Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Strong Electron Donation Induced Differential Nonradiative Decay Pathways for para and meta GFP Chromophore Analogues

Tanmay Chatterjee, Mrinal Mandal, Venkatesh Gude, Partha Pratim Bag, and Prasun K. Mandal*

Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) - Kolkata, Mohanpur, West-Bengal, 741246, India.

e-mail: prasunchem@iiserkol.ac.in

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S1: Materials and methods:

(4-(Diethylamino) salicylaldehyde, N-Acetyl glycine, Sodium acetate, Sodium carbonate were procured from Sigma-aldrich; glycine methyl ester hydrochloride, ethyl acetimidate hydrochloride, methylamine were procured from Acros organics; 5-Nitro salicylaldehyde, Boron tribromide were procured from Spectrochem and Methyl iodide was procured from Oligo Chemicals. Solvents used for spectroscopic measurements were of spectroscopic grade and were procured from Spectrochem. Thin layer chromatography (TLC) analyses were performed on Merck Kieselgel 60 F254 plate using 100-200 mesh size silica gel. ^{1}H NMR and ^{13}C NMR spectra were recorded in both GEOL-400 (400 MHz) and Bruker AVANCE III 500 (500 MHz) spectrometers. IR spectra were recorded on a Perkin Elmer (model – spectrum RX-1) FT-IR spectrometer with the KBr pellets for solid sample and in chloroform for liquid samples. Mass spectra (TOF MS ES+) were taken in a QTOF Micromass system.

S2: Details of single crystal X-ray measurement:

OMIM and OMBO were dissolved in methanol and MOMIM and MOMBO was dissolved in ACN in a 10 mL conical flask. The suspension was heated until a clear solution is obtained. The resulting mixture was boiled for 10 min and then filtered. The filtrate was left to evaporate slowly at ambient condition. The single crystals suitable for X-Ray diffraction were obtained in a single day .The crystals were mounted on a glass pip.

Intensity data for OMIM, OMBO, MOMIM, MOMBO were collected on a Brukar KAPPA APEX II CCD Duo system with graphite monochromatic Mo Kα (λ = 0.71073 Å) radiation. The data for OMIM and OMBO were collected at 100(2) K, for MOMIM at 200(2) K, for MOMBO at 298(2) K temperature. Data reduction was performed using Bruker SAINT Software.[1] Crystal structures were solved by direct methods using SHELEXL-97 and refined by full matrix least squares on F2 with anisotropic displacement parameters for non-H atoms using SHELXL-97.[2] Hydrogen atoms associated with carbon atoms were fixed in geometrically constrained positions. Structure graphics shown in the figures were created using the X-Seed software package version 2.0.[3]

S3: NMR measurements

^{1}H NMR spectra were recorded in $CDCl_3$, DMSO-d_6, CD_3CN in GEOL-400 (400 MHz) and Bruker AVANCE III 500 (500MHz) spectrometer. Chemical shift (δ in ppm) are reported relative to tetramethylsilane (^{1}H NMR) as internal standard to residual signal of the solvents (for ^{1}H NMR : CDCl3, 7.26 ppm; CD_3CN, 1.94 ppm; DMSO-d_6, 2.50 ppm.

^{13}C NMR spectra were recorded in $CDCl_3$ and CD_3CN in Bruker AVANCE III 500 (500MHz) spectrometer (^{13}C NMR : Residual signal - $CDCl_3$, 77.16 ppm; CD_3CN, 1.32 and 118.26 ppm).

S4: Steady state and time resolved optical measurements:

(a) Steady state:

Steady state absorption and corrected emission spectra were taken in a U-4100 Hitachi spectrophotometer and Fluoromax-3, Horiba Jobin Yvon spectrofluorimeter respectively. Solutions of all the compounds, were prepared keeping in mind that the absorbance value is less than 0.1 at the absorption maxima. Φ_f (Quantum Yield) determination was accomplished by comparison of the wavelength integrated intensity of the unknown to that of the standard. Fluorescence quantum yields were calculated with solutions having absorbance less than 0.05 to avoid inner filter effect. To measure the Q.Y. of MOMIM and MOMBO, quinine sulphate was used as the reference compound and for OMBO and OMIM, 4NBD was used as the reference compound. For MOMIM and MOMBO, both the compounds and the reference were excited at 350 nm. For OMBO and OMIM both the compounds and the reference were excited at 450 nm. Φ_f of all the compounds was calculated using the following equation:

$$\Phi_f = \Phi_R \frac{OD_R}{OD} \frac{I}{I_R} \frac{n^2}{n_R^2}$$

where, 'Φ', 'I' and 'n' stands for Quantum yield, Integrated intensity and refractive index of the solvents respectively. Subscript R stands for reference.

(b) Time resolved:

(i) Picosecond TCSPC measurement:

Fluorescence lifetime measurement at ps-ns time domain were carried out using a time correlated single photon counting (TCSPC) spectrometer (Horiba Jobin Yvon IBH). Diode laser with λ_{ex} = 377 nm and 402 nm were used as the excitation sources and an MCP photomultiplier tube (PMT) (Hamamatsu R3809U-50 series) as the detector. The width of the instrument response function (IRF), which was limited by the fwhm of the exciting pulse, was less than 100 ps for 377 nm and 402 nm excitation source. IRF was recorded using a scatterer (dilute solution of ludox in water). Nonlinear least squares iterative reconvolution procedure using IBH DAS6 (Version 2.2) was employed to fit the fluorescence decay curve using a single exponential decay equation. The quality of the fit was assessed from the $\chi 2$ values and the distribution of the residuals.

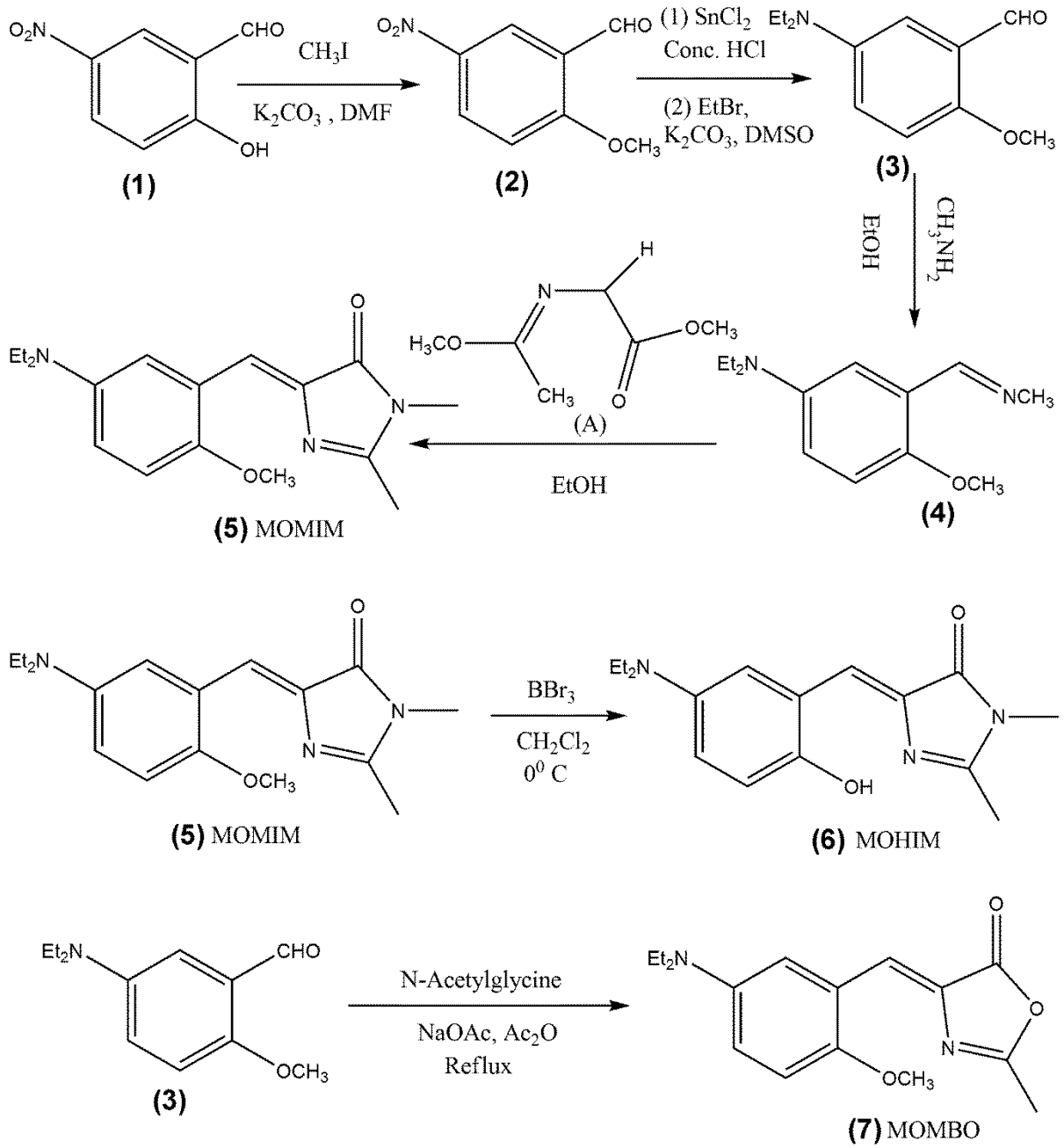
(ii) Femtosecond fluorescence upconversion measurement:

Femtosecond fluorescence transients were collected using Fluorescence Up-conversion technique in femtosecond up-conversion setup (FOG 100, CDP, Russia). The second harmonic (400 nm) of a mode locked Ti-sapphire laser (Tsunami, Spectra physics) was used as the excitation source for the samples. The fundamental beam (800 nm) was frequency doubled in nonlinear crystal (1 mm BBO, Θ =250 ,ϕ =900). The sample was placed inside a 1 mm thick rotating quartz cell. The fluorescence emitted from the sample was up-converted in a nonlinear crystal (0.5 mm BBO, Θ= 380 , ϕ= 900) using the fundamental beam as the gate pulse. The Up-converted light is dispersed in a monochromator and detected using photon counting electronics. The instrument response function of the apparatus is 300 fs. The decays were deconvoluted using a Gaussian shape of the exciting pulse using commercial software (IGOR-Pro, Wavemetrics). All the experiments were performed at 20^0C. Femtosecond up conversion measurements were performed for three molecules in three solvents of different polarity.

S5: Synthesis and characterisation:

Para GFP chromophore analogues (OMIM, OMBO and OHIM) have been synthesized following a literature procedure.[4]

Syntheses of meta GFP chromophore analogues (MOMIM, MOMBO and MOHIM) have been described below:



Scheme-2: Synthesis of the meta GFP chromophore analogues.

Synthesis of 2-Methoxy-5-nitrobenzaldehyde (2) :

2-Hydroxy-5-nitrobenzaldehyde (5.0 g, 30 mmol) was methylated using methyl iodide (12.78 g, 90 mmol) and anhydrous potassium carbonate (13 g, 90 mmol) in DMF (25 mL), by stirring at room temperature for 6h. The reaction mixture was then poured in to crushed ice leading to the precipitation of the product. The product was further purified by column chromatography over silica gel using 1:10 ethyl acetate / hexane to obtain a yield of 83% (4.5 g).

^{1}H NMR (GeOl-400 MHz, $CDCl_3$) δ 10.40 (s, 1H) δ 8.6 (d, 1H, J= 3.6Hz), δ 8.40 (dd, 1H, J= 3.6 Hz, 11.5 Hz), δ 7.63 (d, 1H, J=11.6 Hz), δ 4.07 (s, 3H)

^{13}C NMR (GeOl-400 MHz, $CDCl_3$) : 187.63, 165.68, 141.60, 130.75, 124.62, 124.54, 112.43, 56.852

Synthesis of 5-(diethylamino)-2-methoxy benzaldehyde (3) :

To a concentrated HCl (15 mL) suspension of 2-Methoxy-5-nitrobenzaldehyde (2 g, 11mmol) was added stannous chloride (10 g, 44.2 mmol). 2-Methoxy-5-nitrobenzaldehyde starts dissolving, and a clear, orange solution was obtained. The solution was refluxed for 2 h, and the color turned to red. The solution was cooled in an ice bath, and a paste like orange-red suspension resulted. The precipitate was collected and dried overnight in a vaccumn desiccators under reduced pressure, yielding an orange powder (5.3 g). The orange powder was dissolved in DMSO (15 mL) [solution-A]. The process of dissolution is highly exothermic in nature. Ethyl bromide (12 mL) and potassium carbonate (20 gm) were dissolved in DMSO (20 mL) and was stirred for 30 min at room temperature [solution B]. [Solution A] was then added to [solution B] slowly (dropwise) at room temperature. After addition, the temperature of the system was increased to 55^0C and stirred for another 2 h. The whole solution was then added to 250 mL of ice-cooled water and stirred with a glass rod. The crude product was extracted with DCM. The extracted crude product was then purified by column chromatography using 1:20 ethylacetate/Hexane to yield 320 mg (15 %) of the desired product as yellow oil.

^{1}H NMR (GEOL-400 MHz, $CDCl_3$): δ 10.44 (s, 1H), δ 7.15 (d, 1H, J= 3.9Hz), δ 6.95 (dd, 1H, J= 3.9 Hz, 11.3 Hz), δ 6.91 (d, 1H, J= 11.3 Hz) δ 3.86 (s, 3H), δ 3.30 (q, 4H, J=8.7 Hz), δ 1.12 (t, 6H, J= 8.7 Hz).

^{13}C NMR (GEOL-400 MHz, $CDCl_3$) : 190.40, 154.18, 142.74, 125.32, 121.42, 113.56, 111.51, 56.42, 44.95, 12.54

MS calculated for ($C_{12}H_{17}NO_2 + H^+$) : 208.1 , Found: 208.1

FT-IR: 2970 cm^{-1} (alkane C-H stretching), 1683 cm^{-1} (C=O group stretching), 1500 cm^{-1} (C-C stretching in the aromatic ring), 1217 cm^{-1} (C-O Stretching; strong), 1035 cm^{-1} (in plane C-H bending), 770 cm^{-1} (aromatic out of plane C-H bending; strong).

Synthesis of N,N-diethyl-4-methoxy-3-((methylimino)methyl)aniline (4) :

The Schiff base (**4**) was prepared by mixing 5-(diethylamino)-2-methoxybenzaldehyde (**3**) (300 mg, 1.44 mmol) and methylamine (40 wt% in ethanol) (0.5 mL) in ethanol (5 mL) and stirring the reaction mixture at r.t for 2h. The yield of the reaction was almost quantitative. So after evaporating ethanol and methylamine in a rotavapour, the compound was used for the next step without purification.

^{1}H NMR (Bruker Avance-500MHz, $CDCl_3$) : δ 8.68 (dd, 1H, J= 1.5Hz, 3.2 Hz), δ 7.30 (d, 1H, J=3.1 Hz), δ 6.84 (d, 1H, J= 9Hz), δ 6.80 (dd, 1H, J= 3.1 Hz, 9 Hz), δ 3.81 (s, 3H), δ 3.51 (d, 3H, J= 1.6 Hz), δ 3.30 (q, 4H, J= 7.1 Hz), δ 1.11 (t, 6H, J= 7.1 Hz).

^{13}C NMR (Bruker Avance-500 MHz, $CDCl_3$) : 158.95, 150.96, 142.97, 125.20, 117.70, 113.03, 111.57, 56.48, 48.60, 44.85, 12.47

MS calculated for ($C_{13}H_{20}N_2O + H^+$) : 221.16, Found: 221.19

FT-IR: 2967 cm^{-1} (alkane C-H stretching), 1502 cm^{-1} (C-C stretch in the aromatic ring), 1225 cm^{-1} (C-O Stretching; strong), 1031 cm^{-1} (in plane C-H bending), 770 cm^{-1} (aromatic out of plane C-H bending; strong).

Synthesis of Methyl 2-(1-ethoxyethylidene) aminoethanoate (A):

The compound (**A**) was prepared following a literature procedure.[5] A suspension was formed when K_2CO_3 (6.9 g, 50 mmol) was mixed with methyl glycinate hydrochloride (6.28 g, 50 mmol) in diethylether (150 mL). This was followed by the addition of ethyl acetimidate hydrochloride (6.18 g, 50 mmol). The mixture was shaken for 10 min. The ether layer was decanted off. An additional amount of diethylether (75 mL) was added. Again the mixture was shaken for 10 min and the ether layer was decanted. Then the combined organic portion was dried over anhydrous $MgSO_4$ and the solvent was removed under vacuum. The imidate thus obtained (yield 52%) was used for the next step directly due to its instability.

Synthesis of (*Z*) -4-(5-(diethylamino)-2-hydroxybenzilidene)-1,2-dimethyl-1H-imidazol-5(4*H*)-one (5):

The compound (**5**) was synthesized according to a literature procedure[6] by mixing the Schiff base (**4**) (300 mg, 1.36 mmol) and the imidate (**A**) (238.7 mg, 1.50 mmol) in ethanol (2mL) and stirring the mixture overnight at ambient condition. The product got precipitated out and it was then washed sequentially with diethyl ether (5 mL) and ethanol (2 mL) to get the pure product as a orange powder (210 mg, yield 49%). It was then recrystallised twice from acetonitrile.

^{1}H NMR (GeOl-400 MHz, $CDCl_3$) : δ 8.31 (d, 1H, J= 3.3Hz), δ 7.65 (s, 1H), δ 6.80 (d, 1H, J=11.2 Hz), δ 6.78 (dd, 1H, J= 3.3 Hz, 11.2 Hz), δ 3.81 (s, 3H), δ 3.32 (q, 4H, J= 8.8 Hz), δ 3.17 (s, 3H), δ 2.32 (s, 3H), δ 1.15 (t, 6H, J= 8.83 Hz)

^{13}C NMR (GeOl-400 MHz, $CDCl_3$) : 170.81, 161.135, 151.73, 142.705, 137.91, 123.69, 122.21, 117.945, 117.59, 112.22, 56.38, 45.21, 26.475, 15.68, 12.52.

MS calculated for ($C_{17}H_{23}N_3O_2 + H^+$) : 302.2 , Found: 302.2

FT-IR (neat) : 2930 and 2969 cm^{-1} (alkane C-H stretching), 1708 cm^{-1} (C=O stretching), 1641cm^{-1} (alkene C=C stretching; strong), 1360 - 1502 cm^{-1}(aromatic C=C stretching), 1247 cm^{-1} (C-O Stretching; strong), 1130 cm^{-1} (in plane C-H bending), 792 cm^{-1} (out of plane C-H bending).

Synthesis of (Z)-4-(5-(diethylamino)-2-hydroxybenzylidene)-1,2-dimethyl-1H-imidazol-5 (4H)-one (6):

(*Z*)-4-(5-(diethylamino)-2-methoxybenzylidene)-2-methyloxazol-5(4*H*)-one (**5**) (100 mg, 0.332 mmol) was dissolved in dry dichloromethane (5 mL) in a round bottom flask and the flask was cooled to 0^0C by keeping it in ice bath-salt mixture. To this ice cold solution, BBr_3 solution (in DCM 1 mL, 1.1 mmol) was added drop wise with proper care under nitrogen atmosphere. The reaction was continued for 5h. The reaction mixture was then hydrolyzed with 6 mL of water and extracted two to three times taking 10 mL of DCM in each time. The combined organic phase was then dried over magnesium sulphate. The compound was purified by column chromatography with silica gel and 1:5 ethylacetate/hexane as eluent to yield 75 mg of the desired product (**6**) (yield 79%).

^{1}H NMR (GeOl-400 MHz, $CDCl_3$) : δ 13.07 (broad s, 1H), δ 7.15 (s, 1H), δ 6.89 (dd, 1H, J=11.2 Hz, 3.7 Hz), δ 6.87 (d, 1H, J= 11.2 Hz), δ 6.64 (d, 1H, J=3.7 Hz), δ 3.26 (q, 4H, J= 8.8 Hz), δ 3.25 mixed up with δ 3.26 quartet peak (s, 3H), δ 2.38 (s, 3H), δ 1.11 (t, 6H, J= 8.8 Hz)

^{13}C NMR (GeOl-400 MHz, $CDCl_3$) : 168.385, 157.30, 150.99, 141.65, 132.99, 131.29, 122.75, 120.82, 119.96, 119.77, 45.58, 26.96, 15.35, 12.59.

MS calculated for ($C_{16}H_{21}N_3O_2 + H^+$) : 288.2 , Found: 288.2

FT-IR (neat): 2916 and 2970 cm^{-1} (alkane C-H stretching), 1710 cm^{-1} (C=O stretching), 1637 cm^{-1} (alkene C=C stretching), 1363-1500 cm^{-1}(aromatic C=C stretching), 1225 cm^{-1} (C-O Stretching; strong), 1116 cm^{-1} (in plane C-H bending), 810 cm^{-1} (out of plane C-H bending; strong).

Synthesis of (Z)-4-(5-(diethylamino)-2-methoxybenzylidene)-2-methyloxazol-5(4H)-one (7) :

5-diethylamino-2-methoxybenzaldehyde (**3**) (300 mg, 1.45 mmol), N-acetylglycine (170 mg, 1.45 mmol), anhydrous sodium acetate (118.7 mg, 1.45 mmol), and acetic anhydride (2 mL) were stirred at 90^0C for 4h. After cooling, the whole mixture turned into a dark brown solid and it was directly loaded on silica gel coloum and was eluted by EtOAc/hexane system (1:9) using flash column chromatography. After purification 150 mg desired compound was obtained as a orange solid (yield 36%). It was then recrystallised twice from acetonitrile.

^{1}H NMR (Bruker Avance-500 MHz, CD_3CN) : δ 8.13 (d, 1H, J= 3.1Hz), δ 7.50 (s, 1H), δ 6.93 (d, 1H, J= 9.1 Hz), δ 6.89 (dd, 1H, J= 3.1 Hz, 9.1 Hz), δ 3.82 (s, 3H), δ 3.32 (q, 4H, J= 7.0 Hz), δ 2.34 (s, 3H), δ 1.12 (t, 6H, J= 7.0 Hz)

^{13}C NMR (Bruker Avance-500 MHz, CD_3CN) : 169.18, 166.91, 152.27, 143.57, 132.78, 125.27, 123.12, 119.58, 117.02, 113.56, 56.96, 45.67, 15.84, 12.74.

MS calculated for ($C_{16}H_{20}N_2O_3 + H^+$) : 289.2 , Found: 289.2

FT-IR (neat) : 2919 and 2974 cm^{-1} (alkane C-H stretching), 1780 cm^{-1} (C=O stretching), 1644 cm^{-1} (alkene C=C stretching; strong), 1503 cm^{-1}(aromatic C=C stretching), 1378 cm^{-1} (C=N stretching), 1267 cm^{-1} (C-O Stretching; strong), 1175 cm^{-1} (in plane C-H bending), 893 cm^{-1} (out of plane aromatic C-H bending).

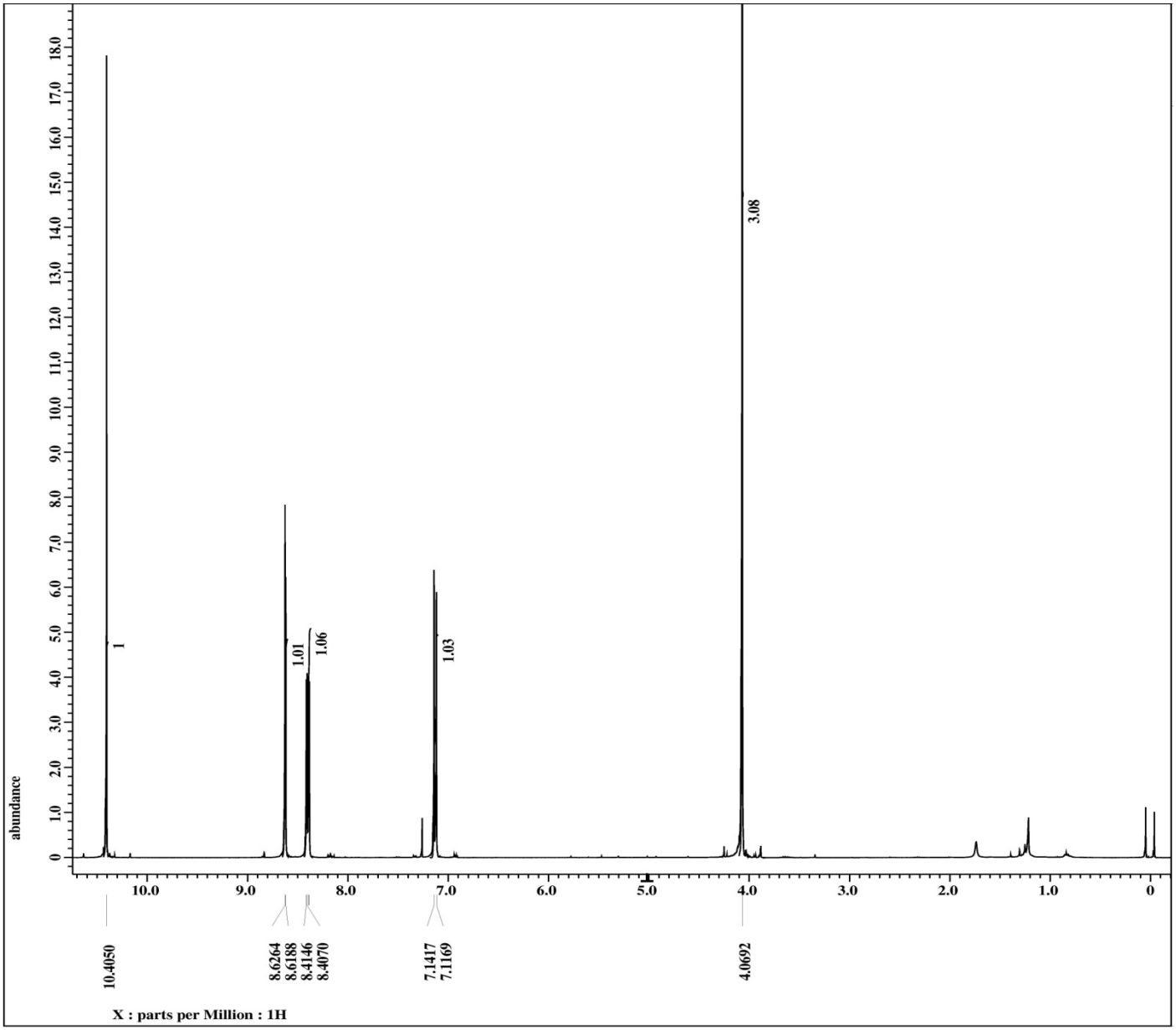


Fig-1: ^{1}H NMR spectrum of compound-**2**

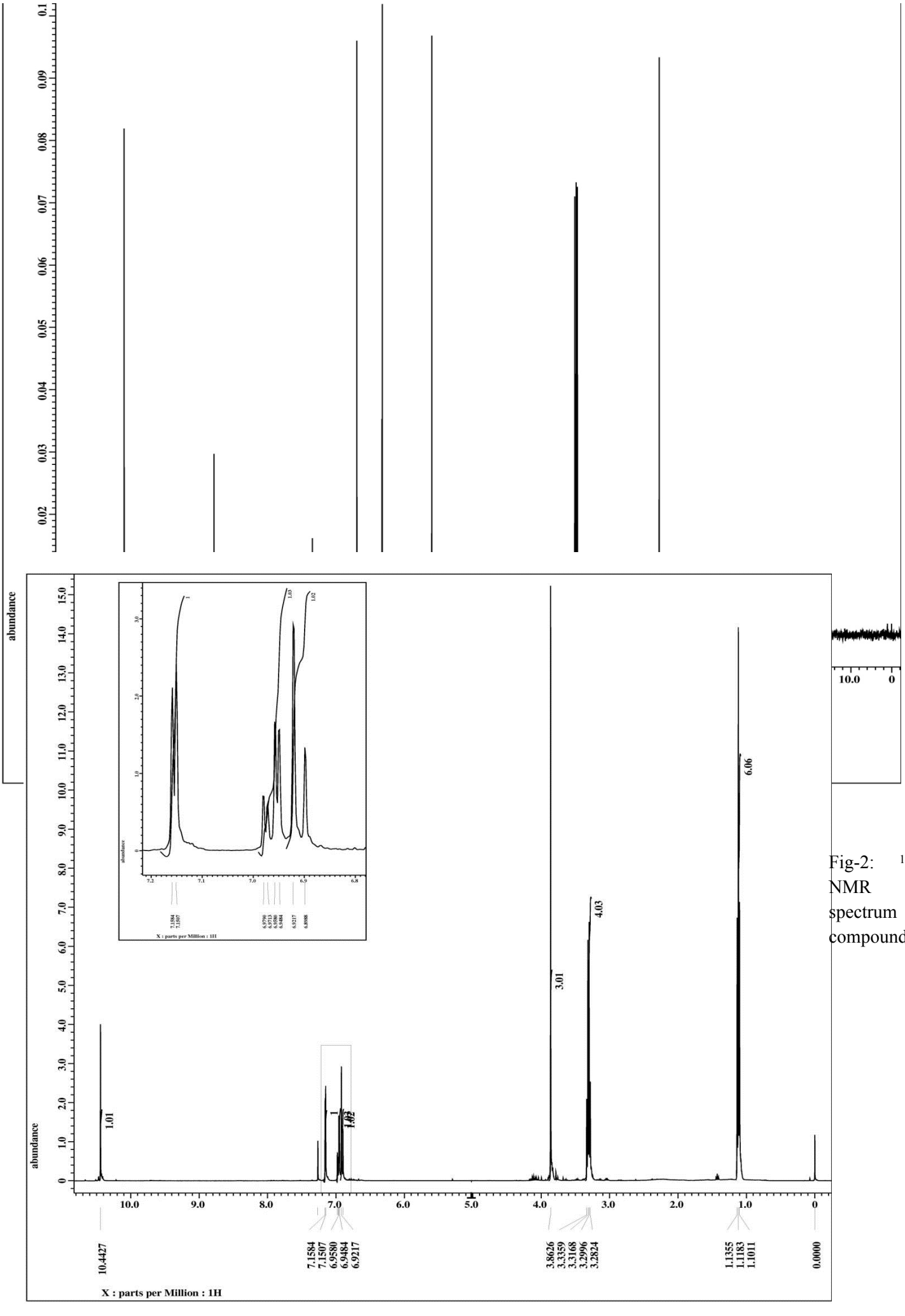


Fig-2: ^{13}C NMR spectrum of compound-**2**

Fig-3: ^{1}H NMR spectrum of compound-**3**

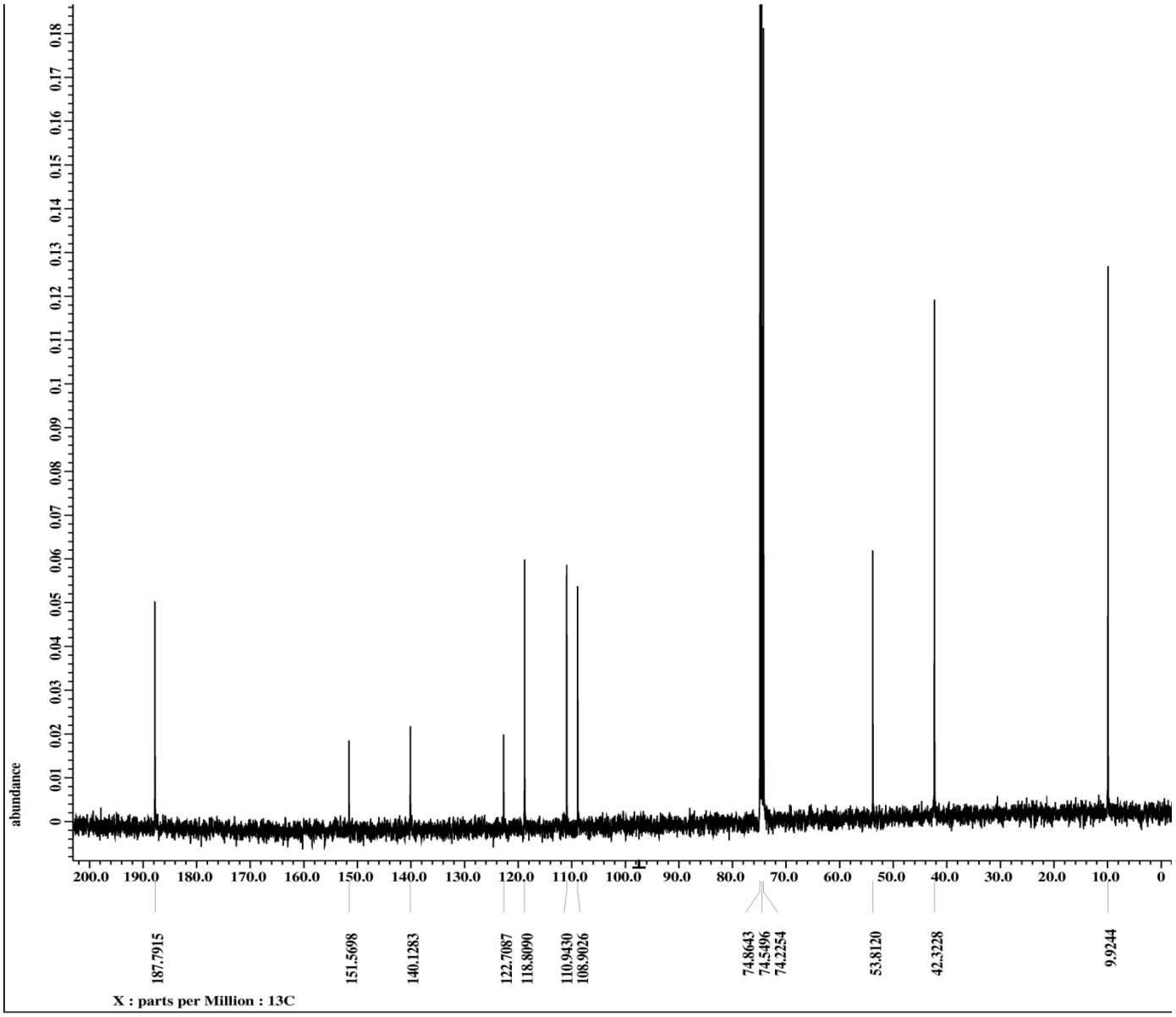


Fig-4: ^{13}C NMR spectrum of compound-**3**

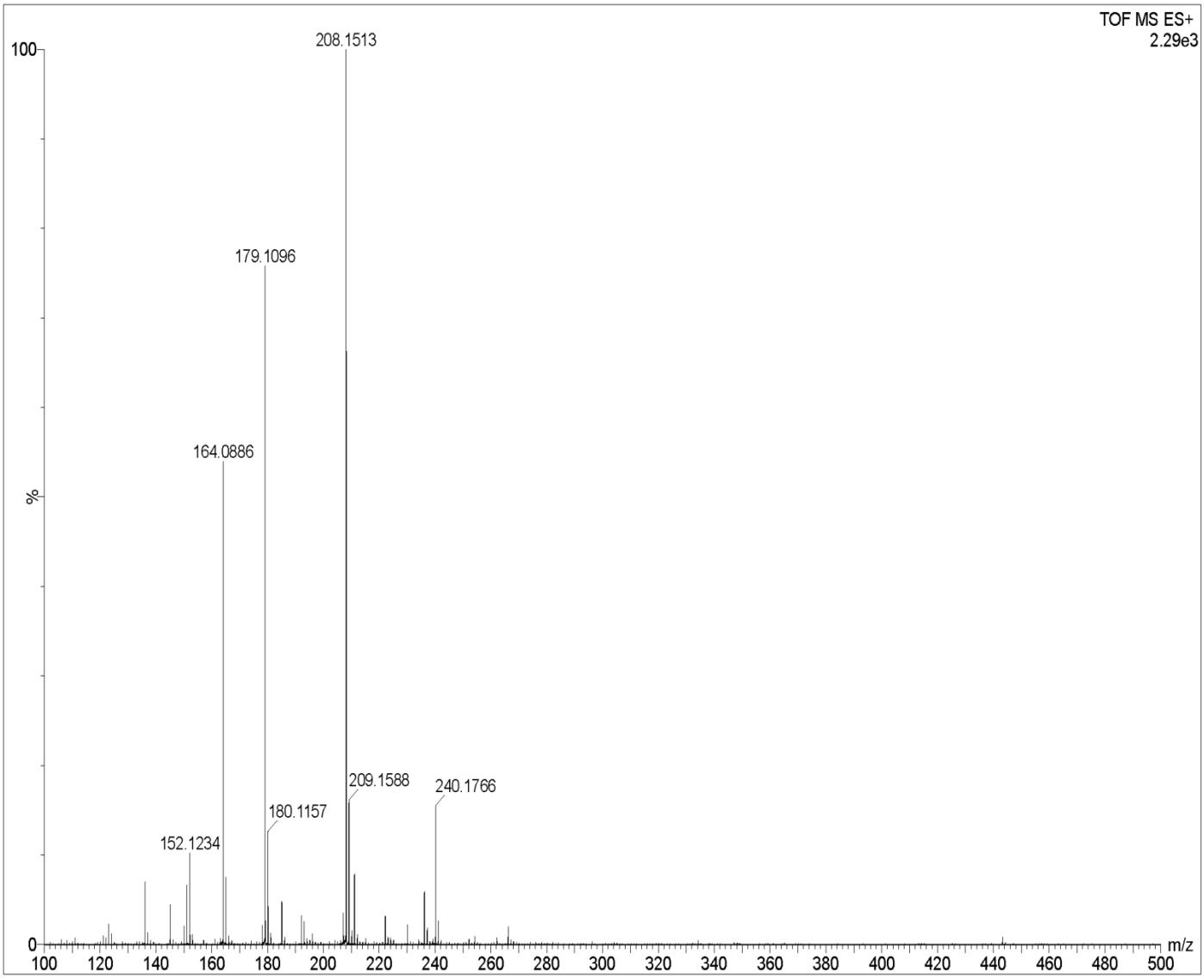


Fig-5: Mass spectrum of compound-**3**

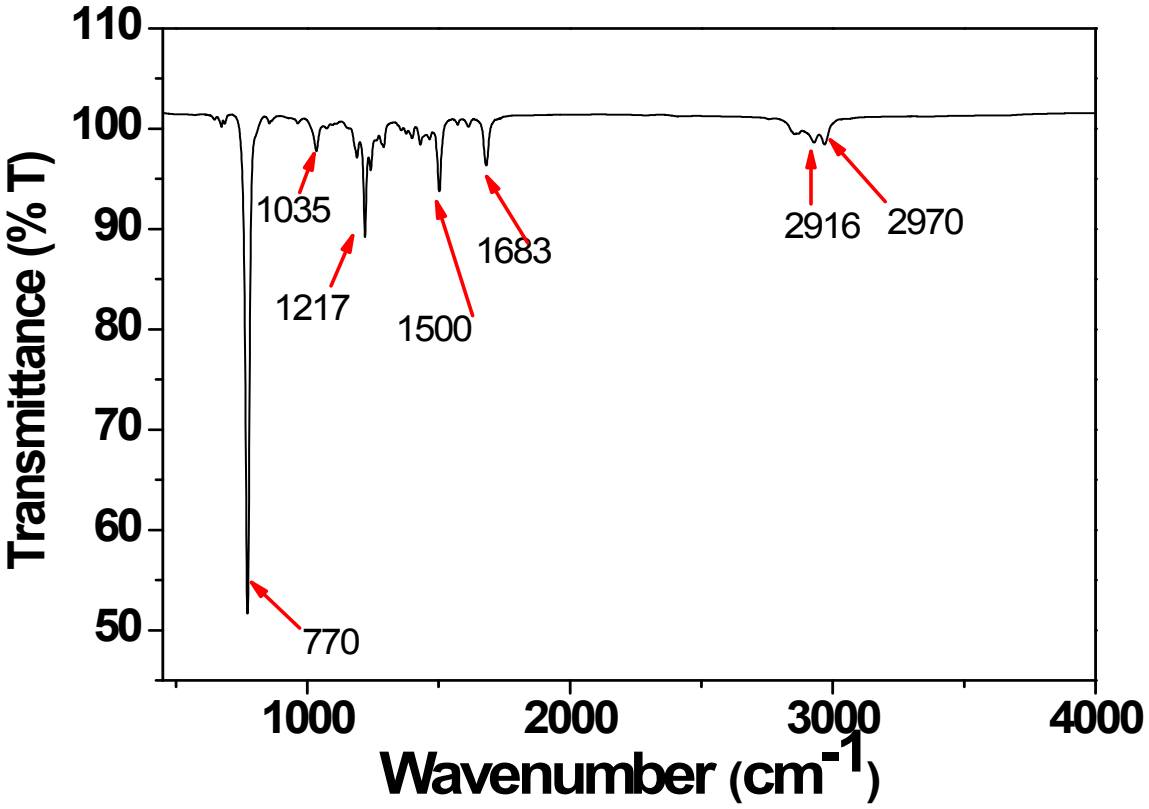


Fig-6: FT-IR spectra of compound-**3**

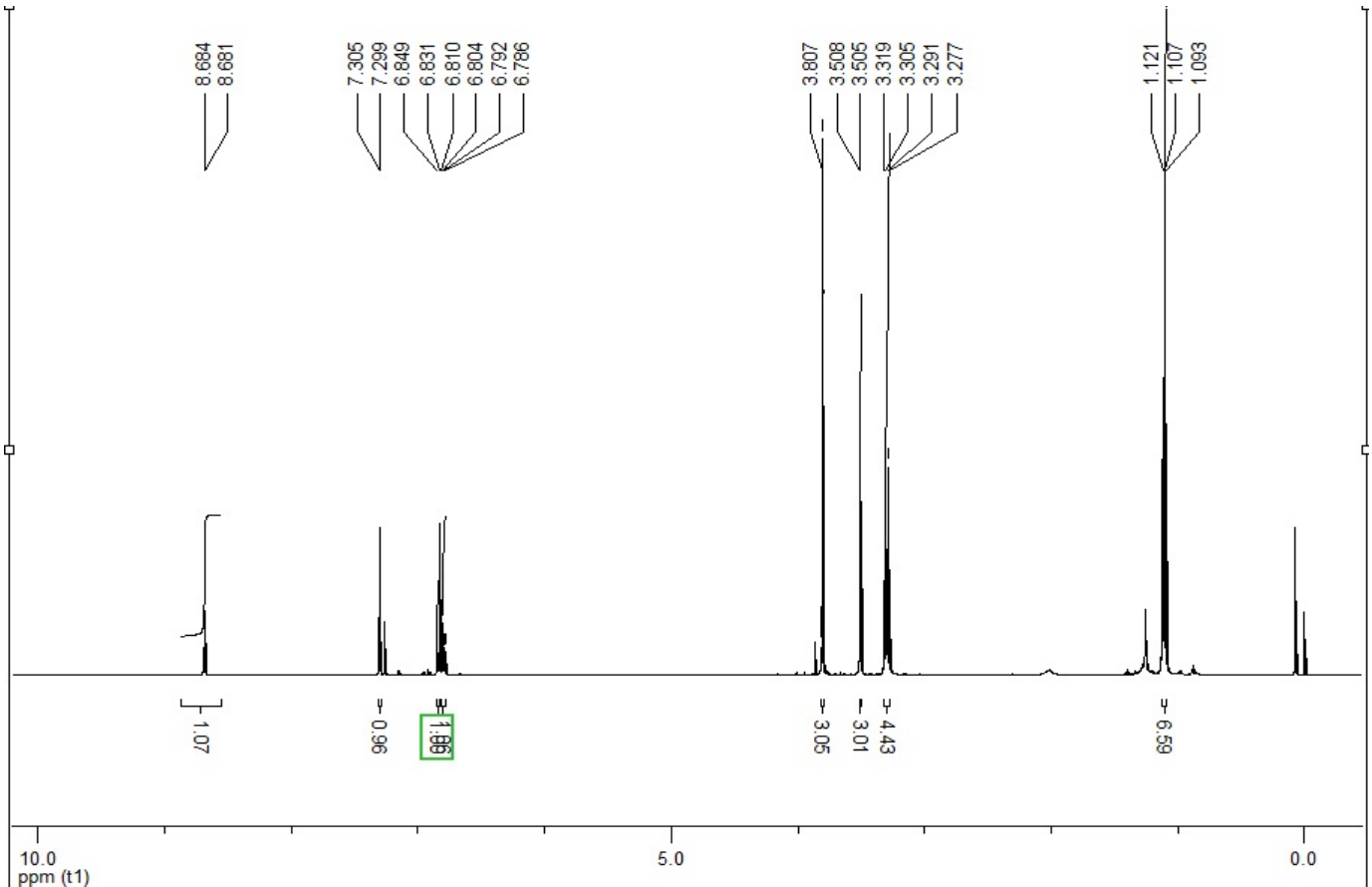


Fig-7: ^{1}H NMR spectrum of compound-**4**

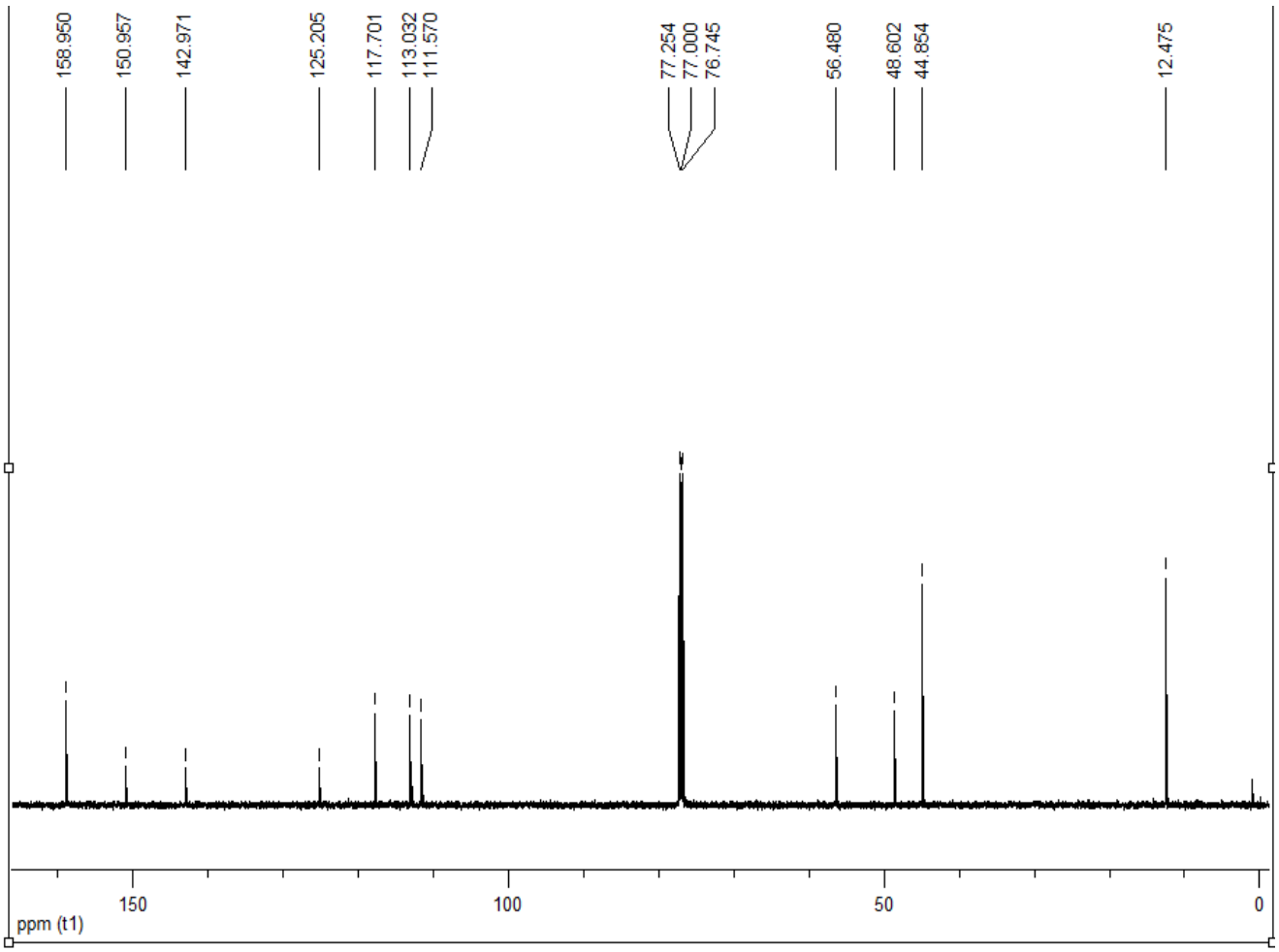


Fig-8: ^{13}C NMR spectrum of compound-**4**

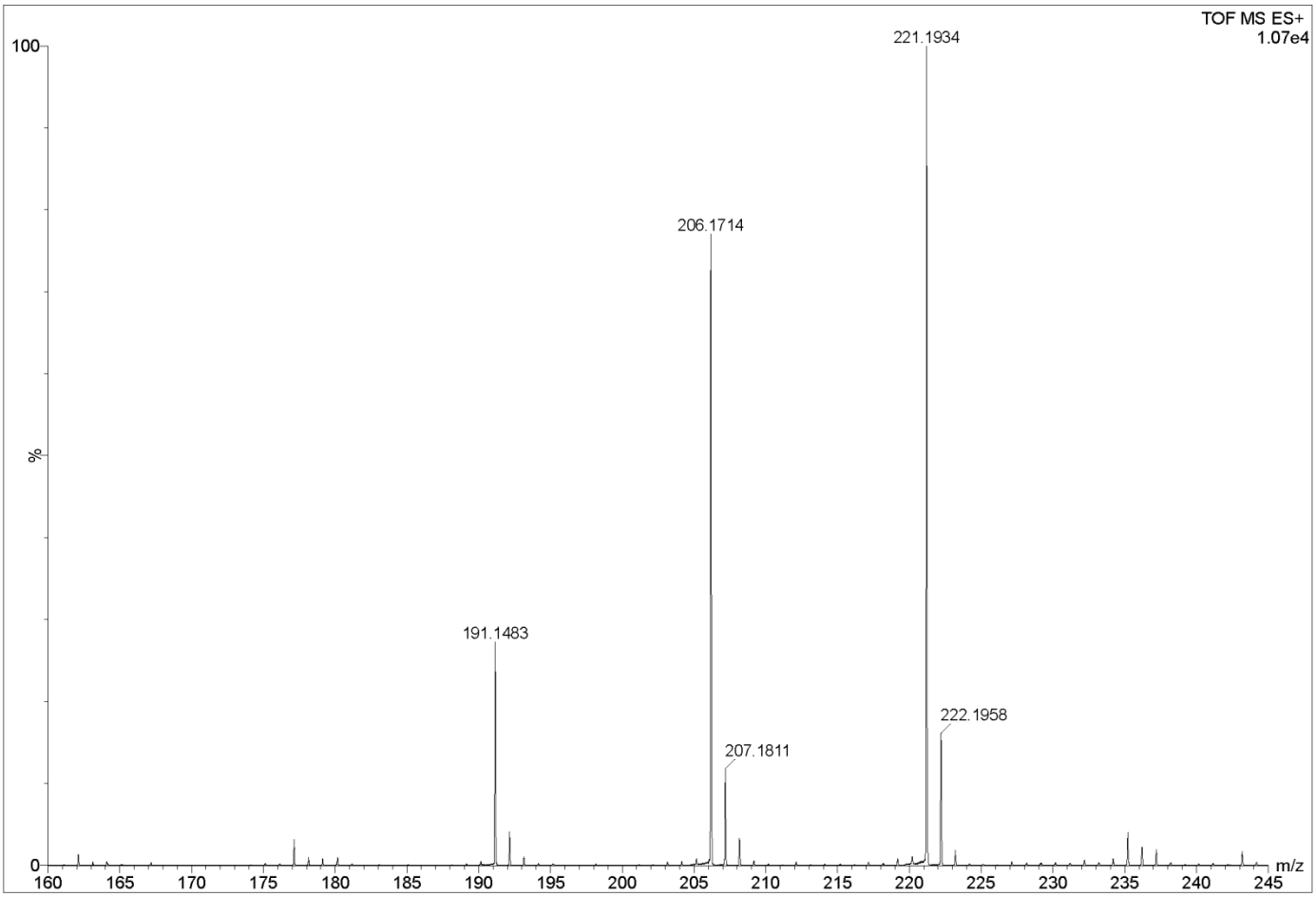


Fig-9: Mass spectrum of compound-**4**

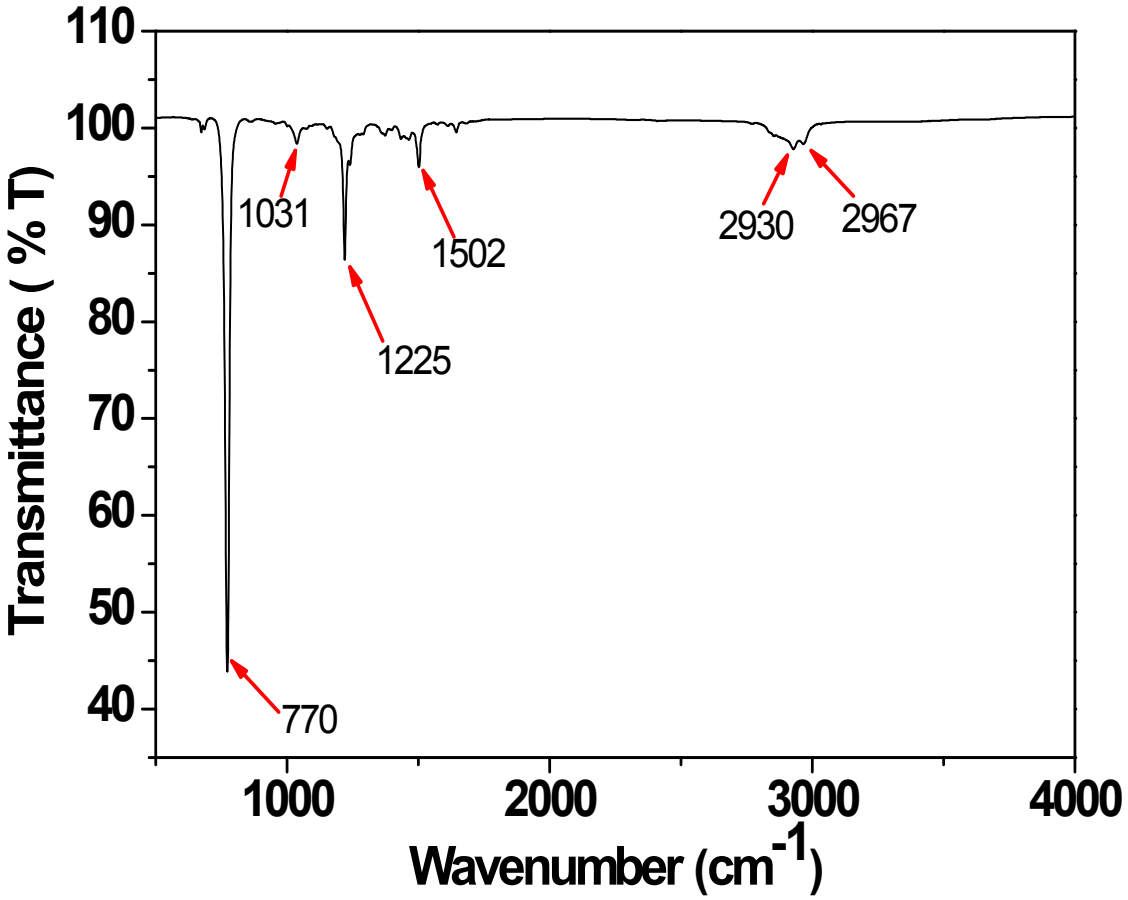


Fig-10: FT-IR spectrum of compound-**4**

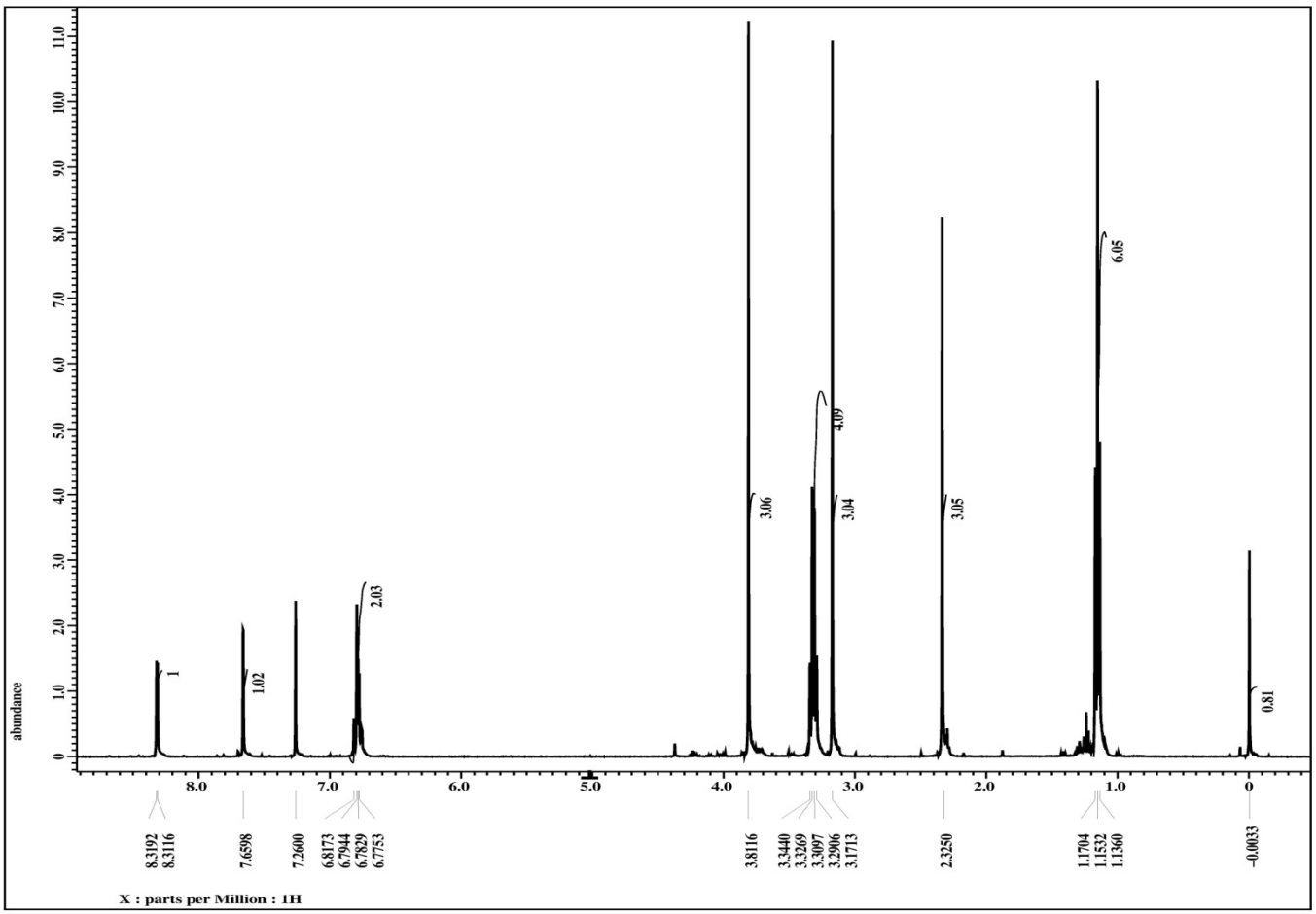


Fig-11: ^{1}H NMR spectrum of compound-**5**

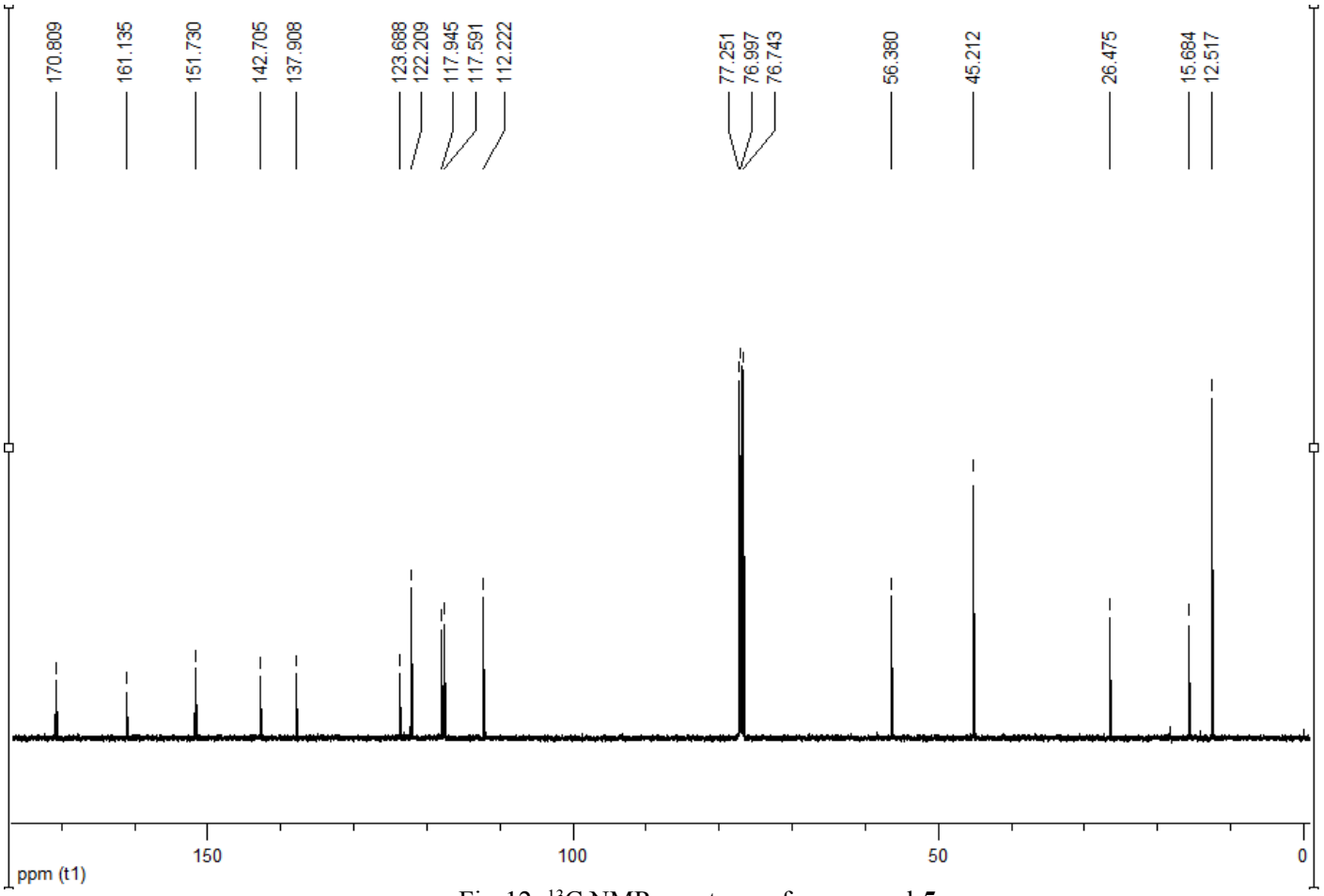


Fig-12: ^{13}C NMR spectrum of compound-**5**

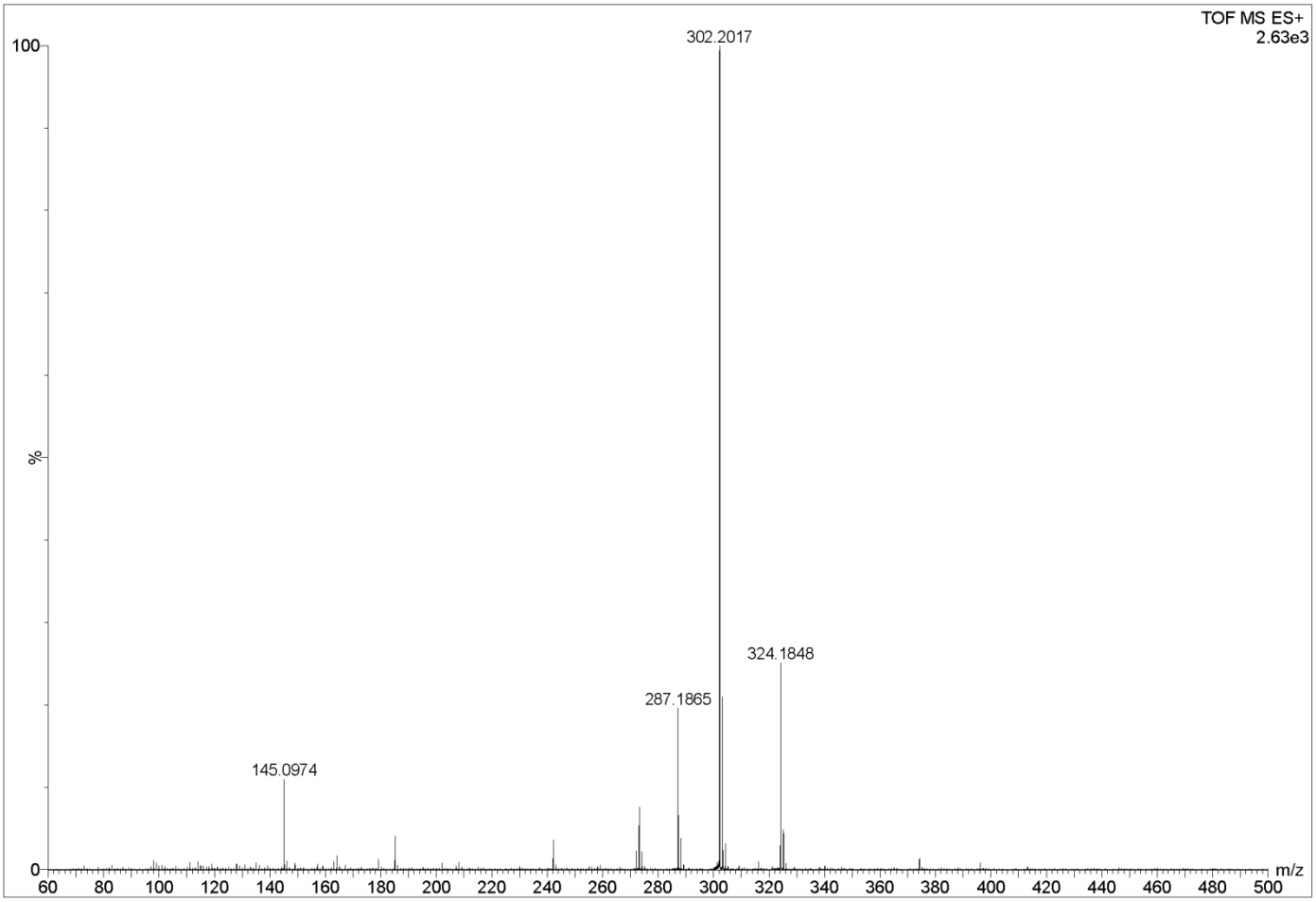


Fig-13: Mass spectrum of compound-**5**

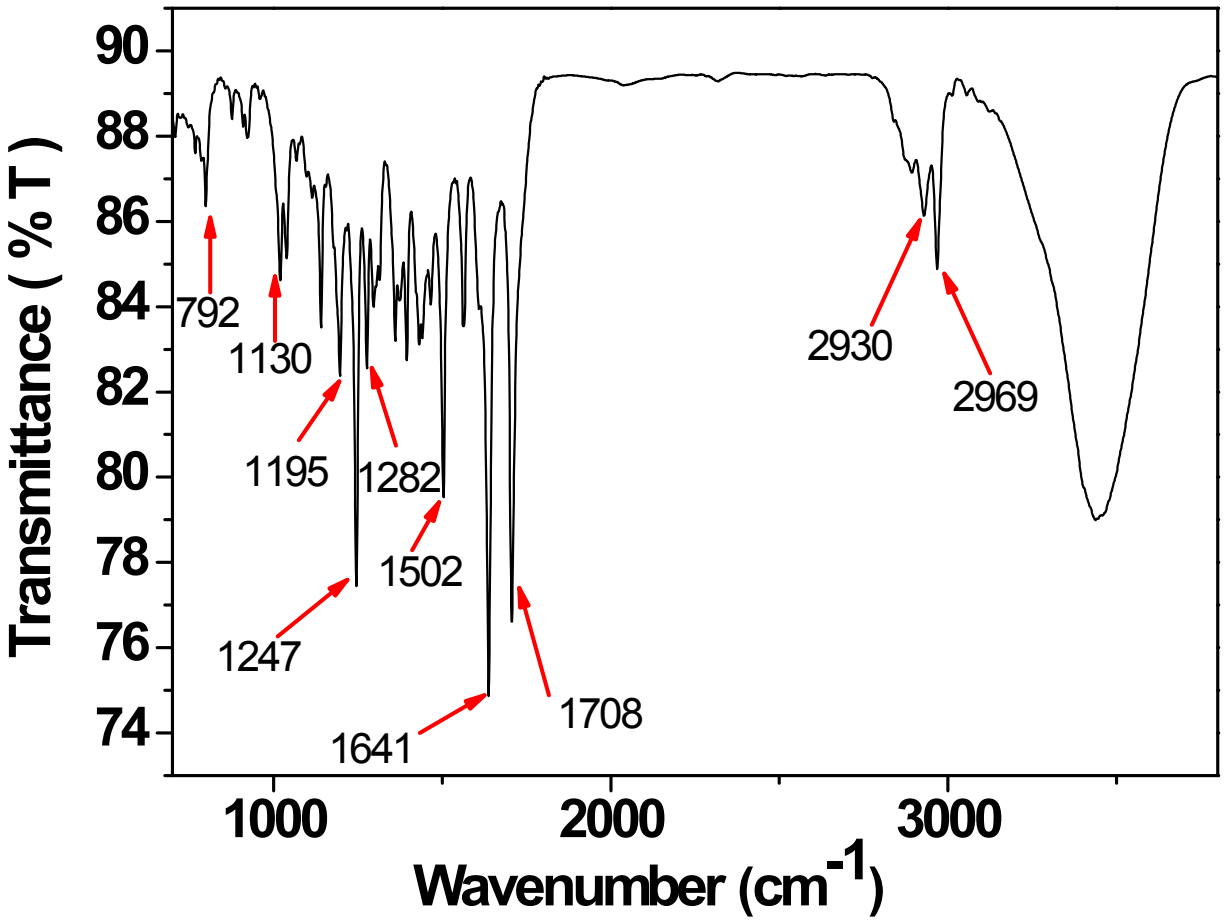


Fig-14: FT-IR spectrum of compound-**5**

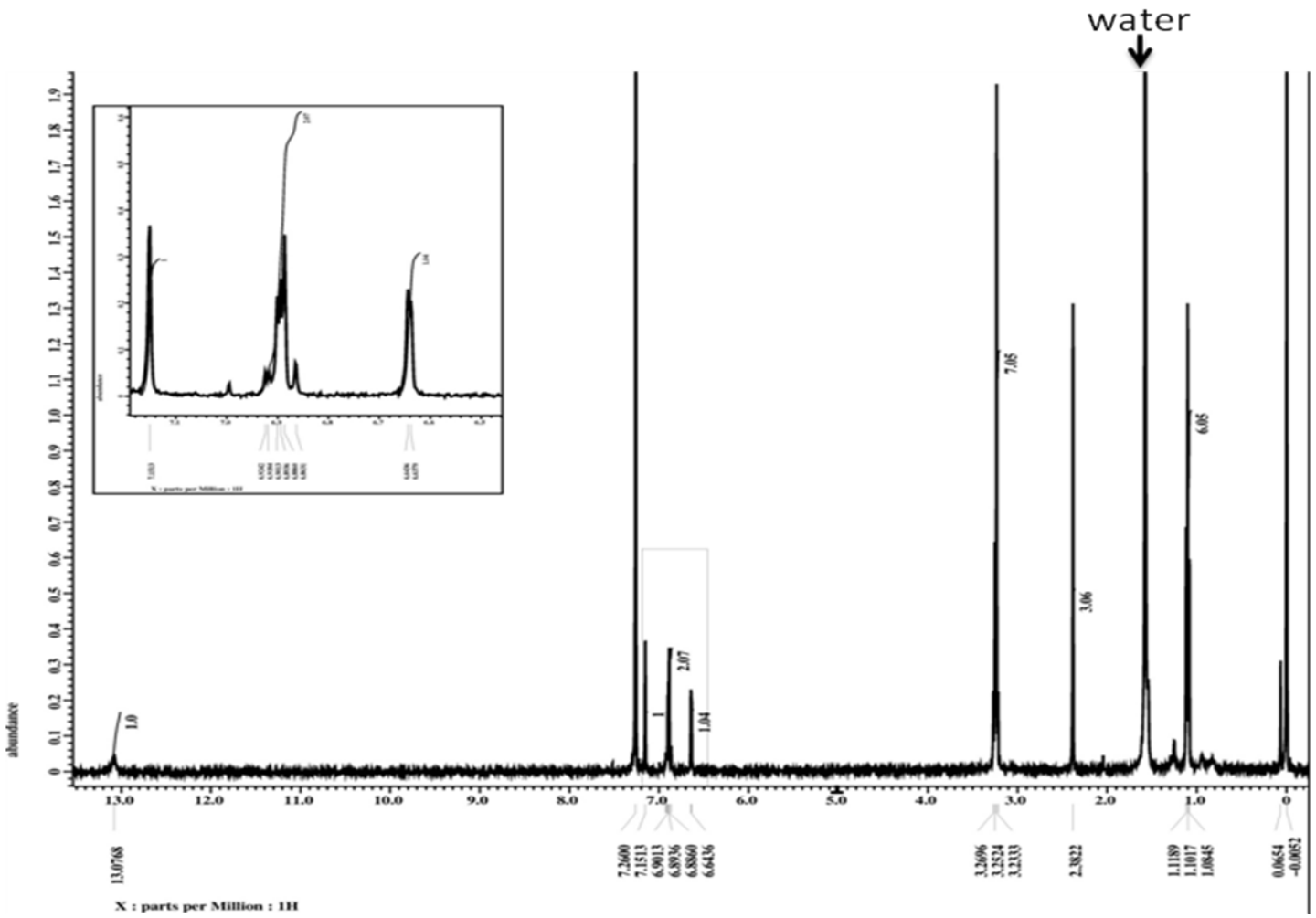


Fig-15: [1]H NMR spectrum of compound-**6**

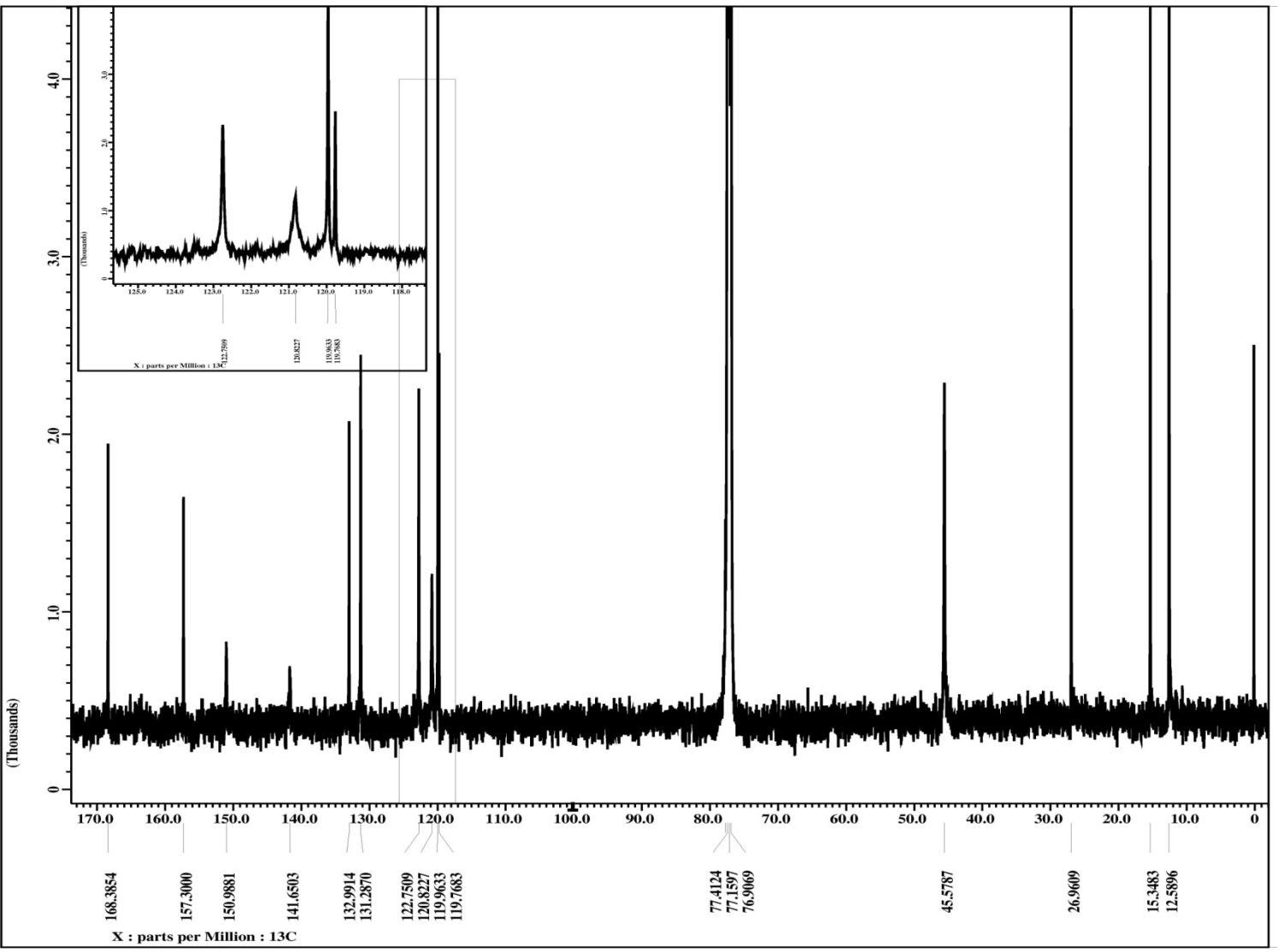


Fig-16: ^{13}C NMR spectrum of compound-**6**

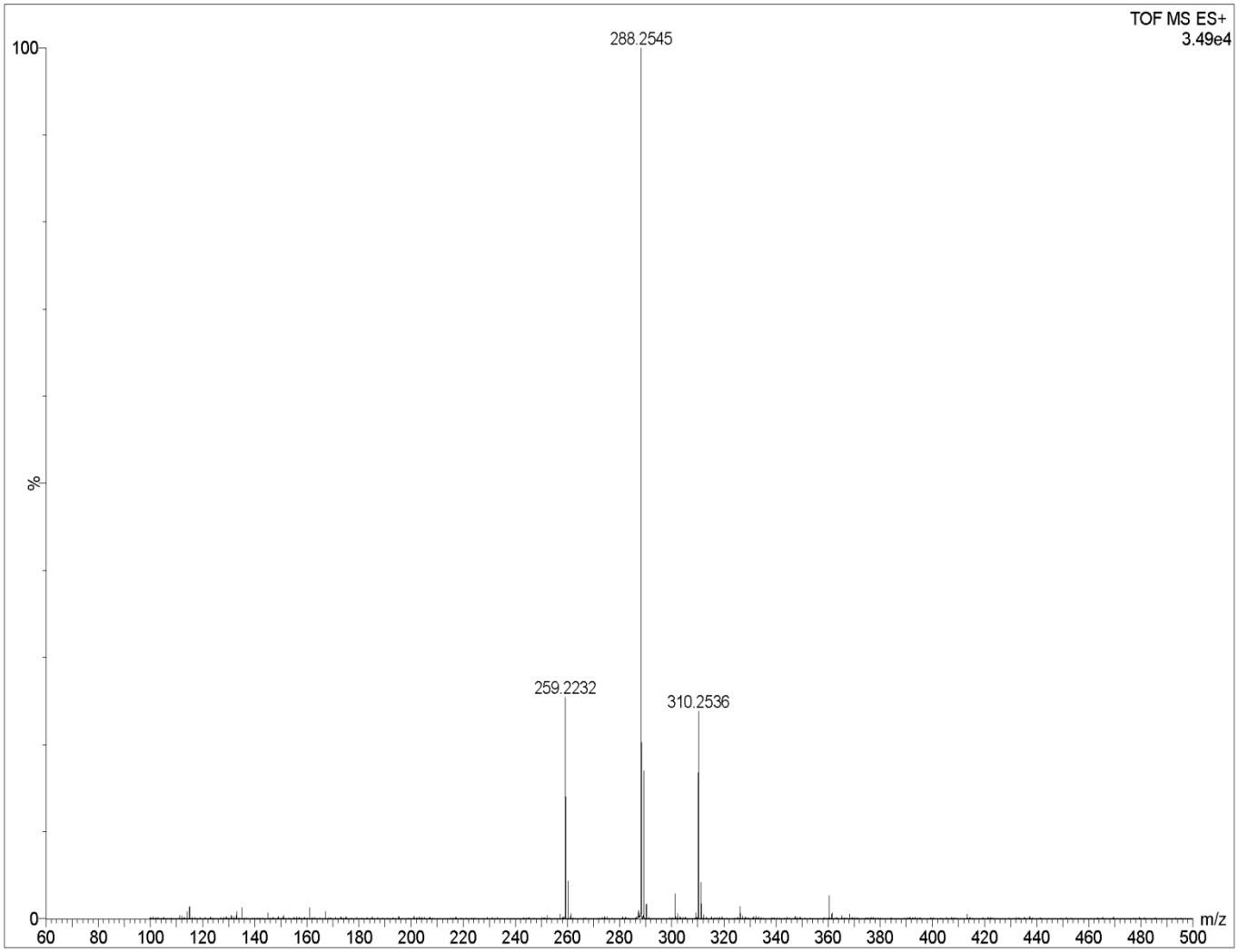


Fig-17: Mass spectrum of compound-**6**

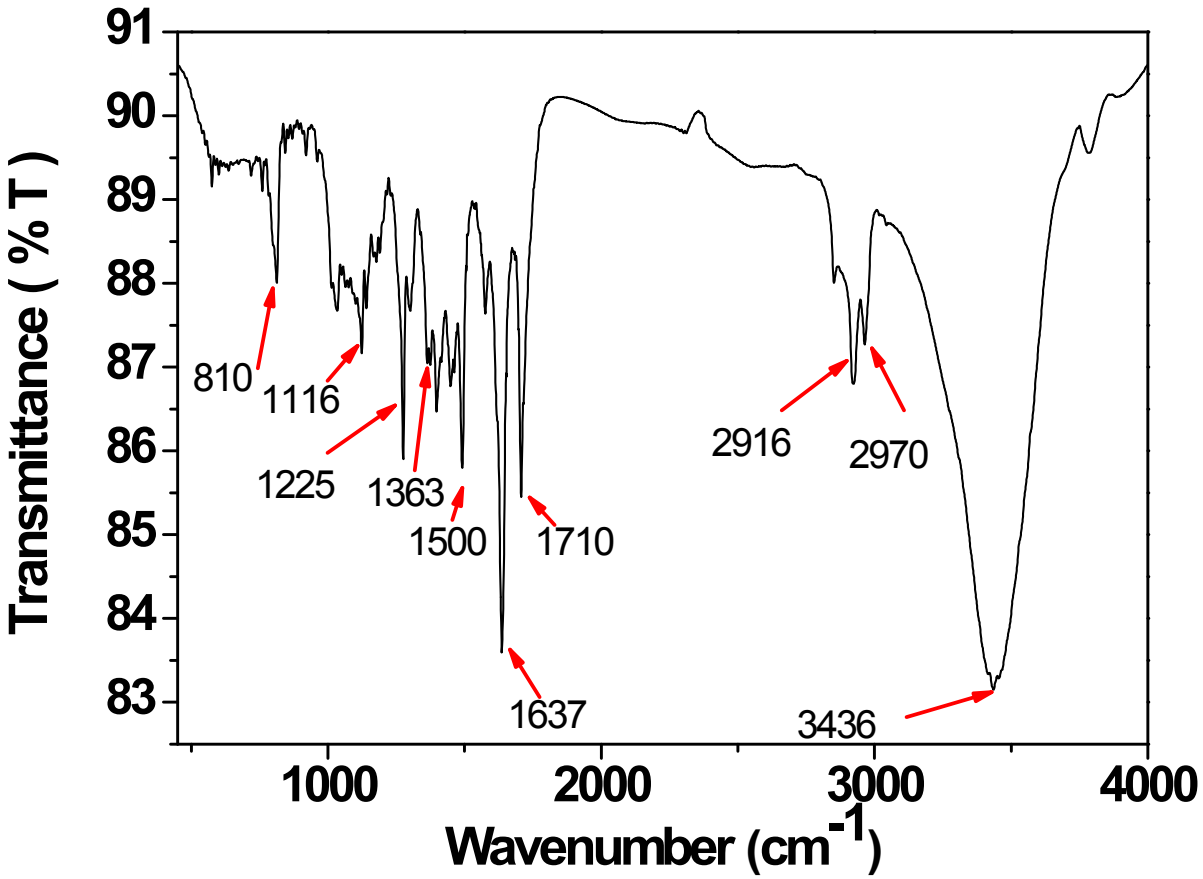


Fig-18: FT-IR spectrum of compound-**6**

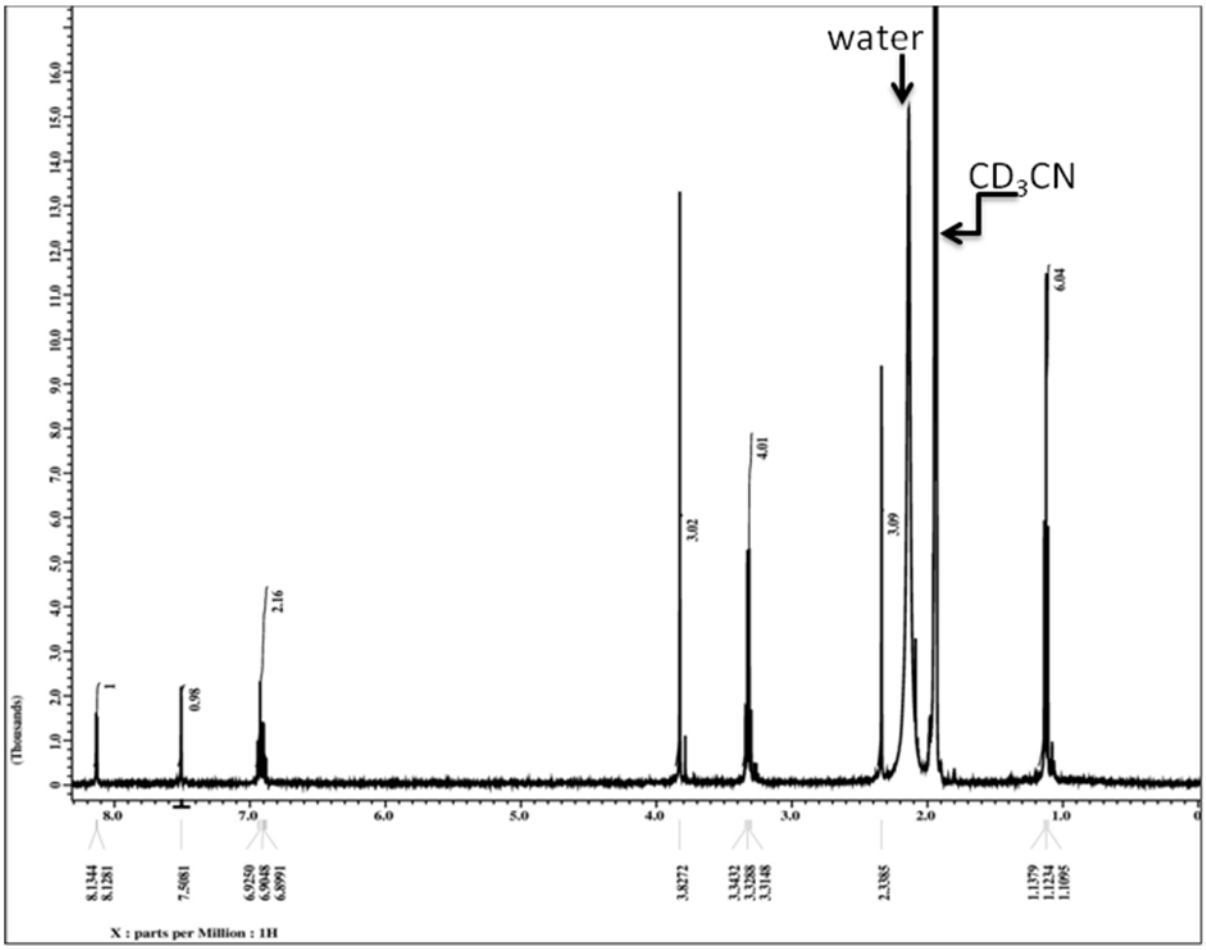


Fig-19: ^{1}H NMR spectrum of compound-**7**

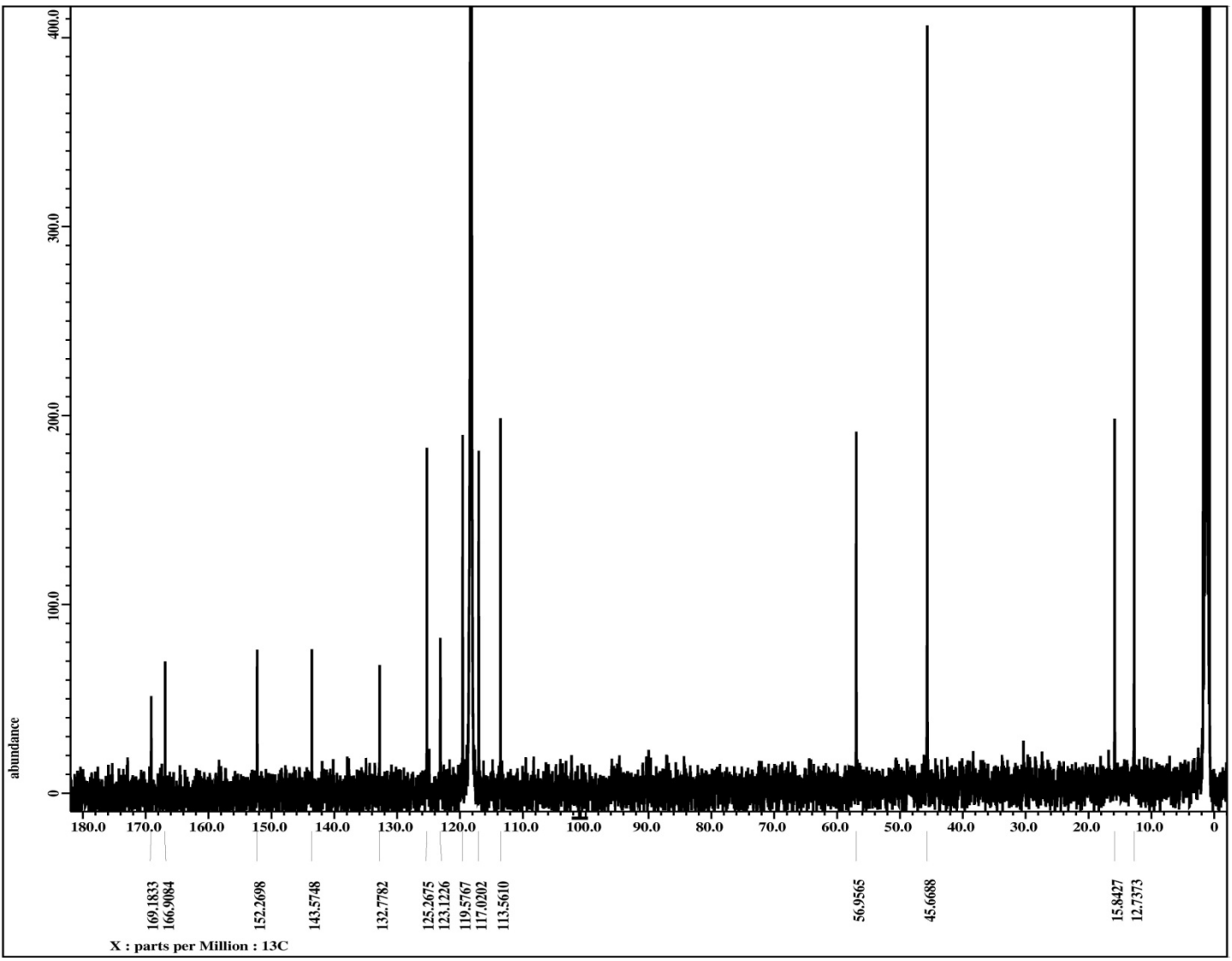


Fig-20: ^{13}C NMR spectrum of compound-**7**

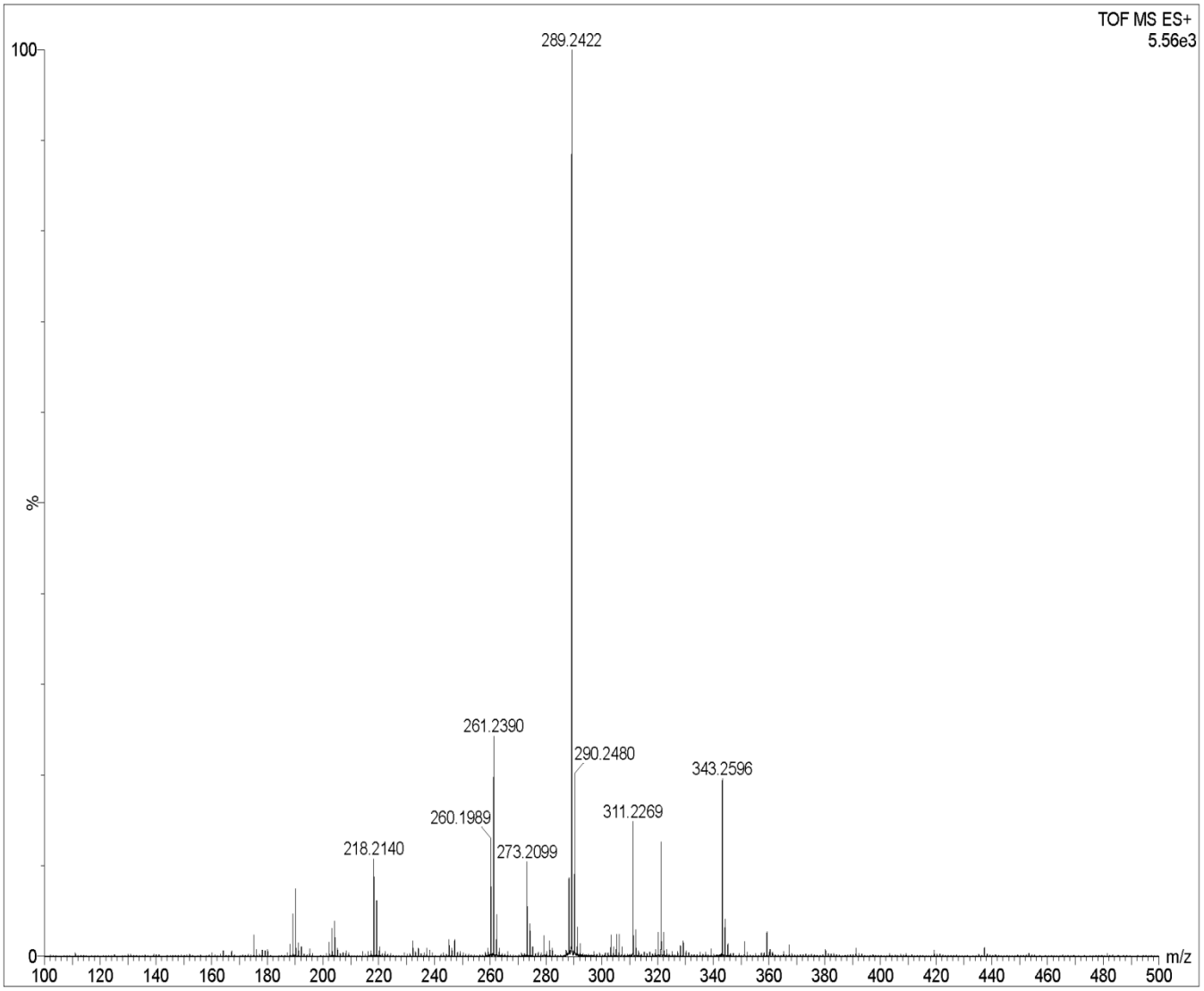


Fig-21: Mass spectrum of compound-**7**

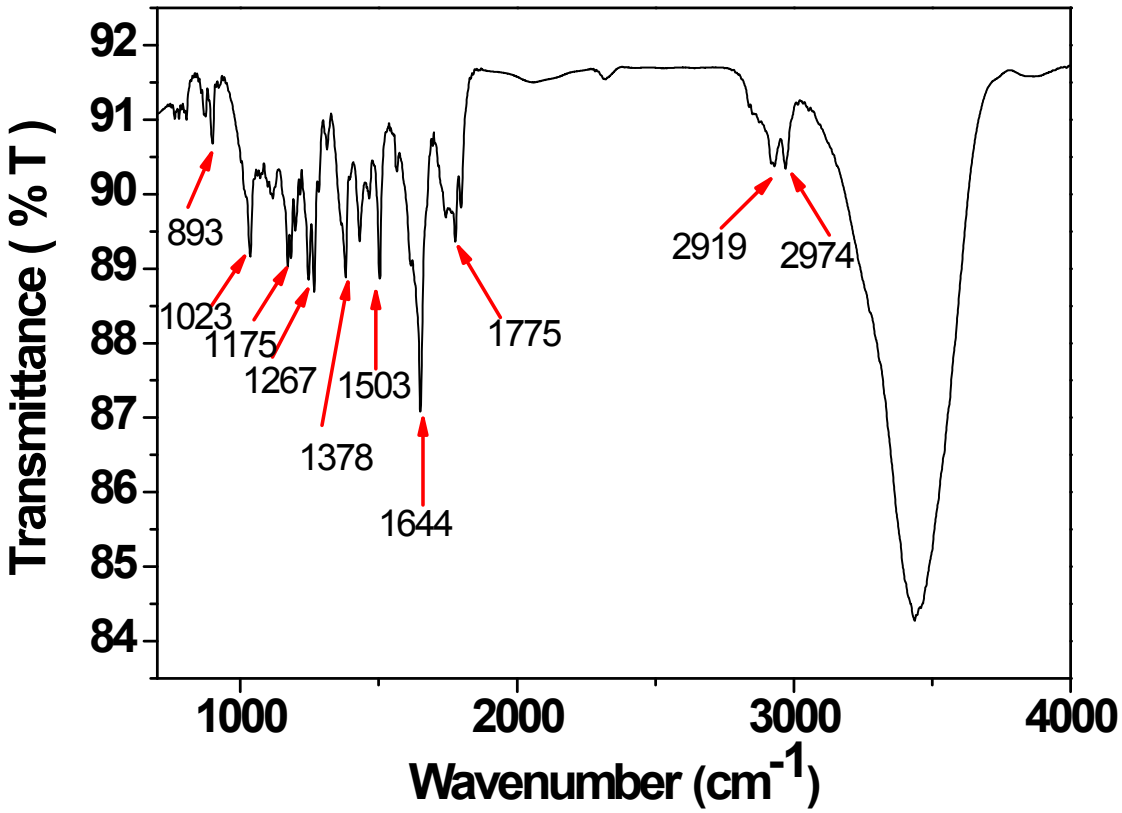


Fig-22: FT-IR spectrum of compound-7

S6: Table-1: Crystallographic Table of all compounds studied :

	OMBO	OMIM	MOMBO	MOMIM
Chemical Formula	C16 H20 N2 O3	C17 H23 N3 O2	C16 H20 N2 O3	C17 H23 N3 O2
Formula weight	288.34	301.38	288.34	301.38
Cryst. system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P2(1)/n*	*P2(1)/n*	*P2(1)/n*	*P2(1)/n*
a (Å)	7.1834 (5)	6.8038(3)	13.818 (6)	10.896 (6)
b (Å)	12.7135 (8)	17.3110(6)	7.428 (3)	7.886 (5)
c (Å)	16.5140 (11)	13.4729(5)	15.482 (7)	19.222 (9)
α (°)	90.00	90.00	90.00	90.00
β (°)	97.201(2)	99.2990(10)	93.055 (9)	94.135 (12)
γ (°)	90	90.00	90.00	90.00
Vol (Å^3)	1496.26 (17)	1565.99(11)	1587.0 (12)	1647.4 (15)
D_{calcd} (g/cm^3)	1.280	1.278	1.207	1.219
μ (mm^{-1})	0.089	0.085	0.084	0.081
θ range (°)	2.49-31.94	2.35-32.01	2.63-19.33	2.79-23.46
Z	4	4	4	4
range *h*	–7 to +9	–8 to+8	-16 to +16	-12 to +12
range *k*	–16 to +14	–21 to +22	-8 to +8	-8 to +8
range *l*	–21 to +20	-17 to +16	-18 to +18	-15 to +21
Reflns collected	13767	14458	19644	8612
Independent reflns	3258	3420	2817	2450
Obsd reflns	2860	2995	1333	1579

T (K)	100(2)	100(2)	298 (2)	200 (2)
*R*1	0.0346	0.0372	0.0759	0.0744
*wR*2	0.1154	0.1469	0.2317	0.2356
GOF	0.754	1.240	1.146	1.242
CCDC No.	1001358	1001355	1001359	1001357

Table-2: Bond distances and bond angles of all derivatives obtained from crystal structure:

Compound	Distance (H^a---sp^2N) Å	Exocyclic double bond distance (Å)	Exocyclic single bond distance(Å)	Dihedral angle-1	Dihedral angle-2
OMIM	2.40	1.361 (C7-C8)	1.441 (C6-C7)	3.22 (C5-C6-C7-C8)	2.49 (N1-C8-C6-C5)
OMBO	2.414	1.362 (C12-C13)	1.427 (C2-C12)	-2.53 (C3-C2-C12-C13)	-2.14 (N2-C13-C2-C3)
MOMIM	2.382	1.365 (C11-C13)	1.451 (C9-C11)	-13.19 (C10-C9-C11-C12)	-10.27(N2-C13-C9-C10)
MOMBO	2.372	1.348 (C11-C12)	1.446 (C9-C11)	-3.72(C10-C9-C11-C12)	-1.62 (N2-C12-C9-C10)

S7: Discussion about NMR results

In order to have an insight regarding the solution phase structure of all these molecules (OMIM, OMBO, MOMIM, MOMBO and also OHIM and MOHIM (see Fig. 23)) ^{1}HNMR studies have been performed. δ values of OH proton for OHIM and MOHIM have been obtained to be > 13 ppm, which indicates the presence of strong intramolecular hydrogen bond in solution phase between the imidazolidinone sp^2 nitrogen and the hydroxyl group of phenyl ring. In this conformation the proton marked "a" (Fig. 23) remains in opposite direction of sp^2 nitrogen of the imidazolidinone ring and appears at δ_{Ha} = 7.1 and 6.65 ppm for OHIM and MOHIM respectively in $CDCl_3$ (see Figure 23). For OMIM, OMBO, MOMIM, and MOMBO the δ values of the proton marked "a" have been obtained to be 8.7, 8.6 , 8.3, 8.2 ppm respectively in $CDCl_3$. In the solid state crystal structure, the orientation of the bulky methoxy group was noted to remain in opposite side of sp^2 nitrogen of imidazolidinone ring. From the structural aspect it is expected that bulky methoxy group will remain in that conformation in the solution phase. In that scenario the proton marked "a" will be spatially closer to the sp^2 nitrogen of the imidazolidinone ring. If that is not the case then the proton marked "a" will have similar orientation as that of OHIM and MOHIM and hence we expect that the proton in OMIM and MOMIM will have nearly same δ value as that of OHIM and MOHIM. However, in analogy to the δ value obtained for OHIM (and MOHIM) it can be concluded that for OMIM, (and MOMIM) the proton marked "a" is deshielded (δ_{Ha} = 8.7 ppm in OMIM, and 8.3 ppm in MOMIM, thus a large difference of (Δδppm) ~ 1.5-1.6 ppm in comparison to OHIM and MOHIM). Thus, it can be concluded that in solution phase, OMIM, MOMIM adopt a conformation in which proton marked "a" will be closer to the sp^2 nitrogen of the imidazolidinone ring. NMR chemical shift values of 'a', 'b', 'c' and 'd' protons in $CDCl_3$ for different compounds are shown in Figure 23 and tabulated in Table-3. Thus, it can be concluded that, the conformation of OMIM and MOMIM & OMBO and MOBMO (each) remains similar both in solid as well as in solution phase

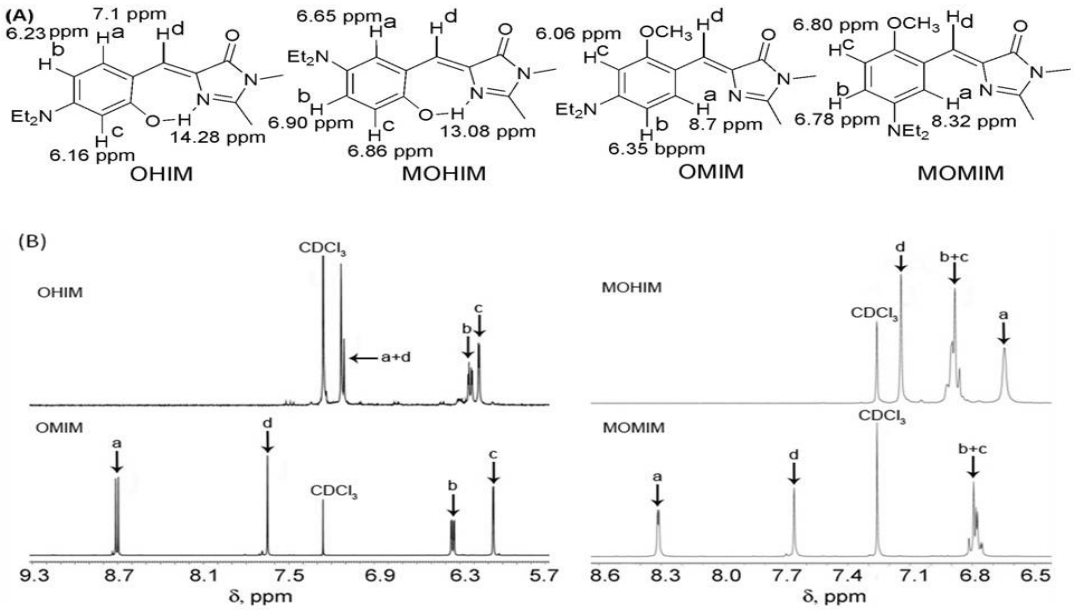
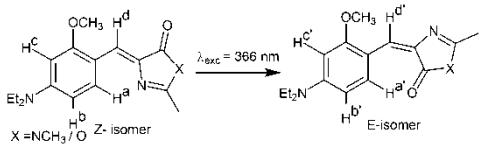


Fig-23: (A) Molecular structure of OHIM, MOHIM, OMIM, MOMIM with the proton NMR chemical shift values in $CDCl_3$. (B) NMR spectra of OHIM (upper left) OMIM (lower left) MOHIM (upper right) MOMIM (lower right). Only aromatic region has been shown for clarity.

S8: Table-3: NMR chemical shift values of 'a'. 'b', 'c' and 'd' protons in $CDCl_3$

Solvent	Compounds	δ, ppm of H^a	δ, ppm of H^d	δ, ppm of H^b	δ, ppm of H^c
$CDCl_3$	OMIM	8.70	7.64	6.35	6.06
	OMBO	8.60	7.68	6.35	6.05
	MOMIM	8.32	7.66	6.78	6.80
	MOMBO	8.2	7.67	6.80	6.82
	OHIM	7.1	7.13	6.23	6.16
	MOHIM	6.65	7.14	6.90	6.86

S9: NMR stack plots of different molecule before and after different time of exposure



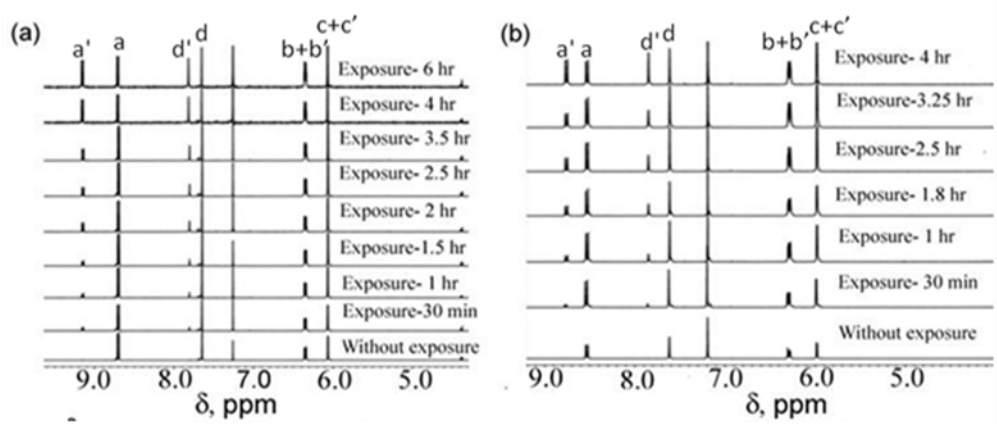


Fig- 24: NMR stack plot in $CDCl_3$ after different time of exposure: (a) for OMIM and (b) for OMBO. Only aromatic region has been shown for clarity.

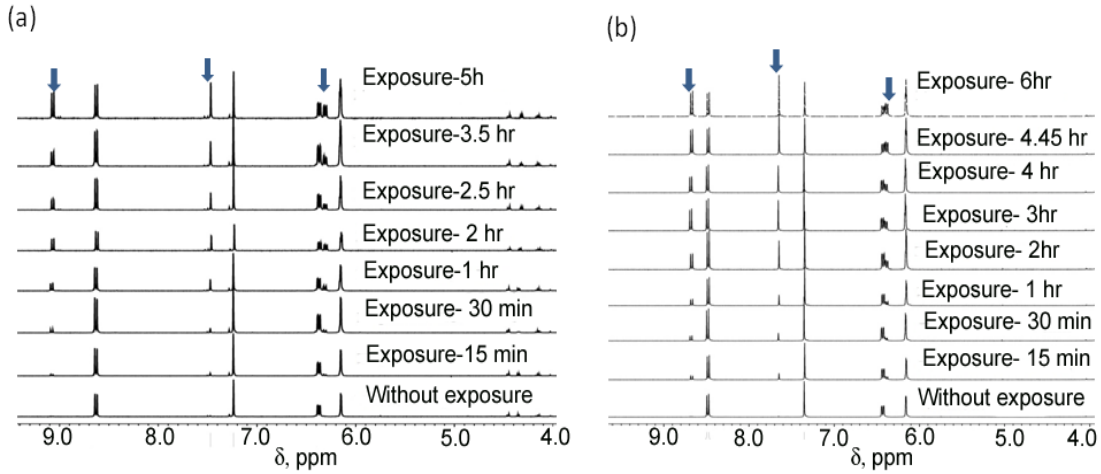


Fig- 25: NMR stack plot in DMSO-d_6 after different time of exposure: (a) for OMIM and (b) for OMBO. Only aromatic region has been shown for clarity.

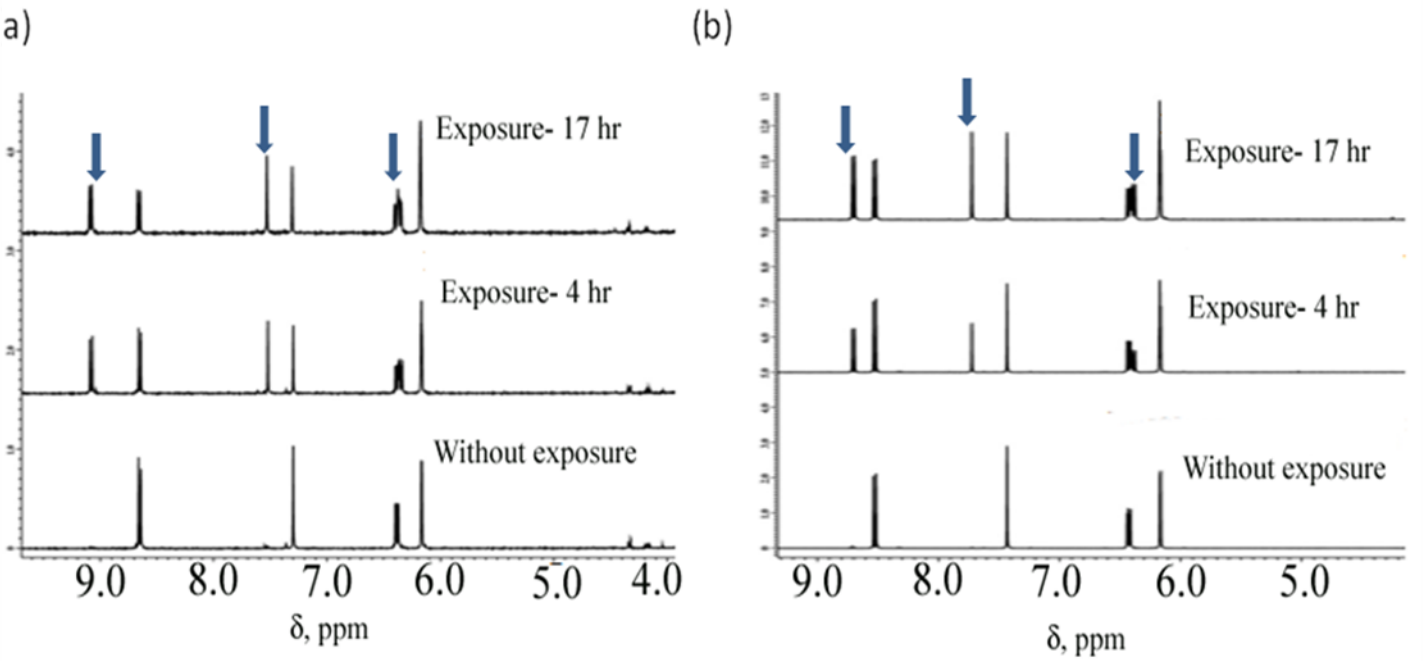
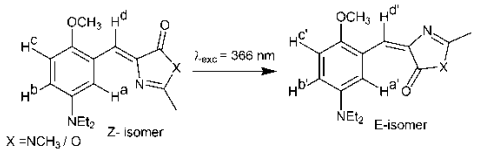


Fig- 26: NMR stack plot in CD_3CN after different time of exposure: (a) for OMIM and (b) for OMBO. Only aromatic region has been shown for clarity.



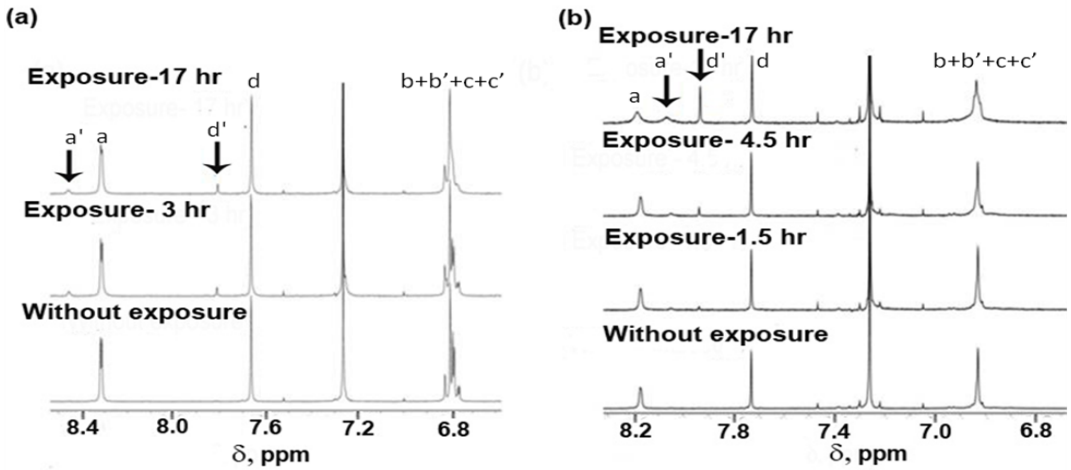


Fig- 27: NMR stack plot in $CDCl_3$ after different time of exposure: (a) for MOMIM and (b) for MOMBO. Only aromatic region has been shown for clarity.

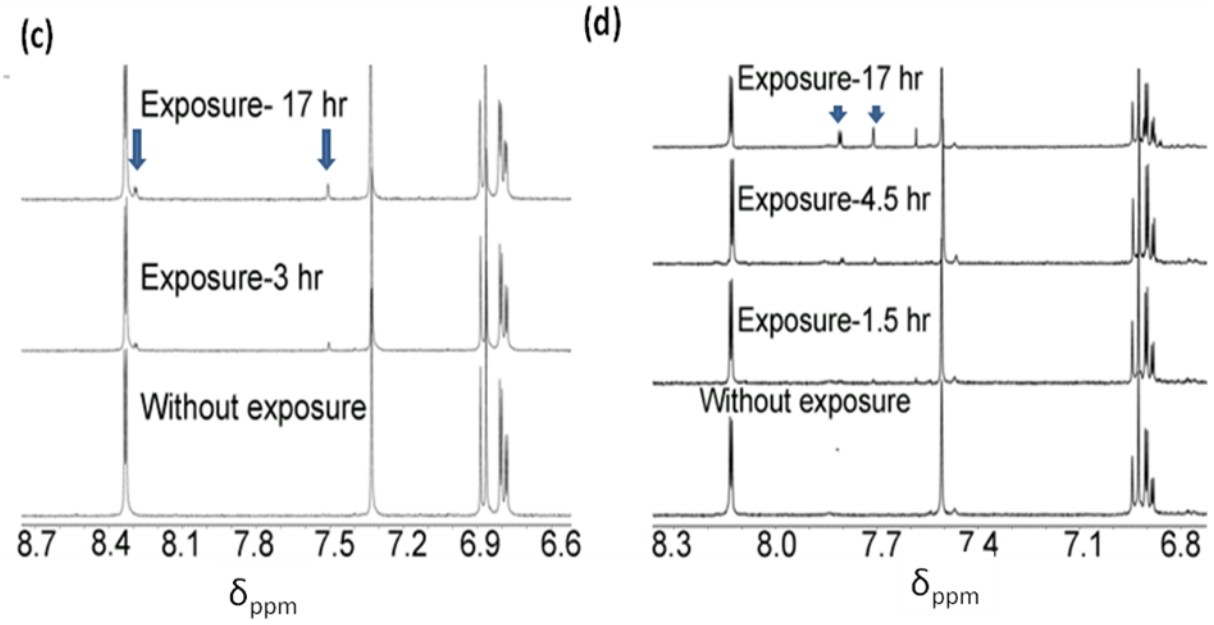


Fig- 28: NMR stack plot in CD_3CN after different time of exposure: (c) for MOMIM and (d) for MOMBO. Only aromatic region has been shown for clarity.

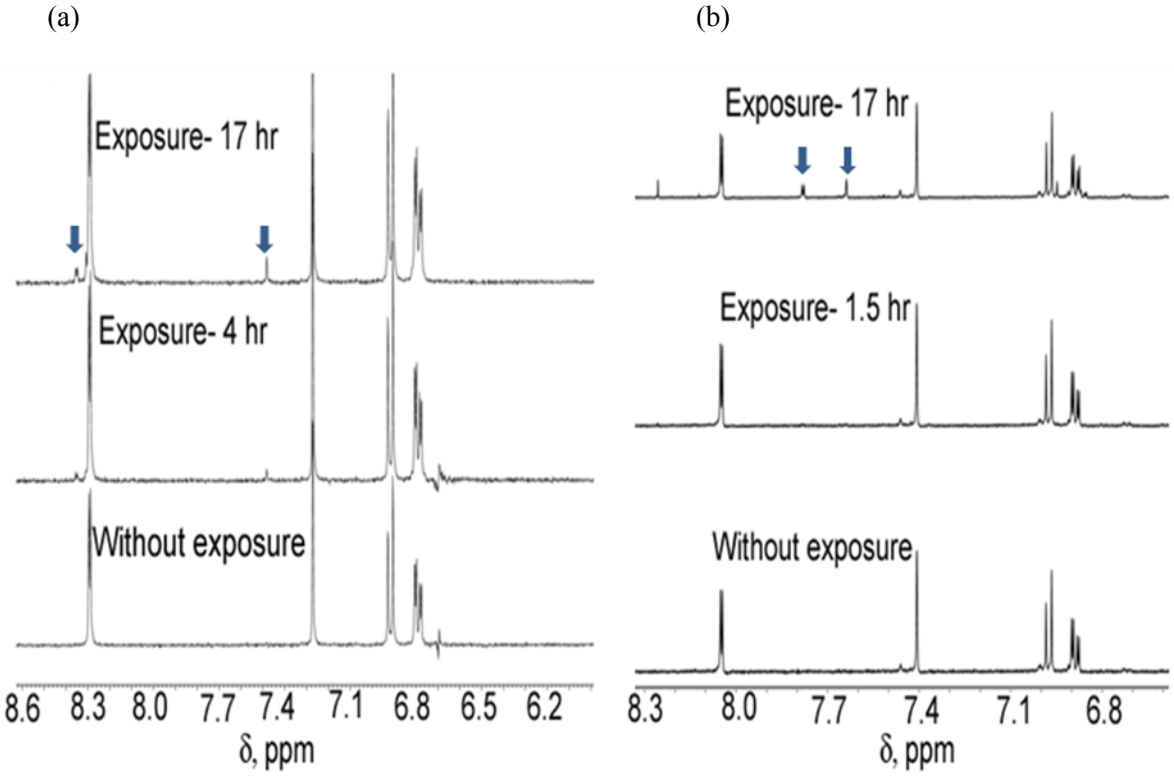
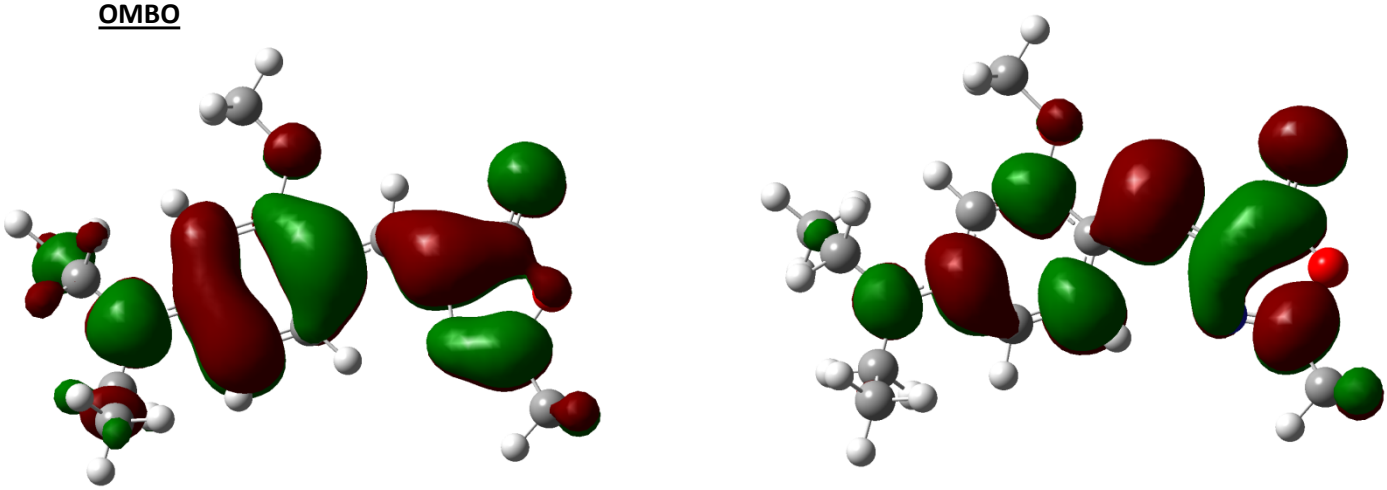


Fig-29: NMR stack plot in DMSO-d_6 after different time of exposure: (a) for MOMIM and (b) for MOMBO. Only aromatic region has been shown for clarity.

S10: Details of computational analysis

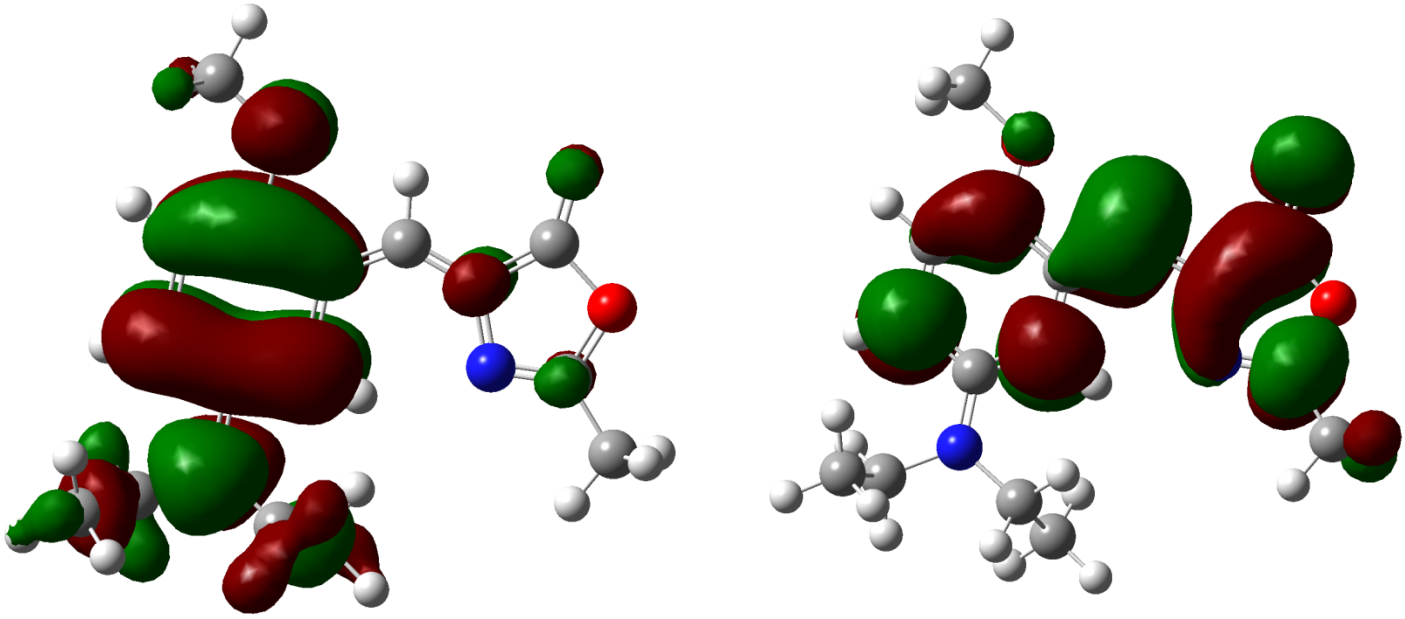
All the calculations were carried out using Gaussian 09 software package.[7] The electronic ground state geometry optimization in the gas phase has been performed using Density Functional Theory (DFT). Becke's three-parameter hybrid exchange functional and Lee-Yang-Parr correlation functional (B3LYP) were utilized in the calculation of Frontier Molecular Orbitals with a 6-31++G basis set. An isosurface value of 0.02 has been used for all the compounds to visualize the orbitals involved in HOMO and LUMO.

OMBO



HOMO LUMO

MOMBO



HOMO

LUMO

Fig. 30: Frontier molecular orbitals of OMBO (above) and MOMBO (below) calculated at B3LYP /6-31G^{++} level.

S11: Steady state absorption, emission and time resolved fluorescence spectra of MOMBO in different solvents.

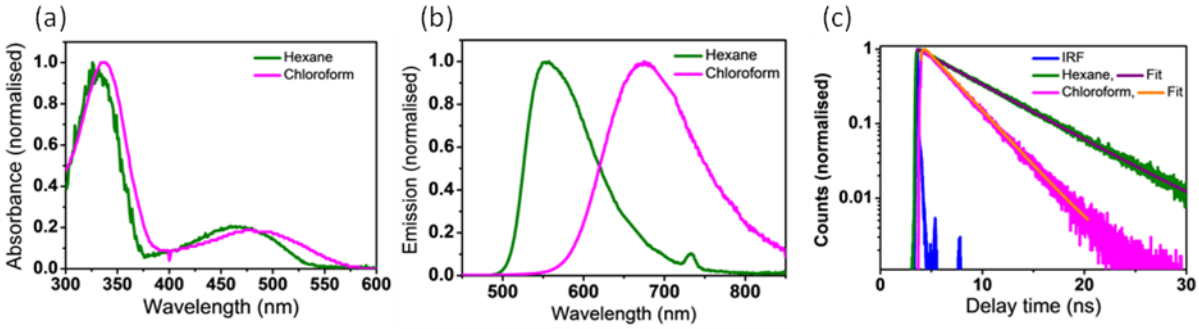


Fig-31: Steady state absorption (a), emission (b) and time resolved fluorescence spectra (c) of MOMBO in Hexane (green line) and chloroform (pink line)

S12: Table-4. Steady state and time resolved optical spectroscopic data in different solvents.

Compound	Solvent	λ_{abs}(nm)	λ_{em}(nm)	Stokes shift (nm)	ϕ_f	τ_f (λ_{mon}=lowest energy band maxima)
OMIM	Hexane	413	465	52	$<10^{-3}$	<64 ps
	$CHCl_3$	442	493	51	$<10^{-3}$	<64 ps
	ψ CH_2Cl_2	437	495	59	$<10^{-3}$	0.83 ps (0.4), 2.02 ps (0.6)
	CH_3CN	438	498	60	$<10^{-3}$	0.69 ps (0.4), 1.9 ps (0.6)
OMBO	Hexane	425	468	43	$<10^{-3}$	<64 ps
	$CHCl_3$	448	487	39	$<10^{-3}$	<64 ps
	ψ CH_2Cl_2	444	495	49	$<10^{-3}$	0.86 ps (0.46), 2.74 ps (0.54)
	CH_3CN	442	497	55	$<10^{-3}$	0.65 ps(0.58), 2.6 ps (0.42)
MOMIM	Hexane	347, 445	547	102	0.12	5.22 ns
	$CHCl_3$	354. 468	652	184	0.04	5.60 ns
	CH_2Cl_2	354, 466	665	199	0.03	4.12 ns
	CH_3CN	353, 460	688	228	0.006	2.78 ns
MOMBO χ	Hexane	332, 465	554	89	0.10	5.83 ns
	$CHCl_3$	337,482	678	196	0.02	2.93 ns
	CH_2Cl_2	339,478	691	213	0.015	1.94 ns
	CH_3CN	336,484	483,730	246	0.002	0.7 ns

ψ These values have already been reported in literature.[4]

χ For this molecule in high polar solvents (CH_3CN) dual emission has been observed by monitoring at some wavelengths. It requires more experiments and analysis to understand the underlying phenomenon.

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