Supplementary Information

Effects of substituents on enriching optical limiting action of novel imidazo[2,1-*b*][1,3,4]thiadiazole fused thiophene based small molecules

Viprabha Kakekochi[a], Udaya Kumar D*[a], Nikhil P P[b], Keloth Chandrasekharan[b]

[a] Synthetic Organic Chemistry Laboratory, Department of Chemistry, National Institute of Technology Karnataka, Srinivasnagar 575 025, Mangaluru, India.

[b] Laser and Nonlinear Optics Laboratory, Department of Physics, National Institute of Technology Calicut, Kozhikode 673601, Kerala, India.

Corresponding Author

*Contact email: udayaravi80@gmail.com, udayakumar@nitk.ac.in

Spectral characterizations

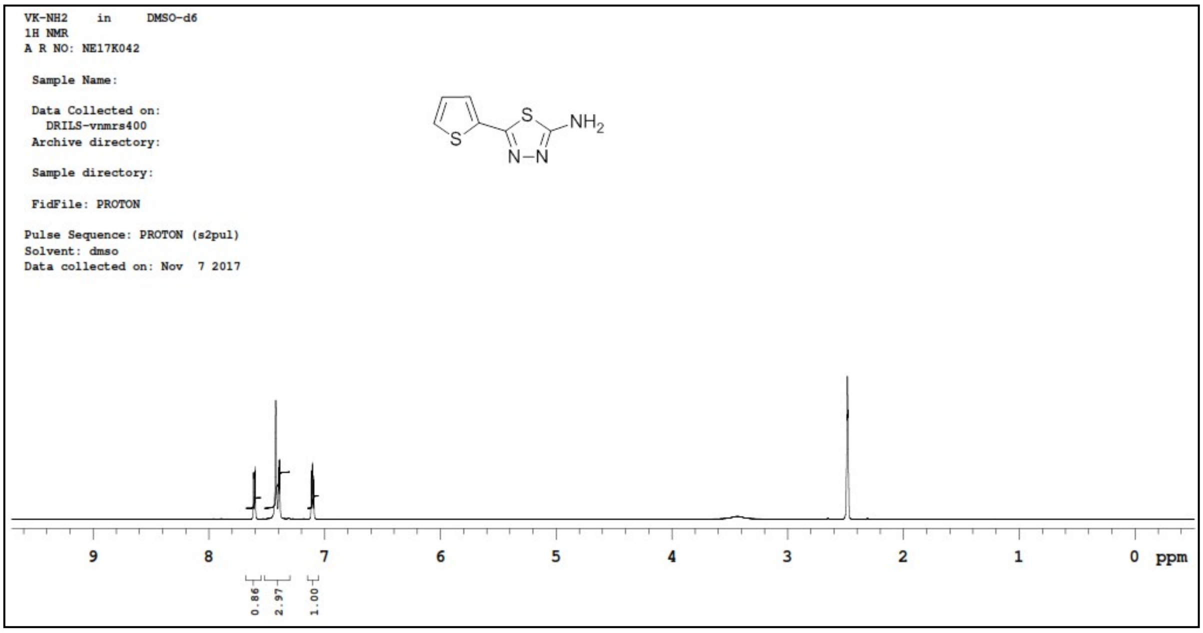

Fig. S1 ^{1}H NMR spectrum of **(3)**

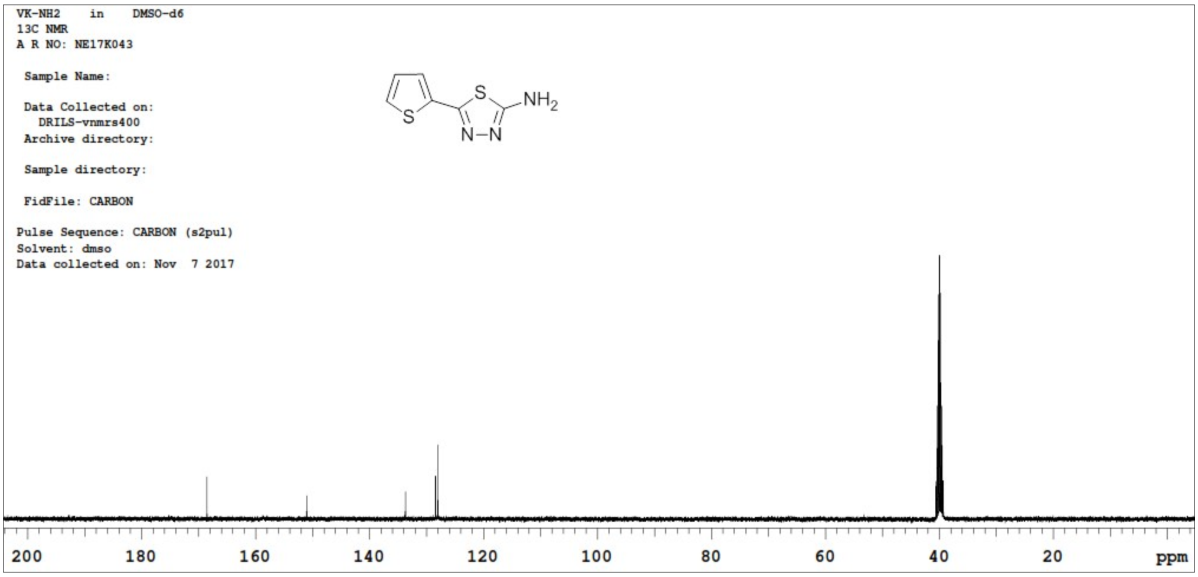

Fig. S2 ^{13}C NMR spectrum of **(3)**

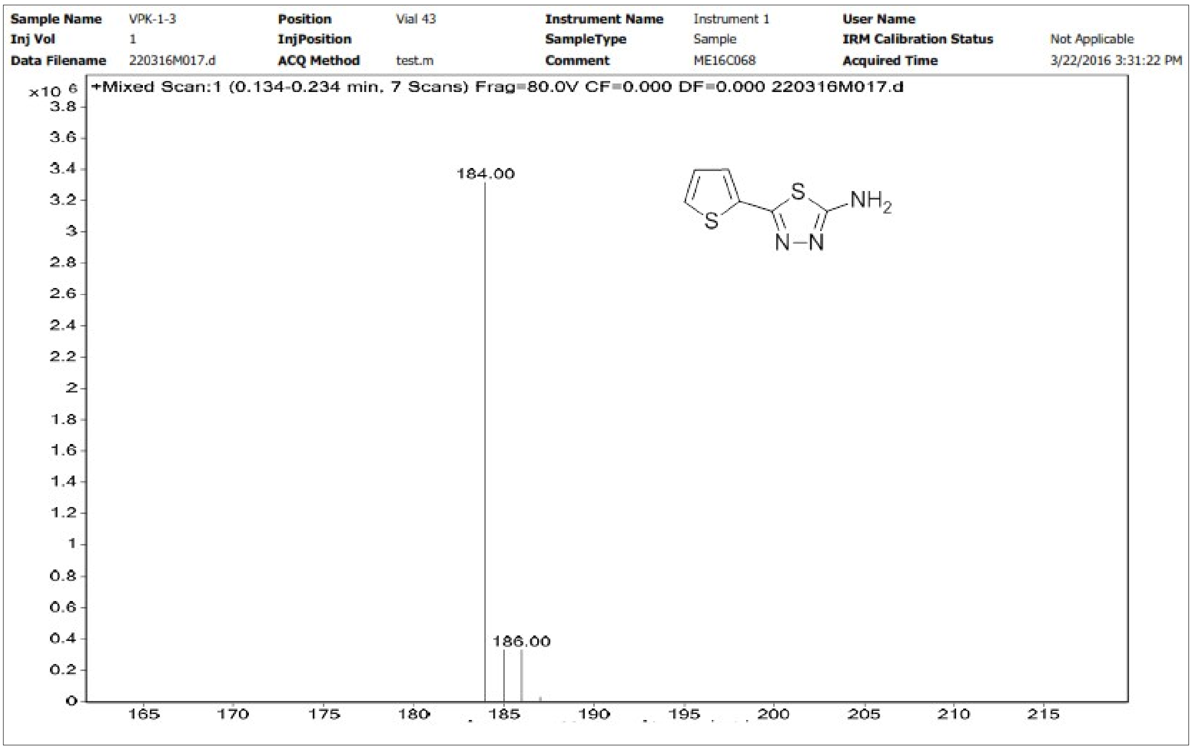

Fig. S3 Mass spectrum of **(3)**

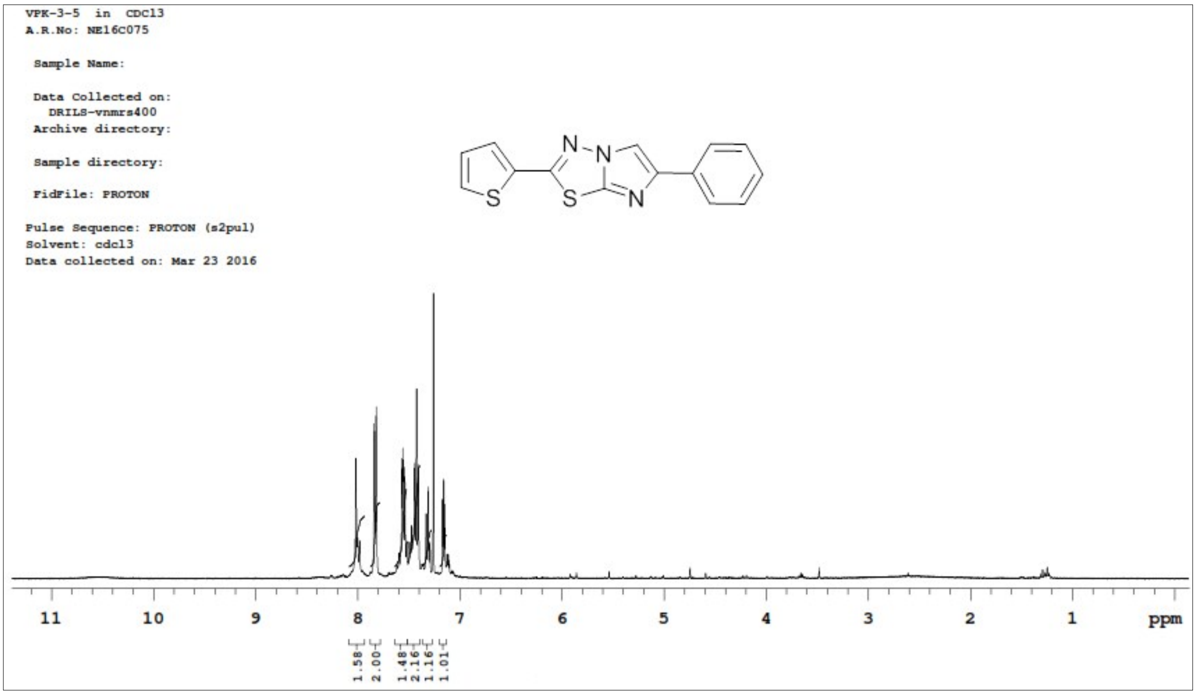

Fig. S4 ^{1}H NMR spectrum of **(4)**

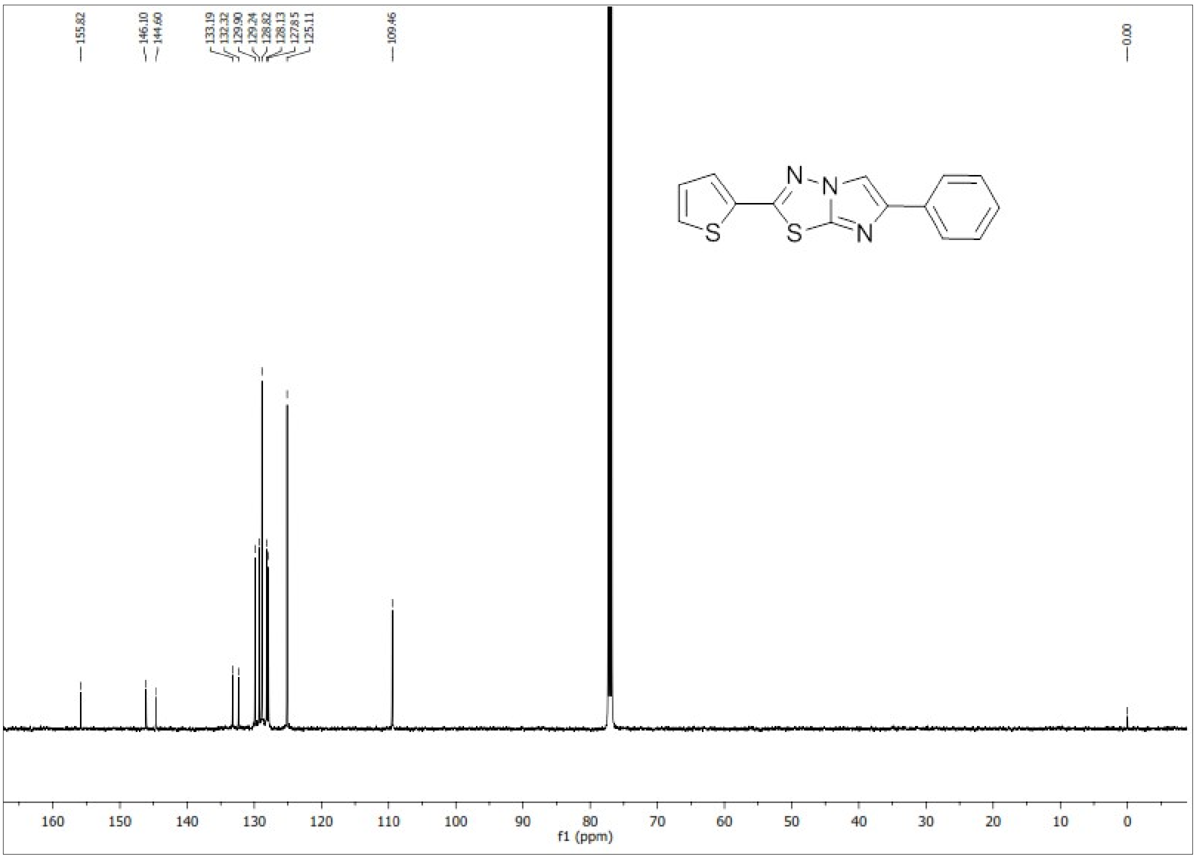

Fig S.5 ^{13}C NMR spectrum of **(4)**

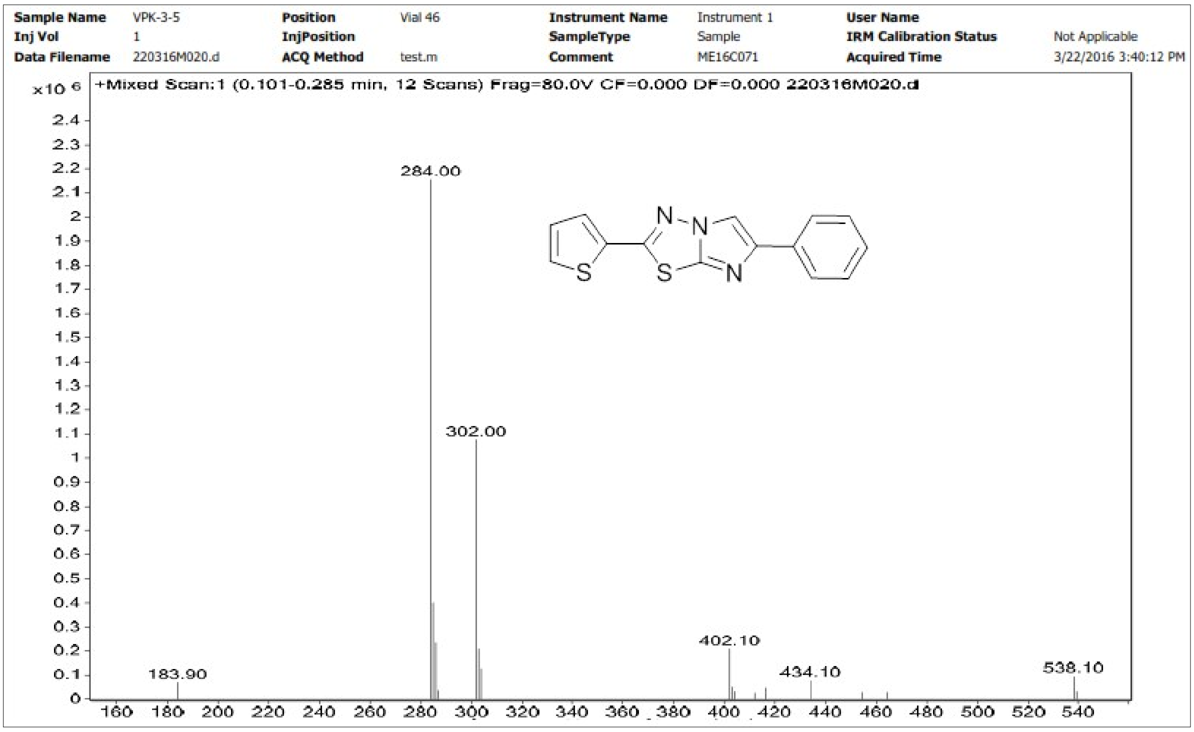

Fig. S6 Mass spectrum of **(4)**

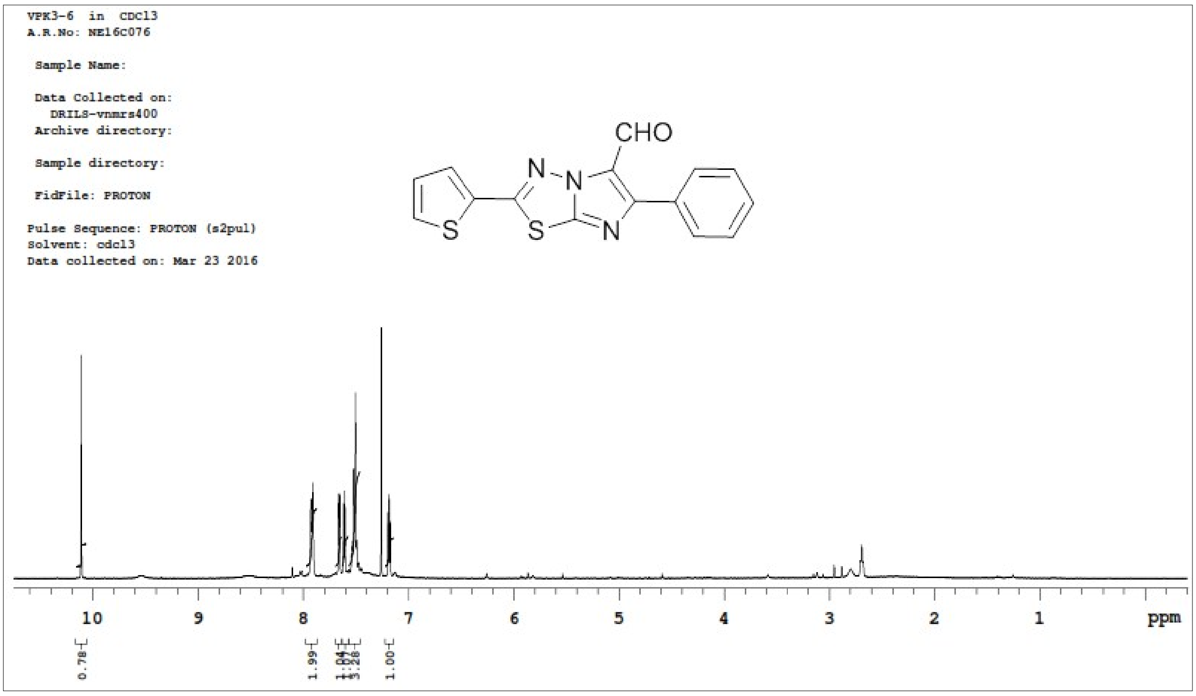

Fig. S7 ^{1}H NMR spectrum of **(5)**

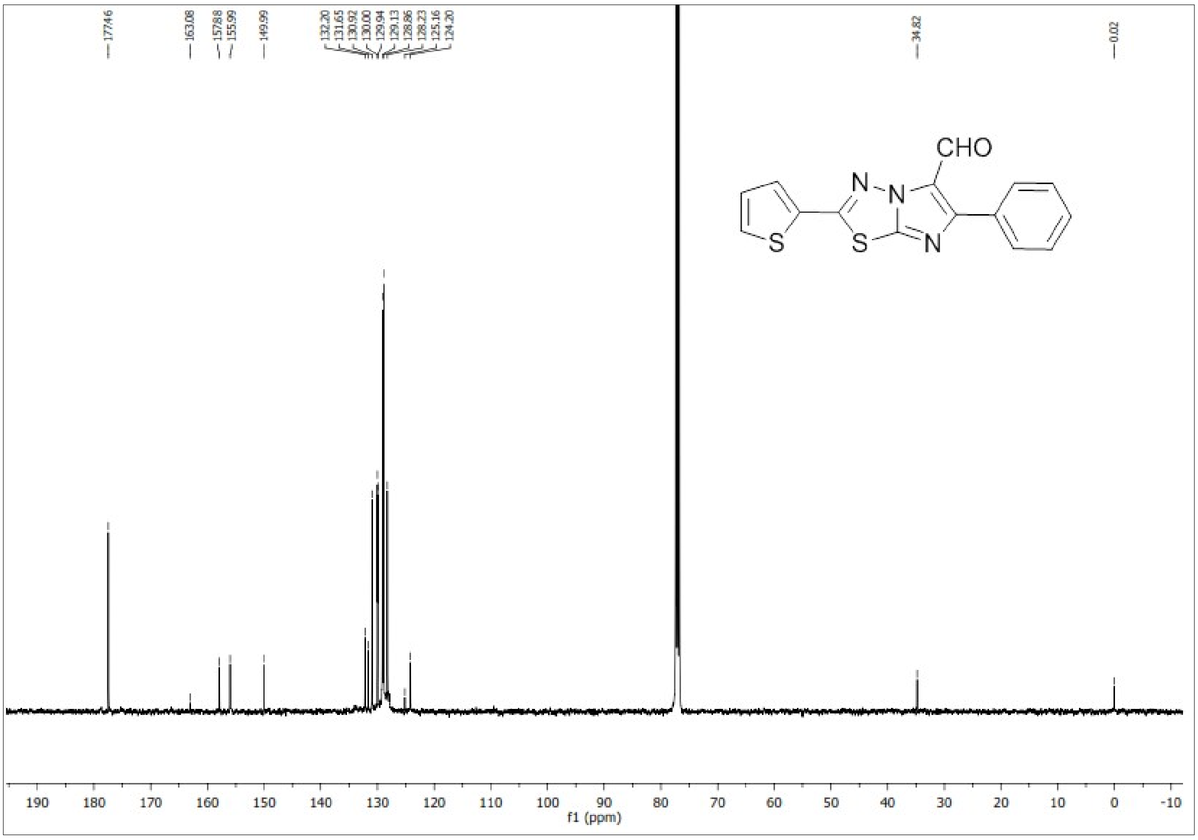

Fig. S8 ^{13}C NMR spectrum of **(5)**

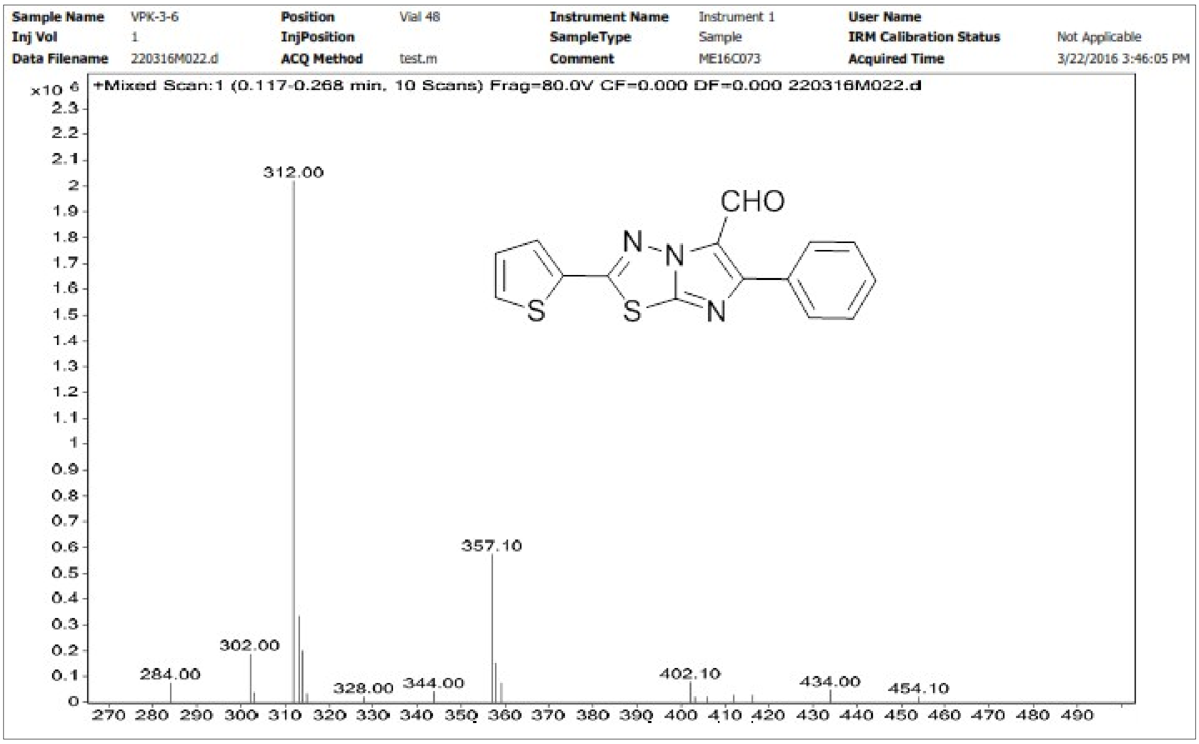

Fig. S9 Mass spectrum of **(5)**

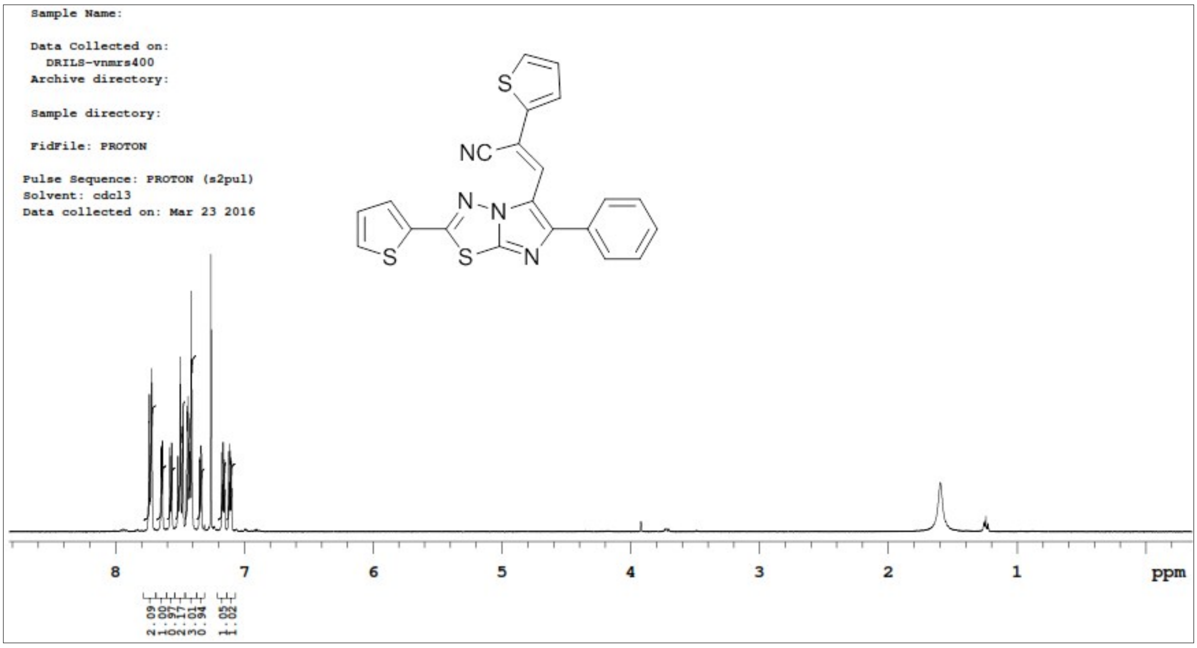

Fig. S10 ^{1}H NMR spectrum of **ThITD1**

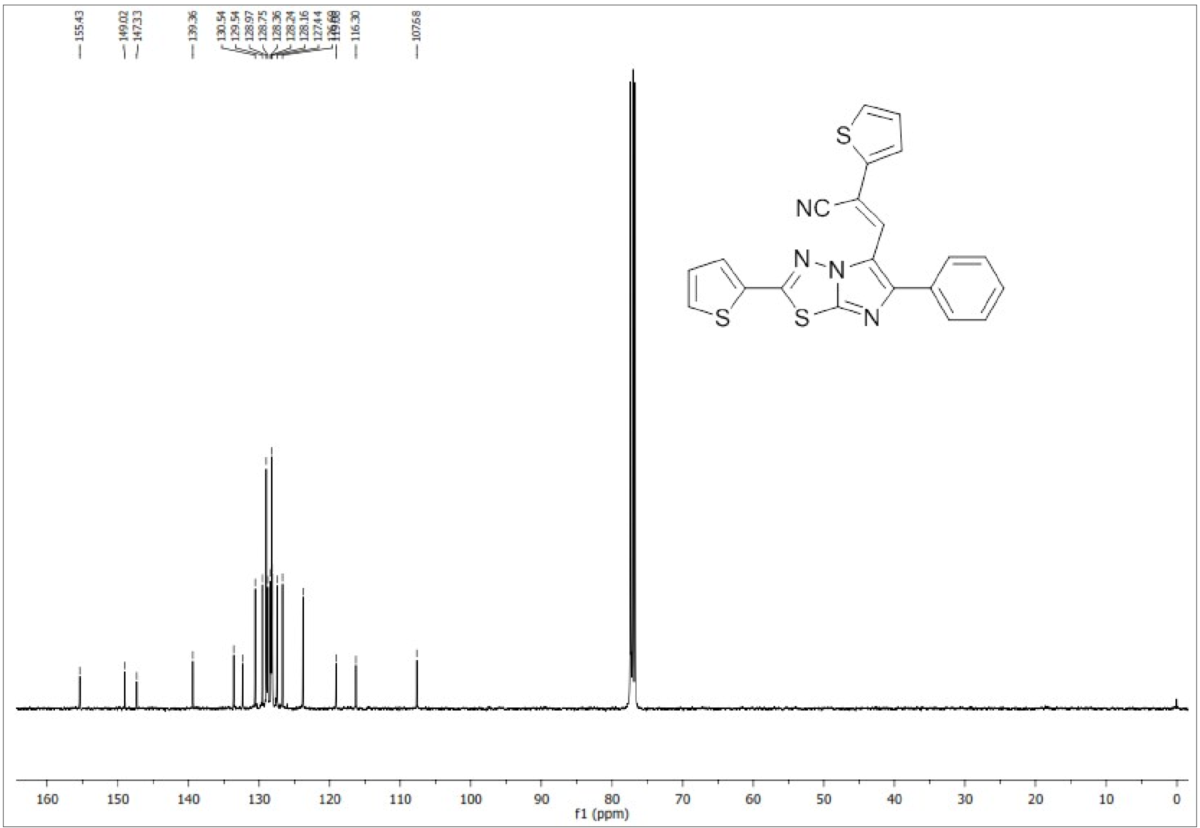

Fig. S11 ^{13}C NMR spectrum of **ThITD1**

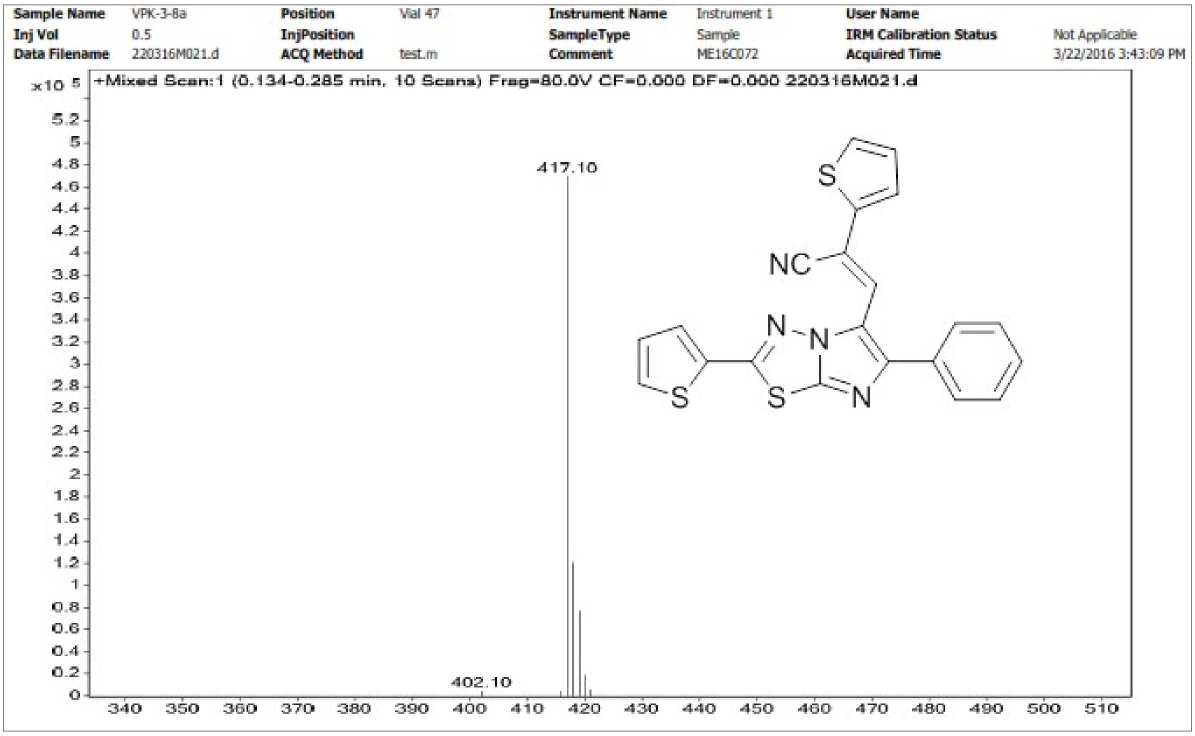

Fig. S12 Mass spectrum of **ThITD1**

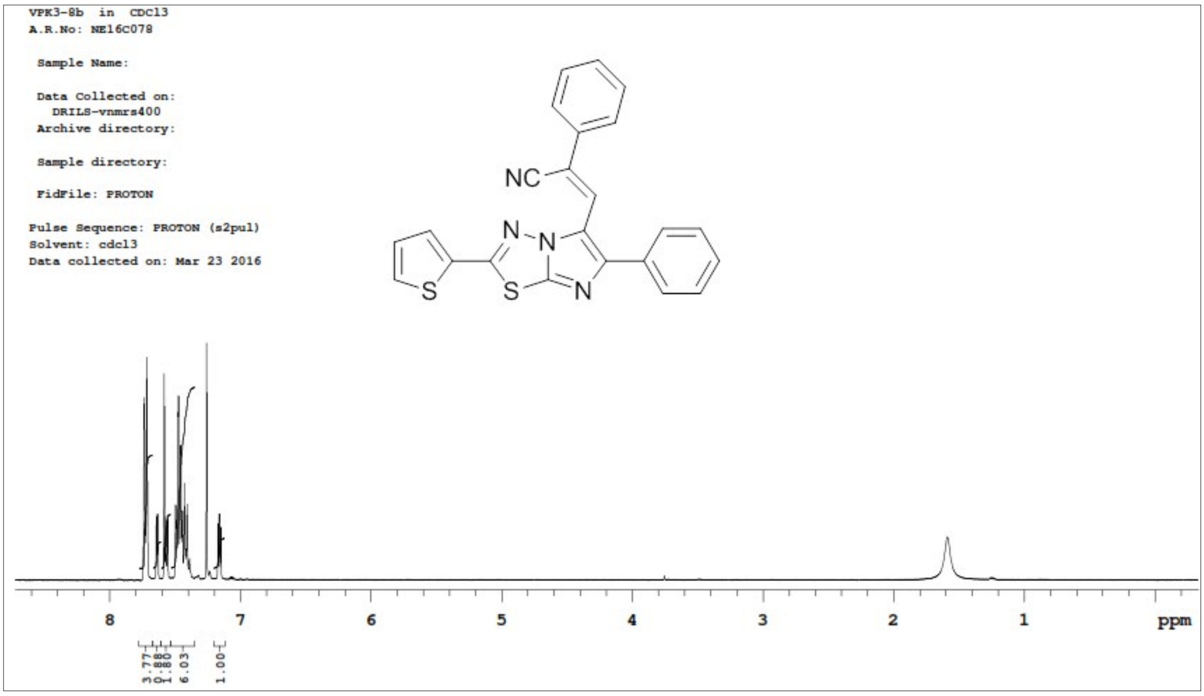

Fig. S13 ^{1}H NMR spectrum of **ThITD2**

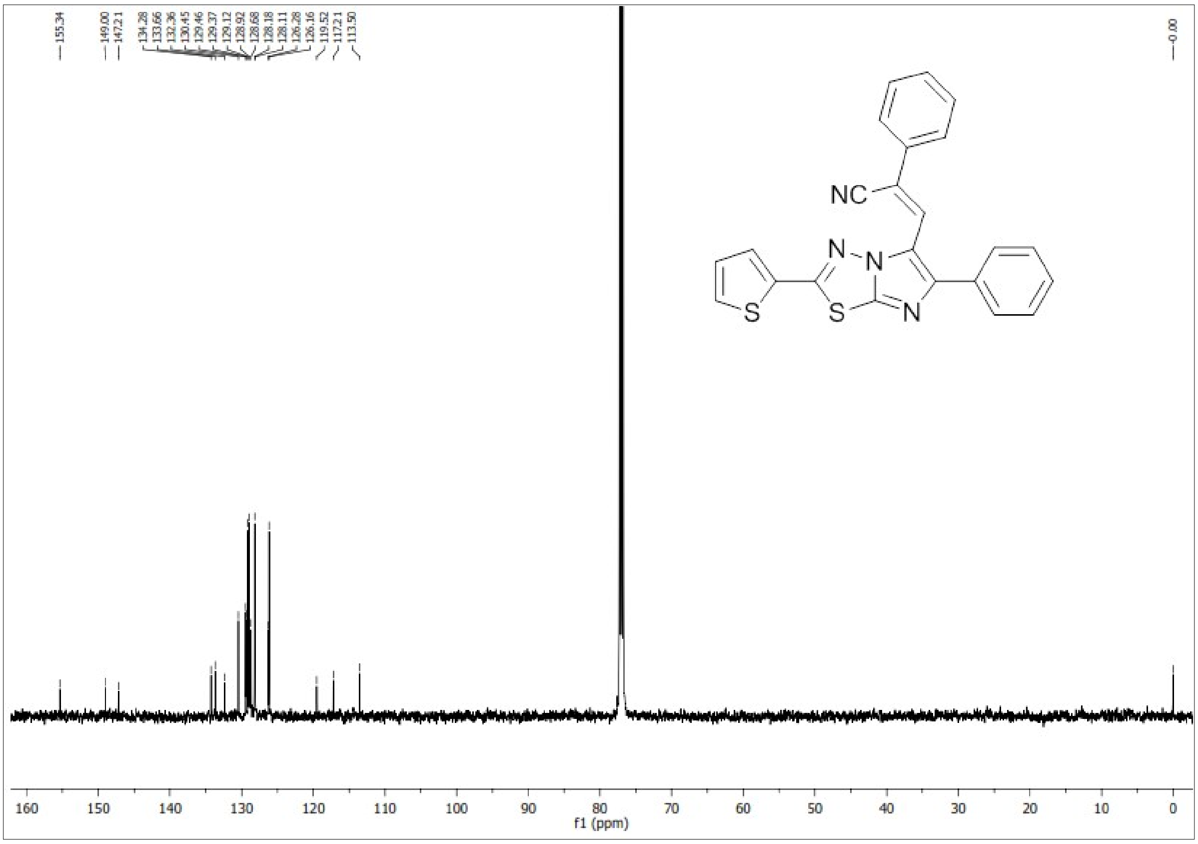

Fig. S14 ^{13}C NMR spectrum of **ThITD2**

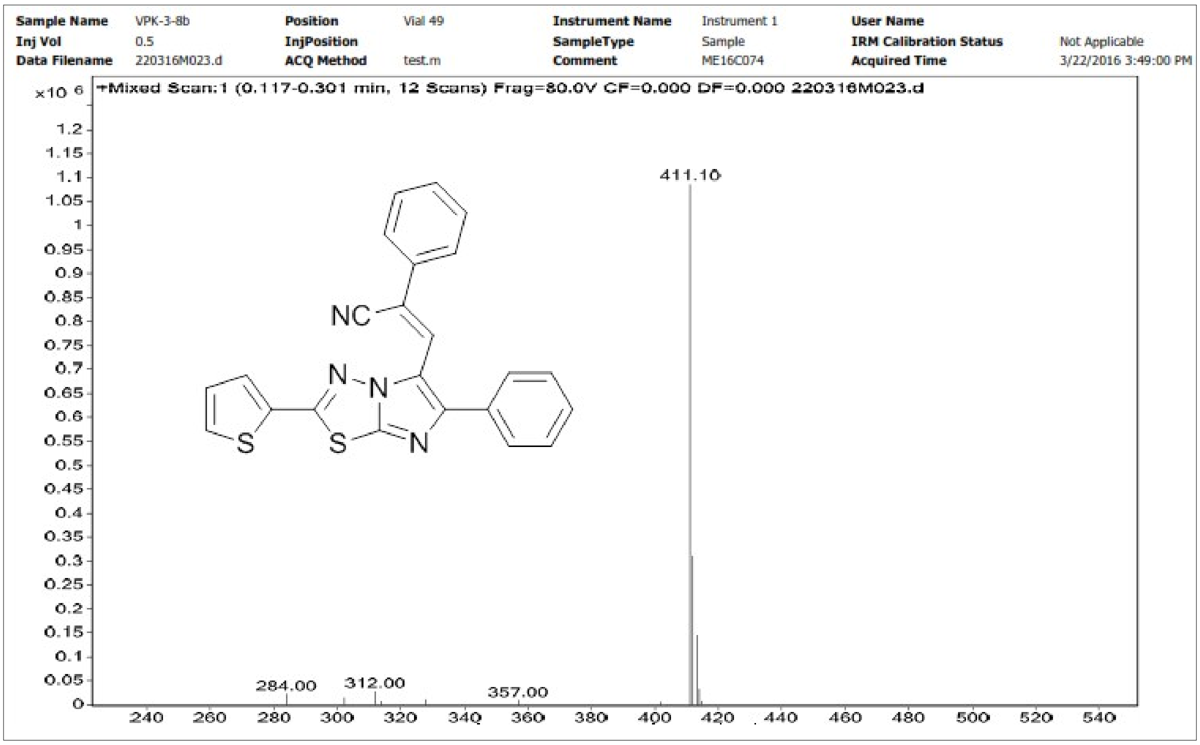

Fig. S15 Mass spectrum of **ThITD2**

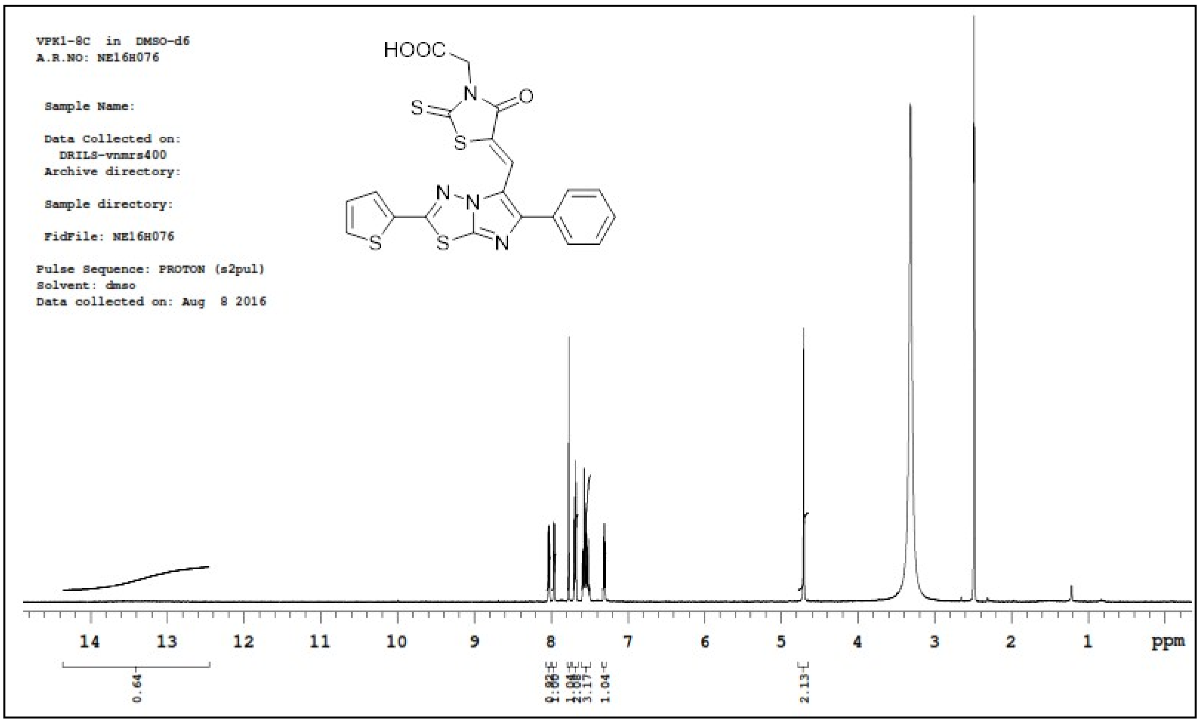

Fig. S16 ^{1}H NMR spectrum of **ThITD3**

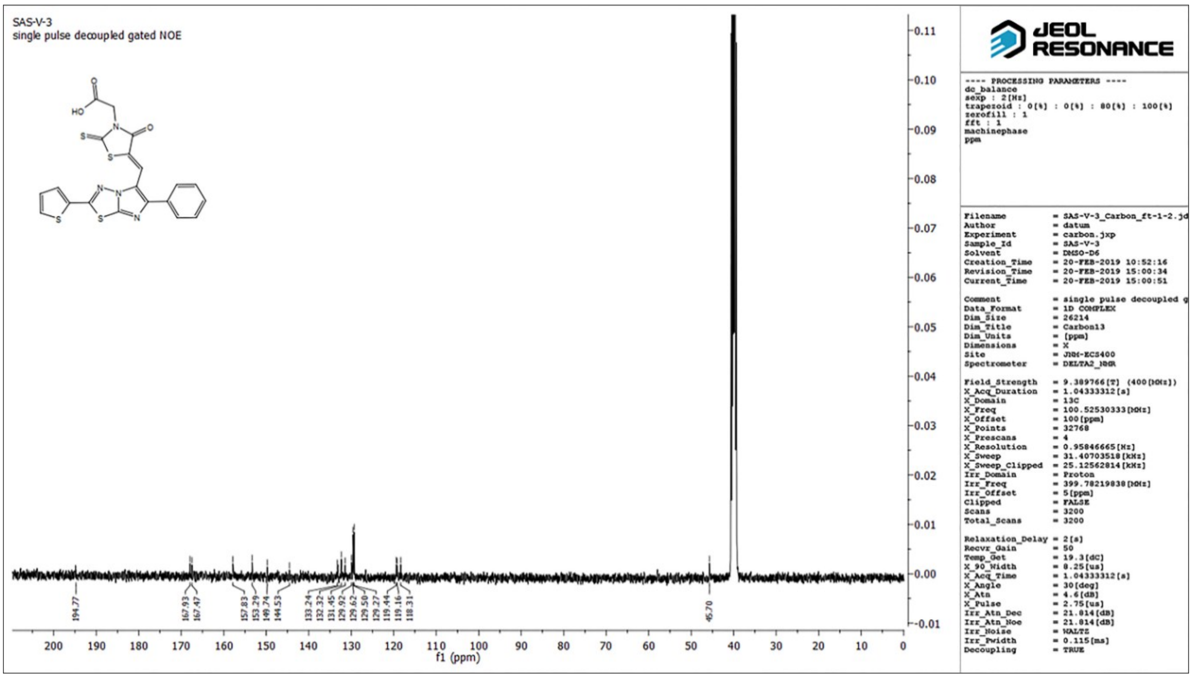

Fig. S17 ^{13}C NMR spectrum of **ThITD3**

Z–scan experimental set up

The Z–Scan experiment was performed using a frequency doubled Q switched Nd:YAG laser (Quanta–Ray INDI–40) operating at 532 nm wavelength, 7 ns pulse width and 10 Hz repeating rate excitation source. The beam splitter divides the beam into two, in which one acts as reference and the other beam has been made to transmit through the sample using a convex lens. All the samples were taken in the solution form in a quartz cuvette of thickness 1mm which was fixed to a computer controlled translation stage. The beam waist at the focus and Rayleigh range of the beam were estimated to be 17.56 μm and 1.82 mm, respectively. During CA scan, an aperture of 3 mm diameter was placed in the front of detector. Two identical pyroelectric detectors (RjP-735, Laser Probe. Corp., USA) were used to measure both the reference as well as transmitted energy from the sample. All the beam energies were recorded in an energy ratio meter (Rj-7620, Laser Probe Corp., and USA). Since the sample thickness was much smaller than Rayleigh range, the experiment was carried out by adopting thin sample approximation method [1].

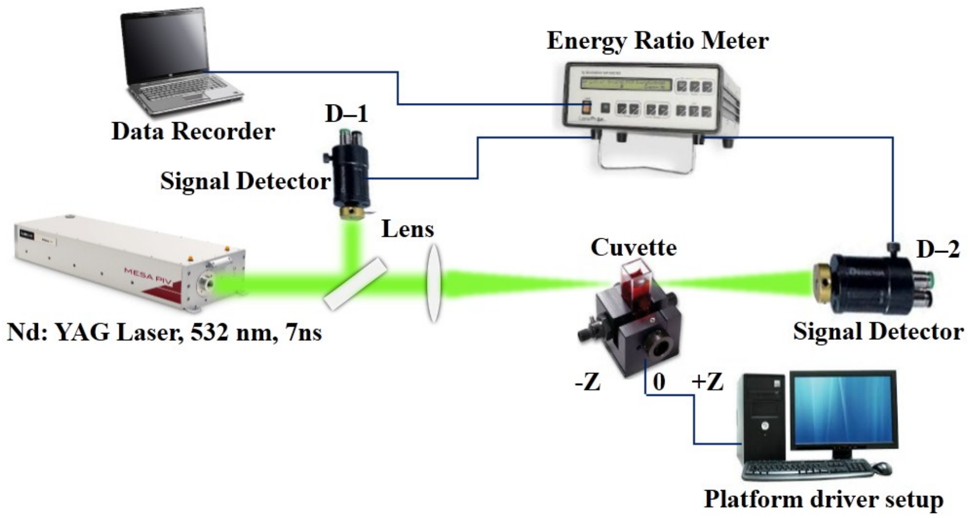

Fig. S18 Schematic representation of Z–scan experimental setup.

Table S1 Selected dihedral angles of **ThITD1–ThITD3**

Dihedral angles	ThITD1	ThITD2	ThITD3
A1-A2	36.5°	39.5°	23.0°
A1-A3	29.3°	30.2°	42.4°

A1- ITD plane, A2- thiophene -2-acetonitrile plane of **ThITD1**, phenyl acetonitrile plane of **ThITD2** and rhodanine–3–acetic acid plane of **ThITD3**, A3- benzene plane

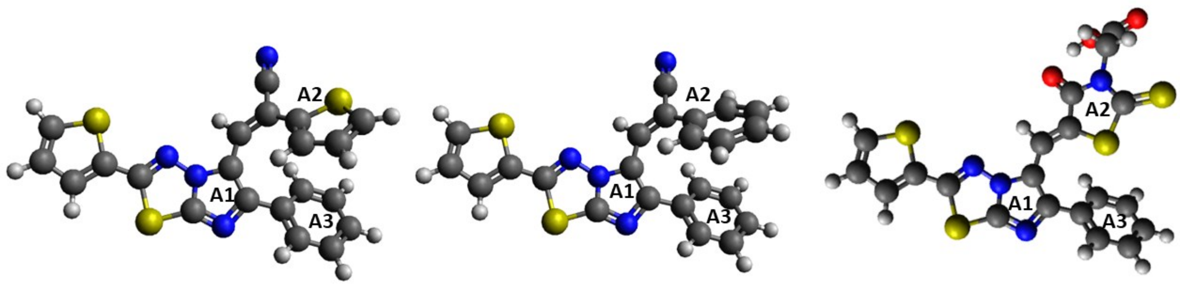

Fig. S19 Optimized geometries of **ThITD1–ThITD3**

The Fig. S20 (a), (b) and (c) show the graph of effective two photon absorption coefficient (β_{eff}) versus input laser intensity (I_o) of **ThITD1–ThITD3**, respectively. There is a decrease in β_{eff} with an increase of beam intensity which is a signature of ESA (RSA) [2]. The high energy incident beam allows partial depletion of ground state with the increase of population in the excited state which significantly decreases β_{eff} [3].

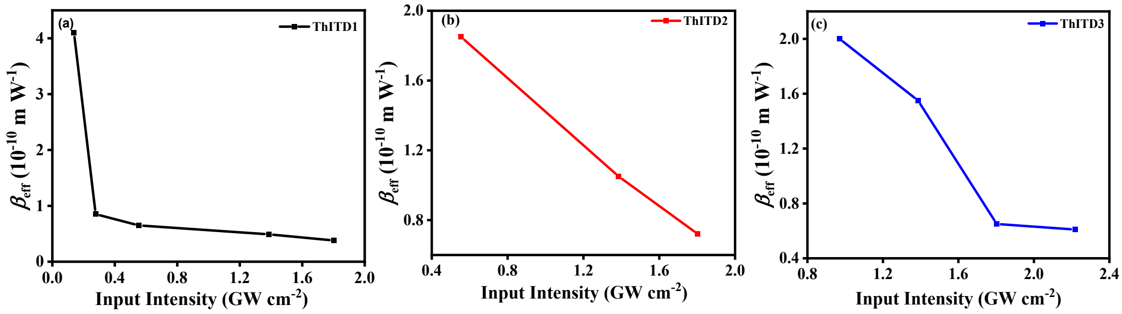

Fig. S20 β_{eff} verses I_o plot of **ThITD1–ThITD3**.

References

1 M. Sheik-Bahae, A. A. Said, T.H. Wei, D. J. Hagan and E. W. Van Stryland, *IEEE J. Quantum Electron.*, 1990, **26**, 760–769.

2 N. S. Narendran, R. Soman, P. Sankar, C. Arunkumar and K. Chandrasekharan, *Opt. Mater.*, 2015, **49**, 59–66.

3 S.L. Guo, L. I. Xu, H.T. Wang, X.Z. You and N. B. Ming, *Opt.Int. J. Light Electron Opt.*, 2003, **114**, 58–62.