

# Complexation of Disperse Dyes Derived from Thiophene with Cu, Co, Zn Metal and Their Application Properties on Polyester and Nylon 6.6 Fabrics

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**Abstract:** Ethyl-4-((4-chlorophenyl)carbamoyl)-2-((5-cyano-2-hydroxy-1,4-dimethyl-6-oxo-1,6-dihydro-pyridin-3-yl)diazanyl)-5-methylthiophene-3-carboxylate and ethyl-4-((4-chlorophenyl) carbamoyl)-2-((5-cyano-1-ethyl-2-hydroxy-4-methyl-6-oxo-1,6-dihydropyridin-3-yl)diazanyl)-5-methylthiophene-3-carboxylate disperse dyes were synthesised in this study by the coupling reaction of synthesised ethyl 2-amino-4-((4-chlorophenyl)carbamoyl)-5-methylthiophene-3-carboxylate with 6-hydroxy-1,4-dimethyl-2-oxo-1,2-dihydropyridine-3-carbonitrile and 1-ethyl-6-hydroxy-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile. Metal complexation of the synthesised disperse dyes with copper, cobalt and zinc metals were carried out. The structure of the synthesised intermediate, coupling components, dyes and their complexes were elucidated by analytical techniques such as proton nuclear magnetic resonance ( $^1\text{H}$  NMR), carbon 13 nuclear magnetic resonance ( $^{13}\text{C}$  NMR), mass spectrometry (MS), fourier transform infra-red (FTIR), ultraviolet-visible spectroscopy as well as the determination of their melting points. The molar extinction coefficient of the dyes and their complexes ranges from 24,800 – 83,200  $\text{Lmol}^{-1}\text{cm}^{-1}$ . The FTIR spectra of the synthesised dyes and their complexes showed the presence of cyano group in the range 2225 – 2229  $\text{cm}^{-1}$ , carbonyl group in the range 1640 – 1692  $\text{cm}^{-1}$ , hydroxyl group in the range 3310 – 3340  $\text{cm}^{-1}$ , azo group in the range 1398 – 1491  $\text{cm}^{-1}$ , stretching vibration of (N-H) in the range 3474 – 3478  $\text{cm}^{-1}$  and stretching vibration of aromatic (C-H) in the range 2882 – 2989  $\text{cm}^{-1}$ . The dyeing performance of the dyes and their metal complex analogous were assessed on polyester and nylon 6.6 fabrics. The dyes and their complexes were found have good levelness, excellent fastness to perspiration and sublimation, good to excellent wash fastness and light fastness on both polyester and nylon 6.6 fabrics with different shades of violet and brown.

**Keywords:** Disperse Dyes, Complexes, Polyester, Nylon 6.6, Fastness Properties

## 1. Introduction

Disperse azo dyes based on the 2-aminothiophene moieties are known to have excellent brightness of shade, they were established as a substitute to the more expensive anthraquinone dyes [1]. Outstanding works and contributions on aminothiophenes have been carried out by various researchers [2-4].

Disperse dyes are sparingly water soluble, nonionic dyes applied to hydrophobic fibres from aqueous dispersions [5-7].

Most heterocyclic dyes of technical interest for application to textiles are derived from diazo components consisting of five-membered rings containing one sulphur heteroatom and to which a diazotisable amino group is directly attached [8-10].

Description and investigation on the synthesis and application properties of monoazo and bis-heterocyclic monoazo dyes based on thiophene ring have been reported by different researchers however, there are few researches on their complexation with metals [11-13].

In this paper, we report the synthesis of azo disperse dyes

derived from ethyl 2-amino-4-[(4-chlorophenyl)carbamoyl]-5-methylthiophene-3-carboxylate and their complexation with Cu, Co, Zn metal. The application of the azo disperse dyes and their complexes on polyester fabrics and nylon 6.6 fabrics have also been evaluated.

## 2. Materials and Methods

### 2.1. Materials and Apparatus

The chemicals employed for the synthesis of the dyes and their complexes were sourced from Sigma Aldrich and British Drug House (BDH), no further purification was carried out. Gallenkamp melting point apparatus (CD10127) was used for the melting point determination, Agilent Technologies Cary 630 FTIR machine was employed for the determination of the infra-red spectra, the wavelength of maximum absorption of the dyes and their complexes were determined in acetone using Jenway 6405 UV-visible spectrophotometer, mass spectrometry was determined on Agilent Technologies 7890R GC system 5977A MSD,  $^1\text{H}$  and  $^{13}\text{C}$  NMR were carried out on Bruker AMX 300 MHz spectrometer and Microsal light fastness tester model no 225 and Blue wool standards were employed for the assessment of the light fastness.

### 2.2. Synthesis of Ethyl 2-Amino-4-[(4-Chlorophenyl)

Carbamoyl]-5-Methylthiophene-3-Carboxylate  
Aminothiophene Intermediate (1)

Ethylcyanoacetate (11.9 ml, 0.1 mol), sulphur (3.37 g, 0.1 mol), 4-chloroacetanilide, (17.84 g, 0.1 mol) were refluxed in ethanol (50 ml) with morpholine (9.1 g, 0.1 mol) for 2 hrs at 55-65°C. The resulting dark thick solution was cooled and stored overnight in a refrigerator, followed by filtration. Washing with a small amount of ethanol and ethanol/ water mixture was carried out followed by drying [11]. The product obtained was recrystallized from ethanol and the yield and melting point were determined.

### 2.3. Synthesis of 1-ethyl-6-hydroxy-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile Pyridone Coupling Component (2a)

A mixture of ethylcyanoacetate (28.2 cm<sup>3</sup>) and ethylamine (72 cm<sup>3</sup>) were stirred until a clear solution was obtained, this was followed by the addition of ethylacetoacetate (39.3 cm<sup>3</sup>). The mixture was refluxed at 110°C for 9 hours and the solution was diluted with water (400 cm<sup>3</sup>) and acidified with hydrochloric acid to give solid precipitate. This was filtered and washed with water and further recrystallized using ethanol.

### 2.4. Synthesis of 6-hydroxy-1,4-dimethyl-2-oxo-1,2-dihydropyridine-3-carbonitrile Pyridone Coupling Component (2b)

The procedure employed for 2a is similar to that employed

here. The difference is in the use of methylamine.

### 2.5. Procedure for Diazotisation

Dry sodium nitrite (1.38 g, 0.02 mol) was added in parts over a period of 30 minutes to 98% H<sub>2</sub>SO<sub>4</sub> (1.98 g, 0.02 mol) with stirring below 65°C. The resulting solution was then cooled to 5°C and a mixture of 20 cm<sup>3</sup> of propionic and acetic acid (3:17) was added dropwise with stirring, allowing the temperature to rise to 15°C. The resulting mixture was then cooled to 0°C, ethyl 2-amino-4-[(4-chlorophenyl)carbamoyl]-5-methylthiophene-3-carboxylate (0.02 mole) was added in portions, and stirring was continued at this temperature for 2 hrs. The excess nitrous acid (tested for by starch-iodide paper) was decomposed using 0.9 g of urea. The diazonium salt solution obtained was then used for the subsequent coupling reaction.

### 2.6. General Procedure for Coupling of the Diazotized Intermediate

0.02 mole of the various coupling components (1-ethyl-6-hydroxy-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile and 6-hydroxy-1,4-dimethyl-2-oxo-1,2-dihydropyridine-3-carbonitrile) were dissolved in 10% sodium hydroxide and cooled to 0°C with the addition of ice. The previously prepared diazonium salt solutions was added dropwise over 30 mins with stirring. The mixture was then stirred for a further 3 hours at 0-5°C, and the pH of the solution adjusted to 4 – 5 with the addition of dilute acetic acid before filtration and recrystallization from ethanol.

### 2.7. Synthesis of Metal Complexes

The metal chelate complexes were synthesised at pH=7.0 value in buffer solution (ammonium acetate) by dissolving 0.002 mole in 30 ml ethanol and then adding drop wise with stirring a stoichiometric amount of [M: 2L] mole ratio to (0.001 mol) of metal chloride, M=Co(III), Cu(II) and Zn(II).

The reaction mixture were refluxed for 30 min, until solid complexes were precipitated and covered with shiny stratum then left over night, then the solid chelate complexes were filtered off and washed with distilled water, until the solution become colourless [14].

## 3. Results and Discussion

The preparation of the intermediates, dyes and their complexes were done according to Figure 1.

### 3.1. Ethyl 2-Amino-4-[(4-Chlorophenyl)Carbamoyl]-5-Methylthiophene-3-Carboxylate Aminothiophene Intermediate (1)

White powder, 91% yield, melting point 175 – 177°C,  $^1\text{H}$  NMR in (DMSO-d<sub>6</sub>), (ppm) 1.27 (3H, t, CH<sub>3</sub>), 2.49 (3H, s, CH<sub>3</sub>) thiophene, 3.34 (3H, s, CH<sub>3</sub>), 4.26 (2H, q, CH<sub>2</sub>), 7.36 (2H, d, ArCH), 7.66 (2H, d, ArCH), 7.77 (2H, NH<sub>2</sub>), 9.80 (1H, s, NH).  $^{13}\text{C}$  NMR in (DMSO-d<sub>6</sub>), (ppm) 14.27-16.53 (CH<sub>3</sub>) thiophene, 39.50 (CHN) Benzene, 59.30 (CH<sub>2</sub>), 105.53

(-COO) thiophene, 112.47 (C,-CN) Benzene, 121.56-128.42 (ArCH), 138.10 (ArC-NH), 140.88 (Ar-C) thiophene, 161.44 (ArC-NH<sub>2</sub>), 164.90 (CO ester), 165.19 (CO amide). (m/z)-338; IR (v cm<sup>-1</sup>) 2941 (ArCH), 820 (ArCH bending), 2117

(R-N-C), 3478 (N-H str), 1506 (N-H bending), 682 (C-Cl), 1662 (C=O), 1461 (-S-C), 1625 (C=C), 3306 (-NH<sub>2</sub>), 1238 (C-N).

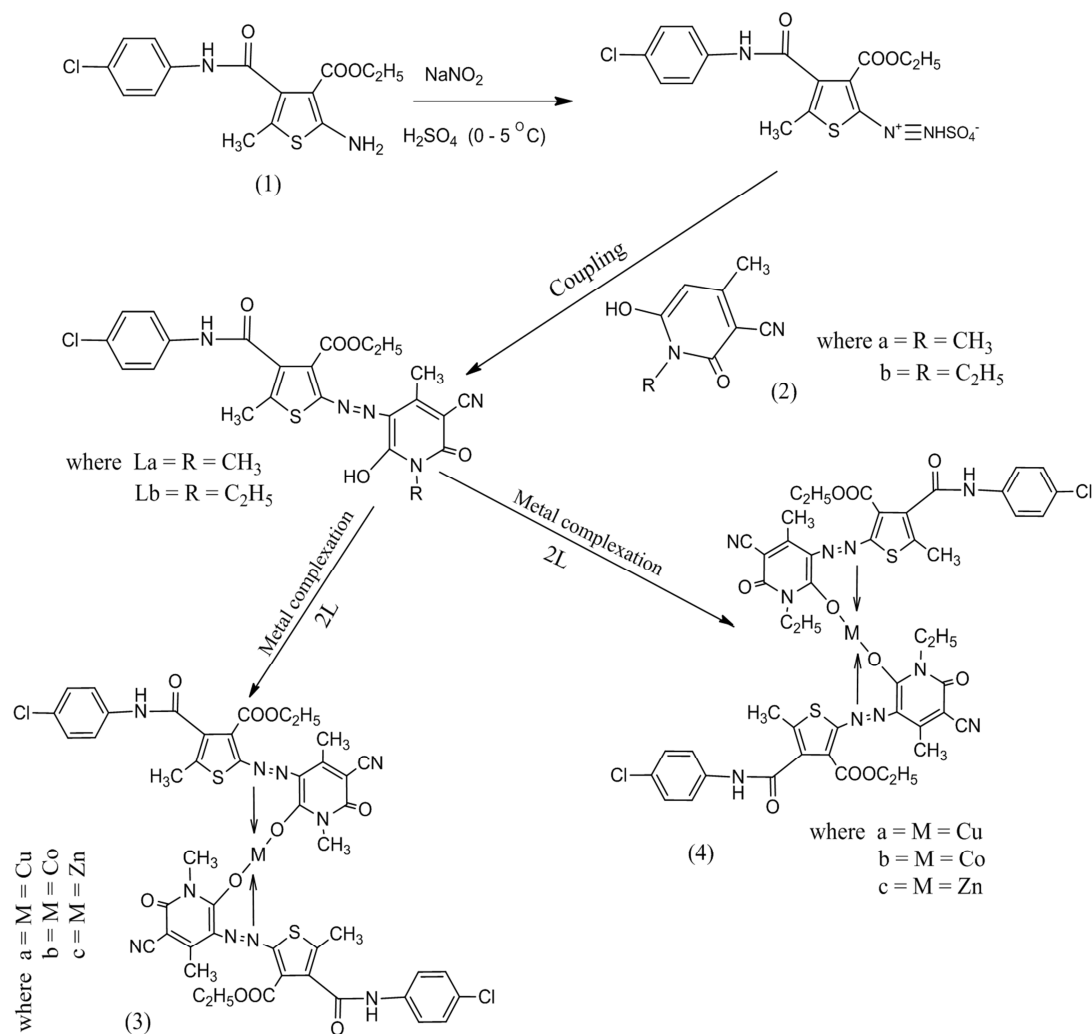


Figure 1. Synthesis of intermediate, dyes and their complexes.

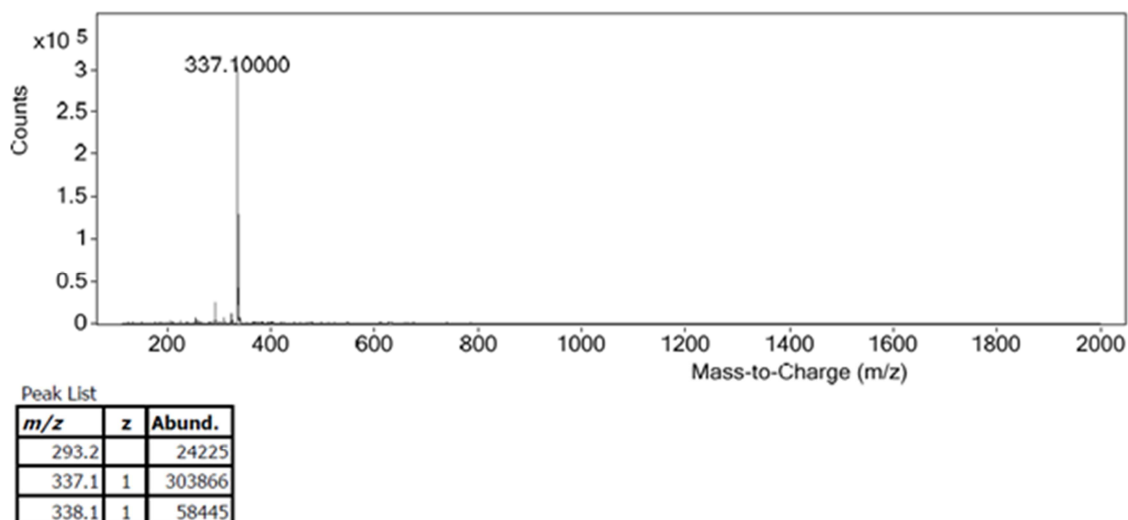


Figure 2. MS Spectrum of (1).

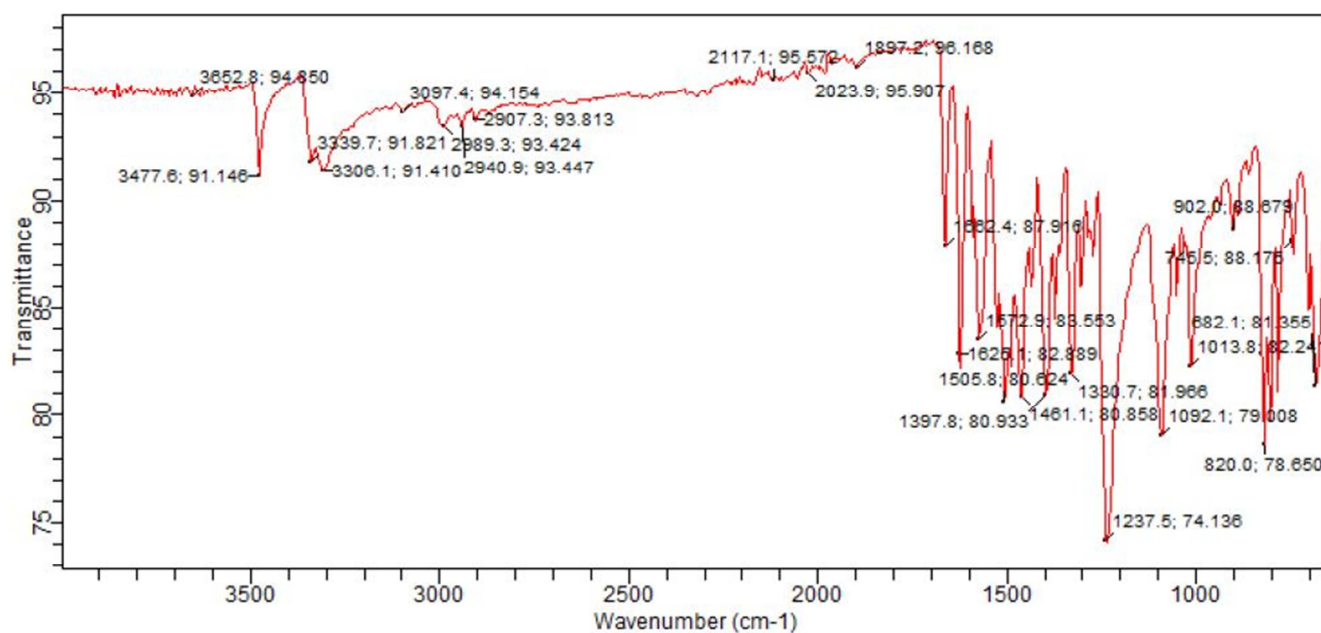


Figure 3. FTIR Spectrum (1).

### 3.2. 6-hydroxy-1,4-dimethyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (2a)

White crystalline powder, 94% yield, melting point 295 – 297°C,  $^1\text{H}$  NMR in (DMSO- $d_6$ ), (ppm) 2.20 (3H, s,  $\text{CH}_3$ ); 3.25 (3H, m,  $\text{CH}_3\text{-N}$ ); 5.62 (1H, s, ArCH); 12.08 (1H, b, Ar-

COH).  $^{13}\text{C}$  NMR in (DMSO- $d_6$ ), (ppm) 20.53-27.56 ( $\text{CH}_3$ ); 88.49 (Ar-C-CN); 91.86 (CH); 117.46 (-CN); 157.92 (Ar-C-); 160.46 (COH); 160.638 (CO). (m/z)-164; IR ( $\nu\text{ cm}^{-1}$ ) 2963 (OH); 828 (ArCH bending); 2214 (CN); 1633 (C=O); 1536 (C=C); 1256 (C-N).

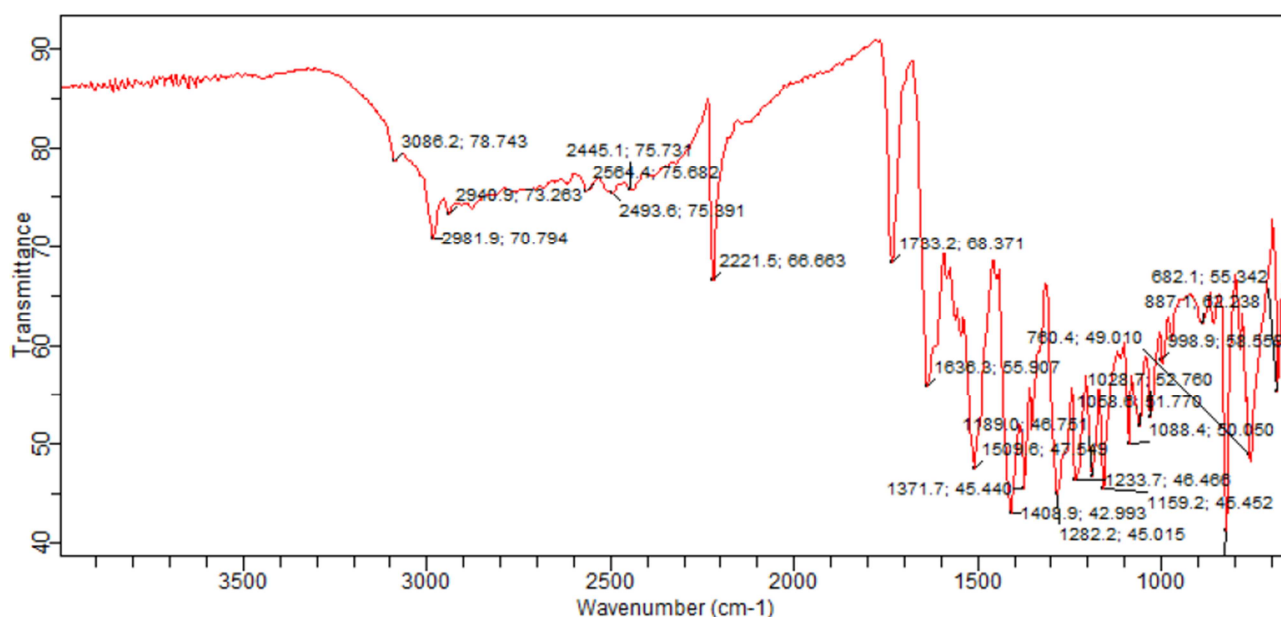


Figure 4. FTIR Spectrum (2a).

### 3.3. 1-ethyl-6-hydroxy-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (2b)

White crystalline powder, 92% yield, melting point 251 – 253°C,  $^1\text{H}$  NMR in (DMSO- $d_6$ ), (ppm) 1.07-1.12 (3H, t,  $\text{CH}_3$ ); 2.19 (3H, m,  $\text{CH}_3$ ); 3.89-3.96 (2H, m,  $\text{CH}_2$ ); 5.61 (1H, s, ArCH) Benzene; 12.16 (1H, s, Ar-COH).  $^{13}\text{C}$  NMR in

(DMSO- $d_6$ ), (ppm) 12.99-20.54 ( $\text{CH}_3$ ); 39.23-40.34 ( $\text{CH}_2$ ); 88.86 (Ar-C-CN); 92.00 (C, C=COH); 117.44 (-CN); 158.16 (Ar-C-); 160.17 (C, COH); 160.25 (C=O). (m/z)-178; IR ( $\nu\text{ cm}^{-1}$ ) 2982 (OH); 887 (ArCH bending); 2222 (CN); 1733 (C=O); 1636 (C=C); 1282 (C-N).

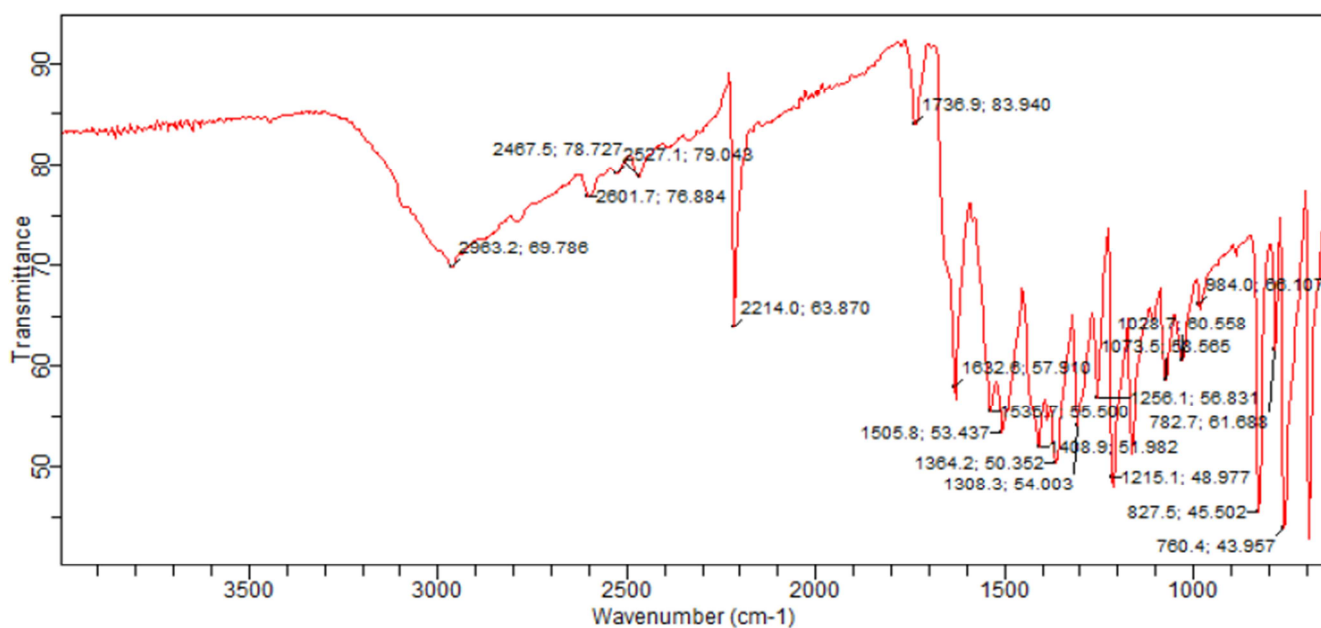
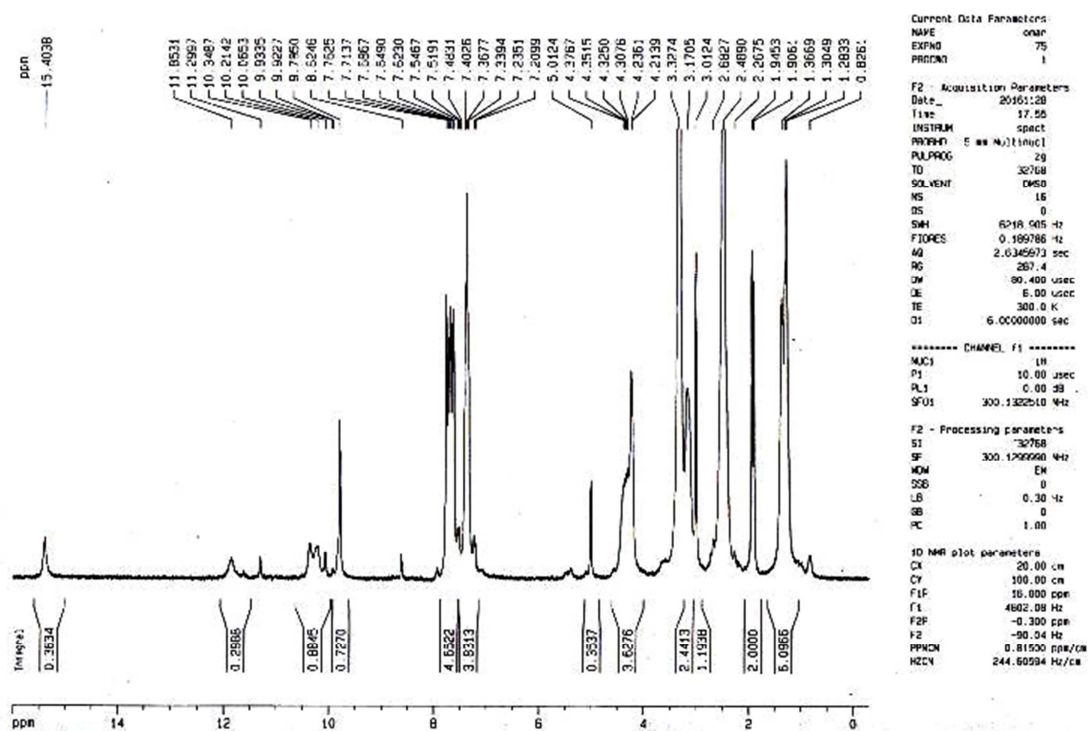


Figure 5. FTIR Spectrum (2b).

### 3.4. Ethyl 4-((4-chlorophenyl)carbamoyl)-2-((5-cyano-2-hydroxy-1,4-dimethyl-6-oxo-1,6-dihydropyridin-3-yl)diazenyl)-5-methylthiophene-3-carboxylate (La)

Red crystalline powder, 96% yield, melting point 273 – 275°C,  $^1\text{H}$  NMR in (DMSO- $d_6$ ), (ppm) 1.28-1.37 (3H, t,  $\text{CH}_3$ ), 1.91-1.95 (3H, d,  $\text{CH}_3$ ), 2.49 (3H, s,  $\text{CH}_3$ ), 3.34 (H, s,  $\text{CH}_3$ ), 4.21-4.38 (2H, m,  $\text{CH}_2$ ), 7.34-7.76 (4H, m, ArCH), 9.79 (H, s, NH), 11.30 (H, s, OH).  $^{13}\text{C}$  NMR in (DMSO- $d_6$ ), (ppm) 14.01-16.47 ( $\text{CH}_3$ ), 39.22 (C,  $\text{CH}_3\text{N}$ ), 59.27 ( $\text{CH}_2$ ),

105.49 (Ar-C-) thiophene, 112.42 (C-CN), 121.53-128.51 (Ar-C-) benzene, 138.06 (ArC-NH), 140.83 (Ar-C) thiophene, 161.38 ( $\text{CONH}_2\text{-C=O}$ ), 164.83-165.12 (Ar-C-OH). (m/z)-513; IR ( $\nu$   $\text{cm}^{-1}$ ) 2989 (ArCH); 861 (ArCH bending); 2225 (CN); 2110 (R-N-C); 3478 (N-H str); 1491 (N-H bending); 664 (C-Cl); 3653 (OH); 1692 (C=O); 1398 (-S-C); 1595 (C=C); 1245 (C-N); 1491 (N=N);  $\lambda_{\text{max}}$  (474.98 nm),  $-(8.32 \times 10^4 \text{ Lmol}^{-1}\text{cm}^{-1})$ .

Figure 6.  $^1\text{H}$  NMR Spectrum of (La).

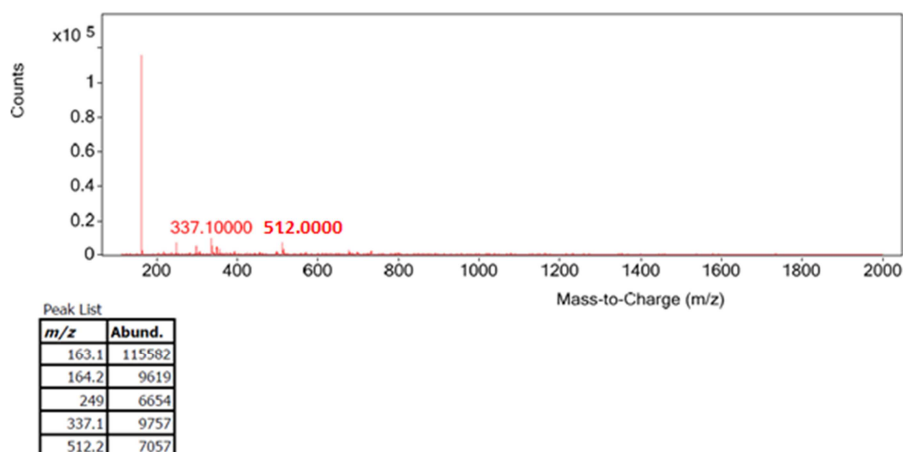


Figure 7. MS Spectrum of (La).

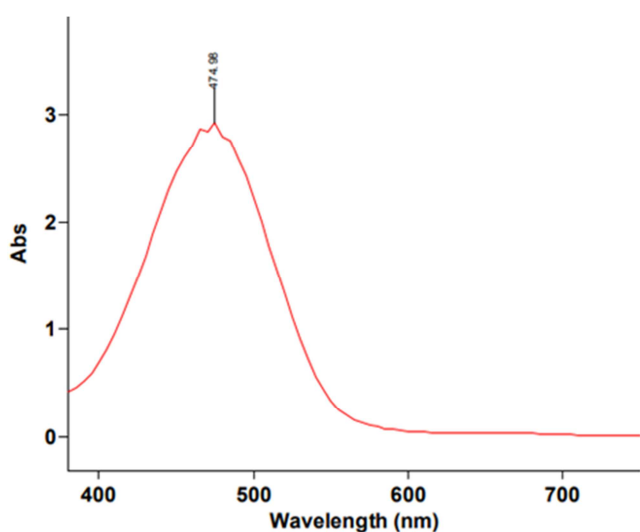
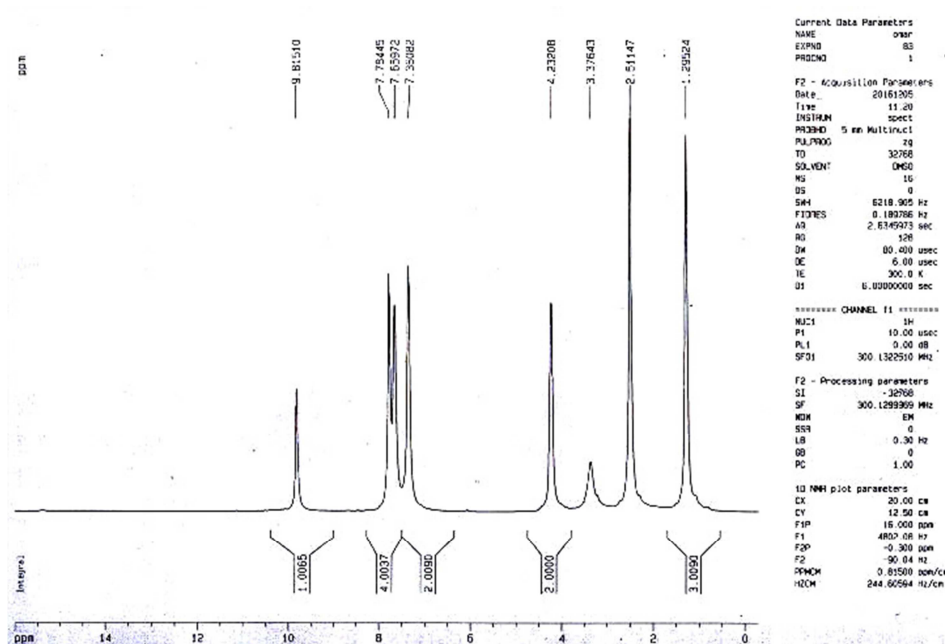


Figure 8. UV Spectrum of (La).

### 3.4.1. Bis((3-((4-((4-chlorophenyl)carbamoyl)-3-(ethoxycarbonyl)-5-methylthiophen-2-yl)diazenyl)-5-cyano-1,4-dimethyl-6-oxo-1,6-dihydropyridin-2-yl)oxy)copper (3a)

Violet red powder, 73% yield, melting point 168 – 169°C, <sup>1</sup>H NMR in (DMSO-d<sub>6</sub>), (ppm) 1.29 (3H, s, CH<sub>3</sub>); 2.51 (3H, s, CH<sub>3</sub>); 3.38 (3H, s, CH<sub>3</sub>); 4.23 (2H, s, CH<sub>2</sub>); 7.36-7.78 (4H, m, ArCH); 9.82 (1H, s, NH). <sup>13</sup>C NMR in (DMSO-d<sub>6</sub>), (ppm) 14.14-16.40 (CH<sub>3</sub>); 38.96-40.02 (C, CH<sub>3</sub>-N); 59.17 (C, H<sub>2</sub>COO); 105.39 (Ar-C-) thiophene; 112.32 (C, -CN); 121.42-128.29 (Ar-C-); 137.97 (Ar-C-NH); 140.75 (Ar-C-) thiophene; 161.29 (CONH); 164.75-165.04 (C=O). IR (ν cm<sup>-1</sup>) 2989 (ArCH); 820 (ArCH bending); 2229 (CN); 2102 (R-N-C); 3478 (N-H str); 1491 (N-H bending); 682 (C-Cl); 3340 (OH); 1662 (C=O); 1238 (C-N); 1465 (N=N). λ<sub>max</sub> (475.00 nm), -(3.80 x 10<sup>4</sup> Lmol<sup>-1</sup>cm<sup>-1</sup>).

Figure 9. <sup>1</sup>H NMR Spectrum of (3a).



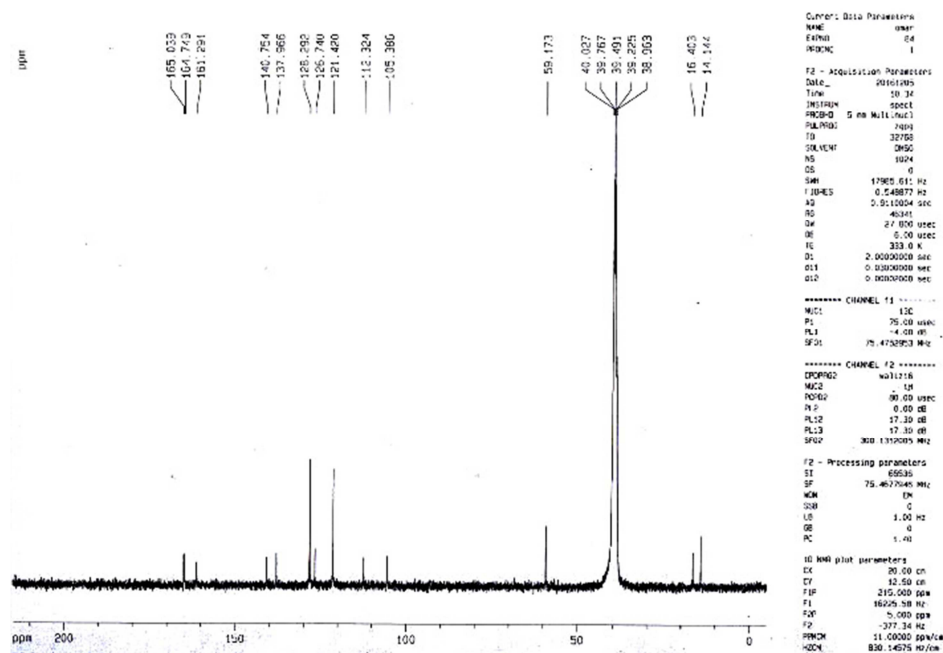


Figure 10.  $^{13}\text{C}$  NMR Spectrum of (3a).

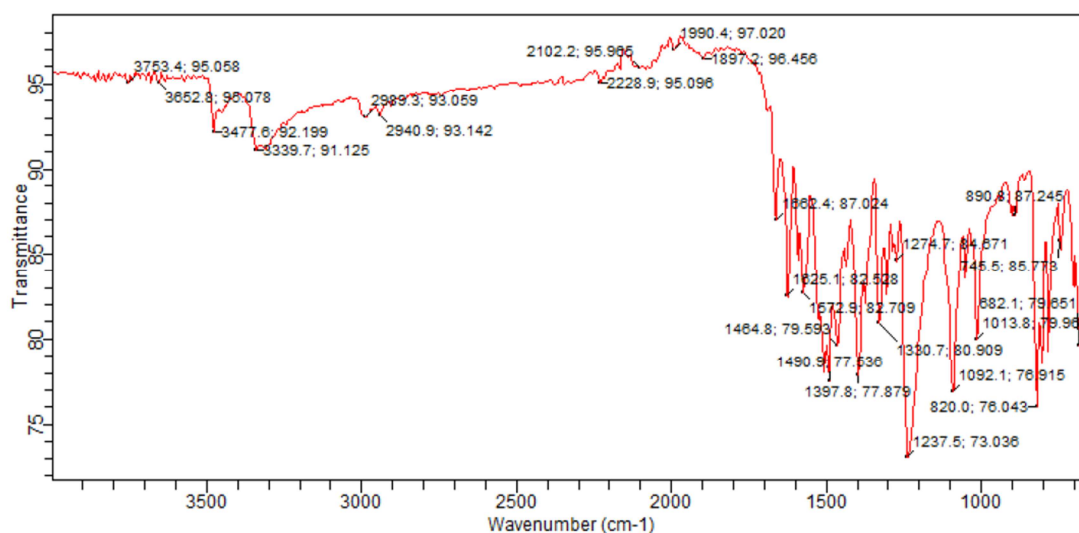


Figure 11. FTIR Spectrum of (3a).

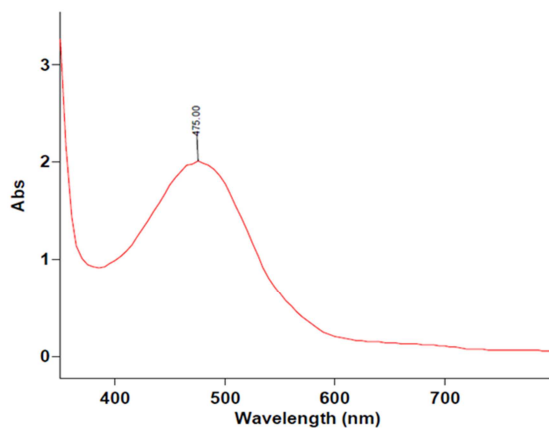
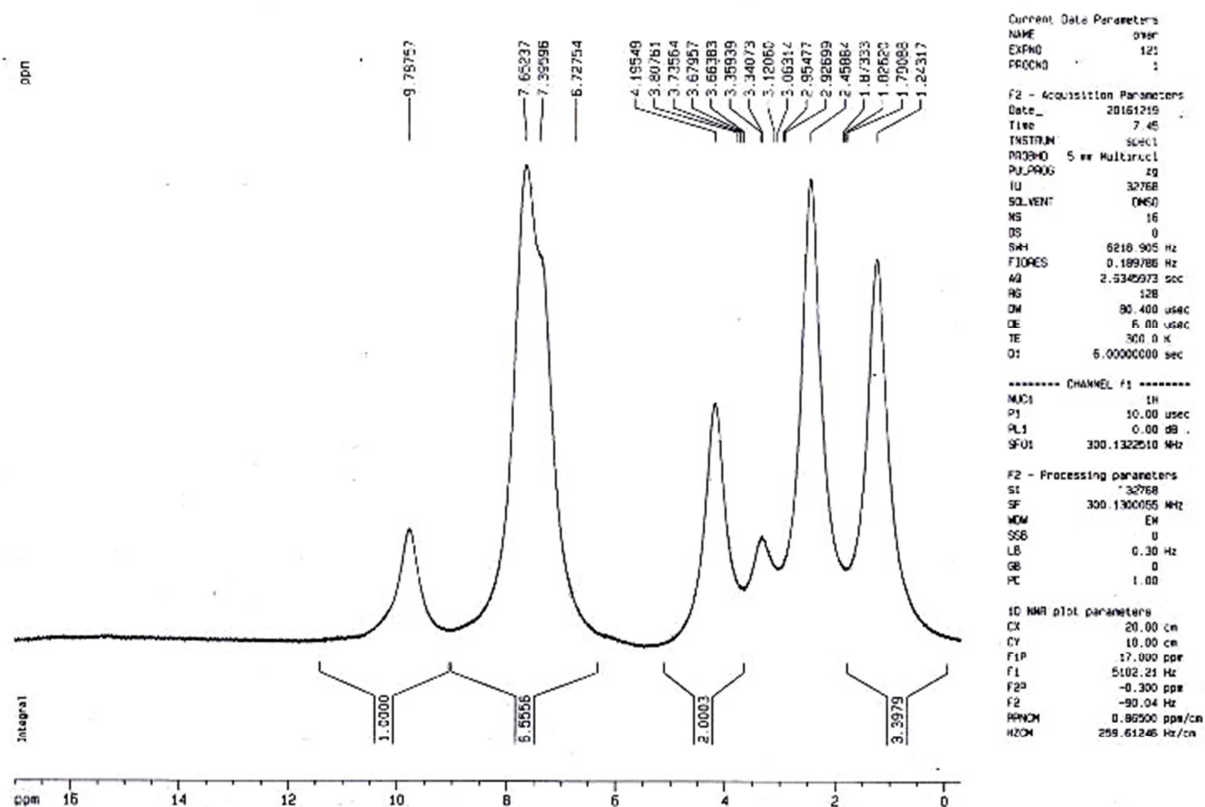
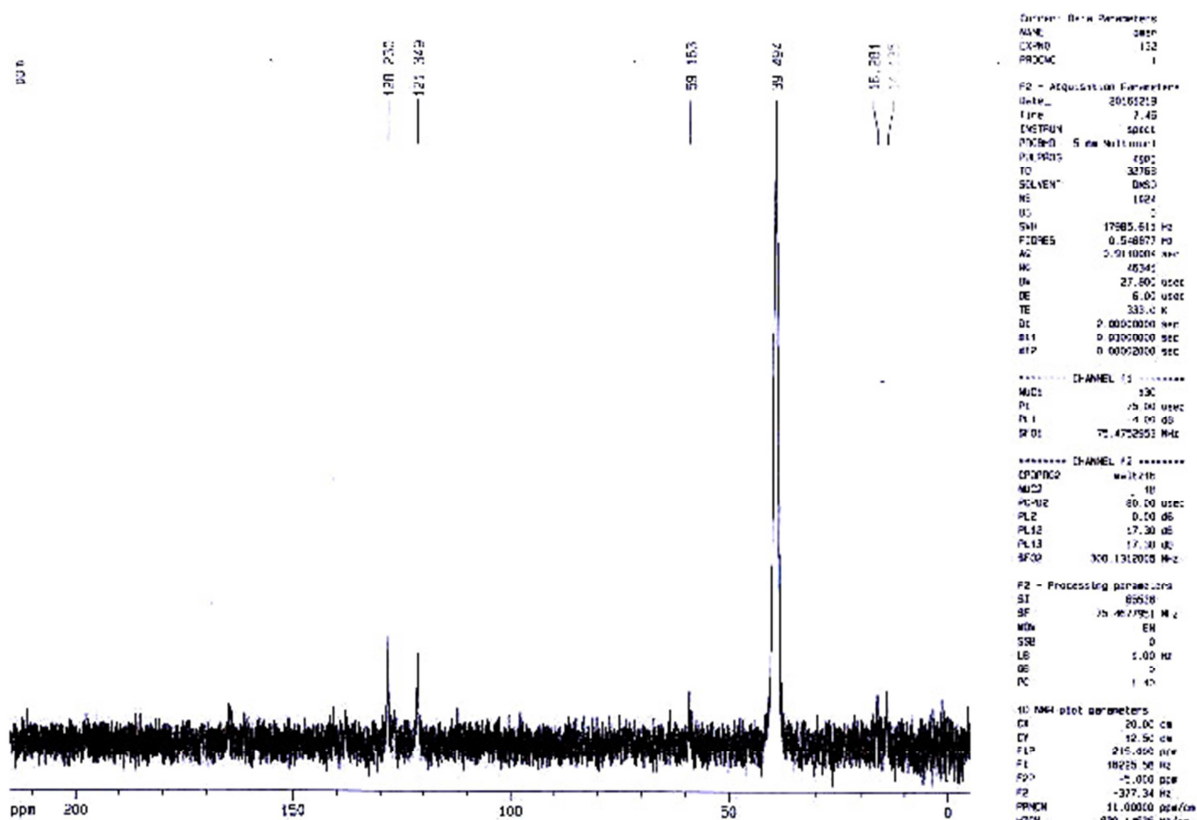


Figure 12. UV Spectrum of (3a).

### 3.4.2. Bis((3-((4-((4-chlorophenyl)carbamoyl)-3-(ethoxycarbonyl)-5-methylthiophen-2-yl)diazenyl)-5-cyano-1,4-dimethyl-6-oxo-1,6-dihydropyridin-2-yl)oxy)cobalt (3b)

Violet red powder, 70% yield, melting point 171 – 172°C,  $^1\text{H}$  NMR in ( $\text{DMSO}-d_6$ ), (ppm) 1.24 (3H, t,  $\text{CH}_3$ ); 2.46 (3H, s,  $\text{CH}_3$ ); 3.34 (3H, s,  $\text{CH}_3$ ); 3.81 (3H, s,  $\text{CH}_3$ ); 4.20 (2H, m,  $\text{CH}_2$ ); 7.39-7.65 (4H, m, ArCH); 9.79 (H, s, NH).  $^{13}\text{C}$  NMR in ( $\text{DMSO}-d_6$ ), (ppm) 14.14-16.28 ( $\text{CH}_3$ ); 39.49 (C,  $\text{CH}_3\text{-N}$ ); 59.16 (C,  $\text{H}_2\text{COO}$ ); 121.49-128.23 (Ar-C-). IR ( $\nu \text{ cm}^{-1}$ ) 2989 (ArCH); 820 (ArCH bending); 2229 (CN); 2102 (R-N-C); 3478 (N-H str); 1491 (N-H bending); 682 (C-Cl); 3340 (OH); 1662 ( $\text{C=O}$ ); 1238 (C-N); 1465 ( $\text{N=N}$ );  $\lambda_{\text{max}}$  (475.02 nm),  $-(1.88 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1})$ .

Figure 13.  $^1\text{H}$  NMR Spectrum of (3b).Figure 14.  $^{13}\text{C}$  NMR Spectrum of (3b).



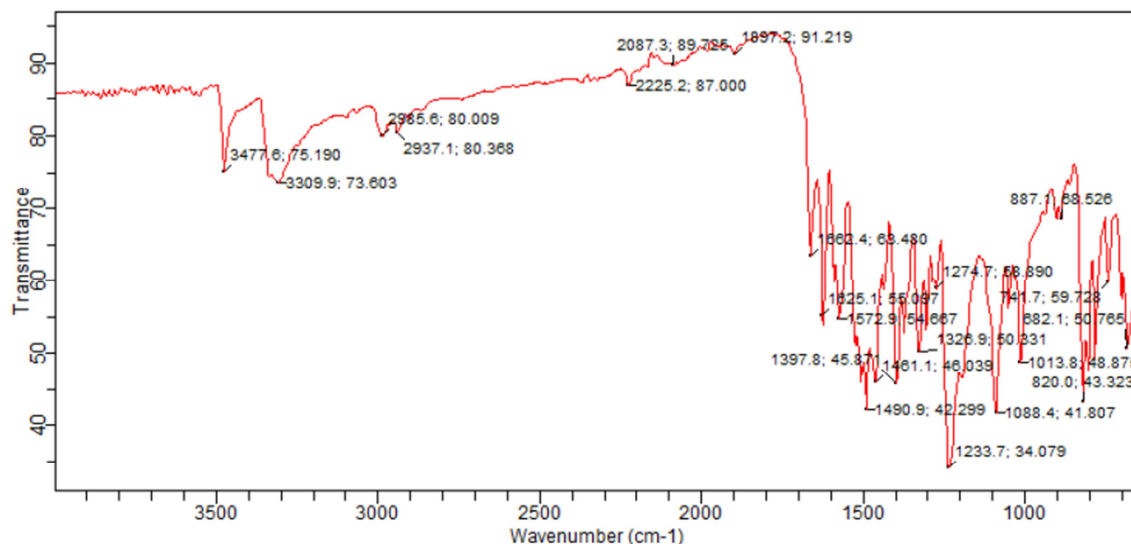


Figure 15. FTIR Spectrum of (3b).

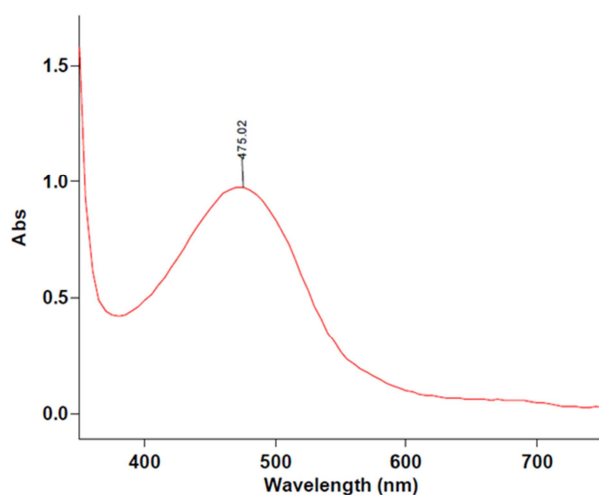


Figure 16. UV Spectrum of (3b).

### 3.4.3. Bis((3-((4-((4-chlorophenyl)carbamoyl)-3-(ethoxycarbonyl)-5-methylthiophen-2-yl)diazenyl)-5-cyano-1,4-dimethyl-6-oxo-1,6-dihydropyridin-2-yl)oxy)zinc (3c)

Red powder, 67% yield, melting point 265 – 267°C, <sup>1</sup>H NMR in (DMSO-d<sub>6</sub>), (ppm) 1.26-1.31 (3H, t, CH<sub>3</sub>); 2.49 (3H, s, CH<sub>3</sub>); 3.20 (3H, s, CH<sub>3</sub>); 3.34 (3H, s, CH<sub>3</sub>); 4.22-4.26 (2H, m, CH<sub>2</sub>); 7.34-7.78 (4H, m, ArCH); 9.81 (H, s, NH). <sup>13</sup>C NMR in (DMSO-d<sub>6</sub>), (ppm) 14.28-16.54 (CH<sub>3</sub>); 39.50-40.34 (C, CH<sub>3</sub>-N); 59.31 (C, H<sub>2</sub>COO); 105.49 (Ar-C-) thiophene; 112.43 (C-CN); 121.53-128.44 (Ar-C-); 138.09 (Ar-C-NH); 140.88 (Ar-C-) thiophene; 161.42 (CONH); 164.88-165.17 (C=O). IR (ν cm<sup>-1</sup>) 2989 (ArCH); 820 (ArCH bending); 2229 (CN); 2102 (R-N-C); 3478 (N-H str); 1491 (N-H bending); 682 (C-Cl); 3340 (OH); 1662 (C=O); 1238 (C-N); 1465 (N=N); λ<sub>max</sub> (473.00 nm), -(2.48 x 10<sup>4</sup> Lmol<sup>-1</sup>cm<sup>-1</sup>).

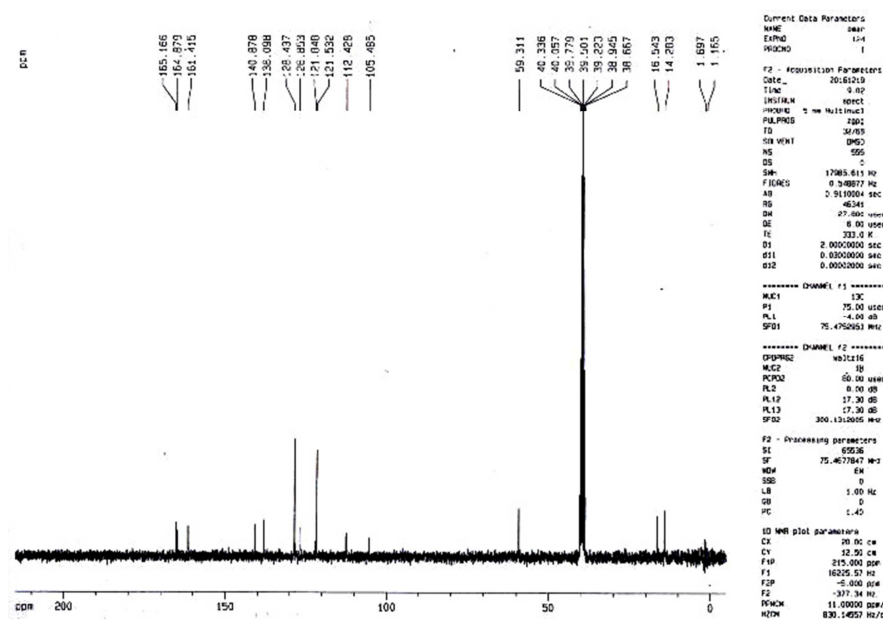


Figure 17. <sup>13</sup>C NMR Spectrum of (3c).

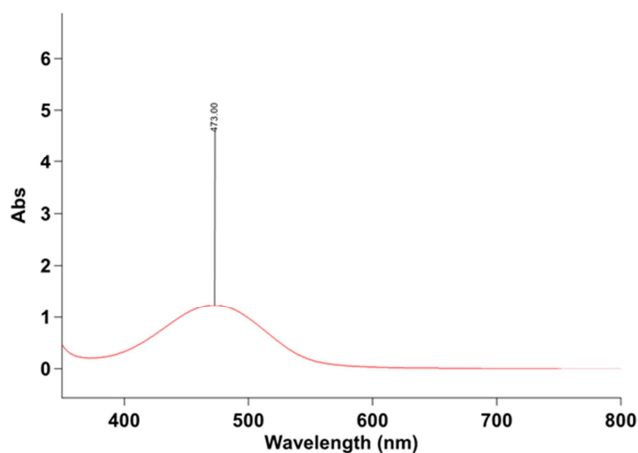


Figure 18. UV Spectrum of (3c).

### 3.5. Ethyl 4-((4-chlorophenyl)carbamoyl)-2-((5-cyano-1-ethyl-2-hydroxy-methyl-6-oxo-1,6-dihydropyridin-3-yl) diazenyl)-5-methylthiophene-3-carboxylate (Lb)

Red crystalline powder, 99% yield, melting point 253-255°C,  $^1\text{H}$  NMR in (DMSO- $d_6$ ), (ppm) 1.29-1.38 (3H, t,  $\text{CH}_3$ ); 1.91 (3H, s,  $\text{CH}_3$ ); 2.49 (3H, s,  $\text{CH}_3$ ) thiophene; 3.34 (2H, s,  $\text{CH}_2\text{N}$ ); 4.22-4.38 (2H, m,  $-\text{CH}_2-\text{O}$ ); 7.24-7.78 (4H, m, ArCH); 9.81 (H, s, NH); 11.32 (H, s, OH).  $^{13}\text{C}$  NMR in (DMSO- $d_6$ ), (ppm) 14.32-16.59 ( $\text{CH}_3$ ); 39.78 ( $\text{CH}_2$ ); 59.35 ( $\text{CH}_2$  ester); 121.55-128.48 (Ar-C-); 138.13 (Ar-C-NH); 140.91 (Ar-C) thiophene; 161.45 ( $\text{CONH}_2-\text{C}=\text{O}$ ); 165.19 (Ar-C-OH). (m/z)-526; IR ( $\nu \text{ cm}^{-1}$ ) 2886 (ArCH); 883 (ArCH bending); 2229 (CN); 2110 (R-N-C); 3474 (N-H str); 1506 (N-H bending); 671 (C-Cl); 3280 (OH); 1689 ( $\text{C}=\text{O}$ ); 1424 ( $-\text{S}-\text{C}$ ); 1592 ( $\text{C}=\text{C}$ ); 1245 (C-N); 1424 (N=N);  $\lambda_{\text{max}}$  (470.00 nm),  $-(8.12 \times 10^4 \text{ Lmol}^{-1}\text{cm}^{-1})$ .

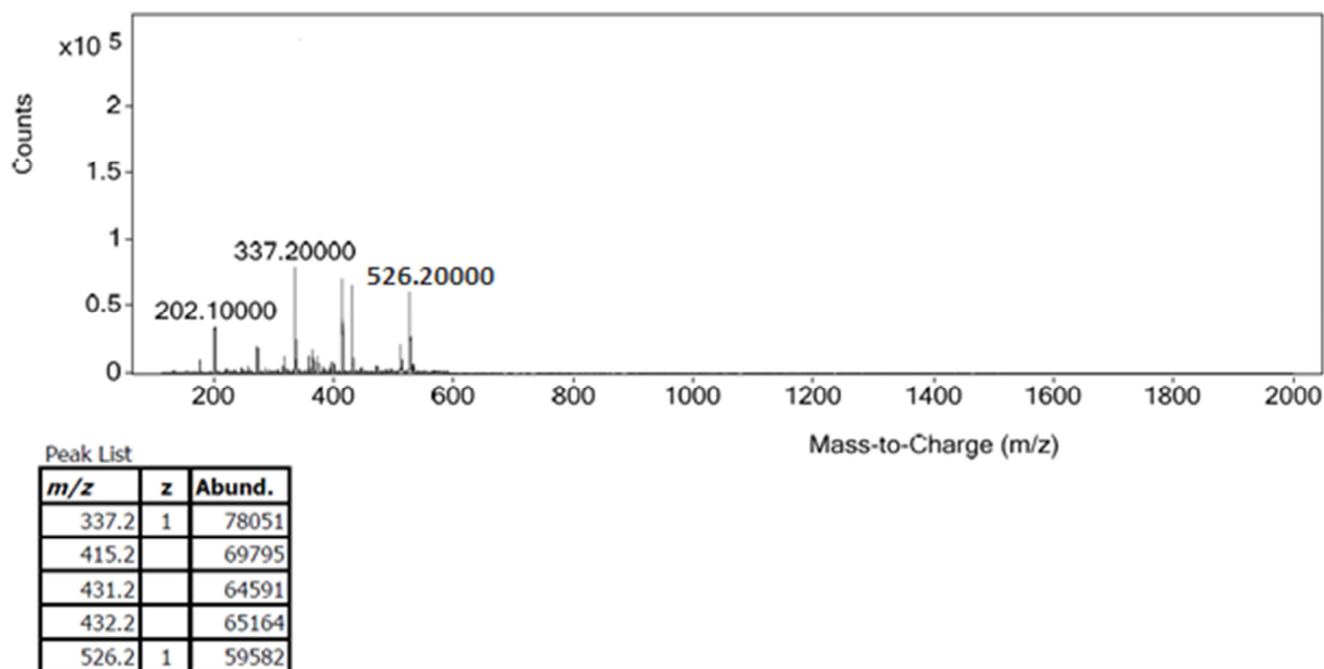


Figure 19. MS Spectrum of (Lb).

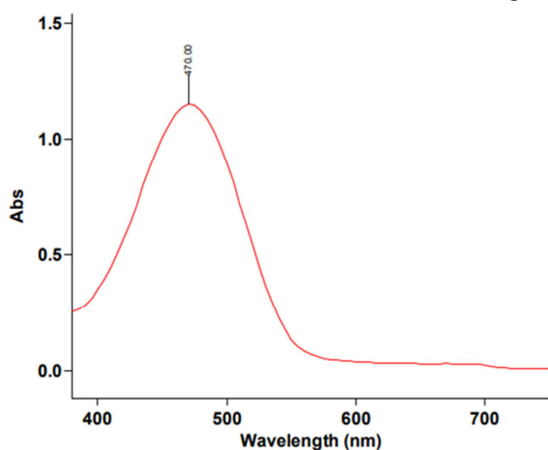


Figure 20. UV Spectrum of (Lb).

### 3.5.1. Bis((3-((4-((4-chlorophenyl)carbamoyl)-3-(ethoxycarbonyl)-5-methylthiophen-2-yl)diazanyl)-5-cyano-1-ethyl-4-methyl-6-oxo-1,6-dihydropyridin-2-yl)oxy)copper (4a)

Violet red powder, 69% yield, melting point 249 – 251°C,  $^1\text{H}$  NMR in (DMSO- $d_6$ ), (ppm) 1.27 (3H, s,  $\text{CH}_3$ ); 1.83 (3H, s,  $\text{CH}_3$ ); 2.49 (3H, s,  $\text{CH}_3$ ); 3.39 (H, s,  $\text{CH}_3$ ); 4.21 (2H, s,  $\text{CH}_2$ ); 7.35-7.67 (4H, d, ArCH); 10.14-10.58 (H, s, NH).  $^{13}\text{C}$  NMR in (DMSO- $d_6$ ), (ppm) 14.16 ( $\text{CH}_3$ ); 39.50 (C,  $\text{CH}_3-\text{N}$ ); 59.18 (C,  $\text{H}_2\text{COO}$ ); 121.42-128.33 (Ar-C-); 137.86 (Ar-C-NH); 140.81 (Ar-C) thiophene; 161.308 ( $\text{CONH}_2-\text{C}=\text{O}$ ); 164.70-165.07 (C,  $\text{C}=\text{O}$ ). IR ( $\nu \text{ cm}^{-1}$ ) 2882 (ArCH); 876 (ArCH bending); 2229 (CN); 2110 (R-N-C); 3478 (N-H str); 1491 (N-H bending); 686 (C-Cl); 3310 (OH); 1640 ( $\text{C}=\text{O}$ ); 1238 (C-N); 1398 (N=N).  $\lambda_{\text{max}}$  (469.99 nm),  $-(5.23 \times 10^4 \text{ Lmol}^{-1}\text{cm}^{-1})$ .

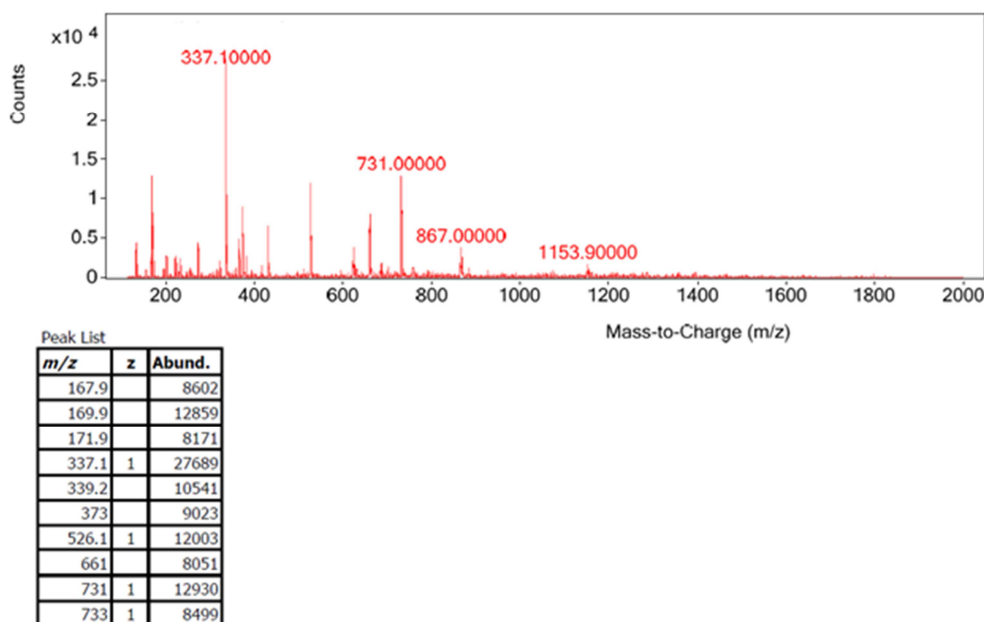


Figure 21. MS Spectrum of (4a).

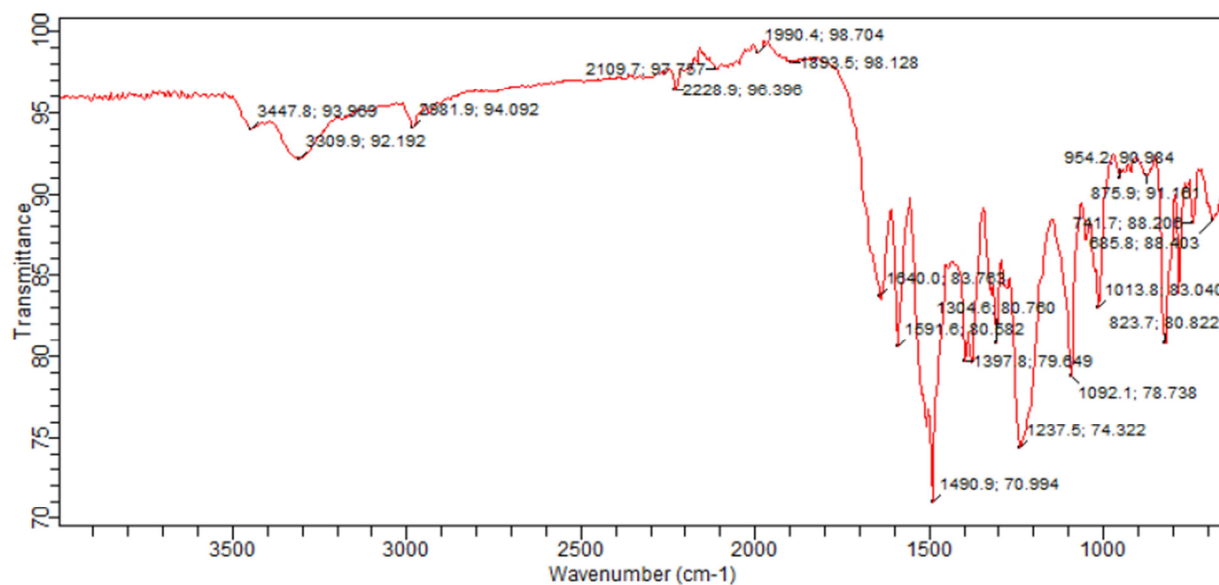


Figure 22. FTIR Spectrum of (4a).

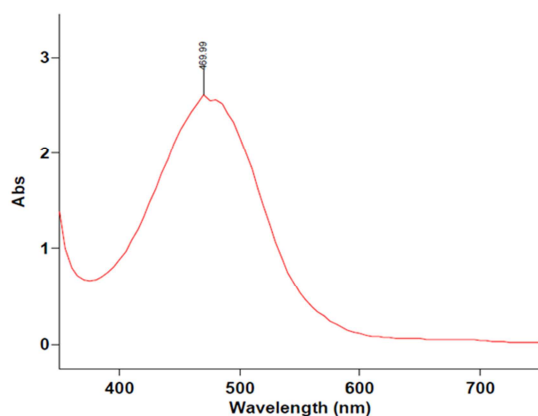


Figure 23. UV Spectrum of (4a).

### 3.5.2. Bis((3-((4-(4-chlorophenyl)carbamoyl)-3-(ethoxycarbonyl)-5-methylthiophen-2-yl)diazanyl)-5-cyano-1-ethyl-4-methyl-6-oxo-1,6-dihydropyridin-2-yl)oxy)cobalt (4b)

Violet red powder, 63% yield, melting point 162 – 163°C, <sup>1</sup>H NMR in (DMSO-d<sub>6</sub>), (ppm) 1.28 (3H, s, CH<sub>3</sub>); 2.43 (3H, s, CH<sub>3</sub>); 3.38 (H, s, CH<sub>3</sub>); 7.50 (4H, d, ArCH); 9.81 (H, s, NH). <sup>13</sup>C NMR in (DMSO-d<sub>6</sub>), (ppm) 39.50 (C, CH<sub>3</sub>-N); 121.21-128.08 (Ar-C-). IR (ν cm<sup>-1</sup>) 2886 (ArCH); 880 (ArCH bending); 2225 (CN); 2113 (R-N-C); 3478 (N-H str); 1525 (N-H bending); 682 (C-Cl); 3317 (OH); 1662 (C=O); 1238 (C-N); 1398 (N=N). λ<sub>max</sub> (485.02 nm), -(4.78 × 10<sup>4</sup> Lmol<sup>-1</sup>cm<sup>-1</sup>), (m/z)-274, 432, 526, 657, 684, 1125.

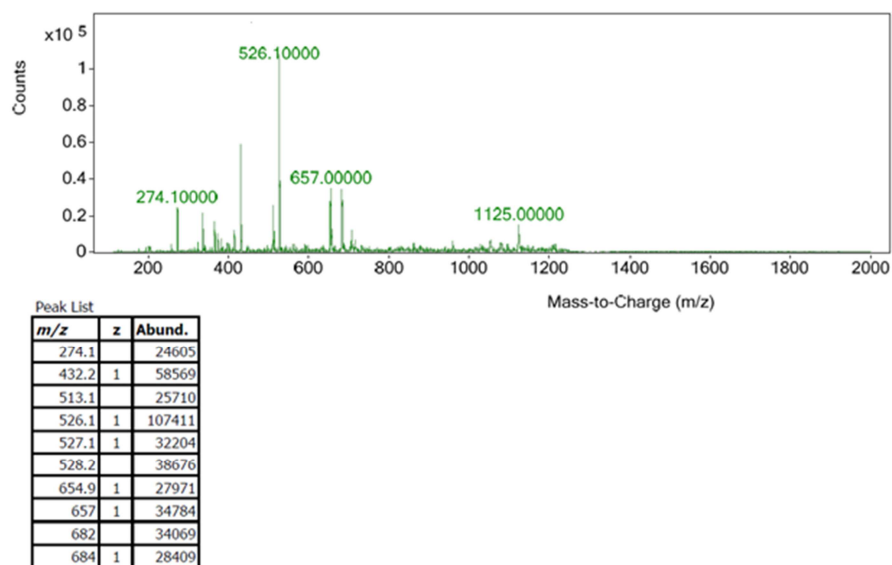


Figure 24. MS Spectrum of (4b).

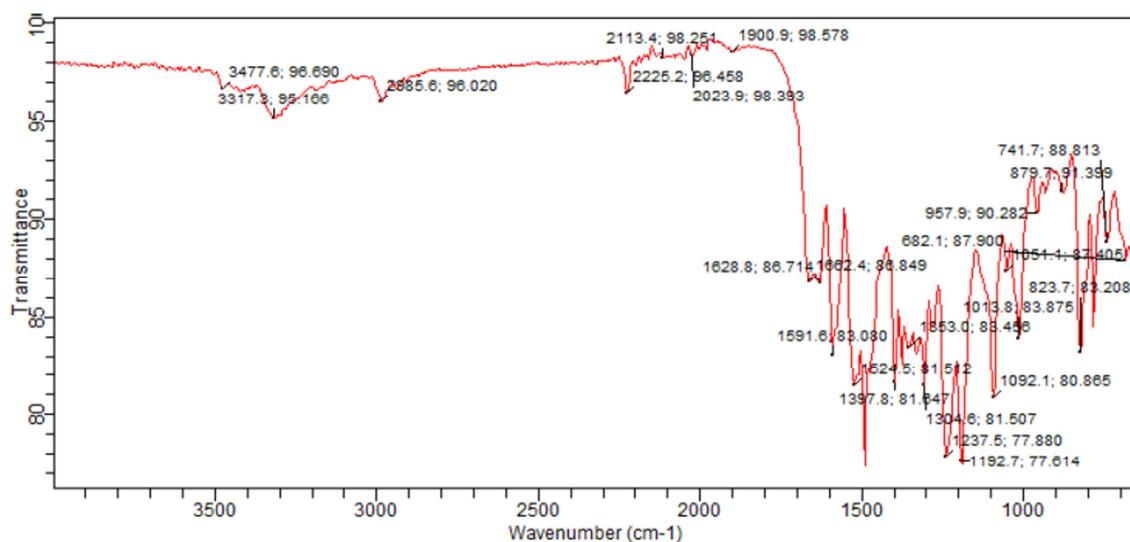


Figure 25. FTIR Spectrum of (4b).

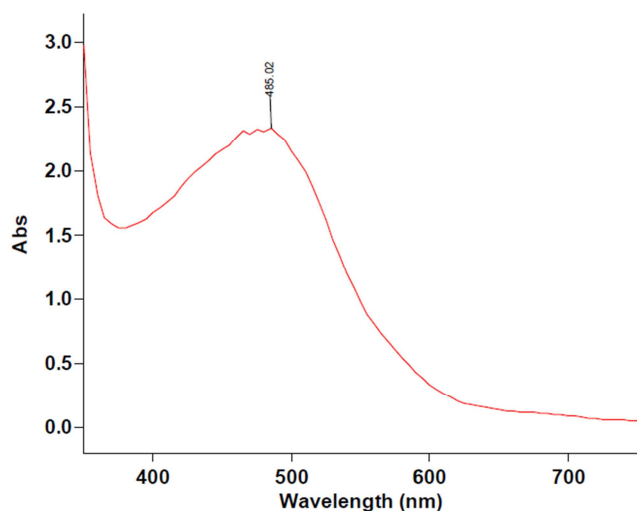


Figure 26. UV Spectrum of (4b).

### 3.5.3. Bis((3-((4-((4-chlorophenyl)carbamoyl)-3-(ethoxycarbonyl)-5-methylthiophen-2-yl)diazenyl)-5-cyano-1-ethyl-4-methyl-6-oxo-1,6-dihydropyridin-2-yl)oxy)zinc (4c)

Red powder, 61% yield, melting point 246 – 248°C.  $\lambda_{\text{max}}$  (469.00 nm),  $-(2.52 \times 10^4 \text{ Lmol}^{-1}\text{cm}^{-1})$ .

### 3.6. Dyeing Properties

The disperse dyes and the metal complexes were applied at 4% depth on polyester and 2% depth nylon 6.6 fabrics according to the standard method of dyeing polyester and nylon 6.6 [15] and their fastness properties also determined according to the procedure described by the American Association of Textile Chemists and Colourists (AATCC) standard methods [16]. Their dyeing properties are given in Tables 1 and 2. The dyes gave different shades of brown and violet red on the fabrics depending on the metal used for the

complexation of the dyes. They generally had good levelness, brightness and depth on the fabrics. The dyeings showed very good fastness to light, washing, perspiration and excellent

fastness to sublimation. A remarkable degree of levelness after washing indicates good penetration and affinity of these dyes to the fabrics.

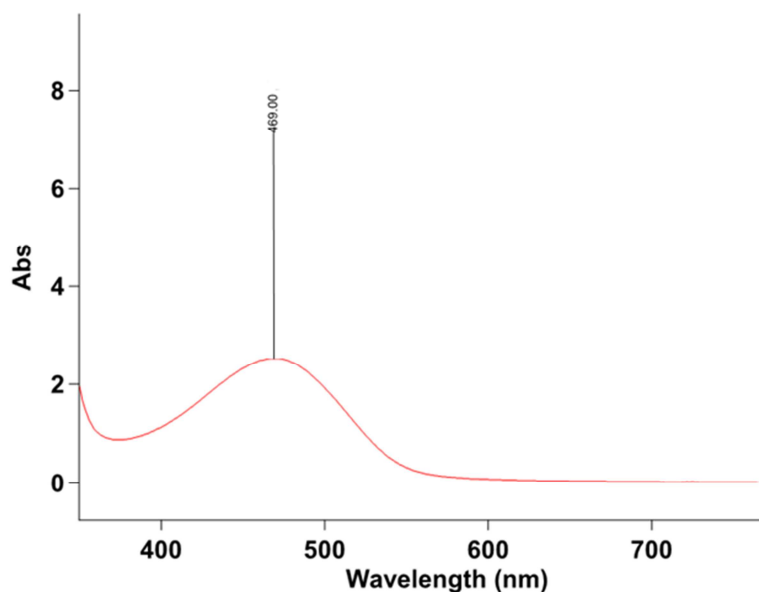


Figure 27. UV Spectrum of (4c).

Table 1. Dyeing Properties of the Synthesised Dyes and their complexes on Polyester Fabrics.

Dye/ Complex	Staining	Colour Fastness	Light	Perspiration	Sublimation
(La)	4	4/5	5	5	5
(Lb)	4	4/5	6	5	5
(3a)	4	4/5	8	5	5
(3b)	5	5	7	5	5
(3c)	4	4/5	7	5	5
(4a)	4	4/5	7	5	5
(4b)	5	5	5	5	5
(4c)	5	5	5	5	5

Table 2. Dyeing Properties of the Synthesised Dyes and their complexes on Nylon 6.6 Fabrics.

Dye/ Complex	Staining	Colour Fastness	Light	Perspiration	Sublimation
(La)	4	4/5	7	5	5
(Lb)	4	4	6	5	5
(3a)	4	4/5	6	5	4
(3b)	4	4/5	7	5	4
(3c)	4	4	7	5	5
(4a)	4	4/5	5	5	4
(4b)	4	4	7	5	5
(4c)	4	4	5	5	5

Table 3. Shade on Polyester and Nylon 6.6.

POLYESTER				
	(La)	(3a)	(3b)	(3c)
NYLON				
	(Lb)	(4a)	(4b)	(4c)
POLYESTER				
	(La)	(3a)	(3b)	(3c)
NYLON				
	(Lb)	(4a)	(4b)	(4c)

## 4. Conclusion

The intermediate, coupling components, dyes and their metal complexes synthesised in this work had good yields in the range of 63-99%. After application of the dyes and their complexes on polyester and nylon 6.6 fabrics, they were found to have very good (4) to excellent (5) fastness to perspiration and sublimation on nylon 6.6 while on polyester it had excellent (5) fastness to perspiration and sublimation on polyester which could be attributed to the crystalline structure of the polyester which disallowed the migration of dye out of the fabric when it has entered the fabric. Both polyester and nylon 6.6 were also found to have good to excellent light fastness and wash fastness. The dyes and the complexes obtained from the aminothiophene intermediate used for this research have practical viability for the colouration of most hydrophobic fibres due to the good application properties they exhibited.

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