

Supporting Information

Entry of Chiral Phthalimides With Significant Second Order Nonlinear Optical and Piezoelectric Properties[†]

Anil K. Singh^a, Ram Kishan^b, N. Vijayan^c, V. Balachandran^d, Taruna Singh^b, Hemandra K. Tiwari^a, Brajendra K. Singh^a and Brijesh Rathi^{a*}

^aBio-organic Research Laboratory, Department of Chemistry, University of Delhi, Delhi-110 007, India

^bDepartment of Chemistry, University of Delhi, Delhi-110 007, India

^cCSIR-National Physical Laboratory, Dr. K. S. Krishnan Road, New Delhi-110 012, India

^dPG & Research Department of Physics, Aringer Anna Government Arts College, Musiri – 621 211, India

General Consideration. Homogeneity/purity of all the products was assayed by thin-layer chromatography (TLC) on alumina-coated plates (Merck). Product samples in chloroform (CHCl₃) were loaded on TLC plates and developed in CHCl₃-MeOH (9.5:0.5, v/v). When slight impurities were detected by iodine vapor/UV light visualization, compounds were further purified by chromatography on silica gel columns (100-200 mesh size, CDH), using petroleum ether-ethyl acetate (1:1, v/v) as the eluent. Melting points were determined on pyris-6 DSC (Perkin Elmer). Infrared (IR) spectra were recorded in KBr medium using a Perkin-Elmer Fourier Transform-IR spectrometer, whereas ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded in CDCl₃ medium on a JNM ECX-400P (JEOL, USA) spectrometer with tetramethylsilane (TMS) as internal reference. Absorption frequencies (ν) are expressed in cm⁻¹, chemical shifts in ppm (δ -scale) and coupling constants (J) in Hz. Splitting patterns are described as singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m). Chemicals and solvents used in the experiment were commercially available. The chemical structures of final products were confirmed by a high-resolution Biosystems QStar Elite time-of-flight electrospray mass spectrometer. UV-Vis spectra were recorded on

Evolution 300 Series UV-Vis spectrophotometer m/s Thermofisher USA. The TGA thermogram was measured on Perkin Elmer Diamond instrument under nitrogen atmosphere at 10 °C/min heating rate.

Single Crystal X-ray Structure Determination. Intensity data of suitably sized crystals of **1-3** were collected on Oxford Xcalibur S diffractometer (4-circle kappa goniometer, Sapphire-3 CCD detector, omega scans, graphite monochromator, and a single wavelength Enhance X-ray source with MoK α radiation).^{S1} The crystallographic details are summarized in Table S1. The bond distances and angles within are summarized in Table S2. The hydrogen bonding parameters are given in Table S3. Pre-experiment, data collection, data reduction and absorption corrections were performed with the CrysAlisPro software suite.^{S2} The frames were collected by ω , ϕ and 2θ rotation at 10 s per frame with SMART. The measured intensities were reduced to F^2 and corrected for absorption with SADABS.^{S3} The structures were solved by direct methods using SIR 92^{S4} which revealed the atomic positions, and refined using the SHELX-97 program package^{S5} and SHELXL97^{S6} (within the WinGX program package).^{S7} Non-hydrogen atoms were refined anisotropically. C-H hydrogen atoms were placed in geometrically calculated positions by using a riding model. The molecular structures were created with a Diamond program.^{S8}

Table S1. Crystallographic Data of Compound 1–3

	1	2	3
Formula	C ₁₈ H ₂₂ N ₂ O ₃	C ₂₁ H ₂₀ N ₂ O ₃	C ₂₂ H ₂₂ N ₂ O ₃
Fw	314.38	348.39	362.42
T/K	298(2)	298(2)	298(2)
λ/Å	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	<i>P2₁2₁2₁</i>	<i>P2₁2₁2₁</i>	<i>P2₁</i>
a/Å	6.0436(11)	10.5272(10)	6.3444(10)
b/Å	15.9764(17)	11.4411(11)	14.8943(19)
c/Å	17.130(4)	14.6077(14)	10.1015(15)
α/deg	90	90	90
β/deg	90	90	101.140(12)
γ/deg	90	90	90
V/Å ³	1654.0(5)	1759.4(3)	936.6(2)
Z	4	4	2
D _{calcd} /g/cm ⁻³	1.263	1.315	1.285
F(000)	672	736	384
μ/mm ⁻¹	0.086	0.089	0.086
θ range/deg	3.49–26.37	2.98–26.37	3.27–26.37
reflns measured	3369	3593	3805
reflns used	2910	3373	3389
Parameters	208	235	244
R1	0.0433	0.0423	0.0374
wR2	0.1043	0.1031	0.0812
goodness of fit on <i>F</i> ²	0.950	1.034	1.049

Table S2 Selected Bond Distances (Å) and Angles (deg) for compound **1–3**

	1	2	3
C1-N1	1.465(2)	1.446(2)	1.458(2)
C1-C14/C1-C17	1.534(5)	1.535(3)	1.544(2)
C1-C2	1.510(3)	1.524(3)	1.533(2)
O3-C14/O3-C17	1.219(2)	1.224(2)	1.222(2)
N2-C14/N2-C17	1.336(2)	1.333(2)	1.342(2)
N2-C15/N2-C21	1.466(3)	1.467(3)	1.467(3)
N2-C18	1.466(3)	1.466(3)	1.463(2)
N1-C13/N1-C16	1.394(2)	1.390(2)	1.393(2)
N1-C6/N1-C9	1.404(2)	1.403(2)	1.402(2)
O1-C6/O1-C9	1.198(2)	1.199(2)	1.208(2)
O2-C13/C16-O2	1.202(2)	1.200(2)	1.202(2)
C1-N1-C13/C1-N1-C16	125.3(1)	124.7(1)	124.2(1)
C1-N1-C6/C1-N1-C9	122.8(1)	122.3(1)	123.9(1)
C6-N1-C13/C9-N1-C16	111.9(2)	111.7(1)	111.6(1)
N1-C1-C14/N1-C1-C17	111.3(1)	112.8(1)	111.6(1)
N1-C1-C2	112.1(1)	111.3(1)	110.3(1)
C2-C1-C14/C2-C1-C17	111.7(1)	110.3(2)	110.3(1)
C15-N2-C14/C17-N2-C21/C17-N2-C18	128.6(2)	128.2(2)	126.6(1)
C14-N2-C18/C18-N2-C21/C17-N2-C19	119.8(2)	120.3(2)	119.4(1)
C15-N2-C18/C17-N2-C18/C18-N2-C19	111.5(2)	111.2(2)	113.5(1)

Table S3 Selected Non-covalent interaction values in **1–3**

Interaction	D-H (Å)	D-A (Å)	D-H...A (°)
1			
C2-H2B...O1	0.970	3.517	175.20
C10-H10...O3	0.930	3.296	129.23
C17-H17B...O1	0.971	3.518	144.39
2			
C6-H6...O2	0.930	3.247	137.89
C12-H12...O1	0.930	3.535	174.86
C14-H14...O3	0.930	3.357	142.23
C18-H18A...O3	0.970	3.483	144.47
C21-H21A...O2	0.970	3.550	155.89
3			
C6-H6...O3	0.930	3.472	140.87
C13-H13...O3	0.930	3.281	158.31
C18-H18B...O2	0.970	3.213	126.84
C20-H20B...O1	0.970	3.556	166.52

Second order NLO and Piezoelectric measurements The relative second harmonic conversion efficiency was carried out using modified setup of Kurtz and Perry.^{S9} The powder of identical particle size of potassium dihydrogen phosphate (KDP) crystals was used as reference material for the present measurement. The powdered samples were sieved with the particle size of 120 micron and packed in triangular cell and kept in a cell holder. The Nd:YAG laser source produces nanosecond pulses (8 ns) of 1064 nm light and the input beam energy was around 4.7 mJ/pulse. The beam emerging through the sample was focused on to a Czerny Turner monochromator using a pair of lenses. The detection was carried out using a Hamamatsu R 928 photomultiplier tube. The signals were captured with an Agilent infinity digital storage oscilloscope interfaced to a computer. The monochromator is set at

532 nm NLO signal is captured by the oscilloscope through the photomultiplier tube. After the 4 average, the signal light is measured (peak to peak volts). Piezoelectric charge coefficient d_{33} was measured by Piezometer system (Piezotest PM 300) and P-E loop was traced by an indigenously-built Sawyer-Tower circuit interfaced with computer controlled loop tracer at room temperature.

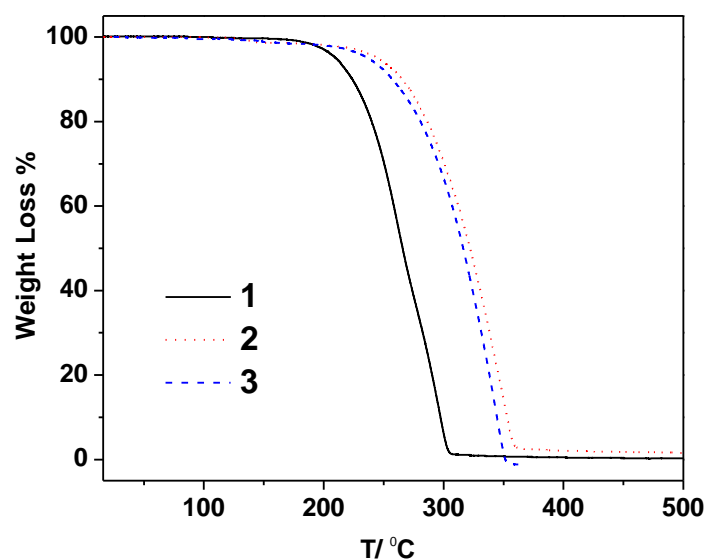
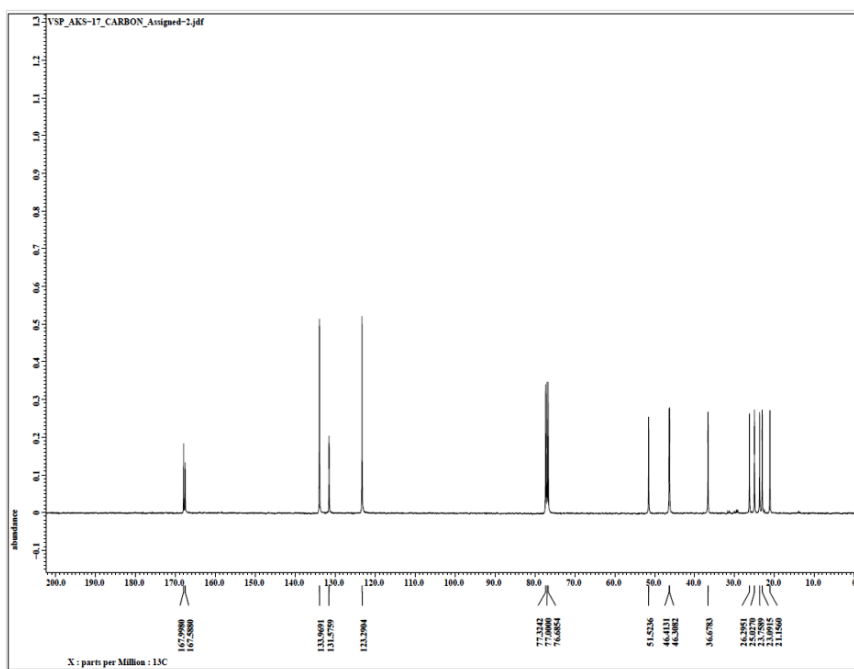
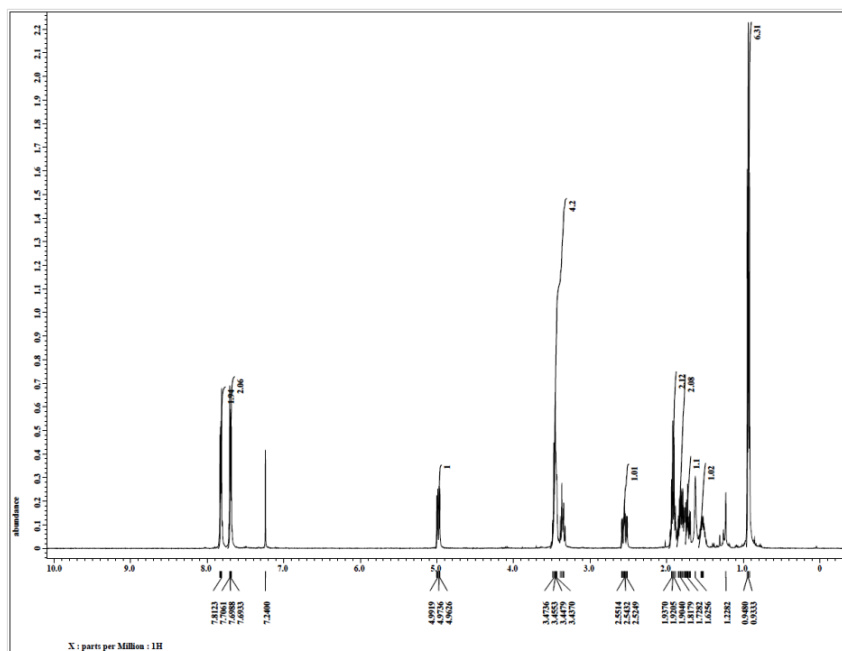


Fig. S1 TGA curve for **1-3**



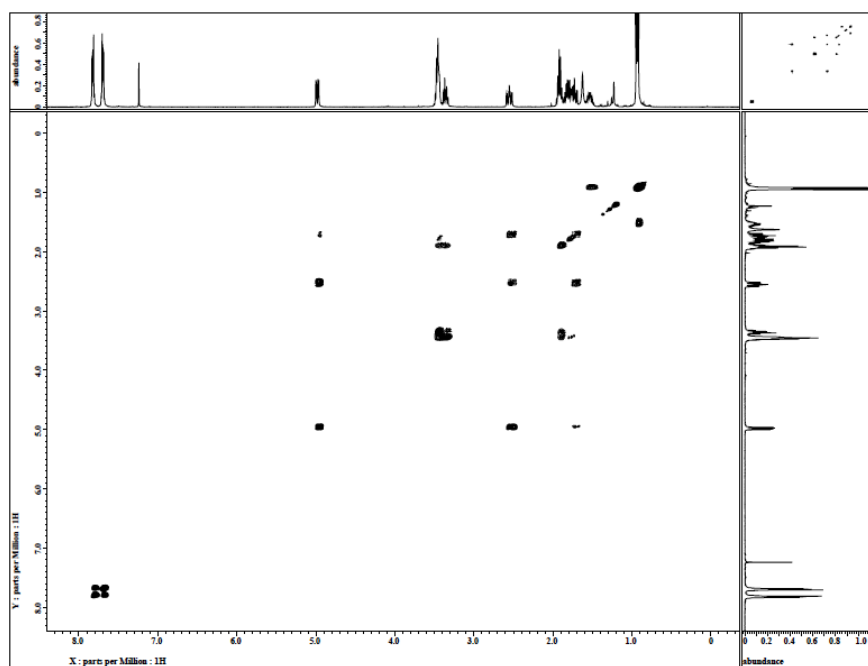


Fig. S4 Cosy spectrum of compound 1.

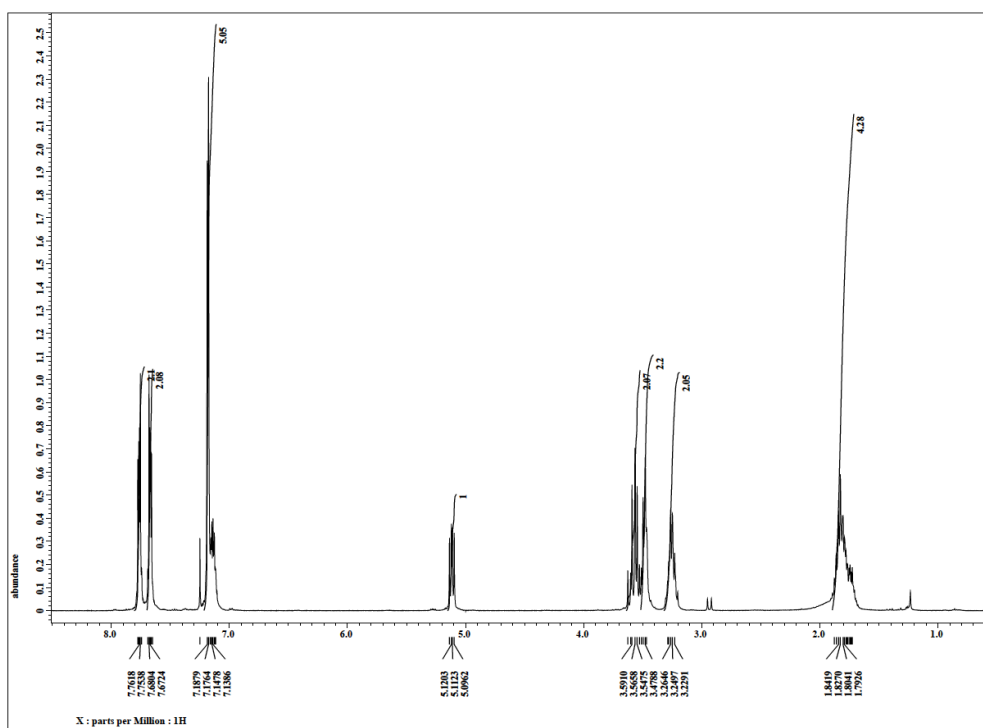


Fig. S5 ^1H NMR spectrum of compound 2 in CDCl_3

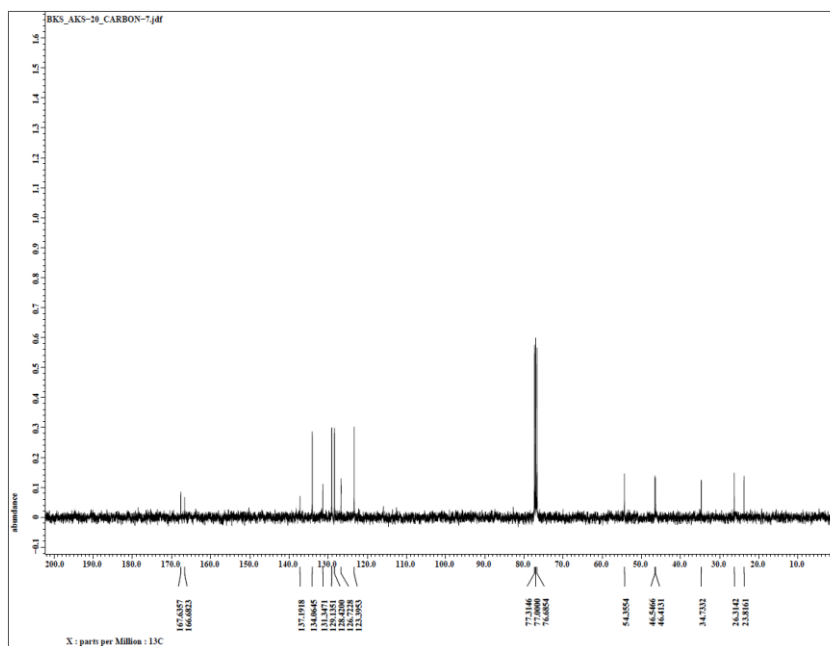


Fig. S6 ^{13}C NMR spectrum of compound **2** in CDCl_3 .

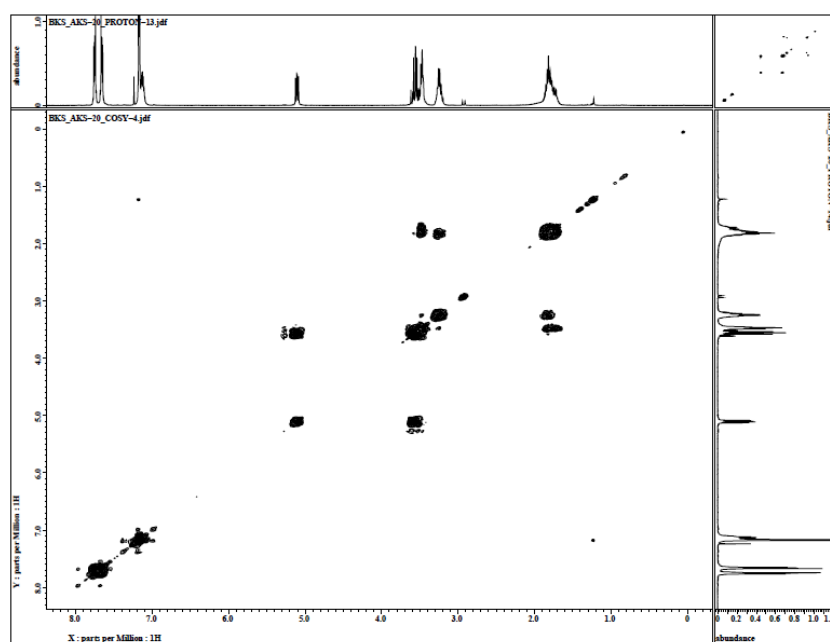


Fig. S7 Cosy spectrum of compound **2**.

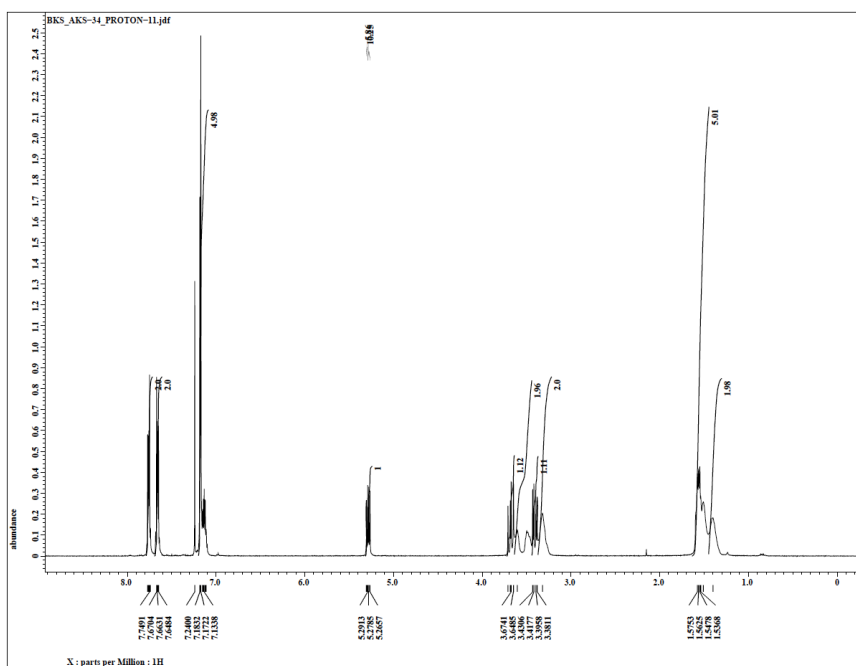


Fig. S8 ^1H NMR spectrum of compound **3** in CDCl_3

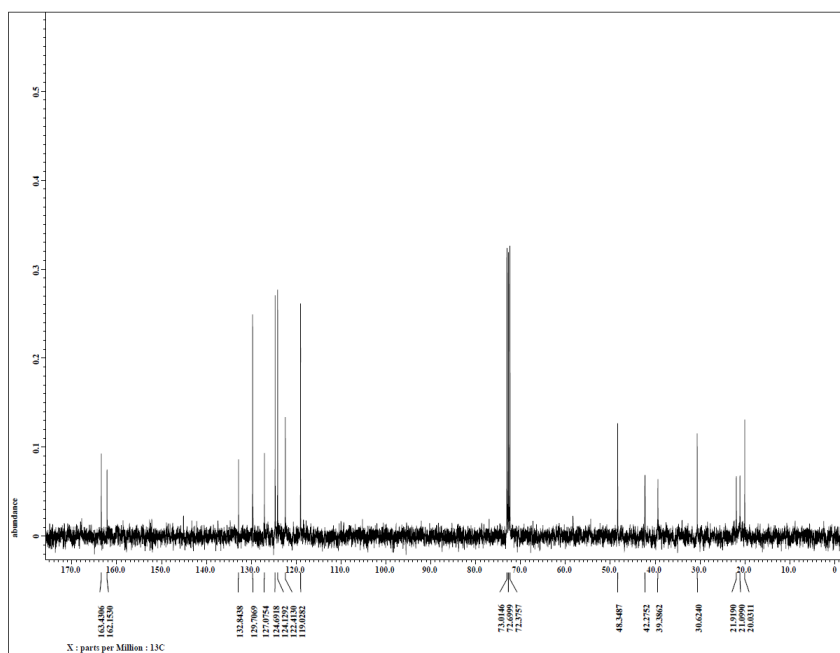


Fig. S9 ^{13}C NMR spectrum of compound **3** in CDCl_3

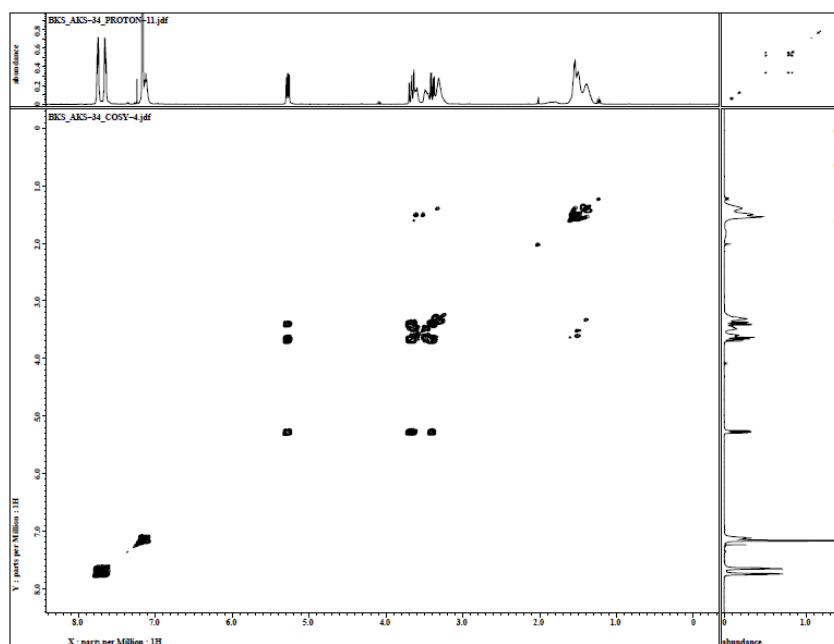


Fig. S10 Cosy spectrum of compound **3**.

References

- S1. *ENHANCE*: Oxford Xcalibur Single Crystal Diffractometer, version 1.171.34.40 (Oxford Diffraction Ltd: Oxford, U. K, 2006).
- S2. *CrysAlisPro*, version 1.171.34.40 (Oxford Diffraction Ltd: Oxford, U. K, 2006).
- S3. *SAINT-NT*, version 6.04, Bruker Analytical X-ray Systems (Madison, WI, 2001).
- S4. A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. J. Camalli, *Appl. Crystallogr.* 1994, **27**, 435.
- S5. G. M. Sheldrick, *SHELXL-97*: Program for crystal structure refinement (University of Gottingen: Gottingen, Germany, 1997).
- S6. G. M. Sheldrick, *Acta Crystallogr.* 2008, **A64**, 112.
- S7. L. J. Farrugia, *J. Appl. Crystallogr.* 1999, **32**, 837.

S8. B. Klaus, *DIAMOND*, version 2.0 c (University of Bonn, Bonn, Germany, 2004).

S9. S. K. Kurtz, T. T. Perry, *J. Appl. Phys.* 1968, **39**, 3798.