

## Electronic Supporting Information

### Terahertz Radiation- and Second-Harmonic-Generation from a Single-Component Polar Organic Ferroelectric Crystal

Uppari Venkataramudu,<sup>†</sup> Chakradhar Sahoo,<sup>‡</sup> Solaiappan Leelashree,<sup>‡</sup> Mottamchetty Venkatesh,<sup>‡</sup> Damarla Ganesh,<sup>‡</sup> Sri Ram Gopal Naraharisetty,<sup>‡</sup> Anil Kumar Chaudhary,<sup>‡</sup> Sanyadanam Srinath,<sup>‡</sup> Rajadurai Chandrasekar<sup>†\*</sup>

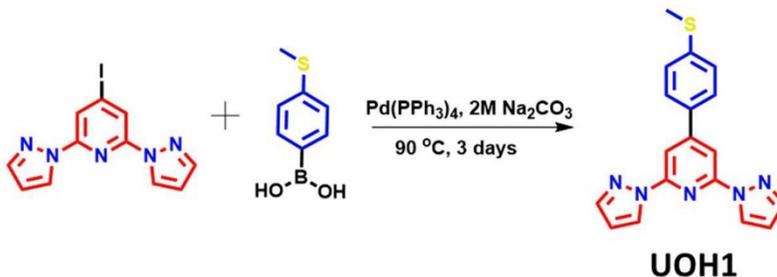
<sup>†</sup>School of Chemistry, <sup>‡</sup>School of Physics, and <sup>‡</sup>Advance Center for High Energy Materials, University of Hyderabad, Prof. C. R. Rao Road, Gachibowli, Hyderabad 500046, India

Email. r.chandrasekar@uohyd.ac.in

#### Experimental Section

Synthesis of UOH1: 4-iodo-2,6-di(1H-pyrazol-1-yl)pyridine (0.2 g, 0.593 mmol 1 equiv.), 4-(methylthio)phenylboronic

acid (0.13 g, 0.77 mmol, 1.2 equiv.) and Pd(PPh<sub>3</sub>)<sub>4</sub> (34 mg, 0.0003 mmol, 0.15 equiv.) were suspended in degassed 1,4-dioxane (20 mL). To this



Na<sub>2</sub>CO<sub>3</sub> (2M, 4 mL) was added and heated at 90 °C for 3 d under nitrogen atmosphere. The course of the reaction was monitored by thin layer chromatography (Eluent: dichloromethane/hexane). After disappearance of starting materials, the reaction mixture was cooled room temperature and then 1,4-dioxane was removed using a rotary solvent evaporator. The resulting residue was treated with water and extracted with dichloromethane (DCM) solvent. The extracted organic fraction was dried over MgSO<sub>4</sub> and the solvent was removed in vacuo. The resulting white colour residue was subjected to silica gel flash column chromatography (1:1 DCM/hexane) to get compound UOH1 as white powder (130 mg, 61%). <sup>1</sup>H-NMR: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub> - d<sub>1</sub>, δ): 8.61 (s, 2H), 8.10 (s, 2H), 7.80 (s, 2H), 7.75 (d, 2H), 7.35 (d, 2H), 6.51 (s, 2H), 2.24 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub> - d<sub>1</sub>, δ): 153.4, 150.6, 142.5, 141.3, 133.7, 127.5, 126.3, 115.5, 109.97, 106.7, 15.3; IR

(KBr):  $\nu = 3112, 3084, 2953, 2920, 2871, 1610, 1550, 1512, 1446, 1391, 1210, 1068, 1046, 936, 893, 838, 783 \text{ cm}^{-1}$ ; ESI-MS  $m/z$ :  $[M+H]$  calcd for  $C_{18}H_{15}N_5S$ , 333.416, found 333.113. Anal. calcd for  $C_{18}H_{15}N_5S$ : C, 64.88; H, 4.53; N 21.01. found: C, 64.78; H, 4.46; N, 21.01.

Crystallization: 120 mg of UOH1 was dissolved in 12 mL of chloroform and then 8 mL of methanol was added dropwise. The solution was kept under slow solvent evaporation condition for crystal growth. After 3 days colorless coffin-shaped crystals along with needle-shaped fibers were obtained. Both crystals are solved with same parameters with the help of single crystal XRD.

Materials and Methods. All chemicals (Citrazanic acid,  $POCl_3$ ,  $(CH_3)_4N^+Cl^-$ ,  $K_2CO_3$ , pyrazole, potassium metal,  $(COCl)_2$ , LiOH,  $NaN_3$ , KI, iodine,  $Pd(PPh_3)_4$ , (4-(methylthio)phenyl)boronic acid) were used as purchased. The solvents were distilled and dried before reactions and for extraction. Column chromatography was performed using Merck silica gel (particle size 100-200 mesh). For UV-Vis, Fluorescence measurements spectroscopic grade solvents were used.

$^1H$  and  $^{13}C$  NMR spectroscopy studies were performed on a Bruker DPX 500 spectrometer with solvent proton as an internal standard ( $CDCl_3-d_1 = 7.26 \text{ ppm}$ ). UV-Visible absorption spectra were recorded on a SHIMADZU-UV-3600 UV-VIS-NIR Spectrophotometer. Size and morphology of the microspheres were examined by using a Zeiss field-emission scanning electron microscope (FESEM) operating at 3 kV. IR spectra were recorded on Nicolet 5700 FTIR or JASCO FT/IR 5300. For thin-layer chromatography (TLC), silica gel plates Merck 60 F254 were used and compounds were visualized by irradiation with UV light

X-ray Crystallography: X-ray crystal structure of UOH1 crystal was obtained at 298 K using Oxford Xcalibur Gemini Eos CCD diffractometer using radiation Cu Ka ( $\lambda = 1.54056 \text{ \AA}$ ). OLEX2-1.046 software was used to solve and refine the structure. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on heteroatoms were located from difference electron density maps, and all C-H hydrogens were fixed geometrically. Hydrogen bond geometries were determined in Platon. Crystal structures are deposited as part of the Supporting Information and may be accessed at [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif) (CCDC Nos. 1824689).

Optical Absorbance and Emission Studies. UV-Visible absorption spectra of the solid and solution state compounds were recorded on a Shimadzu UV-3600 spectrometer. For solid sample,

diffuse reflectance UV-visible (DR-UV-vis) mode was used and the reflectance spectrum was converted to an absorbance spectrum using the Kubelka-Munk function. Fluorescence spectra were recorded on a FluoroLog-3, Horiba Jobin Yvon spectrofluorimeter.

DFT (density functional theory). DFT calculations were performed using B3LYP hybrid functional and 6-31G(d) basis set for all the atoms as incorporated in Gaussian 09 software. Optimization of molecular structures with consequent frequency test provided structures with close similarity to the X-ray crystallographic geometry.

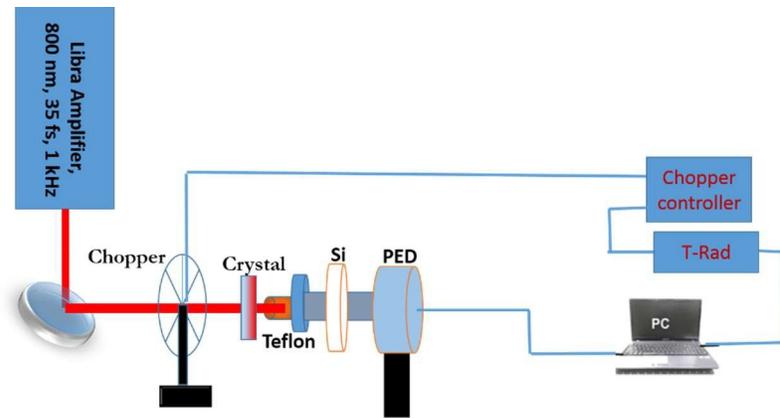
Differential Scanning Calorimetry. DSC was performed on a Mettler Toledo DSC 822e module. Samples were placed in crimped but vented aluminum sample pans. The typical sample size is 3-5 mg; temperature range was 25–180 °C @ 10 °C/min. Samples were purged by a stream of nitrogen flowing at 60 mL/min.

Ferro-electric and dielectric measurements. Temperature-dependent dielectric constant and ferroelectric hysteresis measurements were performed on a single crystal of UOH1. The crystal was painted by silver paste on the opposite sides to have a metal-insulator-metal configuration. The crystal was treated thermally at 60°C for 30 minutes to increase the adhesion between the sample and the electrodes. All measurements were performed at room temperature. The dielectric measurement was carried out using LCR meter (Agilent E4980A) for the frequency range between 20 Hz to 2 MHz. And the ferroelectric measurement was done using Precision Premier II (Radiant Technologies).

Experimental Setup for SHG and TPL. For SHG/ TPL measurement a home build experimental set up was developed by using a commercial Ti: Sapphire laser having central wavelength 800 nm, pulse width 100 fs, Repetition rate 1 KHz. The laser output is directed by a half-wave plate and polarizer combination to control the laser power, a lens having a focal length of 50 cm is used to focus the laser beam on the sample. The reflected beam is filtered by a notch filter to cut down the fundamental excitation wavelength, the filtered beam is collected by a fiber-coupled spectrometer, and the spectrometer output is displayed by a computer. The experiment is performed by keeping the sample at focal volume having a spot size of 102  $\mu\text{m}$  and is exposed by linearly polarized light with different input powers.

Powder SHG measurement for calculation of second-order nonlinear optical coefficient: The powder SHG measured by the Kurtz–Perry method. The samples were placed in a quartz cell and measured SHG signals at 800 nm Ti: Sapphire pulse laser (pulse width 100 fs, repetition rate 1 kHz, linear polarization). We measured the intensity of the frequency-doubled output emitted from the sample using a photomultiplier tube. The second harmonic efficiency of the sample was compared to that of a standard powder sample of Urea.

THz transmission experiment set-up 1: The experimental layout for measurement of THz intensity is shown below.

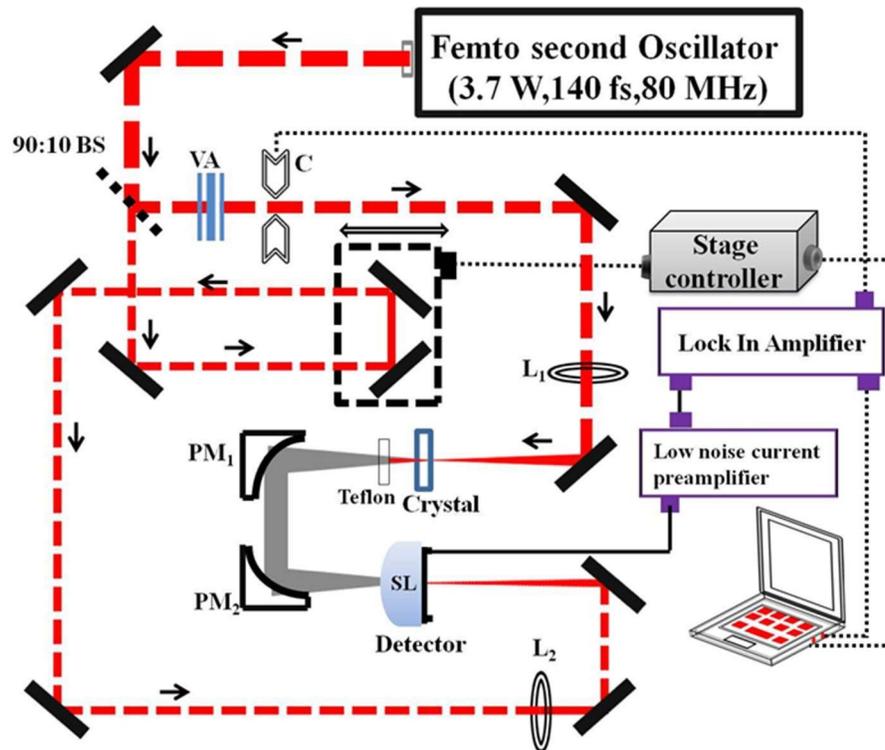


Coherent LIBRA amplifier pulse having pulse width 35 fs at 800 nm wavelength was used as a pump to generate THz radiation from the UOH1 crystal. Teflon sheet and silicon plate were used to filter out the unconverted pump from THz. The optical chopper (23.5 Hz) is used as a reference for the pyroelectric detector (PED). The intensity of THz was measured by focusing on pyroelectric detector connected to a T-Rad system and the output of the T-Rad was fed to the personal computer for measuring the power of the generated THz signal.

THz generation experiment set-up 2:

The THz generation was achieved using a coherent chameleon ultra-II laser which provides an output wavelength of 800 nm, pulse duration 140 fs at repetition rate 80 MHz. A variable attenuator was used to attenuate the incident laser pulses and the laser beam with selective average power was allowed to an incident on the UOH1 nonlinear crystal to generate the THz signal. The employed pump and probe beam powers were  $\sim 700$  mW, and  $\sim 175$  mW for emission and detection of THz radiation, respectively. Teflon filter was used to eliminate the unconverted pump beam

from the crystal. The generated THz was detected by dipole photoconductive antennas (gap  $\sim 5 \mu\text{m}$ , length  $\sim 20 \mu\text{m}$ ) using photoconductive sampling technique. The antenna output was



VA- Variable attenuator, BS-Beam splitter,  $\text{PM}_1$  &  $\text{PM}_2$ : Parabolic mirror,  $L_2$  &  $L_1$ : Lenses, Crystal: UOH1, Detector: Photoconductive antenna, C: chopper,

connected to low noise current preamplifier which is fed to the Lock-in Amplifier (Stanford Research Systems, Model no.SR830). The S/N ratio is enhanced using mechanical chopper operating at 1.569 kHz frequency. The temporal profile of THz radiation is measured by varying the delay of the probe beam with respect to THz pulse reaching to the antenna.

Raman Spectroscopy Studies. Variable Temperature Raman spectra of the samples were recorded on a WI-Tec confocal Raman spectrometer connected to a Peltier-cooled CCD detector. A 600 grooves/mm grating BLZ = 500 nm was used. The accumulation time was 10 s and integration time was typically 2.0000 s. To acquire a single spectrum 10 accumulations were performed. A 785 nm laser ( $\text{Ar}^+$  ion) was used as an excitation source.

Other methods:  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic data were recorded on a Bruker DPX 400 MHz spectrometer with a solvent proton as internal standard ( $\text{CDCl}_3\text{-d}_1 = 7.26$  and  $\text{DMSO-d}_6 = 2.50$ ). Deuterated solvent  $\text{CDCl}_3\text{-d}_1$  was obtained from Aldrich. The high-resolution mass analysis was performed on a Bruker ESI-TOF mass spectrometer. IR spectra were recorded on JASCO FT/IR-5300. Elemental analysis was recorded on a Thermo Finnigan Flash EA 1112 analyzer. For thin layer chromatography (TLC), silica gel plates Merck 60 F254 were used and compounds were visualized by irradiation with UV light.

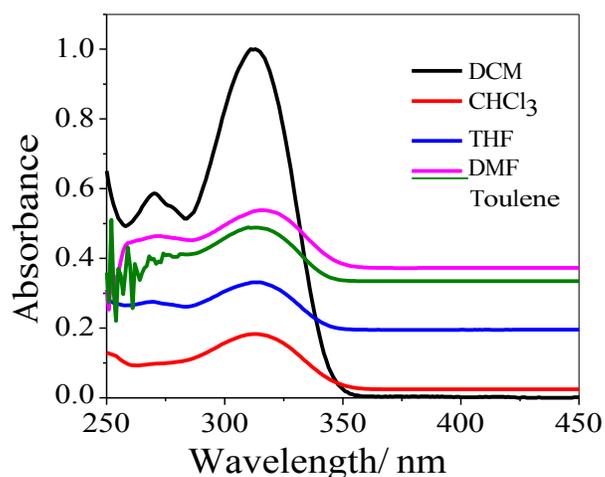


Figure S1. UV-Vis absorbance of UOH1 in various solvents.

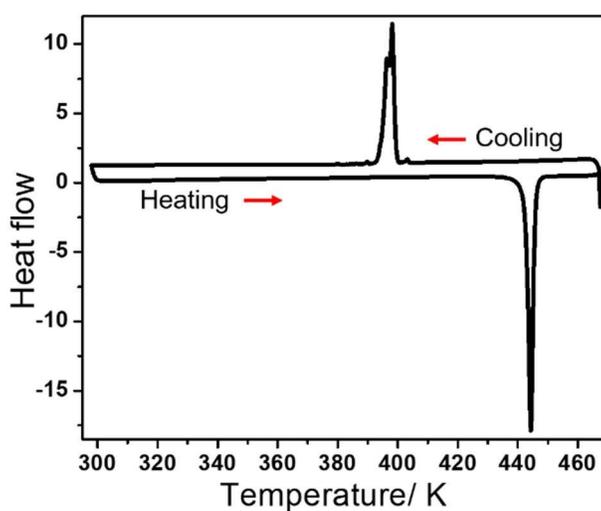


Figure S2. DSC thermogram of UOH1 crystal.

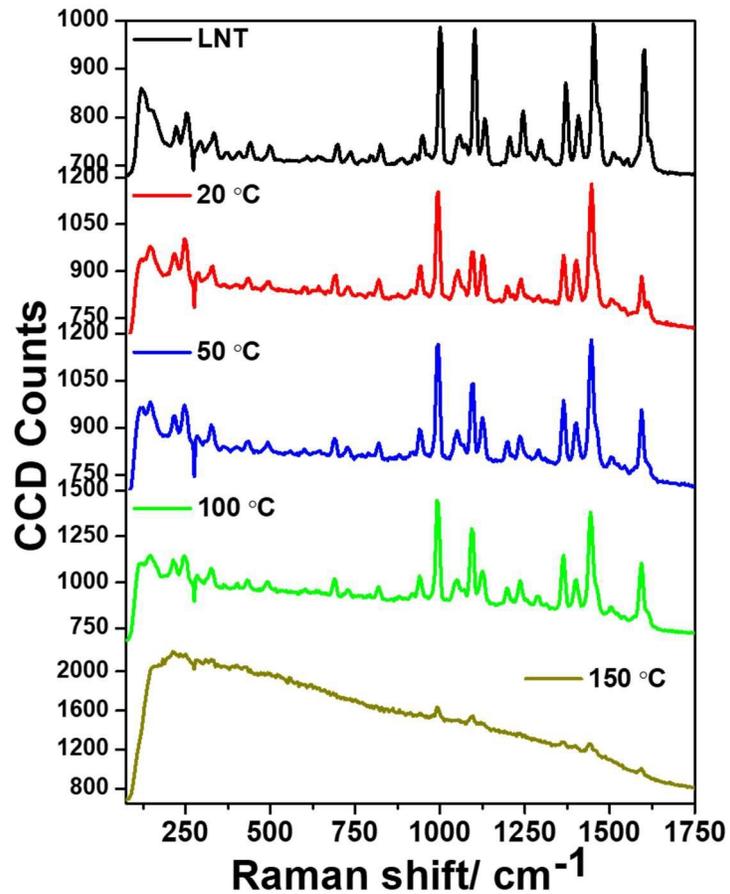


Figure S3. Variable-temperature Raman spectra of UOH1 crystal at -140 °C (LNT), 20 °C, 50 °C, 100 °C and 150 °C.

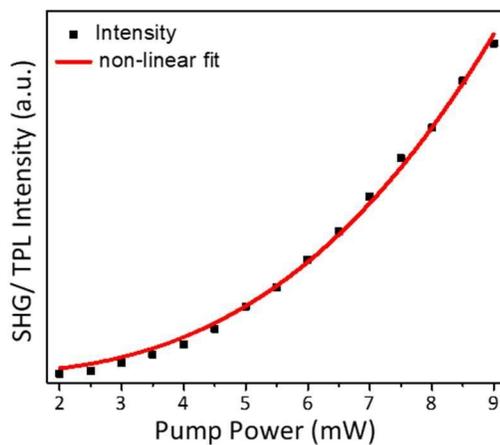


Figure S4. Pump power dependent NLO study with 800 nm laser excitation. NLO signal quadratically increases with pump power. The red line shows the non-linear fit.

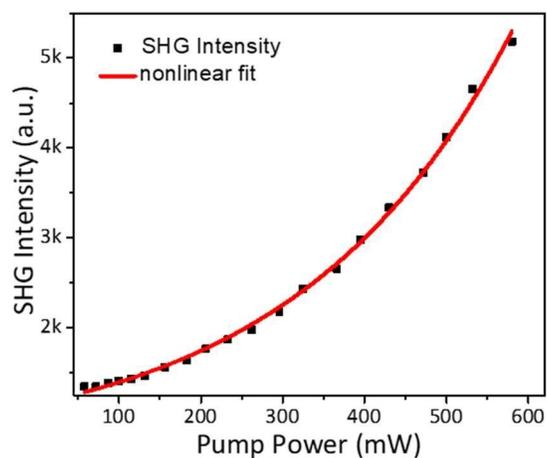


Figure S5. Pump power dependent SHG study with fundamental 1030 nm harmonic light. SHG signal quadratically increases with pump power. The red line shows the non-linear fit.

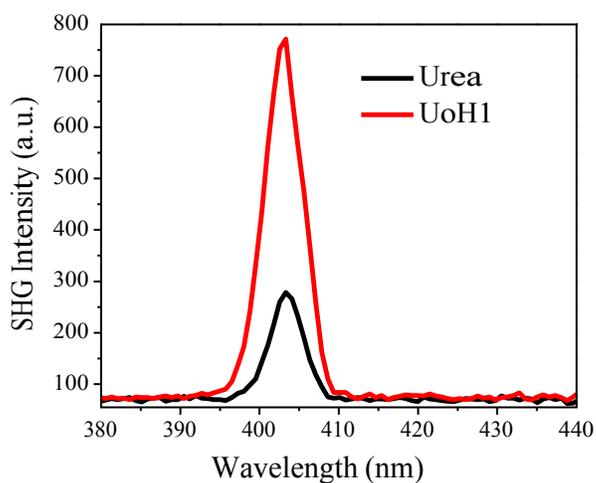


Figure S6. Second-order nonlinear optical coefficient calculations.

The second order non-linear coefficient of UOH1 crystal was calculated with reference to urea. The magnitude of SHG signal is 3.3 times greater than urea.

$$\beta_{\text{urea}} = 3.39 \times 10^{-9} \text{ e.s.u.}, \text{ then } \beta_{\text{MTP-BPP}} = (\beta_{\text{urea}}) \times 3.3$$

$$\beta_{\text{MTP-BPP}} = 11.187 \times 10^{-9} \text{ e.s.u.}$$

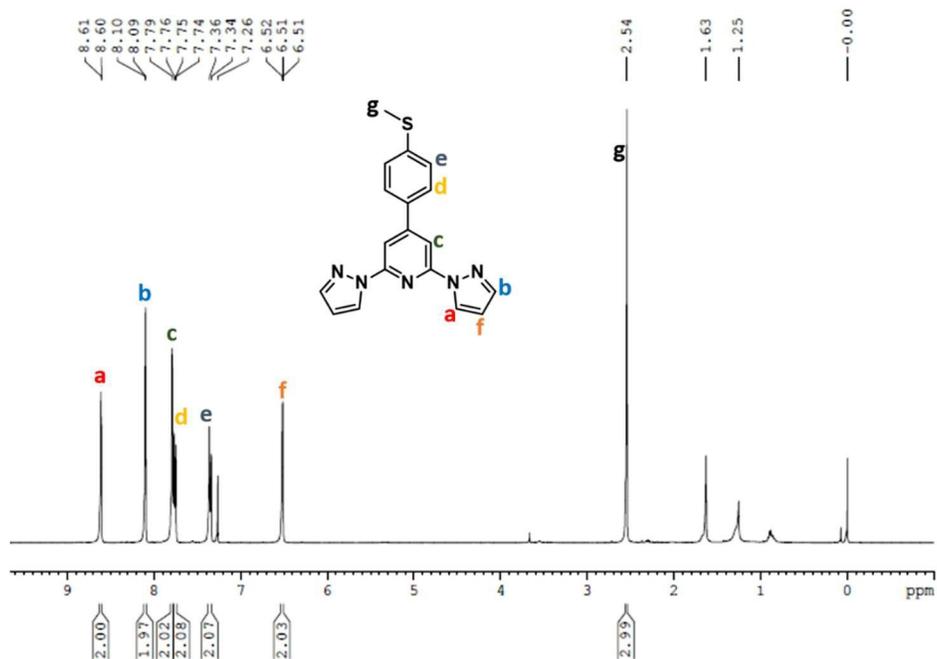


Figure S7. <sup>1</sup>H-NMR spectrum of UOH1.

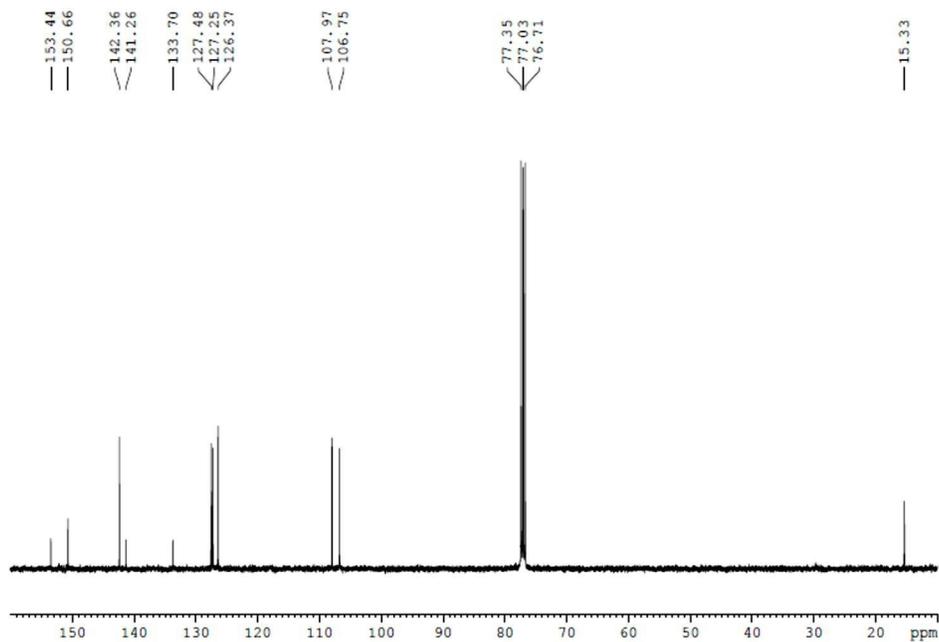


Figure S9. <sup>13</sup>C-NMR spectrum of UOH1.

# BRUKER MAXIS HRMS REPORT

School of Chemistry  
University of Hyderabad

## Analysis Info

Analysis Name D:\Data\2015\DR\_RCJULYWR-43.d  
Method Tune\_low.m  
Sample Name VR-43  
Comment

Acquisition Date 7/16/2015 3:29:47 PM

Operator Ramu Sridhar  
Instrument maXis 10138

## Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	4.4 psi
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1800 m/z	Set Collision Cell RF	350.0 Vpp	Set Divert Valve	Waste

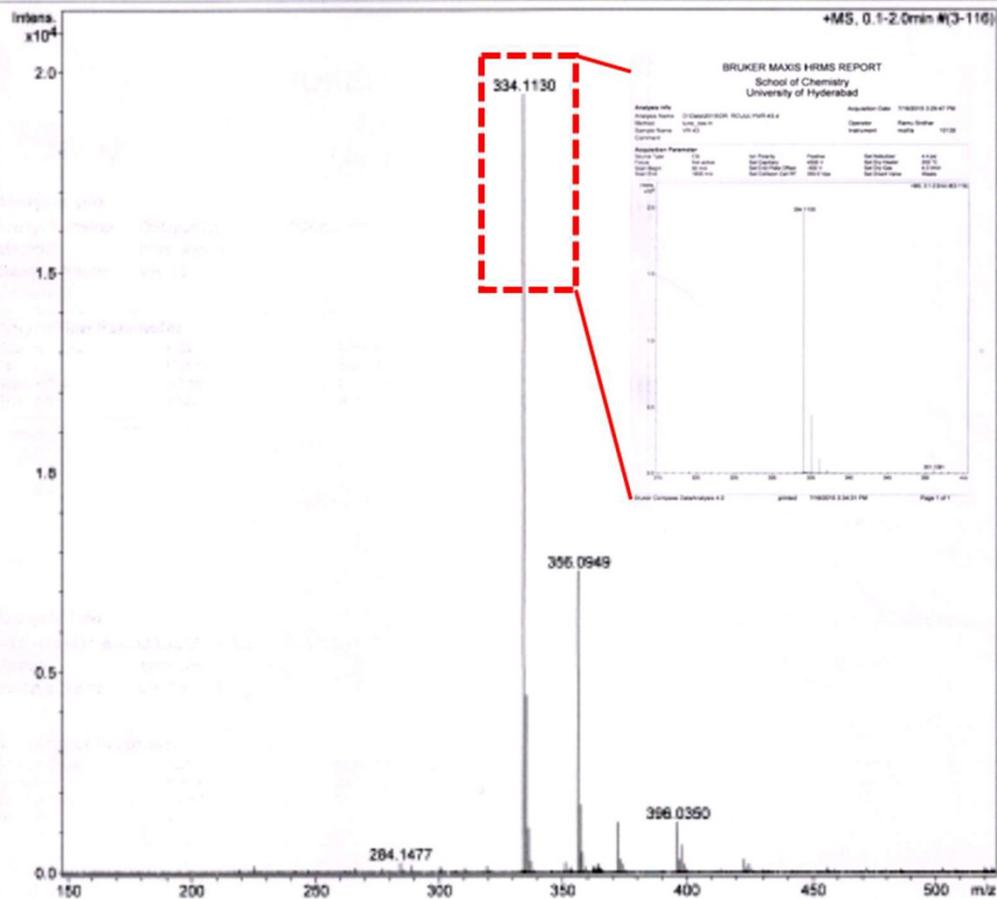
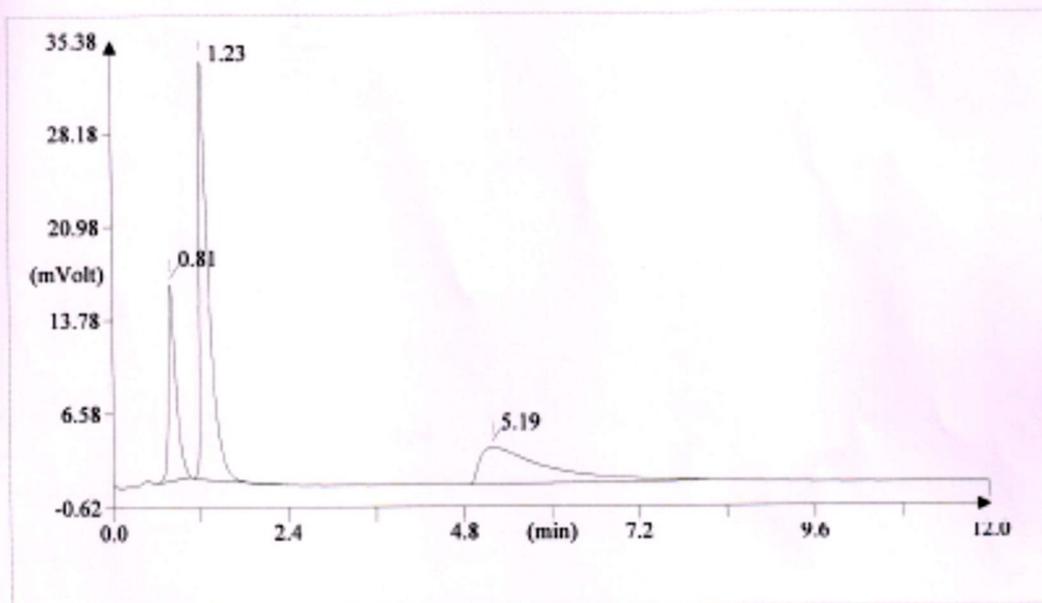


Figure S10: The HR-MS of UOH1 compound.

# FLASH EA 1112 SERIES CHN REPORT THERMO FINNIGAN

Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys\_data\_ex  
Sample ID: VR-26 (# 101)  
Analysis type: UnkNown  
Chromatogram filename: UNK-31012018-1.dat  
Sample weight: 1.086



Element Name	Element %	Ret. Time
Nitrogen	21.12	0.81
Carbon	64.78	1.23
Hydrogen	4.46	5.19

Figure S11. The CHN analysis of UOH1 compound.

Supplementary Table 1. X-ray crystal structure data of UOH1 [CCDC Nos. 1824689]

Chemical Formula	C <sub>18</sub> H <sub>15</sub> N <sub>5</sub> S
FW	333.41
Color	Colorless
Crystal system	Tetragonal
Spacegroup	I 4 <sub>1</sub>
a	12.8855(4)
b	12.8855(4)
c	19.6018(10)
$\alpha$	90.0
$\beta$	90.0
$\gamma$	90.0
V (Å <sup>3</sup> )	3254.6(3)
Z	8
$\rho$ (g/cm <sup>3</sup> )	1.361
T	298 K
$\Lambda$ (Å)	1.54184
F (000)	1392.0
Theta	0.530
Index Ranges (h, k, l)	15,15,24
R1 (Reflections)	0.0348( 1989)
Goodness of Fit on F <sup>2</sup> . S	1.042