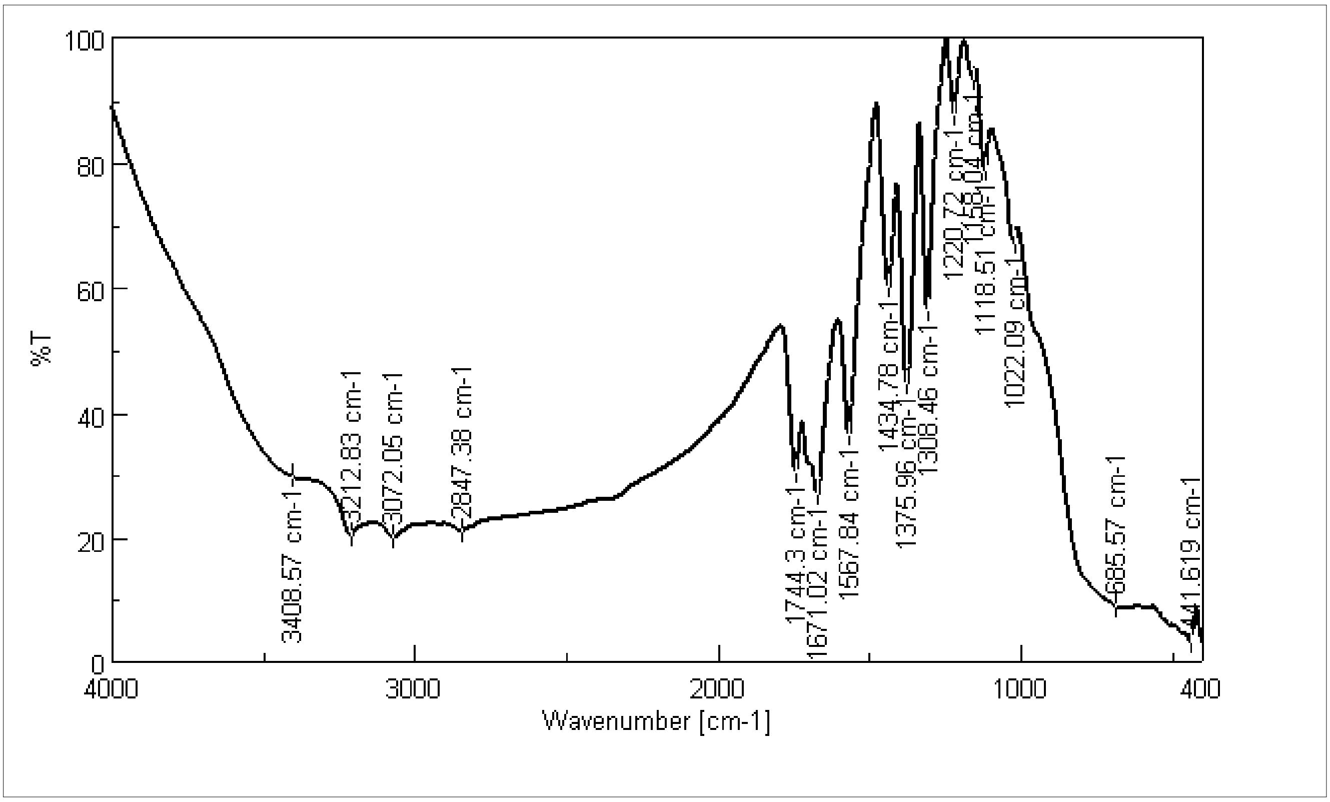


Figure S34: FTIR spectrum of compound HB-2 over TiO_2.

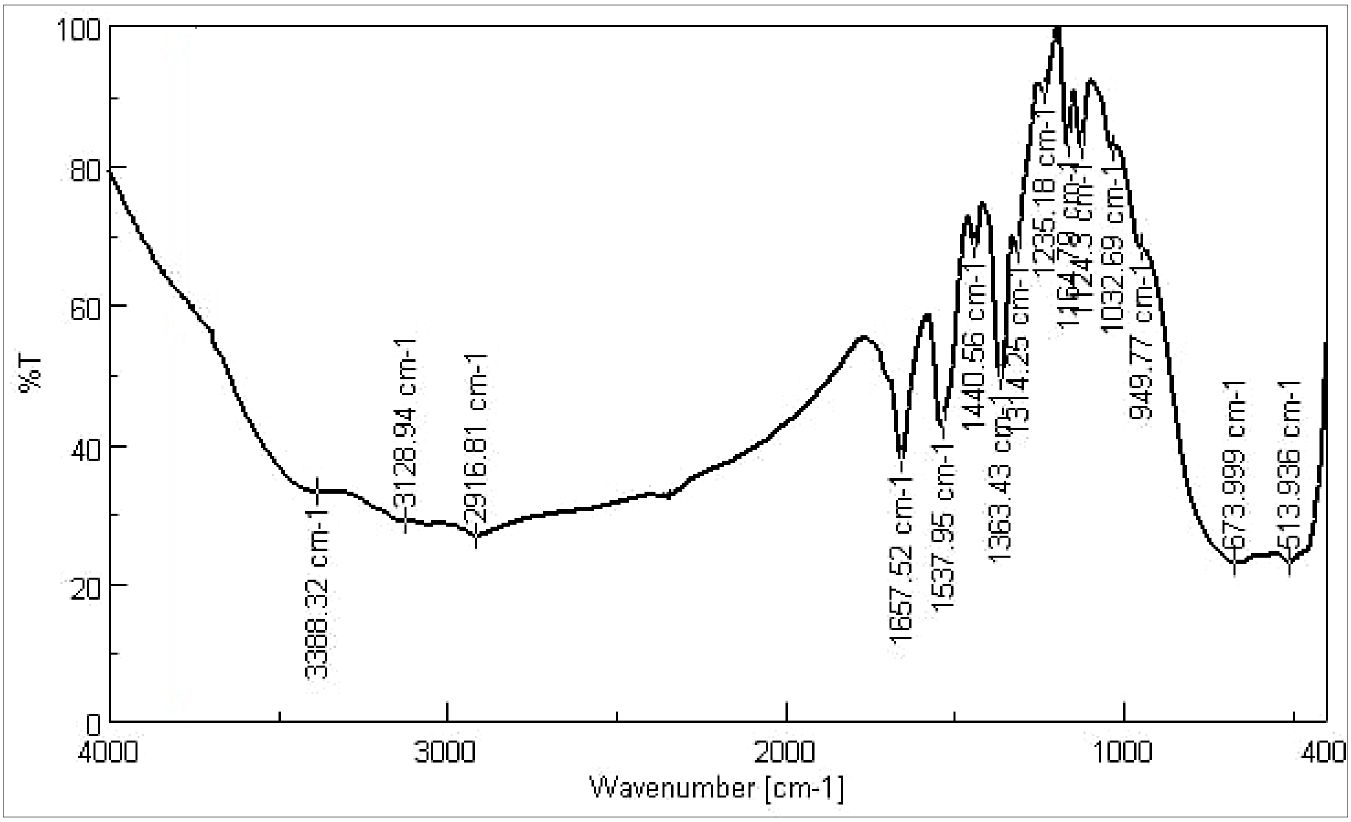


Figure S35: FTIR spectrum of compound HB-3 over TiO_2.

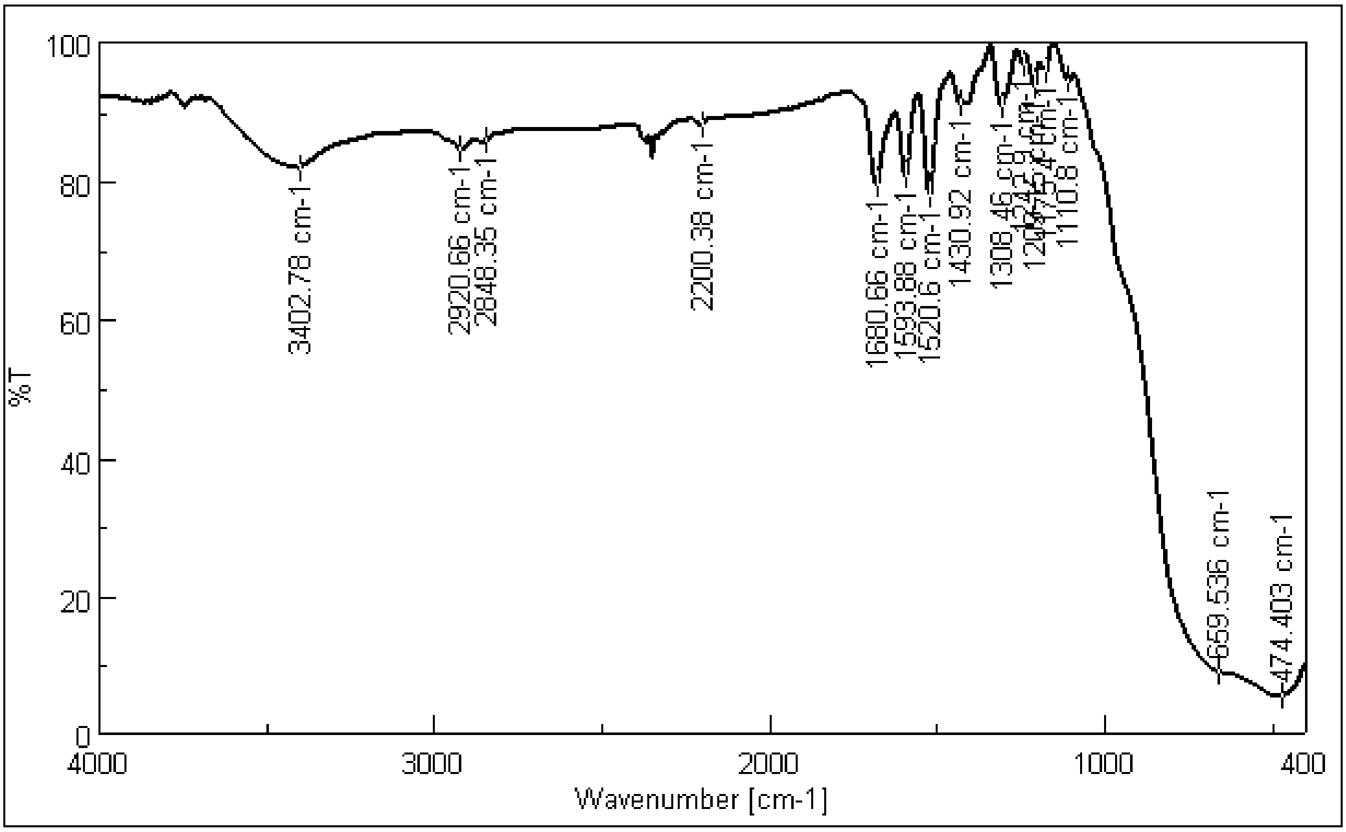


Figure S36: FTIR spectrum of compound HB-4 over TiO_2.

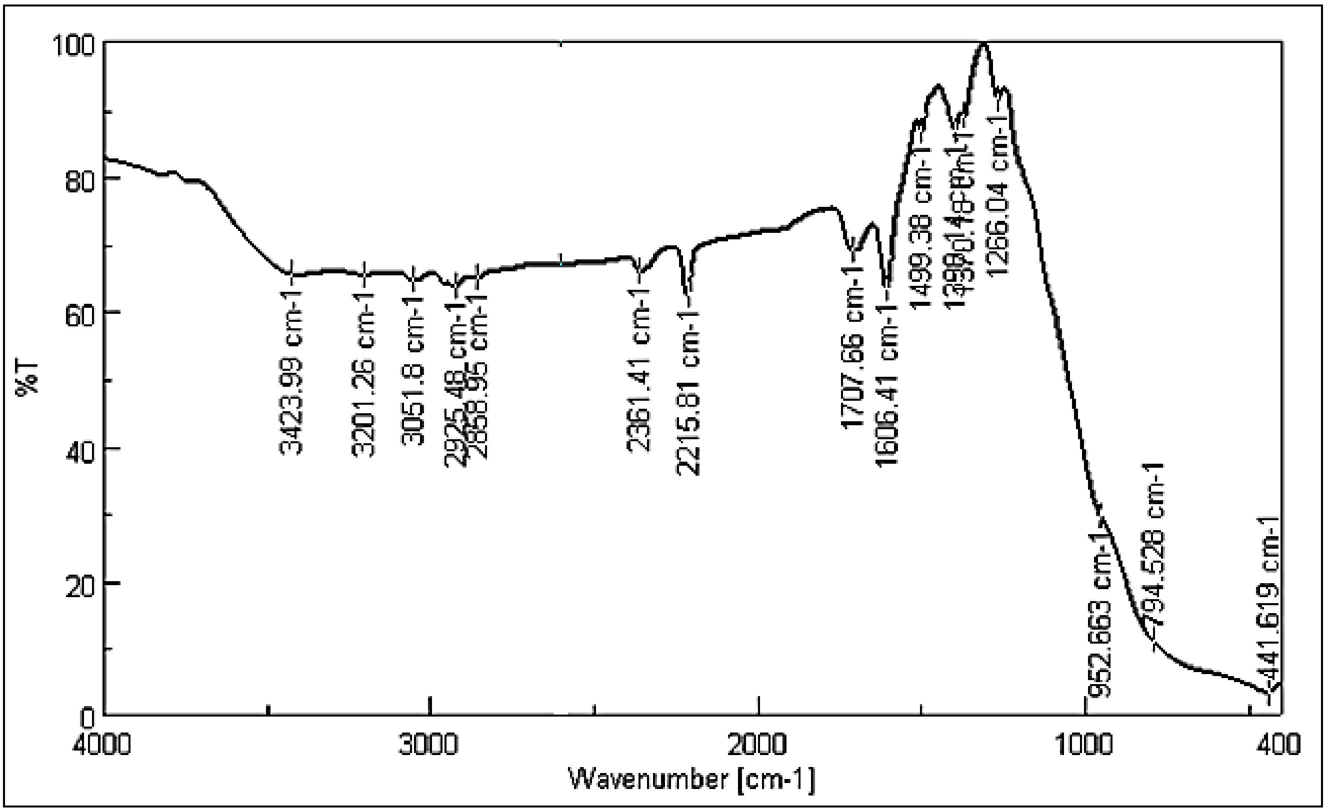


Figure S37: FTIR spectrum of compound HB-5 over TiO_2.

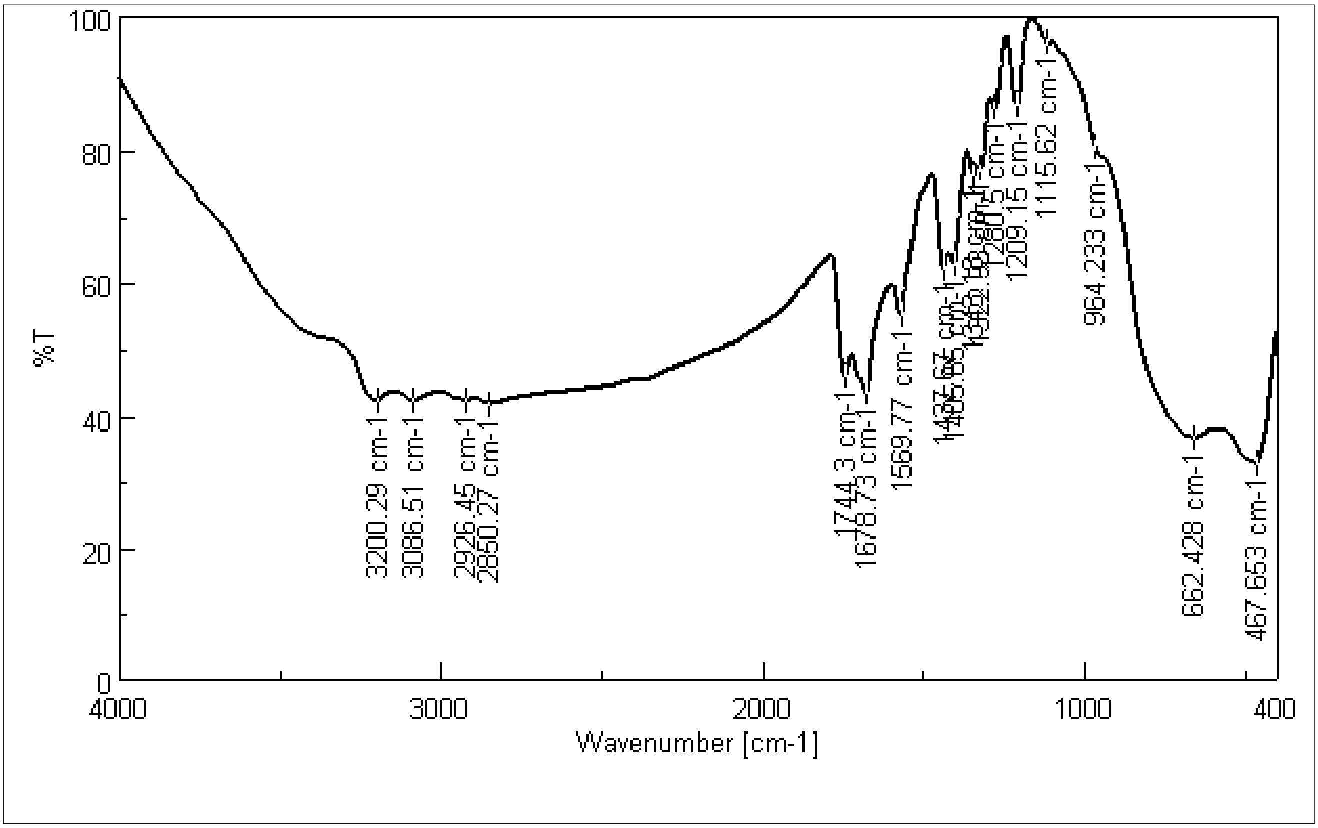


Figure S38: FTIR spectrum of compound HB-6 over TiO_2.

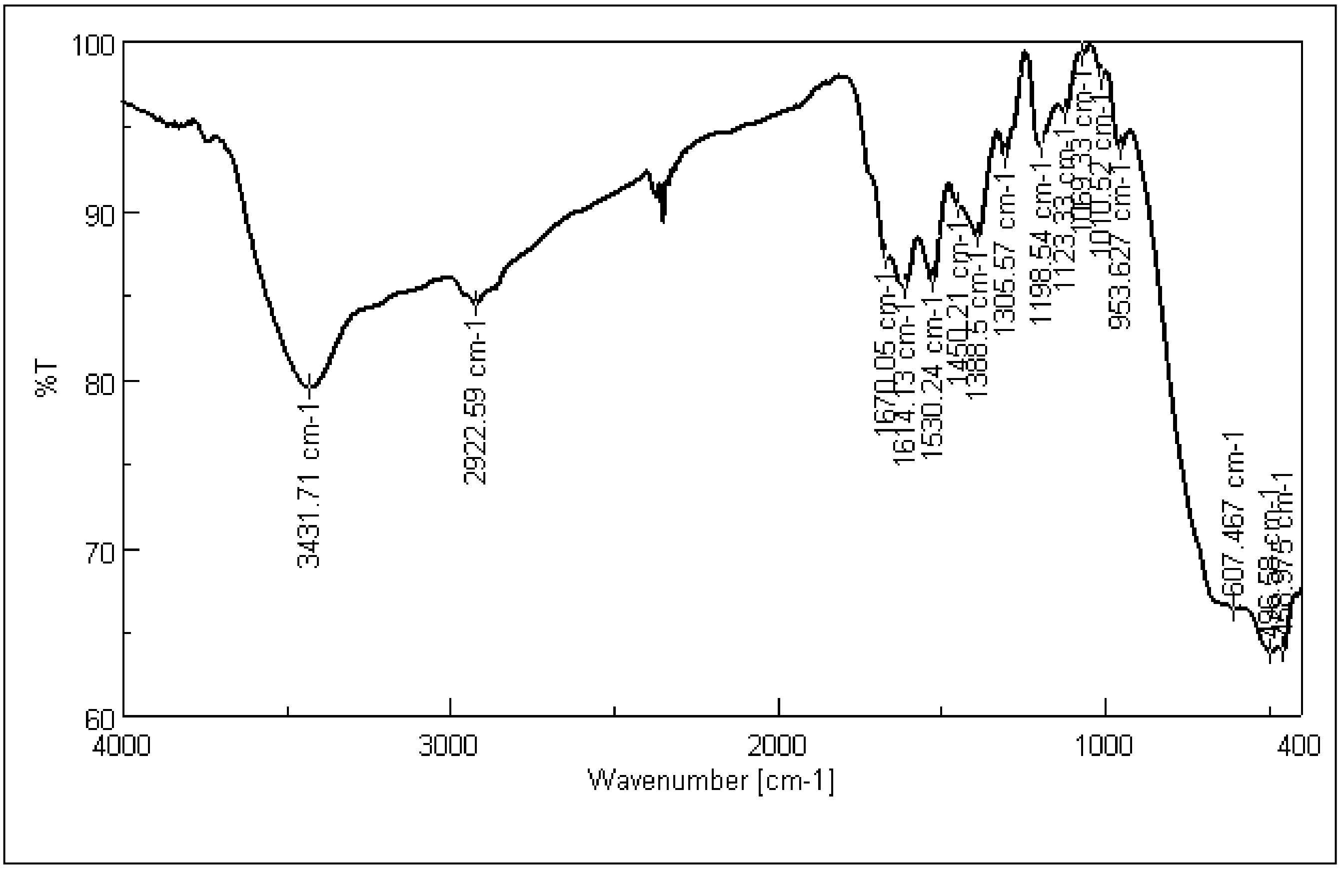


Figure S39: FTIR spectrum of compound HB-7 over TiO_2.

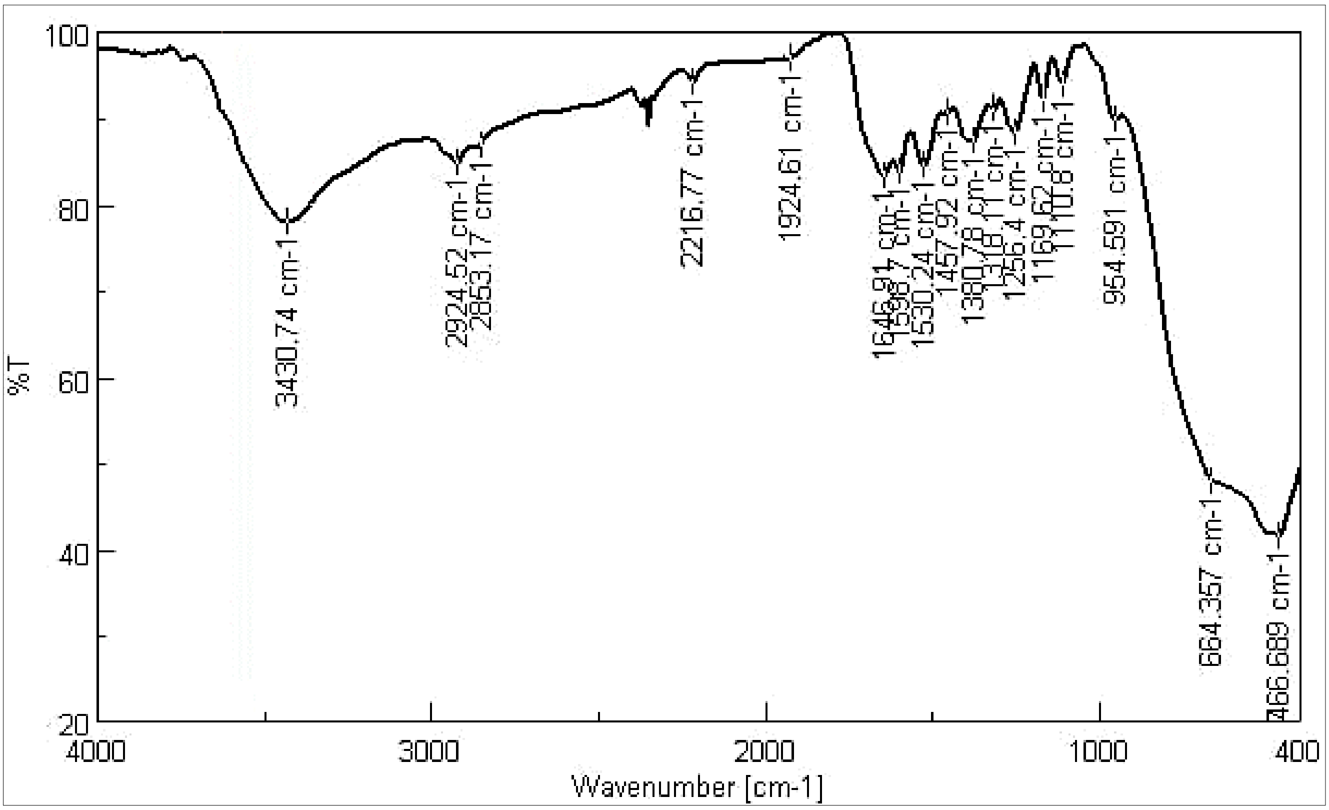


Figure S40: FTIR spectrum of compound HB-8 over TiO_2.

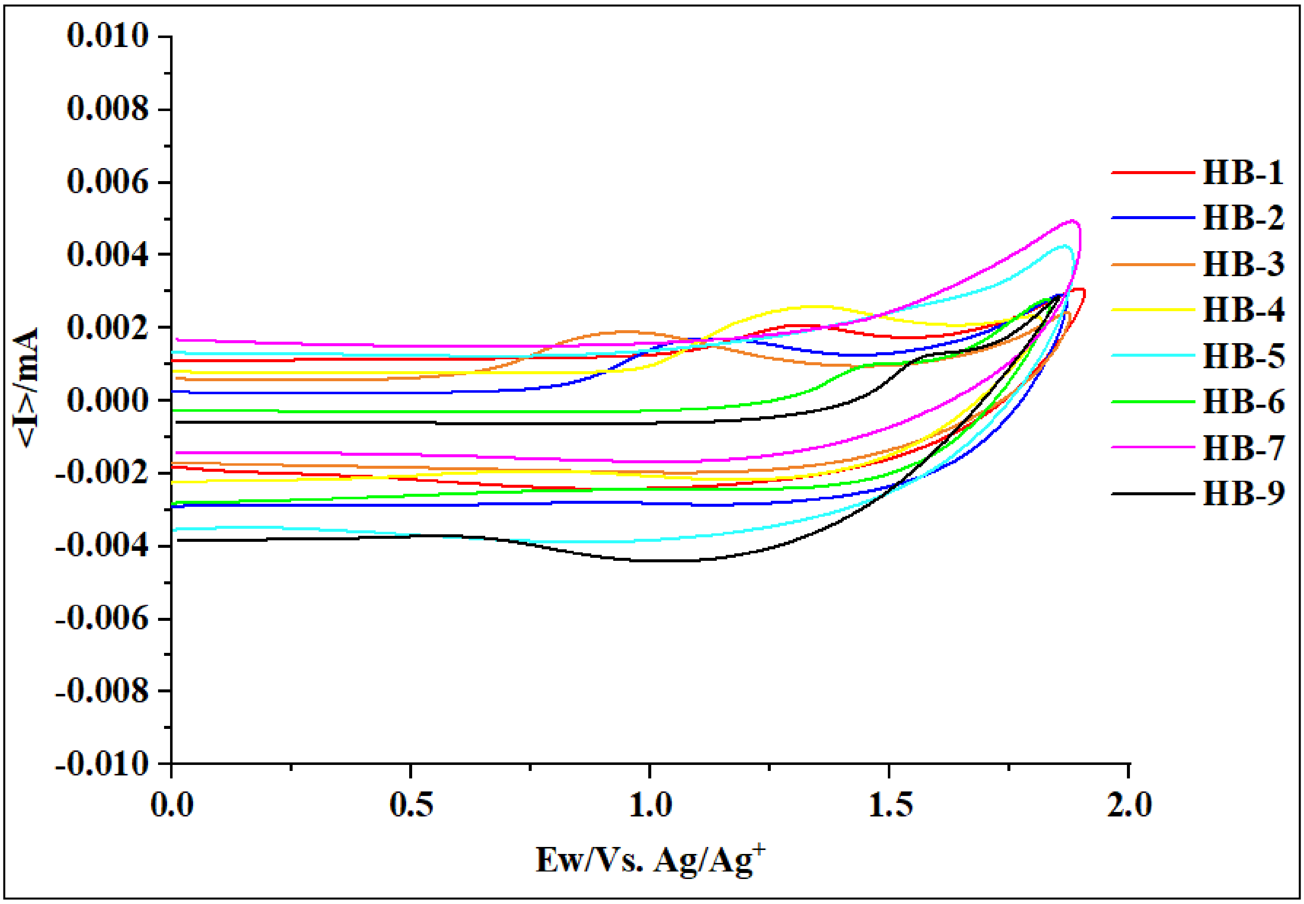


Figure S41: The cyclic voltammetry plots of co-sensitizers HB-1-8.

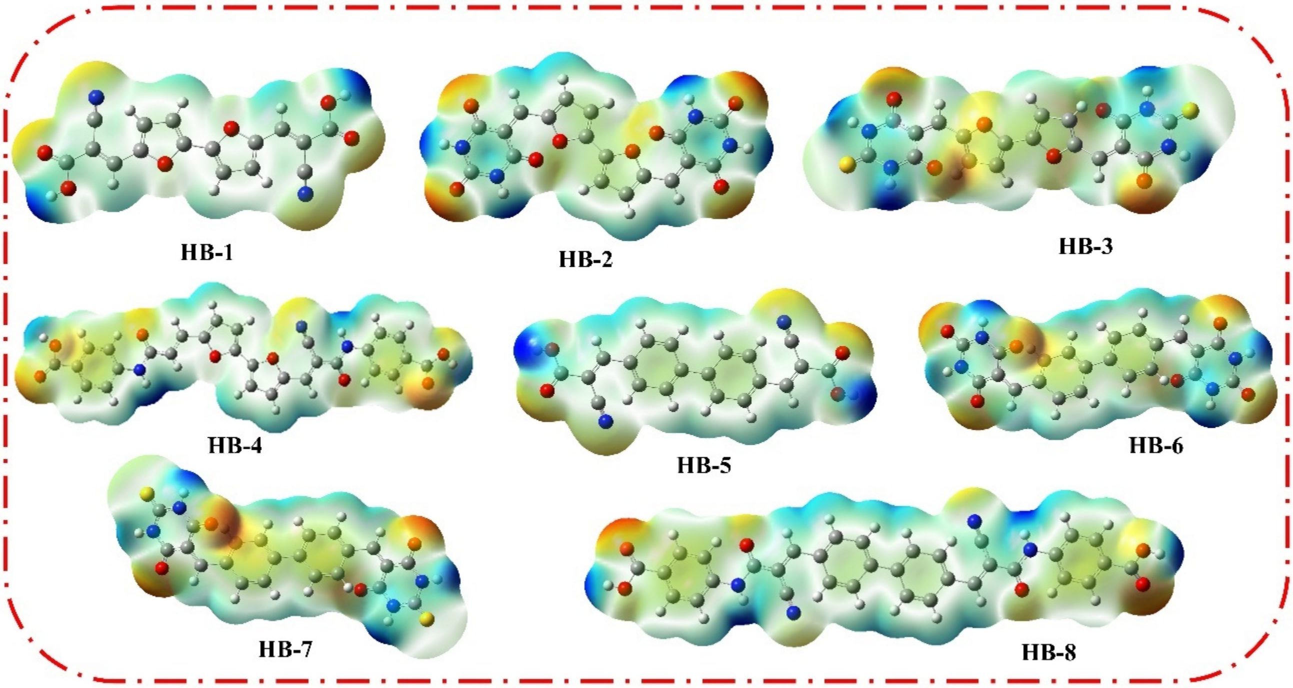


Figure S42: Molecular electronic potential diagram (**MEP**) of bifuran/biphenyl sensitizers **HB-1-8.**

2. Experimental Section:

2.1. Materials and methods:

The chemicals and solvents necessary for the chemical reactions and synthetic procedures were acquired from Sigma-Aldrich, TCI America, Alfa Aesar, and Acros chemical companies and utilized exactly as supplied. The measured melting points (uncorrected) are just in degrees Celsius, employing a Gallenkamp electric melting point instrument. A Thermo Scientific Nicolet iS10 FTIR spectrometer was used for recording the IR spectra (KBr). Nuclear magnetic resonance (NMR) spectra were obtained on a Bruker NMR spectrometer/ or A JEOL spectrometer using DMSO-d_6 as a solvent at 400, 500 MHz (^{1}H-NMR) and 100, 125 MHz (^{13}C-NMR) with an internal standard (TMS), chemical shifts are given as δ/ppm. A Schimadzu Qp-2010 Plus (GC-MS) and Thermo Scientific ISQ (GC-MS) spectrometers were used for recording mass spectra of the newly synthesized compounds. The elemental analysis data was collected using the Perkin Elmer 2400 analyzer. The UV-Visible spectra were measured by using the high-performance double beam spectrophotometer (T80 series).

3. Cell preparations and photovoltaic characterizations

3.1. TiO_2 electrode preparation

A double-layer TiO_2 photoelectrode (10 + 5) μm in thickness with a 10 μm thick nanoporous layer and a 5 μm thick scattering layer (area: 0.25 cm^2) was prepared using a reported method. Fluorine-doped tin oxide (FTO) coated glasses (Nippon Sheet Glass Co., Japan) with a sheet resistance of 8-10 ohm-2 and an optical transmission of greater than 80% in the visible range were screen printed using anatase TiO_2 colloids (particle size ~ 13 nm) obtained from commercial sources (Ti-Nanoxide D/SP, Solaronix). Nanocrystalline TiO_2 thin films were deposited onto the conducting glass by screen-printing, which was then sintered at 500 °C for 1 h. The film thickness was measured with a Surfcom 1400A surface profiler

(Tokyo Seimitsu Co. Ltd.). The electrodes were impregnated with a 0.05 M titanium tetrachloride solution and sintered at 500 °C. The films were further treated with 0.1 M HCl(aq) before examination.

The dye solutions of the main sensitizer N3 (0.2 mM) and HB1-8 (0.2 mM) were prepared in 1:1:1 mixture of acetonitrile, tert-butyl alcohol and dimethyl sulfoxide (DMSO). The electrodes were immersed in the dye solutions and then kept at 25 ° C for 20 h to adsorb the dye onto the TiO_2 surface.

For preparing the counter electrode, pre-cut TCO glasses were washed with water followed by 0.1M HCl in EtOH, and sonication in acetone bath for 10 min. These washed TCO were then dried at 400 °C for 15 min. Thin layer of Pt-paste (Solaronix, Platisol T/SP) on TCO was printed and the printed electrodes were then cured at 450 °C for 10 min.

3.2. Fabrication of dye-sensitized solar cell

Photovoltaic and incident photon-to-current efficiency (IPCE) measurements were made on sandwich cells, which were prepared using TiO_2 coated working electrodes and platinum coated counter electrodes and were sealed using a 40 μm Syrlyn spacer through heating of the polymer frame. The redox electrolyte (Solaronix, Iodolyte HI-30) consisted of a solution of 0.6 M DMPII, 0.05 M I_2, 0.1 M LiI and 0.5 M TBP in acetonitrile.

3.3. Photovoltaic measurements

Photovoltaic measurements of sealed cells were made by illuminating the cell through the conducting glass from the anode side with a solar simulator (WXS-155S-10) at AM 1.5 illuminations (light intensity: 100 mW cm^{-2}).

3.4. Incident photon to current efficiency (IPCE) conversion

IPCE measurements were made on a CEP-2000 system (Bunkoh-Keiki Co. Ltd.). IPCE at each wavelength was calculated using Equation 1, where I_{SC} is the short-circuit photocurrent density (mA. cm^{-2}) under monochromatic irradiation, q is the elementary charge, λ is the wavelength of incident radiation in nm and P0 is the incident radiative flux in W/m^2.

$$IPCE(\lambda) = 1240\left(\frac{I_{SC}}{q\lambda P_o}\right) \qquad (1)$$

3.5. Electrochemical impedance spectroscopy (EIS)

The electrochemical impedance spectra were measured with an impedance analyzer potentiostat (Bio-Logic SP-150) under illumination using a solar simulator (SOL3A, Oriel) equipped with a 450 W xenon lamp (91160, Oriel). EIS spectra were recorded over a frequency range of 100 mHz to 200 kHz at room temperature. The applied bias voltage was set at the V_{OC} of the DSSCs, with AC amplitude set at 10 mV. The electrical impedance spectra were fitted using Z-Fit software (Bio-Logic).

3.6. Cyclic voltammetry

Cyclic voltammetry (CV) was performed in DMF with the electrolyte 0.1 M [TBA][PF_6] at a scan rate of 50 mV s^{-1}. The working electrode used is the Glassy carbon, Pt wire represented the counter electrode, and the reference electrode is Ag/Ag^+ in ACN. Fc/Fc^+ was introduced as internal reference.

4. Molecular Modeling

Equilibrium molecular geometries of **HB1-8** calculated using the Becke's three parameter hybrid functional, Lee–Yang–Parr's gradient corrected correlation functional (B3LYP) and *d*-polarized 6–311G [1, 2, 3, 4]. The geometry optimization calculations were followed by energy calculations using time-dependent density functional theory (TD-DFT) utilizing the energy, functional B3lyp and the basis set *d*-

polarized 6–311G. The solvent (DMF) effect was accounted for by using the conductor-like polarizable continuum model (C-PCM), implemented in Gaussian 09.

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