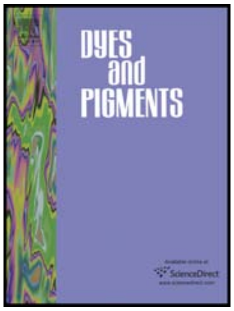

Synthesis, characterization and evaluation of the photophysical and nonlinear optical behaviour of novel 4-substituted arylidene-2-[5-(2,6-dichlorophenyl)-3-methyl-1,2-oxazol-4-yl]-1,3-oxazol-5-ones

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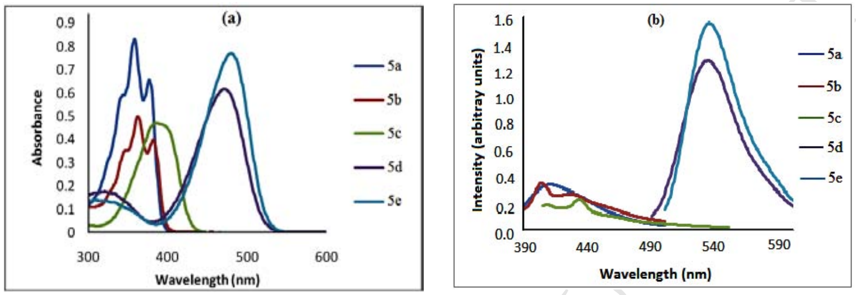
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0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
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400
500
600
Wavelength (nm)
5a
5b
5c
5d
5e
(b)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Intensity (arbitray units)
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440
490
540
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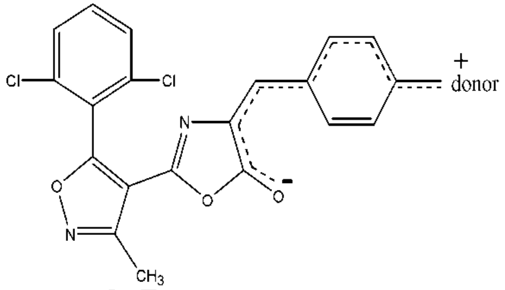
Wavelength (nm)
5a
5b
5c
5d
5e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CH3
N
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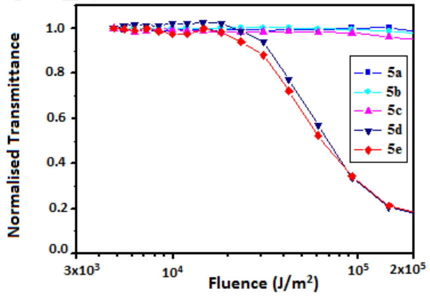
+
donor


1.0
0.8
0.6
0.4
0.2
0.0
Normalised Transmittance
3x10³
10⁴
10⁵
2x10⁵
Fluence (J/m²)
5a
5b
5c
5d
5e

Highlights

- Amongst the oxazolyloxazolones the dialkylamino substituted derivatives exhibited the highest λ_{max} and λ_{em} in DMF.
- The nonlinear refractive index is found to be negative and its magnitude is of the order of 10^{-11} esu.
- The molecular two photon absorption cross-sections are of the order of 10^{-46} cm^4 s/photon.
- Values of two photon absorption cross-section are nearly two orders of magnitude larger than of Rhodamine 6G.
- Molecules with $–NR_2$ substituents exhibited better optical limiting behavior.

Synthesis, characterization and evaluation of the photophysical and nonlinear optical behaviour of novel 4-substituted arylidene-2-[5-(2,6-dichlorophenyl)-3-methyl-1,2-oxazol-4-yl]-1,3-oxazol-5-ones

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Abstract : Five new 4-substituted arylidene-2-[5-(2,6-dichlorophenyl)-3-methyl-1,2-oxazol-4-yl]-1,3-oxazol-5-ones have been designed and synthesized in order to study their third-order nonlinear optical properties. These novel compounds were characterized by advanced spectroscopic techniques (IR, ^{1}H, ^{13}C NMR, ESI-MS spectroscopy and elemental analyses). In addition, the evaluation of absorption and emission wavelengths of the new 5-oxazolone derivatives was carried out in seven different solvents of varying polarity, which showed intense absorption maxima at 350–480 nm and emission maxima at 390-535 nm respectively. The third-order nonlinear optical properties of the target molecules have been investigated in *N*,*N*-dimethylformamide using a single beam Z-scan technique with nanosecond laser pulses at 532 nm. The nonlinear refractive index, nonlinear absorption coefficient, magnitude of third-order susceptibility and molecular two photon absorption cross-sections have been determined. All of the compounds showed excellent optical limiting behaviour at 532 nm, with the best optical limiting behaviour observed with strong electron donor [dimethyl and *N*,*N*-diethyl amino] substituents.

Keywords : 5-oxazolones, fluorescent probes, optical properties, third-order nonlinear, optical limiting, Z-scan.

1. Introduction

Derivatives of 4-arylidene-3-aryl-5-oxazolones have been extensively studied as precursors of organic molecules, such as amino acids, amides, peptides and a wide range of biologically active compounds [1-7]. On the other hand, they exhibit interesting photophysical and photochemical properties, which proved them to be good candidates for semiconductor devices (electrophotographic photoreceptors), nonlinear optical (NLO) materials, biosensors and wide variety of dyes [8-15].

Thus, in continuation of our investigations on NLO properties of 5-oxazolones [10], it is aimed to study the effect of different acceptor and donor groups on the oxazolone moiety and understand the structure-property relationship on NLO behaviour. In view of this study, a series of five new 5(4*H*)-oxazolones **(5a-5e)** with a novel heterocyclic acceptor group [5-(2,6-dichlorophenyl)-3-methyl-1,2-oxazole] at the C-2 position and various *p*-substituted aryl groups as donors at the C-4 position were designed, synthesized (Scheme-1) and characterized.

The present work describes the synthesis of the title compounds, 4-substituted arylidene-2-[5-(2,6-dichlorophenyl)-3-methyl-1,2-oxazol-4-yl]-1,3-oxazol-5-ones **(5a-5e)** and the study of their third-order nonlinear optical properties in DMF solution by Z-scan technique.

In order to find the suitability of a material for nonlinear applications one needs to study its photophysical as well as its optical characteristics such as type of nonlinearity, magnitude and response time [16]. Hence, the photophysical properties of these target molecules were evaluated in seven different solvents with a range of polarities (benzene, 1,4-dioxane, tetrahydrofuran (THF), acetonitrile, 2-proponol, ethanol and *N*,*N*-dimethylformamide (DMF)). The influence of substituted donor/acceptor strength on the third-order NLO properties of the newly synthesized oxazolones was discussed. The potent optical limiting behaviour exhibited by these molecules is also demonstrated.

2. Experimental

2.1 Materials and methods

N,*N*-dimethylformamide (DMF) was vacuum distilled from calcium hydride before being used for NLO studies. All other organic solvents were commercially available and dried using standard procedures. The title compounds **(5a-5e)** were recrystallized twice from hot benzene to enhance the degree of purity for the studies. ^{1}H NMR and ^{13}C NMR spectra were recorded by a "Mercury-400" spectrometer using deuteriated chloroform ($CDCl_3$) as solvent and tetramethylsilane (TMS) as internal standard. IR spectra were obtained on a Perkin-Elmer 1330 infrared spectrophotometer in KBr, UV absorption spectra on a Unicam-540 spectrophotometer by using quartz cuvette and Fluorescence emission spectra on Horiba Jobinyuon Fluoromax-4 spectrofluorometer with concentration of 10^{-3} mol/L. The nonlinear transmission of the samples, with and without the aperture in front of the detector was measured in the far-field using Laser Probe Rj-7620 Energy Meter with pyroelectric detectors.

Solutions of the title compounds **(5a-5e)** were prepared using spectroscopic grade *N*,*N*-dimethylformamide (DMF) with concentration 1×10^{-3} mol/L. Single beam Z-scan technique [17, 18] was employed to measure the third-order optical nonlinearities of the series of novel 5-oxazolones, which enabled simultaneous measurement of nonlinear refraction (NLR) and nonlinear absorption (NLA). Basically, in this technique a Gaussian laser beam is focused, using a lens on the cuvette containing the liquid sample. The cuvette is translated across the focal region and changes in the far-field intensity pattern are monitored. The experiments were performed using a Q-switched, frequency doubled, Nd: YAG laser (Spectra-Physics GCR170) which produces 7 ns pulses at 532 nm, at a repetition rate of 10 Hz. The laser beam was focused by using a lens of 25 cm focal length whose beam waist at the focused spot was estimated to be 18.9 μm and the corresponding Rayleigh length at 2.11 mm. The Z-scan measurements with an input peak intensity of 2.39 GW/cm^2 were carried out using a cuvette of 1 mm thickness, which is less than the Rayleigh length. Hence, the thin sample approximation is valid.

2.2 Synthesis of 5-(2,6-dichlorophenyl)3-methyl-1,2-oxazole-4-carbonylchloride ***(2)***

A mixture of 5-(2,6-dichlorophenyl)-3-methyl-1,2-oxazole-4-carboxylicacid **(1)** (0.1 mol) in acetonitrile (30 mL) was added slowly to thionyl chloride (0.3 mol) and the reaction mixture was heated under reflux for 4 hours under anhydrous conditions. The excess thionyl chloride was distilled off under reduced pressure and the resultant acid chloride **(2)** in the form of viscous liquid, was collected.

2.3 Synthesis of 5-(2,6-dichlorophenyl)3-methyl-1,2-oxazol-4-yl carbonyl aminoacetic acid ***(3)***

Glycine (0.1 mol) was dissolved in NaOH (30 mL, 2N) and stirred vigorously with mechanical stirrer, until the total solid completely dissolved. This was added dropwise to the crude acid chloride **(2)** (0.1 mol) and stirred vigorously for 1 hour. Later it was poured into crushed ice and concentrated hydrochloric acid was added slowly with stirring, until the mixture was acidified to Congo red. The obtained crude compound **(3)** was washed with cold water, dried and recrystallized from boiling water.

White crystalline powder; Yield : 90%. m.p. : 198°C. IR (KBr, υ, cm^{-1}) : 785, 1191, 1447, 1675, 1732. ^{1}H NMR (400 MHz, DMSO, δ, ppm) : 2.70 (s, CH_3, 3H), 3.79 (s, CH_2, 2H), 7.53 (m, Ar-

H, 3H) , 8.19 (s, NH, 1H), 12.68 (br s, COOH, 1H). ^{13}C NMR (100 MHz, DMSO, δ, ppm) : 12.9, 41.1, 113.6, 127.6, 128.6, 132.5, 134.9, 158.4, 160.4, 170.6, 171.2. ESI-MS *(m/z)* : 329 [M$^+$], 331 [M+2], 333 [M+4]. Anal. Calcd. for $C_{13}H_{10}Cl_2N_2O_4$: C, 47.44, H, 3.96 %; Found : C, 47.41, H, 3.98 %.

2.4 Synthesis of 2-[5-(2,6-dichlorophenyl)-3-methyl-1,2-oxazol-4-yl]-4-(4-substituted arylidene)-1,3-oxazol-5-ones ***(5a-5e)***

A mixture of dry 5-(2,6-dichlorophenyl)-3-methyl-1,2-oxazol-4-yl carbonyl aminoacetic acid **(3)** (0.01 mol), substituted aromatic aldehyde **(4a-4e)** (0.01 mol), powdered anhydrous sodium acetate (0.01 mol) and high-grade acetic anhydride (0.03 mol) was heated at 110°C on a hot plate, with constant shaking until the solid gradually liquified to light yellow solution. Then the reaction mixture was added 4°A molecular sieves (2g) and heated on a water bath for 1 hour with occasional stirring. The molecular sieves were removed by filtration of the warm reaction mixture. On cooling, ethanol (10 mL) was added slowly to the reaction mixture and left overnight at room temperature. The crystalline product thus obtained was filtered under suction pump, washed with ice cold alcohol, finally with boiling water and dried. The crude 5-oxazolones obtained **(5a-5e)** were recrystallized from hot benzene.

2.4.1. 2-[5-(2,6-Dichlorophenyl)-3-methyl-1,2-oxazol-4-yl[-4-(4-arylidene)-1,3-oxazol-5-one ***(5a).*** Pale yellow crystals. Yield : 85%. m.p. : 167°C. IR (KBr, υ, cm^{-1}) : 941, 1143, 1456, 1656, 1765. ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm) : 2.93 (s, 3H), 7.12 (s, 1H), 7.29 (d, J = 7.6 Hz, 2H). 7.38 (d, J = 7.2 Hz, 1H), 7.50 (m, Ar-H, 3H), 7.64 (d, J = 7.6 Hz, 2H), ^{13}C NMR (100 MHz, CDCl$_3$, δ, ppm) : 13.8, 105.5, 128.0, 128.1, 128.7, 131.2, 131.3, 131.6, 132.0, 132.5, 133.5, 136.0, 156.7, 158.3, 166.5, 174.3. ESI-MS *(m/z)* : 399 [M$^+$], 401 [M+2],: 403 [M+4]. Anal. Calcd. for $C_{20}H_{12}Cl_2N_20_3$: C, 60.17, H, 3.03, N, 7.02 %; Found : C, 60.15, H, 3.05, N, 6.99 %.

*2.4.2. 2-[5-(2,6-Dichlorophenyl)-3-methyl-1,2-oxazol-4-yl[-4-(4-chloroarylidene)1,3-oxazol-5-one **(5b)***. Bright yellow crystals. Yield : 82%. m.p. : 163°C. IR (KBr, υ, cm^{-1}) : 784, 960, 1164, 1419, 1667, 1792. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) : 2.92 (s, 3H), 7.04 (s, 1H), 7.23 (d, J = 8.4 Hz, 2H), 7.51 (m, Ar-H, 3H), 7.56 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm) : 13.8, 105.3, 127.8, 128.0, 129.0, 130.3, 131.3, 131.8, 131.9, 133.5, 135.8, 137.4, 156.9, 158.2, 166.2, 174.5. ESI-MS *(m/z)* : 433 [M$^+$], 435 [M+2], 437 [M+4], 439 [M+6]. Anal. Calcd. for $C_{20}H_{11}Cl_3N_2O_3$: C, 55.39, H, 2.56, N, 6.46 %; Found : C, 55.35, H, 2.59, N, 6.45 %.

2.4.3. 2-[5-(2,6-Dichlorophenyl)-3-methyl-1,2-oxazol-4-yl[-4-(4-methoxyarylidene)1,3-oxazol-5-one ***(5c).*** Yellow crystals. Yield : 88%. m.p. : 179°C. IR (KBr, υ, cm^{-1}) : 773, 959, 1157, 1455, 1668, 1789, 1805. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) : 2.92 (s, 3H), 3.87 (s, 3H), 6.79 (d, J = 8.8 Hz, 2H), 7.10 (s, 1H), 7.50 (m, Ar-H, 3H), 7.62 (d, J= 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm) : 13.7, 55.6, 105.6, 114.3, 126.5, 128.0, 129.3, 131.1, 132.2, 134.6, 135.9, 155.4, 158.2, 162.2, 166.9, 173.8. ESI-MS *(m/z)* : 429 [M$^+$], 431 [M+2], 433 [M+4]. Anal. Calc. for $C_{21}H_{14}Cl_2N_2O_4$: C, 58.76, H, 3.29, N, 6.53 %; Found : C, 58.73, H, 3.23, N, 6.50 %.

2.4.4. 2-[5-(2,6-Dichlorophenyl)-3-methyl-1,2-oxazol-4-yl[-4-(4-N,N-dimethylaminoarylidine) 1,3-oxazol-5-one ***(5d).*** Deep red crystals. Yield : 86%. m.p. : 233°C. IR (KBr, υ, cm^{-1}) : 790, 958, 1159, 1377, 1586, 1760, 1787. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) : 2.91 (s, 3H), 3.10 (s, 6H), 6.53 (d, J = 8.8 Hz, 2H), 7.07 (s, 1H), 7.43-7.51 (m, Ar-H, 3H), 7.59 (d, J = 8.8 Hz, 2H), ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm) : 13.7, 40.1, 105.9, 111.5, 121.6, 126.5, 128.0, 128.2, 130.9, 133.6, 134.9, 136.0, 152.3, 153.5, 158.1, 167.5, 173.0. ESI-MS *(m/z)* : 442 [M$^+$], 444 [M+2], 446 [M+4]. Anal. Calcd. for $C_{22}H_{17}Cl_2N_3O_3$: C, 59.74, H, 3.87, N, 9.50 %; Found : C, 59.76, H, 3.93, N, 9.47 %.

2.4.5. 2-[5-(2,6-Dichlorophenyl)-3-methyl-1,2-oxazol-4-yl[-4-(4-N,N-diethylaminoarylidene)1,3-oxazol-5-one ***(5e).*** Orange red crystals. Yield : 83%. m.p.: 245°C. IR (KBr, υ, cm^{-1}) : 791, 957, 1197, 1577, 1664, 1754, 1781. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) : 2.92 (s, 3H), 3.43-3.48 (q, 4H), 6.51 (d, J = 8.8 Hz, 2H), 7.05 (s, 1H), 7.40-7.50 (m, Ar-H, 3H), 7.58 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 12.7, 13.6, 44.8, 106.0, 111.1, 121.0, 126.0, 128.0, 128.3, 130.8, 133.6, 135.2, 136.0, 150.1, 153.2, 158.1, 167.5, 173.0. ESI-MS *(m/z)* : 470 [M^+], 472 [M+2], 474 [M+4]. Anal. Calcd. for $C_{24}H_{21}Cl_2N_3O_3$:C, 61.29, H, 4.50, N, 8.93 %; Found : C, 61.25, H, 4.51, N, 8.91 %.

3. Results and discussion

3.1. Synthesis

5-(2,6-Dichlorophenyl)-3-methylisoxazole-4-carboxylic acid **(1)** in acetonitrile was first converted to its acid chloride using thionyl chloride and the obtained 5-(2,6-dichlorophenyl)3-methylisoxazole-4-carbonyl chloride **(2)** was immediately reacted with glycine (aminoacetic acid) in presence of sodium hydroxide to give 5-(2,6-dichlorophenyl)3-methyl-1,2-oxazol-4-yl carbonyl aminoacetic acid **(3)** in the subsequent step. Finally, the title compounds 4-(substitutedbenzylidene)-2-[5-(2,6-dichlorophenyl)-3-methylisoxazol-4-yl]oxazol-5(4*H*)-ones **(5a-5e)** with various substituents, were synthesized by the condensation of **3** with different *p*-substituted aryl aldehydes **(4a-4e)** in presence of acetic anhydride and sodium acetate in excellent yields by using molecular sieves ($4A^0$) as cyclodehydrating agents. The crude compounds **(5a-5e)** on purification followed by crystallization formed yellow / reddish crystalline solids and confirmed by IR, ^{1}H NMR, ^{13}C NMR, ESI mass spectroscopy and elemental analyses. The detailed experimental procedure is recorded in experimental section (*2.4*). The chemistry used to prepare these compounds is illustrated in Scheme 1.

3.2. Photophysical characterization

The photophysical behaviour of the title compounds **(5a-5e)** in different solvents of varying polarity was investigated and presented in Table 1. These compounds exhibited the excitation and emission wavelengths in the range of 350-480 nm and 390-535 nm respectively in all the solvents employed.

From the observed data, the influence of different substituents towards their absorption and fluorescence emission maxima is clearly evidenced (Table 1). With the acceptor remaining constant throughout the series **(5a-5e)** at one end, the red shift observed is due to donor strength of the groups at the other end. Upon formation of the target 5-oxazolone from its reactant molecules, the transition of an electron from the highest filled molecular orbital (HOMO) of the donor to the lowest unoccupied molecular orbital (LUMO) of the acceptor takes place forming a charge transfer complex, where π-electron delocalization takes place from the donor groups to more or less the carbonyl group in the oxazolone ring (Fig.1).

From Table 1, no considerable changes have been observed in the absorption maxima of compounds **(5a-5e)** due to solvent polarity. However, substantial shifts were observed in their emission maxima, probably due to the interaction of the molecules in their excited states with the solvent molecules. The compounds **5d** and **5e** exhibited longest wavelength absorption (λ_{max}) at 471 nm and 479 nm and emission (λ_{em}) at 533 nm and 535 nm respectively in DMF (Fig.2). Consequently, in compounds **5d** and **5e**, the enhanced π-electron delocalization due to $-N(CH_3)_2$ and $-N(C_2H_5)_2$ groups on the phenyl ring is responsible for these effects.

Furthermore, the molar absorption coefficients (ε_{max}) of **5a-5e** were calculated by recording absorbance values of each compound at a given wavelength in seven different solvents and listed in Table 1. The Stokes shift values of **5a-5e** were also calculated in terms of nm (difference in wavelength between the excitation and emission maxima) and cm^{-1} (the transition energy between absorption and emission) and presented in Table 1.

The fluorescence quantum yields (φ_f) were measured using dilute solutions to avoid re-absorption effect, relative to rhodamine 6G as a reference standard [19]. The quantum yields observed (Table 1) were low for the series of compounds **(5a-5e).** A slight increase in these values was observed in **5d** and **5e** in all the solvents employed. The low quantum yields exhibited by oxazolones might be due to an efficient non-radiative deactivation channel of the excess energy [20]. Finally, these studies reveal that the title compounds have potent photophysical properties which make them interesting candidates for NLO studies.

3.3. NLO characterization

The nonlinear transmission of compound **5a** without aperture (open aperture) was measured in the far field as the sample was moved through the focal point. This allowed us to determine the nonlinear absorption β. Here, the transmission is symmetric with respect to focus (z = 0), where a minimum transmission, showing an intensity dependent absorption effect is observed. To study the variation in the nonlinear optical parameters with the nature of the substituent group, Z-scan experiments have been conducted on other samples **(5b-5e)** of this series and similar curves have been obtained. The open aperture curves of samples **5c** & **5e** are shown in Fig. 3(a) and 4(a). The shape of the open aperture curves suggests that the compounds exhibit two-photon absorption [21-23]. The normalized transmittance for the open aperture Z-scan is given by eq. (1) [24]

$$T(z) = \frac{\ln[1+q_0(z)]}{q_0(z)} \quad \text{for } |q_0(z)| < 1 \qquad (1)$$

where q_0 is a free factor, defined as

$$q_0(z) = \frac{I_0\beta(1-e^{-\alpha L})}{(1+z^2/z^2{}_0)\alpha} \qquad (2)$$

and α is the linear absorption coefficient, L is the thickness of the sample, I_0 is the on axis peak irradiance at the focus, and z_0 is the Rayleigh length.

It is known that nonlinear absorption coefficient β, depends on the number of absorptive centers in a unit volume. Assuming that this number is N_0, in units of cm^{-3}, we have [25, 26],

$$\beta = \sigma_2 N_0 = \sigma_2 N_A d \times 10^{-3} \qquad (3)$$

Here, N_0 is the molecular density of the sample (in units of $1/cm^3$), σ_2 is the molecular TPA coefficient (or cross-section) (in units of cm^4/GW), d is the concentration of the sample and N_A is the Avogadro number. For known β and d, the value of σ_2 can be obtained. Molecular TPA cross-section (in units of cm^4 s/photon) is also defined as [26, 27],

$$\sigma_2' = \sigma_2 h\upsilon, \qquad (4)$$

Now the nonlinear absorption coefficient β, is related to the imaginary part of third-order nonlinear optical susceptibility through the equation [24],

$$\mathrm{Im}\,\chi^{(3)} = n_0^2 \varepsilon_0 c \lambda \beta / 2\pi, \qquad (5)$$

where n_0 is the linear refractive index, ε_0 is the permittivity of free space and c is velocity of light in vacuum.

From the open aperture Z-scan data, the measured values of nonlinear absorption coefficient β, molecular TPA cross-sections σ_2 and σ'_2 and the imaginary part of third-order nonlinear optical susceptibility $\chi^{(3)}$ of samples **(5a-5e)** are given in Table 2. The σ'_2 value of the newly synthesized 5-oxazolones **(5a-5e)** are nearly two orders of magnitude larger than that of Rhodamine 6G which is 10^{-48} to 10^{-50} cm^4 s/photon [28]. It is also comparable with values obtained in stilbazolium like dyes such as *trans*-4-[2-(pyrryl)vinyl]-1-methylpyridium iodide [29].

To determine the sign and magnitude of nonlinear refraction, closed-aperture Z-scan was performed by placing an aperture in front of the detector. The closed aperture Z-scan curves of **5c** & **5e** are shown in Fig. 3(b) and 4(b). To obtain the pure nonlinear refraction curve we adopted the division method [24]. The investigated samples **(5a-5e)** were found to exhibit peak–valley characteristics, indicating negative nonlinear refraction or self defocusing effects as shown in Fig. 3(c) and 4(c) for compounds **5c** and **5e**.

The nonlinear refractive index γ (m2/W) is given by the formula [24],

$$\gamma \ = \ \frac{\Delta\phi_0 \lambda}{2\pi L_{\text{eff}} I_0}(m^2/W), \qquad (6)$$

where $L_{\text{eff}} = \frac{(1-\exp^{-\alpha L})}{\alpha}$ and ΔΦ0 is the on-axis phase change given by the equation,

$$\Delta\phi_0 \ = \ \frac{\Delta T\text{p}-\text{v}}{0.406(1-S)^{0.25}} \quad \text{for } |\Delta\phi_0| \ \leq \ \pi, \qquad (7)$$

Here ΔT_{p-v} is the peak to valley transmittance difference and S is the linear aperture transmittance. Then nonlinear refractive index n_2 (in esu) is related to γ (m^2/W) by,

$$n_2 \ (\text{esu}) \ = \ (cn_0/40\pi)\gamma \ (\text{m}^2/\text{W}), \qquad (8)$$

The normalized transmittance for pure nonlinear refraction is given by [24],

$$T(Z) = 1 - \frac{4x\Delta\phi_0}{[(x^2+9)(x^2+1)]}, \qquad (9)$$

The nonlinear refractive index n_2 (esu) is related to the real part of third-order nonlinear optical susceptibility through equation [24],

$$\text{Re}\,\chi^{(3)} \ = \ 2n_0^2\varepsilon_0 c n_2(esu), \qquad (10)$$

where n_0 is the linear refractive index, ε_0 is the permittivity of free space and c is velocity of light in vacuum.

From the pure nonlinear refraction Z-scan data, the real part of third-order nonlinear optical susceptibility $\chi^{(3)}$ and nonlinear refractive index n_2, for samples **(5a-5e)** have been calculated and tabulated in Table 2.

The nonlinear absorption coefficients (β) of some of the organic compounds and metal complexes studied previously are listed in Table 3. Azoaromatic compounds such as Disperse Orange 3, Disperse Red 13, Disperse Red 19 and azobenzene, which are conjugated molecules with donor/acceptor groups, have large values of β [30]. Similarly, styryl dyes and octupolar metal complexes are found to have large values [31,32], exceeding that of semiconductors such as ZnSe, CdS and ZnTe, Cu nanocomposite glasses [33] and bismuth nanorods [34]. The nonlinear absorption coefficients of the tested samples **5d** and **5e** are also found to be in the same range as that of the materials shown in Table 3.

The magnitude of susceptibility ($\chi^{(3)}$) values of the title compounds **(5a-5e)** were found to be increasing from **5a** to **5e**. This can be attributed to the increase in the electron donating abilities of the donor groups and is pronounced in **5d** and **5e** [-$N(CH_3)$ and -$N(C_2H_5)_2$]. Thus, the compounds **5d** and **5e**, containing the -NR_2 substituent groups showed the highest third-order nonlinear response amongst the title compounds **(5a-5e)** studied. Thus, the knowledge of variation of nonlinear response with substituents could be employed to design suitable organic materials for future specific applications in photonics and other optoelectronics fields.

3.4. Optical limiting

The optical power limiting efficiency of the target molecules **(5a-5e)** was investigated by means of nonlinear transmittance measurements as a function of the input fluence, to determine the limiting threshold. The optical limiting threshold determines the ability of the limiter and it is noted that the lower the threshold value, the better the optical limiter [35]. Fig.5 shows the clear optical limiting behaviour of the tested samples **5a-5e**. The optical limiting threshold (the fluence value at which the transmittance starts decreasing) of the molecules **5a-5e** from the Fig.5, are found to be $2.25x10^5$ J/m^2, $8x10^4$ J/m^2, $6x10^4$ J/m^2, $2x10^4$ J/m^2 and $2x10^4$ J/m^2 respectively. The results demonstrated that the molecules **5d** and **5e** with strong electron donating $–N(CH_3)_2$, $–N(C_2H_5)_2$ substituents on the phenyl ring, exhibited better optical limiting behaviour with lower threshold values than all the other molecules tested **(5a-5c).**

Moreover, the optical limiting parameters of the tested molecules **(5a-5e)** compare very well with those of the materials mentioned in Table 3 and are also comparable with those values for mixed metal clusters [36-39].

4. Conclusion

In conclusion, five novel 5-oxazolones with delocalized π-conjugated systems having novel acceptor and different donor groups **(5a-5e)** were synthesized and their third-order nonlinear optical response was screened using the Z-scan technique in DMF solution. In addition, the photophysical properties of the title compounds in seven different solvents have also been determined. The substituent effect on the NLO properties is clearly noticed. The Z-scan results indicate that the target molecules exhibit good negative nonlinear refractive index (n_2) and nonlinear absorption (NLA). The nonlinear index is found to be negative and its magnitude is of the order of 10^{-11} esu. The molecular two-photon absorption cross-section of these molecules was also measured and is of the order of 10^{-46} cm^4 s/photon which is nearly two orders of magnitude larger compared to that of Rhodamine dyes. The molecules studied **(5a-5e),** exhibit good optical power limiting behaviour of nanosecond laser pulses at 532 nm wavelength.

A good correlation was found between the theoretical and experimental values, suggesting that the samples investigated seem to be promising candidates for future photonic and optoelectronic applications.

Acknowledgements

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Table 1. The absorption and emission maxima of (5a-5e) in different solvents of varying polarity

Table 2. Third-order nonlinear optical parameters of title compounds (5a-5e) in DMF solution at the concentration of $1x10^{-3}$ mol/L.

Table 3. Nonlinear absorption coefficient (β) of various compounds reported in the literature.

Table 1.

Compound	Solvent	Absorption Maxima (λ_{abs} in nm)	Molar extension coefficient (ε_{max} (cm^{-1} M^{-1}))	Emission maxima (λ_{em} in nm)	Stokes shift ($\Delta\lambda$)		Fluorescence quantum yield φ_f
					nm	cm^{-1}	
5a	Benzene	360	59,000	409	49	3343	0.009
	1,4-dioxane	356	84,000	407	51	3504	0.008
	Tetrahydrofuran (THF)	357	52,000	399	42	2964	0.002
	Acetonitrile	355	29,000	397	43	3012	0.001
	2-propanol	356	38,000	398	43	2980	0.004
	Ethanol	356	75,000	399	43	3059	0.002
	N,*N*-Dimethylformamide (DMF)	357	82,000	413	56	3782	0.002
5b	Benzene	365	89,000	417	52	3401	0.004
	1,4-dioxane	361	80,000	413	52	3472	0.003
	Tetrahydrofuran (THF)	361	70,000	414	53	3531	0.004
	Acetonitrile	359	52,000	404	45	3087	0.003
	2-propanol	361	25,000	404	43	3009	0.006
	Ethanol	360	78,000	405	45	3010	0.005
	N,*N*-Dimethylformamide (DMF)	362	48,000	405	43	2841	0.005
5c	Benzene	383	78,000	437	54	3213	0.003
	1,4-dioxane	379	47,000	427	48	2952	0.002
	Tetrahydrofuran (THF)	382	99,000	432	50	3016	0.09
	Acetonitrile	382	63,000	434	52	3137	0.001
	2-propanol	386	99,000	437	51	3050	0.001
	Ethanol	386	92,000	435	49	2945	0.006
	N,*N*-Dimethylformamide (DMF)	385	47,000	433	48	2859	0.003

5d	Benzene	463	90,000	497	34	1487	0.06
	1,4-dioxane	454	62,000	498	44	1966	0.08
	Tetrahydrofuran (THF)	460	87,000	512	52	2198	0.09
	Acetonitrile	464	54,000	528	66	2622	0.14
	2-propanol	465	69,000	516	51	2126	0.10
	Ethanol	465	86,000	525	60	2284	0.12
	N,*N*-Dimethylformamide (DMF)	471	66,000	533	62	2465	0.18
5e	Benzene	470	52,000	500	30	1249	0.05
	1,4-dioxane	464	62,000	502	38	1650	0.07
	Tetrahydrofuran (THF)	470	89,000	515	45	1914	0.09
	Acetonitrile	471	44,000	530	59	2354	0.12
	2-propanol	471	36,000	518	47	1908	0.09
	Ethanol	475	53,000	528	53	2131	0.10
	N,*N*-Dimethylformamide (DMF)	479	78,000	535	56	2177	0.15

Table 2.

Compound	n_2 (x10^{-11} esu)	β (cm/GW)	**Re** $\chi^{(3)}$ (x10^{-13}esu)	**Im** $\chi^{(3)}$ (x10^{-13}esu)	σ_2 (x10^{-19} cm^4/GW)	σ'_2 (x10^{-46} cm^{4}s /photon
5a	-0.4073	0.3219	-0.4363	0.0495	5.344	1.993
5b	-0.6924	0.4603	-0.7417	0.0708	7.643	2.851
5c	-0.7495	0.9065	-0.8029	0.1395	15.051	5.614
5d	-3.0783	9.8652	-3.2974	1.5181	163.792	61.094
5e	-3.2442	9.8971	-3.4751	1.5230	164.322	61.292

Table 3.

Compounds	β **(cm/GW)**	**References**
Diazobenzene	6.5	[30]
Styryl dyes	4.87	[31]
Octupolar metal complexes	5.07	[32]
ZnSe, CdS, and ZnTe	3.6, 4.9 and 4.7	[33]
Bismuth nanorods	5.3	[34]
5-oxazolones (5d & 5e)	9.8	Present work

Scheme 1. Synthetic pathway of title compounds (5a-5e)

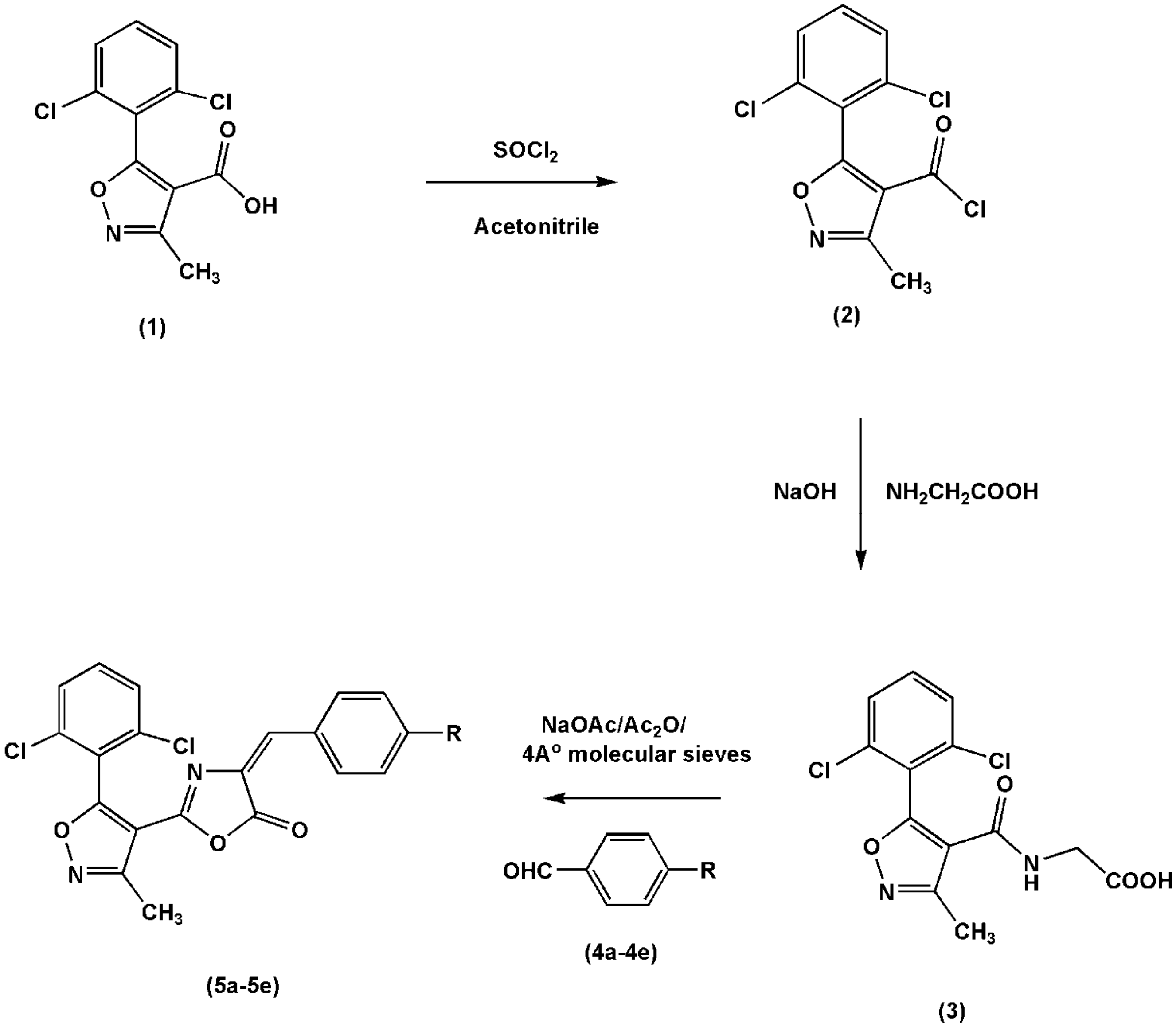
Fig. 1. Charge transfer complex of 5-oxazolones (5a-5e)

Fig. 2. (a) Absorption and (b) Emission spectra of title compounds (5a-5e) in DMF

Fig. 3. (a) Open aperture (b) Closed aperture and (c) Pure nonlinear refraction Z-scan curve of 5c in DMF solution. Solid line is a theoretical fit to the experimental data.

Fig. 4. (a) Open aperture (b) Closed aperture and (c) Pure nonlinear refraction Z-scan curve of 5e in DMF solution. Solid line is a theoretical fit to the experimental data.

Fig. 5. Optical limiting behaviour of title compounds (5a-5e)



R in 4a-4e and 5a-5e = (a) H, (b) *p*-Cl, (c) *p*-OCH_3, (d) *p*-*N*$(CH_3)_2$, (e) *p*-*N*$(C_2H_5)_2$

Scheme 1.

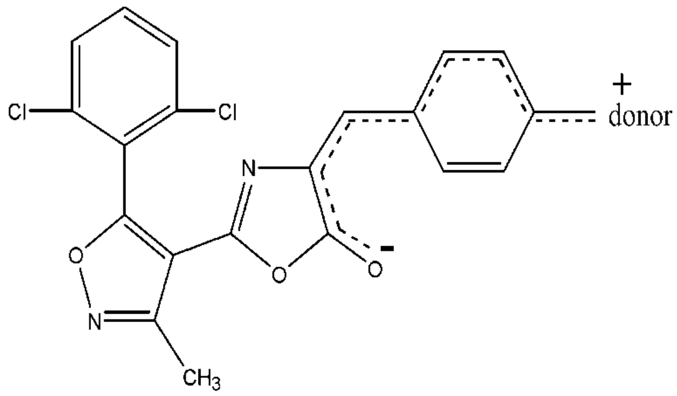

Cl
Cl
N
O
O
N
CH3
O
+
donor
-

Fig. 1.

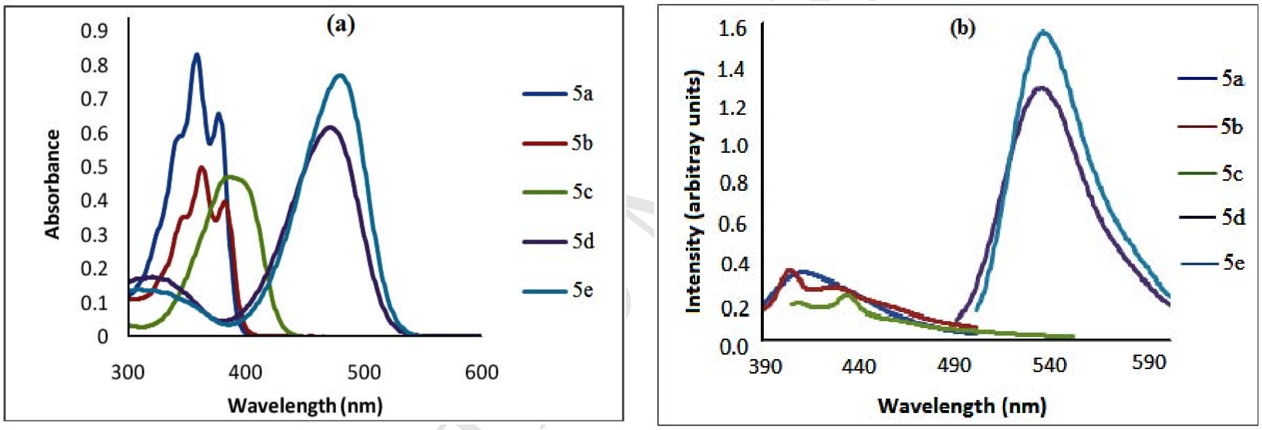

(a)
Absorbance
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
300
400
500
600
Wavelength (nm)
5a
5b
5c
5d
5e
(b)
Intensity (arbitray units)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
390
440
490
540
590
Wavelength (nm)
5a
5b
5c
5d
5e

Fig. 2.

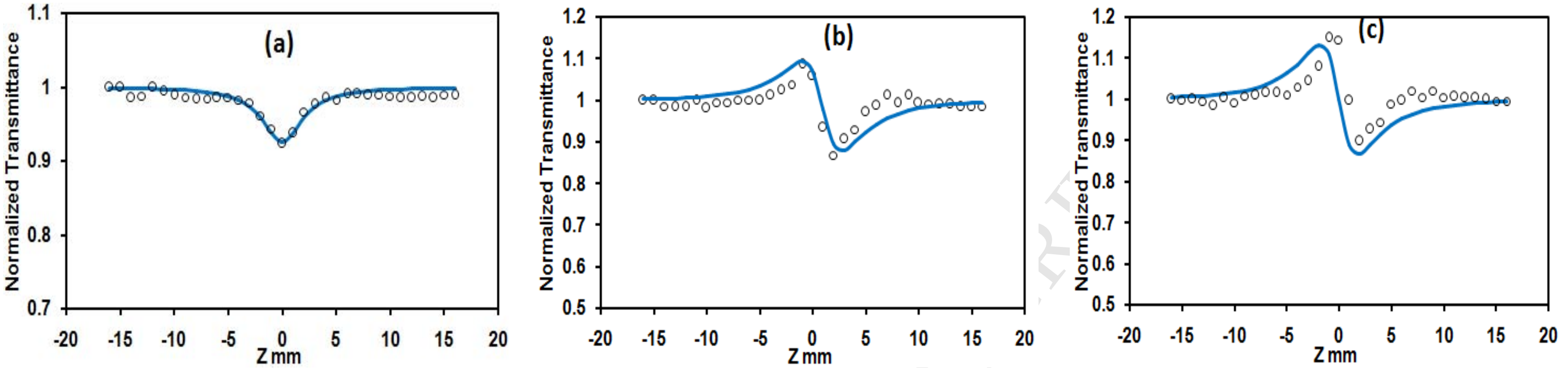

(a)
(b)
(c)
Normalized Transmittance
Z mm
1.1
1
0.9
0.8
0.7
1.2
0.6
0.5
-20
-15
-10
-5
0
5
10
15
20

Fig. 3.

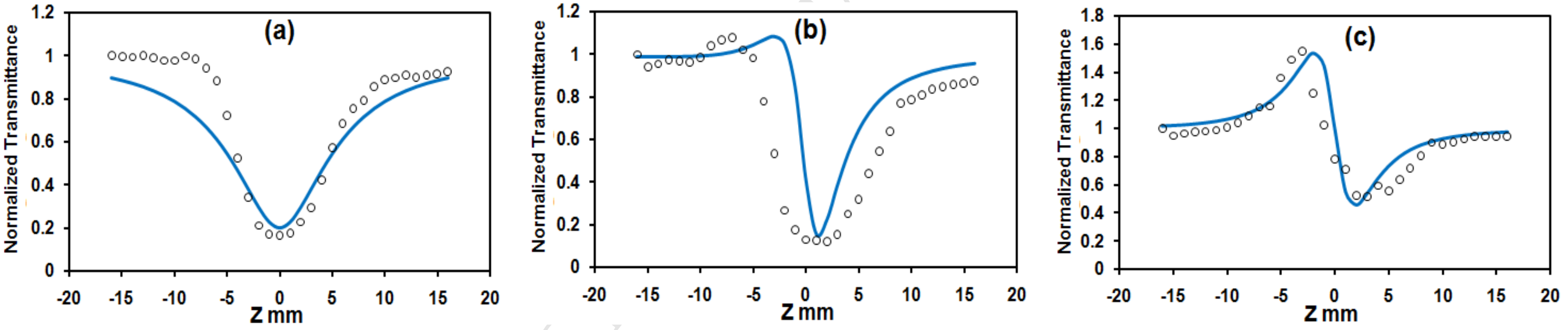

(a)
(b)
(c)
Normalized Transmittance
Z mm
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-20
-15
-10
-5
0
5
10
15
20

Fig. 4.

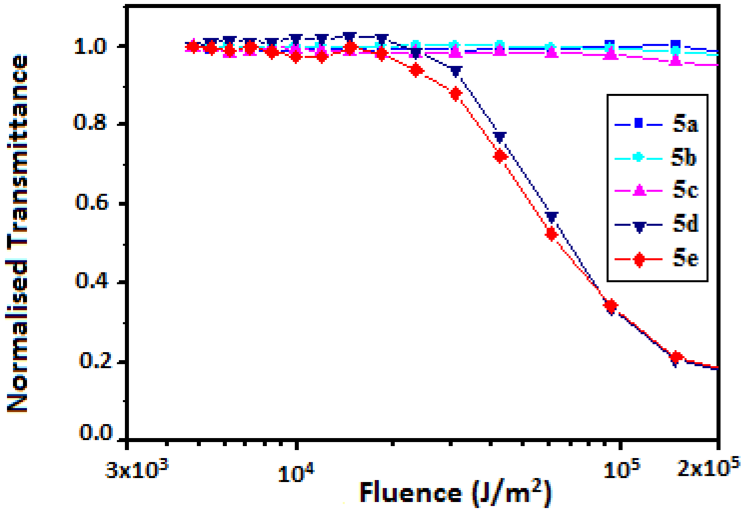
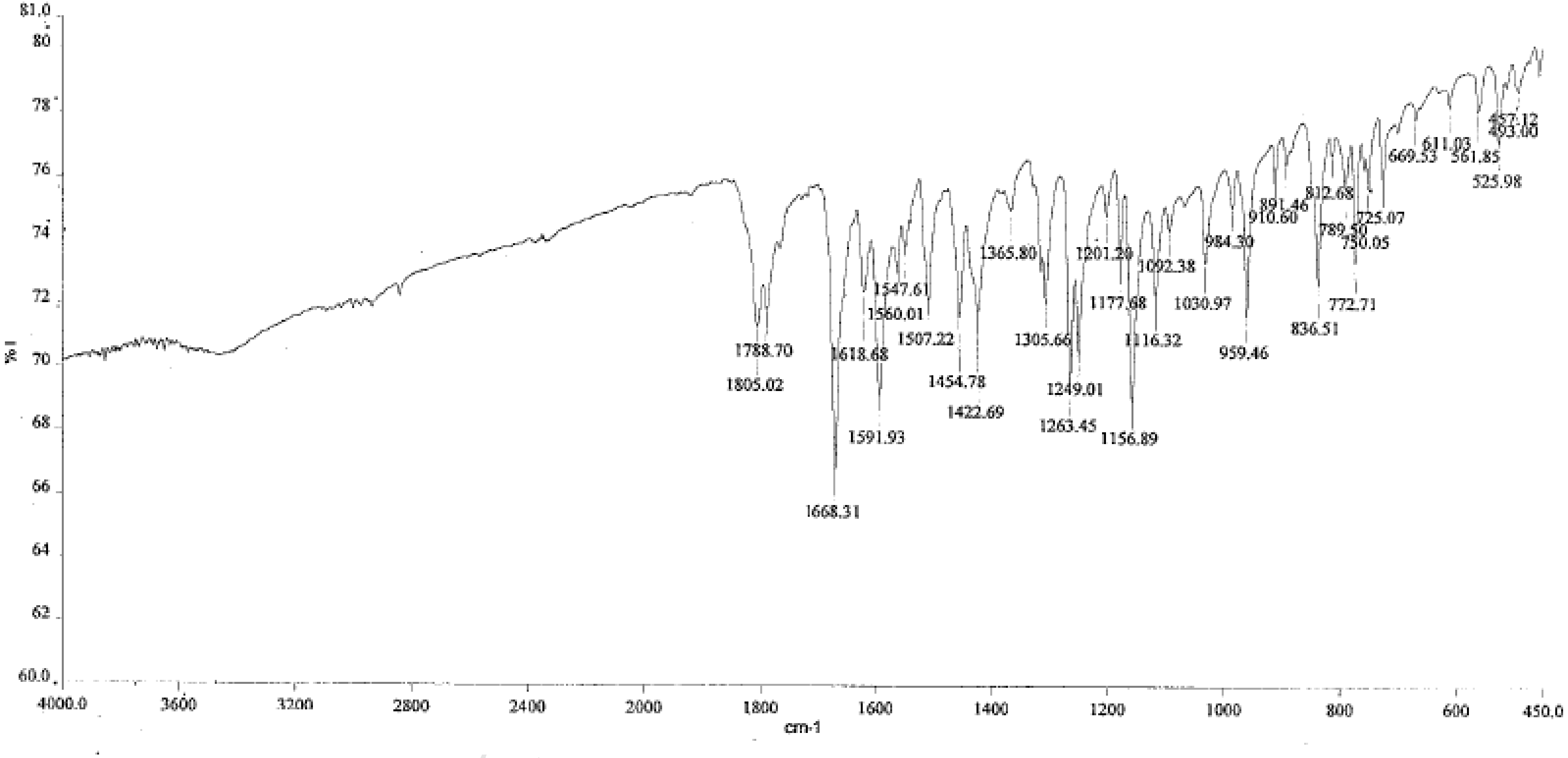
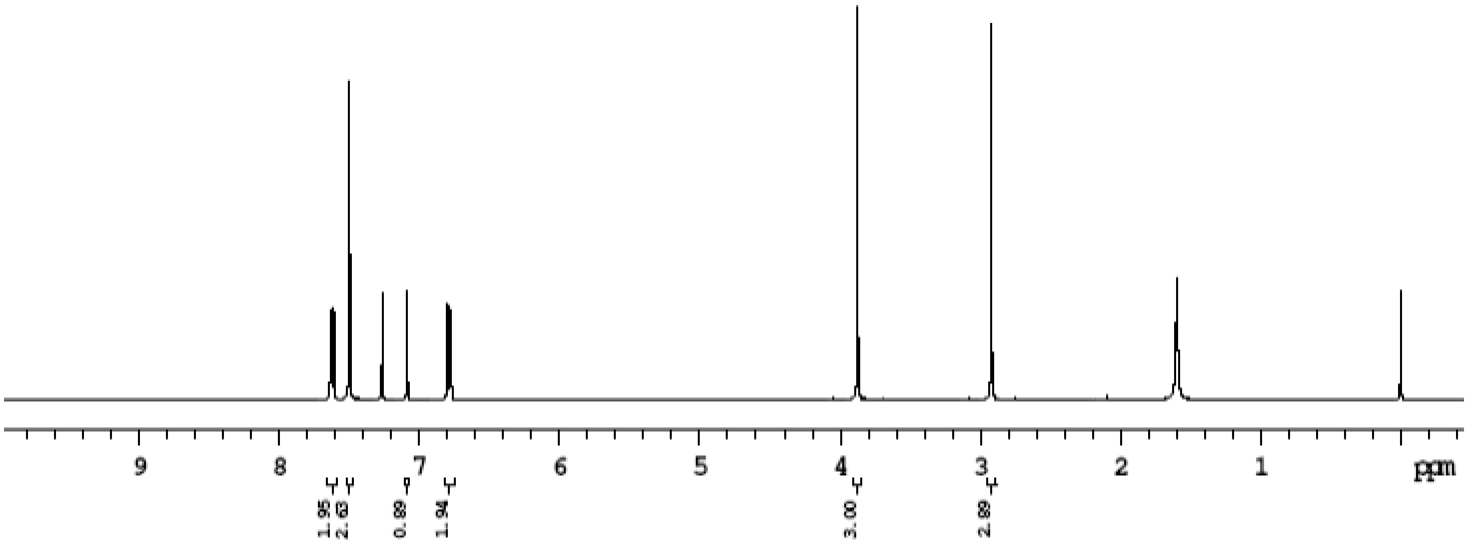

Normalised Transmittance
1.0
0.8
0.6
0.4
0.2
0.0
3x10³
10⁴
10⁵
2x10⁵
Fluence (J/m²)
5a
5b
5c
5d
5e

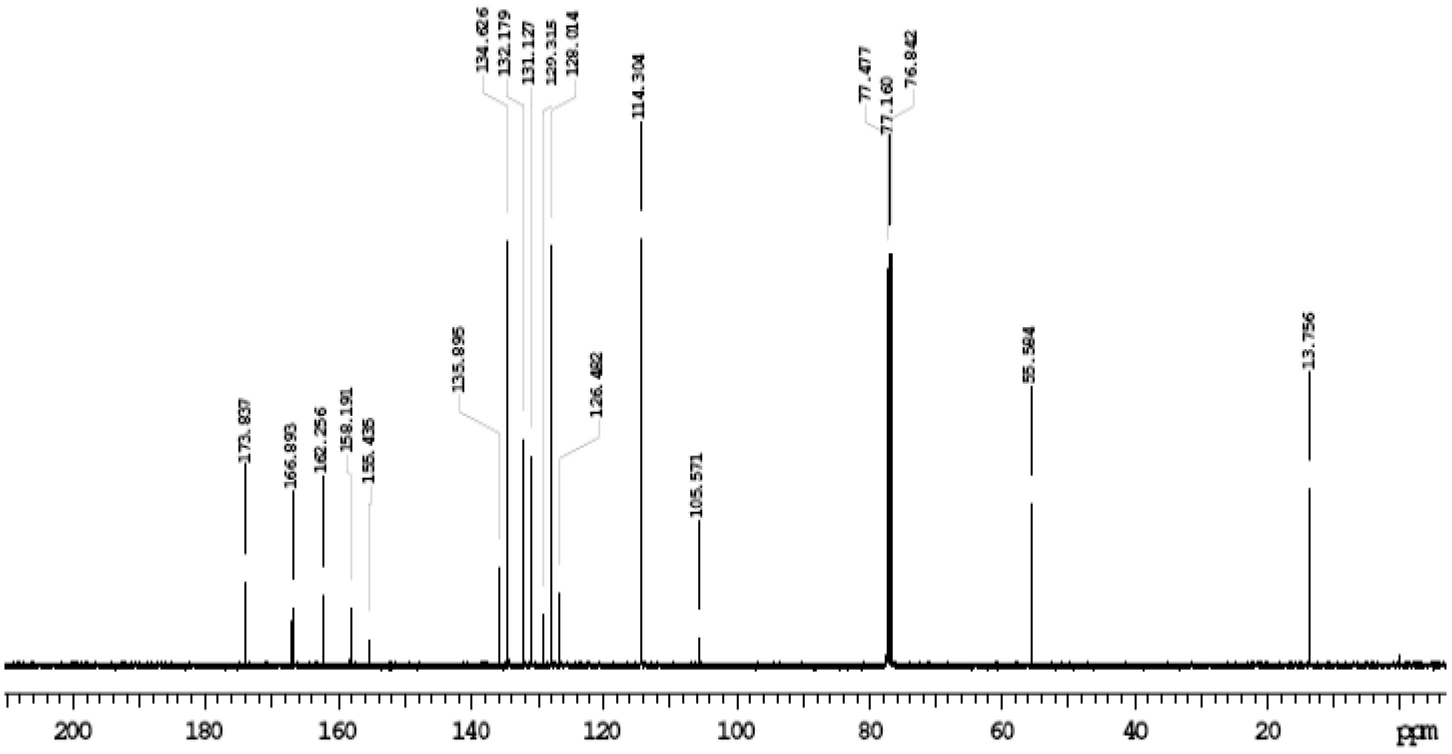
Fig. 5.



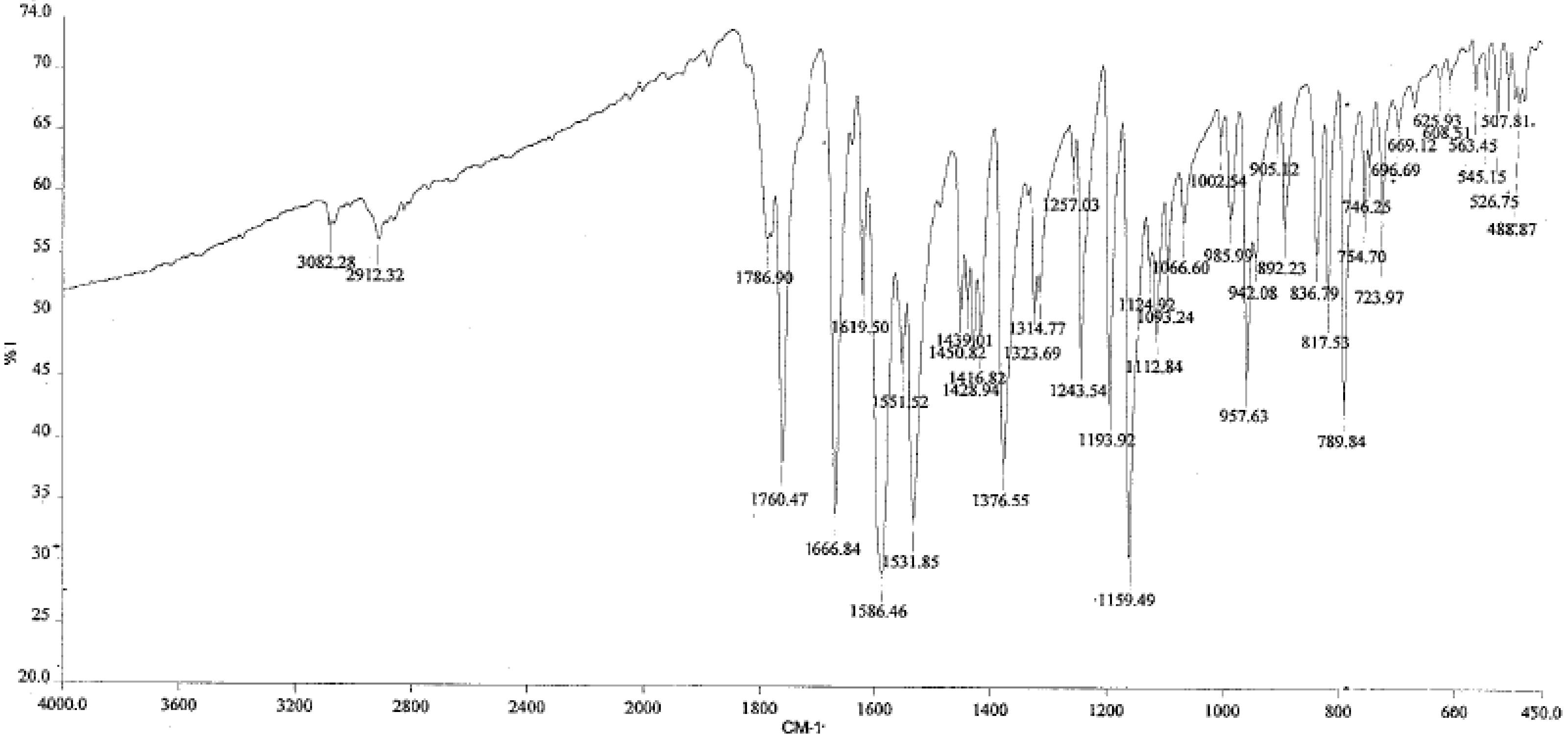
IR of 2-[5-(2,6-dichlorophenyl)-3-methyl-1,2-oxazol-4-yl[-4-(4-methoxyarylidene)1,3-oxazol-5-one ***(5c)***



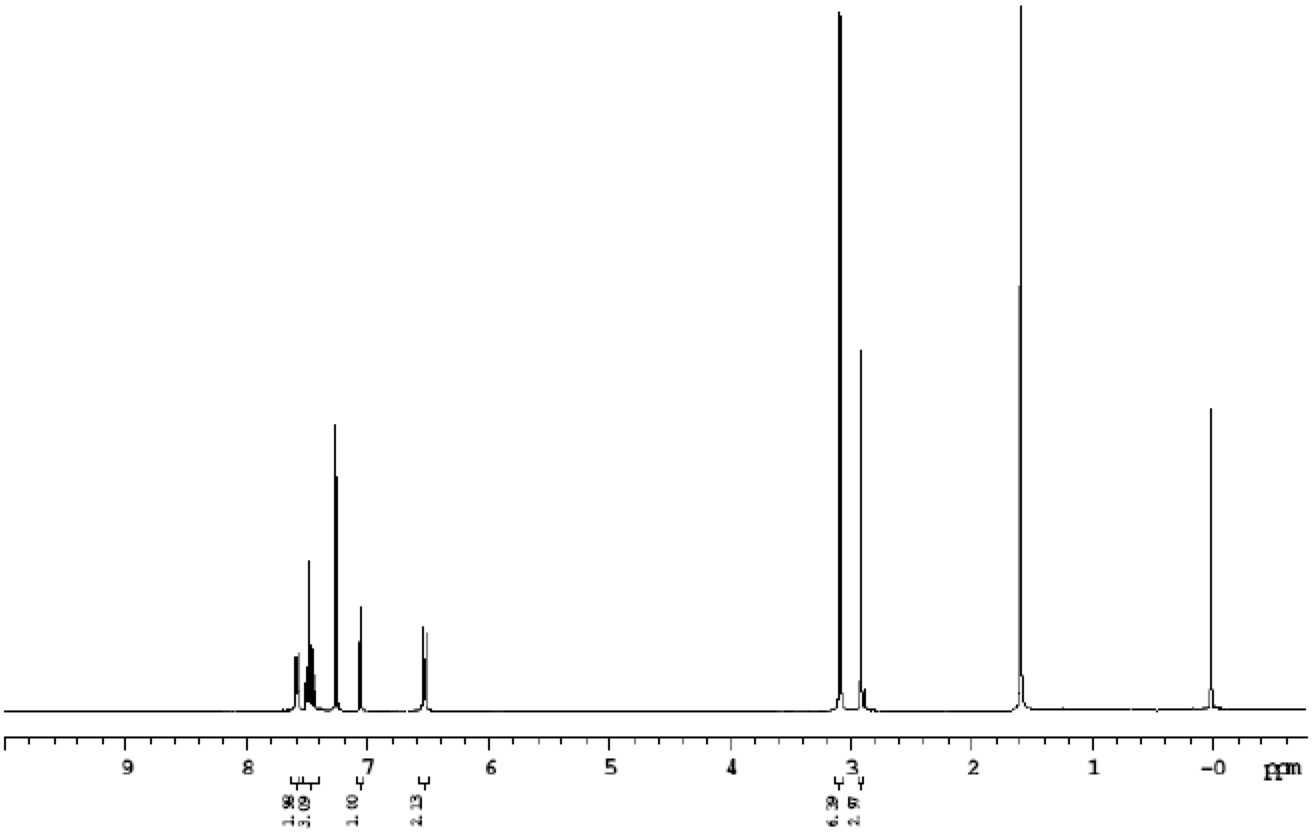
^{1}H NMR of 2-[5-(2,6-dichlorophenyl)-3-methyl-1,2-oxazol-4-yl[-4-(4-methoxyarylidene)1,3-oxazol-5-one ***(5c)***



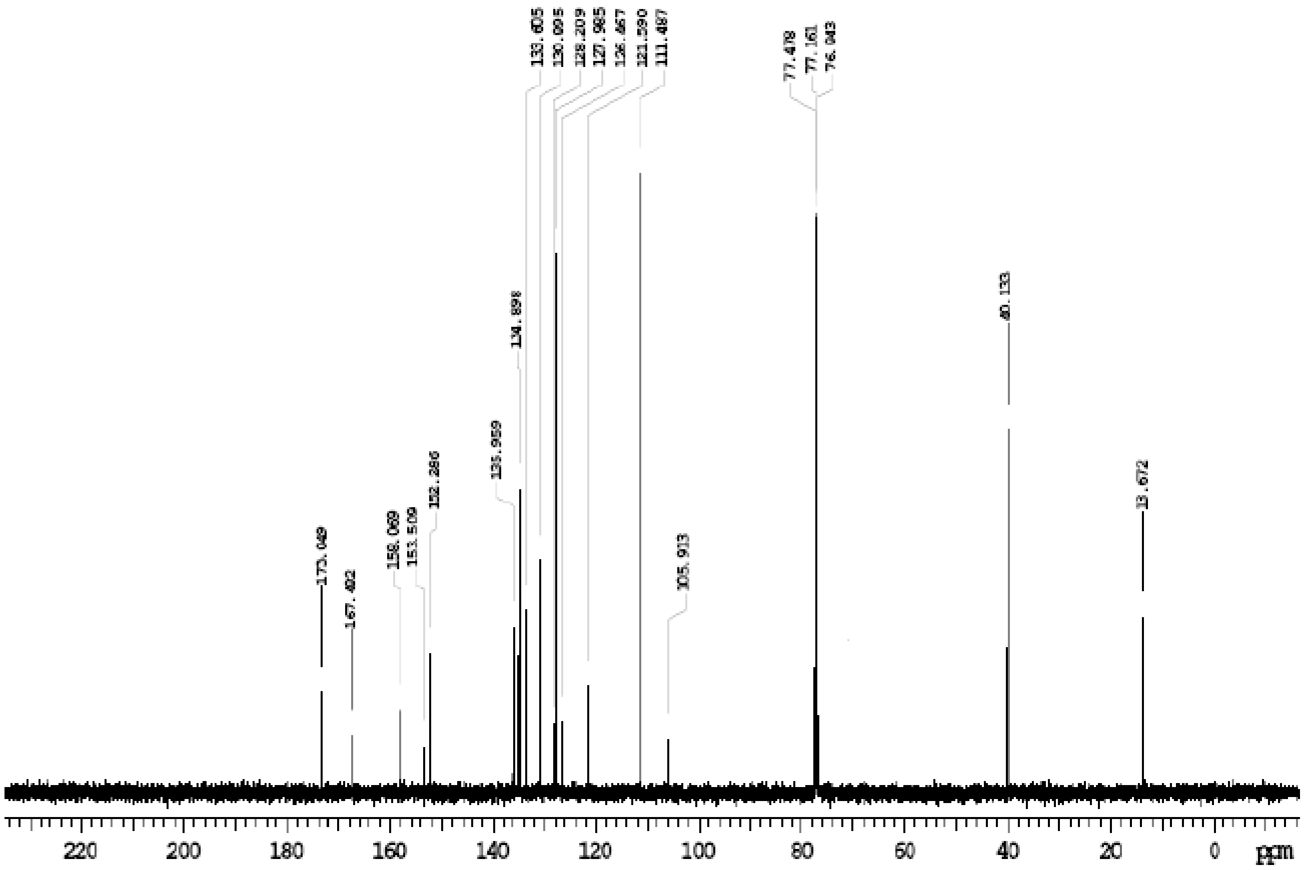
^{13}C NMR of 2-[5-(2,6-dichlorophenyl)-3-methyl-1,2-oxazol-4-yl[-4-(4-methoxyarylidene)1,3-oxazol-5-one ***(5c)***



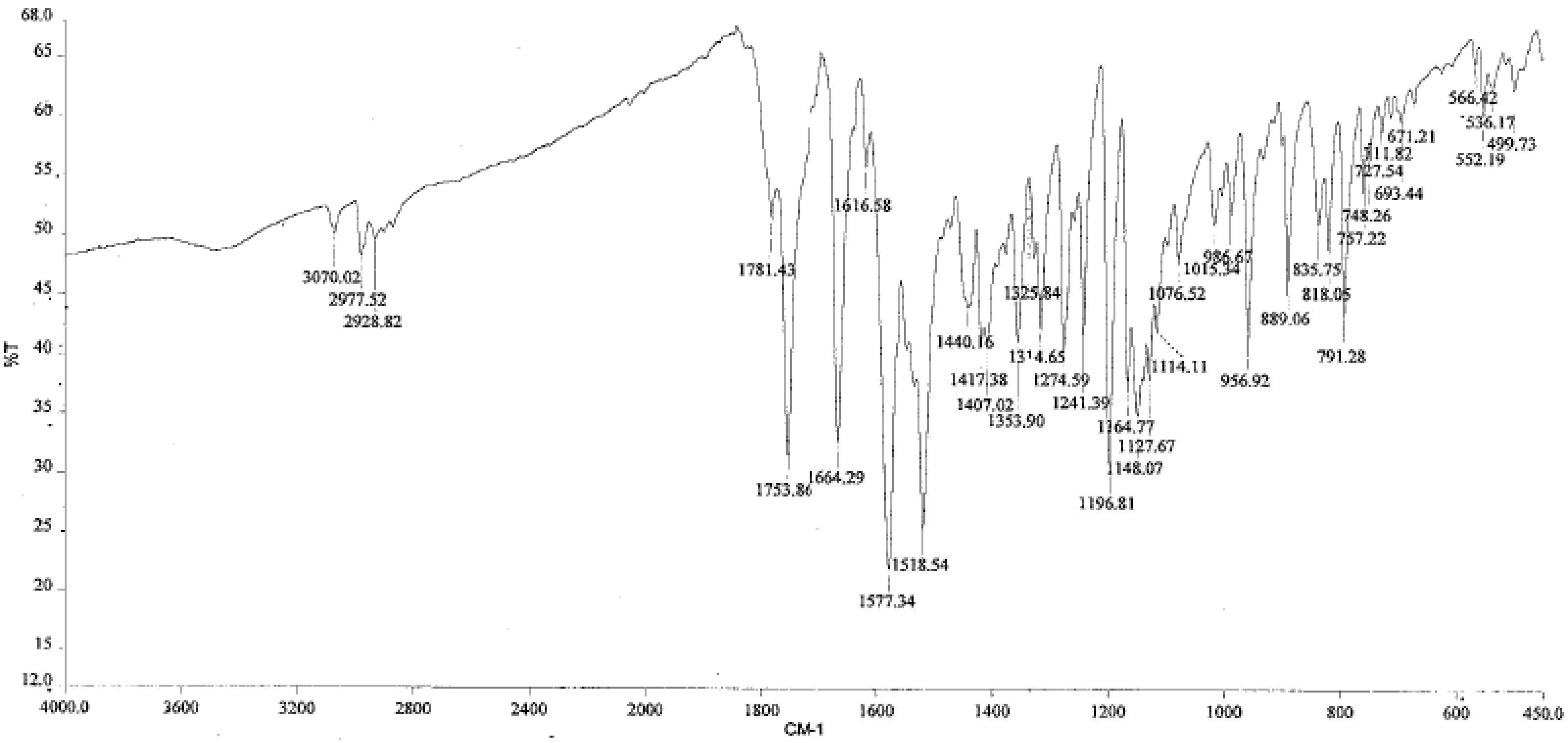
IR of 2-[5-(2,6-dichlorophenyl)-3-methyl-1,2-oxazol-4-yl[-4-(4-*N*,*N*-dimethylaminoarylidene)1,3-oxazol-5-one ***(5d)***



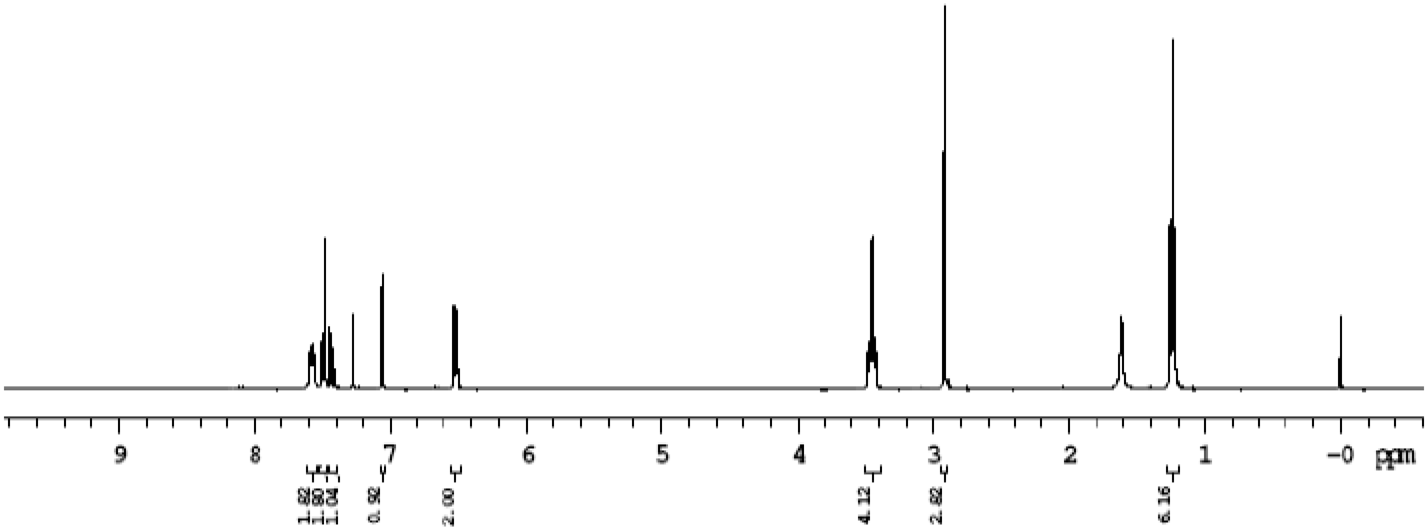
^{1}H NMR of 2-[5-(2,6-dichlorophenyl)-3-methyl-1,2-oxazol-4-yl[-4-(4-*N*,*N*-dimethylaminoarylidene)1,3-oxazol-5-one ***(5d)***



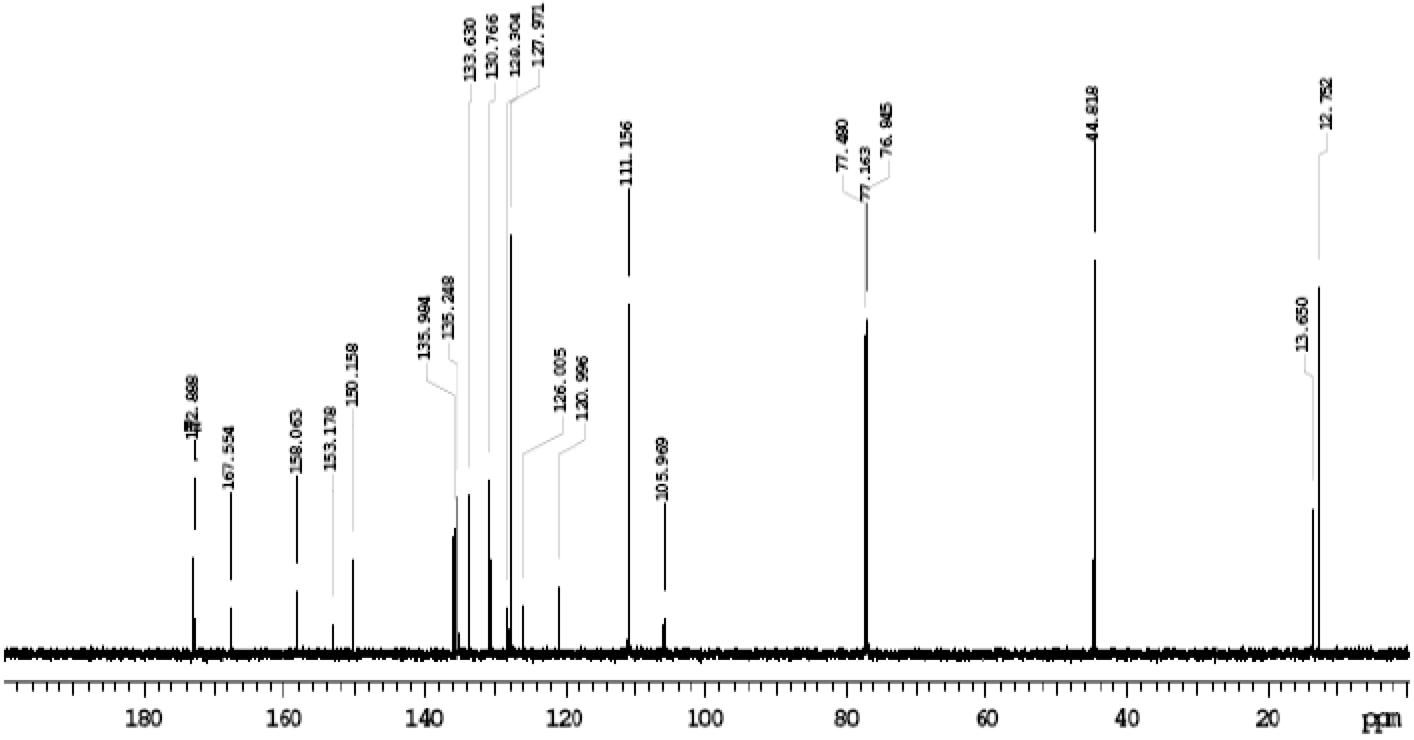
^{13}C NMR of 2-[5-(2,6-dichlorophenyl)-3-methyl-1,2-oxazol-4-yl[-4-(4-*N*,*N*-dimethylaminoarylidene)1,3-oxazol-5-one ***(5d)***



IR of 2-[5-(2,6-dichlorophenyl)-3-methyl-1,2-oxazol-4-yl[-4-(4-*N*,*N*-diethylaminoarylidene)1,3-oxazol-5-one ***(5e)***



^{1}H NMR of 2-[5-(2,6-dichlorophenyl)-3-methyl-1,2-oxazol-4-yl[-4-(4-*N*,*N*-diethylaminoarylidene)1,3-oxazol-5-one ***(5e)***



^{13}C NMR of 2-[5-(2,6-dichlorophenyl)-3-methyl-1,2-oxazol-4-yl[-4-(4-*N*,*N*-diethylaminoarylidene)1,3-oxazol-5-one ***(5e)***