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Synthesis and Characterization of Dissperse Dyes Derived from Methyl 2-amino-4-[(4-chlorophenyl)carbamoyl]-5-methylthiophene-3-carboxylate, their complexation with metal and Their Application Properties on Polyester and Nylon 6.6 fabrics

I. O. Abolude[1*], K. A. Bello[2], P. O. Nkeonye[3], A. Giwa[4],
[1*, 2, 3, 4] *Department of Polymer and Textile Engineering, Ahmadu Bello University, Zaria, Nigeria*
**Corresponding author: I. O. Abolude*

ABSTRACT
Methyl 2-amino-4-[(4-chlorophenyl)carbamoyl]-5-methylthiophene-3-carboxylate was coupled 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 for the syntheses of a series of monoazo disperse dyes. The dyes were further complexed with Cu, Co and Zn metals. Recrystallization method was employed for the purification of the synthesized diazo component and the dyes. Spectroscopic techniques such as UV-visible, FT-IR, NMR and MS were used for the elucidation of the structures of the diazo component, dyes and the metal complexes. The wavelength of maximum absorption and molar extinction co-efficient of the dyes and their metal complexes were assessed using acetone. The synthesised dyes and their metal complexes were applied on polyester and nylon 6.6 fabrics. The light, wash, perspiration and sublimation fastness properties were tested and found to be very good on both polyester and nylon 6.6.

KEYWORDS: *Aminothiophenes, Azo, Disperse dyes, Complexation, Metal, Fabrics, Fastness properties*

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I. INTRODUCTION

Azo disperse dyes represent the single largest chemical class of industrial colourants used for colouring hydrophobic fibres. Azo dyes are generally cost effective due to their simplicity of manufacture and their high tinctorial strength (Adedokun, 2011).

Heterocyclic based azo dyes have wide application for the dyeing of polyester fabrics due to their excellent fastness properties; they have also been utilized in non-textile applications such as photodynamic therapy, lasers, reprographic technology, functional dye applications and non-linear optical systems (Maradiya, 2010; Khalifa *et al.*, 2015).

The aim of the study was to synthesize novel monoazo disperse dyes derived from methyl 2-amino-4-[(4-chlorophenyl)carbamoyl]-5-methylthiophene-3-carboxylate using coupling components such as 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; complexation of the synthesized dyes with metals such as Cu, Co and Zn and the assessment of their fastness properties on polyester fabrics.

II. MATERIALS AND METHODS

All the chemicals used in the synthesis were of commercial grade and purchased from Sigma-Aldrich and British Drug House (BDH). Agilent Technologies Cary 630 FTIR machine, Jenway 6405 uv/vis spectrophotometer, Agilent Technologies 7890R GC system 5977A MSD, ^{1}H and ^{13}C NMR Bruker AMX 300 MHz spectrometer, Pro phenom X SEM machine, Gallenkamp melting point apparatus (CD10127) were used for the characterization of the compounds.

Synthesis of methyl 2-amino-4-[(4-chlorophenyl)carbamoyl]-5-methylthiophene-3-carboxylate Aminothiophene Intermediate (1)

Morpholine (9.0 g, 0.1 mol) was added to a mixture of 4-chloroacetanilide (21.17 g, 0.1 mol), methylcyanoacetate (10.38 g, 0.1 mol), sulphur (3.37 g, 0.1 mol) and methanol 50 ml. The mixture was refluxed at 70 °C for 3 hours. The resulting solution was cooled by adding crushed ice and placing in a refrigerator overnight for the crystals to precipitate out of the solution. The crystals were filtered, washed and air dried. The product obtained was recrystallized from ethanol. The yield and melting point were determined.

Diazotisation of the methyl 2-amino-4-[(4-chlorophenyl)carbamoyl]-5-methylthiophene-3-carboxylate

Dry sodium nitrite (1.38 g, 0.02 mol) was added in parts over a period of 30 minutes to 98 % H_2SO_4 (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^3 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, methyl 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 the required amount of urea. The diazonium salt solution obtained was then used for the subsequent coupling reaction (Maradiya, 2002).

General procedure for coupling of the diazotized methyl 2-amino-4-[(4-chlorophenyl)carbamoyl]-5-methylthiophene-3-carboxylate intermediate to the various coupling components

0.02 mole of the various coupling components (1-ethyl-6-hydroxy-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile, 6-hydroxy-1,4-dimethyl-2-oxo-1,2-dihydropyridine-3-carbonitril
e) were dissolved in 10 % sodium hydroxide and cooled to ± 0 °C with the addition of ice. The previously prepared diazonium salt solutions were 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.

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 stoichometric 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 (Khalid *et al.*, 2016).

III. RESULTS AND DISCUSSION

The intermediate, dyes and their complexes were prepared according to scheme 1.

Methyl 2-amino-4-((4-chlorophenyl)carbamoyl)-5-methylthiophene-3-carboxylate Aminothiophene Intermediate (1)

White powder, 67 % yield, melting point 195 – 197 °C, ^{1}H NMR in (DMSO-d_6), □ (ppm) 2.49 (3H, s, CH_3); 3.74 (3H, d, CH_3); 7.32 -7.66 (4H, t, ArCH); 7.78 (2H, s, NH_2); 9.79 (1H, s, NH). ^{13}C NMR in (DMSO-d6), □ (ppm) 16.40 (CH_3) thiophene; 40.05 (CHN) Benzene; 50.71 (CH_3COO); 105.42 (-COO) thiophene;121.60 - 128.42 (ArCH);138.09 (ArC-NH); 141.08 (Ar-C) thiophene; 161.43 (ArC-NH_2); 165.14 (CO ester); 165.17 (CO amide). (m/z) -324; IR (v cm^{-1}) 2952.1 (ArCH); 816.3 (ArCH bending); 2102.2 (R-N-C); 3477.6 (N-H str); 1505.8 (N-H bending); 678.4 (C-Cl); 1666.1 (C=O); 1621.4 (C=C); 3309.9 (-NH_2); 1237.5 (C-N).

Methyl 4-((4-chlorophenyl)carbamoyl)-2-((5-cyano-2-hydroxy-1,4-dimethyl-6-oxo-1,6-dihydropyridin-3-yl)diazenyl)-5-methylthiophene-3-carboxylate (2)

Red crystalline powder, 65 % yield, melting point 271 – 273 °C, ^{1}H NMR in (DMSO-d_6), □ (ppm) 2.41 - 2.53 (3H, m, CH_3); 3.19 (3H, s, CH_3); 3.93 (H, s, 7.31 - 7.76 (4H, m, ArCH); 9.75 (1H, s, NH); 10.27 (1H, s, OH). ^{13}C NMR in (DMSO-d_6), □ (ppm) 16.37 (CH_3); 39.22 - 40.06 (CH_3N); 50.71 (CH_3COO); 105.35 (C, -$COOCH_3$); 112.32 (C, -CN); 121.56 - 128.41 (Ar-C-); 138.07 (Ar-C-NH); 161.37 (CONH, -C=O); 165.07 (Ar-C-OH). (m/z) - 499; IR (v cm^{-1}) 2952.1 (ArCH); 820.0 (ArCH bending); 2228.9 (CN); 2191.7 (R-N-C); 3473.9 (N-H str); 1494.7 (N-H bending); 682.1 (C-Cl); 3652.8 (OH); 1688.5 (C=O); 1397.8 (-S-C); 1591.6 (C=C); 1244.9 (C-N); 1438.8 (N=N); λmax (474.98 nm), □ - (8.10 x 10^4 $Lmol^{-1}cm^{-1}$).

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

Violet Red powder, 69 % yield, melting point 227 – 229 °C, ^{1}H NMR in (DMSO-d_6), □ (ppm) 2.49 (3H, s, CH_3); 3.39 (H, s, CH_3N); 3.73 (3H, s, CH_3); 7.34 (2H, m, ArCH); 7.78 (2H, m, ArCH); 9.79 (1H, s, NH). ^{13}C NMR in (DMSO-d_6), □ (ppm) 16.19 (CH_3); 39.23 - 39.77 (C, CH_3N); 50.52 (C, H_3COO); 105.17 (Ar-C-); 112.15 (C, -CN); 121.37 - 128.23 (Ar-C-); 137.89 (Ar-C-NH); 140.87 (Ar-C-) thiophene; 161.19 (CONH, -

C=OO); 164.93 (C, C=O). IR (v cm^{-1}) 2952.1 (ArCH); 816.3 (ArCH bending); 2228.9 (CN); 2083.6 (R-N-C); 3447.8 (N-H str); 1490.9 (N-H bending); 678.4 (C-Cl); 3309.9 (OH); 1666.1 (C=O); 1237.5 (C-N); 1438.8 (N=N). λmax (475.02 nm), □ - (4.01 x 10^4 $Lmol^{-1}cm^{-1}$).

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

Violet Red powder, 65 % yield, melting point 189 – 190 °C, ^1H NMR in (DMSO-d_6), □ (ppm) 2.45 (3H, s, CH_3); 2.49 (3H, s, CH_3); 3.40 (3H, s, CH_3); 3.72 (H, s, CH_3); 7.31 - 7.75 (4H, m, ArCH); 9.76 (1H, s, NH). ^{13}C NMR in (DMSO-d_6), □ (ppm) 15.99 (CH_3); 39.50 - 39.78 (C, CH_3N); 50.33 (C, H_3COO); 104.95 (Ar-C-) thiophene; 111.93 (C, -CN); 121.16 - 128.02 (Ar-C-); 137.67 (Ar-C-NH); 140.64 (Ar-C-) thiophene; 161.00 (CONH, -C=OO); 164.69 (C, C=O). IR (v cm^{-1}) 2952.1 (ArCH); 816.3 (ArCH bending); 2225.2 (CN); 2105.9 (R-N-C); 3473.9 (N-H str); 1490.9 (N-H bending); 678.4 (C-Cl); 3295.0 (OH); 1662.4 (C=O); 1237.5 (C-N); 1397.8 (N=N); λmax (480.00 nm), □ - (3.62 x 10^4 $Lmol^{-1}cm^{-1}$).

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

Red powder, 53 % yield, melting point 196 – 198 °C, ^1H NMR in (DMSO-d_6), □ (ppm) 2.49 (3H, s, CH_3); 3.35 (H, s, CH_3); 3.75 (3H, s, CH_3); 7.37 (2H, m, ArCH); 7.78 (2H, m, ArCH); 9.80 (1H, s, NH). ^{13}C NMR in (DMSO-d_6), □ (ppm) 16.39 (CH_3); 39.23 - 39.78 (C, CH_3N); 50.72 (C, H_3COO); 105.37 (Ar-C-) thiophene; 112.35 (C, -CN); 121.57 - 128.43 (Ar-C-); 138.08 (Ar-C-NH); 141.05 (Ar-C-) thiophene; 161.39 (CONH, -C=OO); 165.09 (C, C=O). λmax (472.00 nm), □ - (2.53 x 10^4 $Lmol^{-1}cm^{-1}$). (m/z) - 1134.15

Methyl 4-((4-chlorophenyl)carbamoyl)-2-((5-cyano-1-ethyl-2-hydroxy-4-methyl-6-oxo-1,6-dihydropyridin-3-yl)diazenyl)-5-methylthiophene-3-carboxylate (3)

Red crystalline powder, 63 % yield, melting point 289 – 291 °C, ^1H NMR in (DMSO-d_6), □ (ppm) 1.11 - 1.16 (3H, t, CH_3); 2.44 - 2.49 (3H, t, CH_3); 3.33 (H, s, CHN); 3.81 - 3.94 (3H, m, CH_3); 7.33 - 7.77 (4H, m, ArCH); 9.79 - 9.82 (H, s, NH); 10.35 (1H, s, ArOH). ^{13}C NMR in (DMSO-d_6), □ (ppm) 12.54 - 16.38 (CH_3); 39.50 (CHN); 52.33 (C, H_3COO); 105.34 (-$COOCH_3$); 111.95 (C, -CN); 121.54 - 128.59 (ArCH); 137.46 (Ar-C-NH); 141.05 (Ar-C) thiophene ; 161.37 (CONH, -C=O); 165.09 (Ar-C-OH). (m/z) - 512; IR (v cm^{-1}) 2989.3 (ArCH); 810.3 (ArCH bending); 2225.2 (CN); 2113.4 (R-N-C); 3473.9 (N-H str); 1539.4 (N-H bending); 711.9 (C-Cl); 3652.8 (OH); 1684.8 (C=O); 1394.0 (-S-C); 1591.6 (C=C); 1248.7 (C-N); 1442.5 (N=N); λmax (470.00 nm), □ - (8.92 x 10^4 $Lmol^{-1}cm^{-1}$).

Bis((3-((4-((4-chlorophenyl)carbamoyl)-3-(methoxycarbonyl)-5-methylthiophen-2-yl)diazenyl)-5-cyano-1-ethyl-4-methyl-6-oxo-1,6-dihydropyridin-2-yl)oxy)copper (3a)

Brown powder, 67 % yield, melting point 180 – 182 °C, ^1H NMR in (DMSO-d_6), □ (ppm) 1.31 (3H, t, CH_3); 2.08 (3H, s, CH_3); 2.49 (3H, s, CH_3); 3.39 (3H, s, CH_3); 3.73 (2H, s, CH_2); 7.33 (2H, m, ArCH); 7.77 (2H, m, ArCH); 9.79 (1H, s, NH). ^{13}C NMR in (DMSO-d_6), □ (ppm) 16.03 (CH_3); 39.50 (C, CH_3N); 50.35 (C, H_3COO); 104.97 (Ar-C) thiophene 111.96 (C, -CN); 121.18 - 128.03 (Ar-C-); 137.69 (Ar-C-NH); 140.68 (Ar-C-) thiophene; 160.99 (CONH, -C=OO); 164.728 (C, C=O). IR (v cm^{-1}) 2952.1 (ArCH); 820.0 (ArCH bending); 2221.5 (CN); 2109.7 (R-N-C); 3421.7 (N-H str); 1524.5 (N-H bending); 678.4 (C-Cl); 3298.7 (OH); 1666.1 (C=O); 1233.7 (C-N); 1438.8 (N=N). λmax (485.02 nm), □ - (5.77 x 10^4 $Lmol^{-1}cm^{-1}$).

Bis((3-((4-((4-chlorophenyl)carbamoyl)-3-(methoxycarbonyl)-5-methylthiophen-2-yl)diazenyl)-5-cyano-1-ethyl-4-methyl-6-oxo-1,6-dihydropyridin-2-yl)oxy)cobalt (3b)

Violet Red powder, 62 % yield, melting point 178 – 180 °C, ^1H NMR in (DMSO-d_6), □ (ppm) 1.19 - 1.88 (3H, t, CH_3); 2.45 - 2.49 (3H, s, CH_3); 2.93 (3H, s, CH_3); 3.39 (3H, s, CH_3); 3.71 (2H, s, CH_2); 7.33 - 7.75 (4H, m, ArCH); 9.77 (1H, s, NH). ^{13}C NMR in (DMSO-d_6), □ (ppm) 16.01 (CH_3); 39.24 - 39.79 (C, CH_3N); 50.35 (C, H_3COO); 104.96 (Ar-C-) thiophene; 111.95 (C, -CN); 121.18 - 128.05 (Ar-C-); 137.69 (Ar-C-NH); 140.66 (Ar-C-) thiophene; 161.02 (CONH, -C=OO); 164.71 (C, C=O). IR (v cm^{-1}) 2985.6 (ArCH); 816.3 (ArCH bending); 2225.2 (CN); 2109.7 (R-N-C); 3477.6 (N-H str); 1490.9 (N-H bending); 678.4 (C-Cl); 3309.9 (OH); 1666.1 (C=O); 1237.5 (C-N); 1438.8 (N=N). λmax (475.02 nm), □ - (5.44 x 10^4 $Lmol^{-1}cm^{-1}$).

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

Red powder, 64 % yield, melting point 224 – 246 °C, ^1H NMR in (DMSO-d_6), □ (ppm) 1.15 (3H, t, CH_3); 2.49 (3H, s, CH_3); 3.81 (3H, s, CH_3); 3.93 (2H, q, CH_2); 7.40 (2H, m, ArCH); 7.76 (2H, m, ArCH); 9.77 - 10.32 (1H, s, NH) . ^{13}C NMR in (DMSO-d_6), □ (ppm) 12.54 - 16.37 (CH_3); 40.06 - 40.34 (CH_3N); 50.71 - 52.30 (C, H_3COO); 105.35 (Ar-C-) thiophene; 112.32 (C, -CN); 121.83 - 128.58 (Ar-C-); 137.47 (Ar-C-NH); 141.06 (Ar-

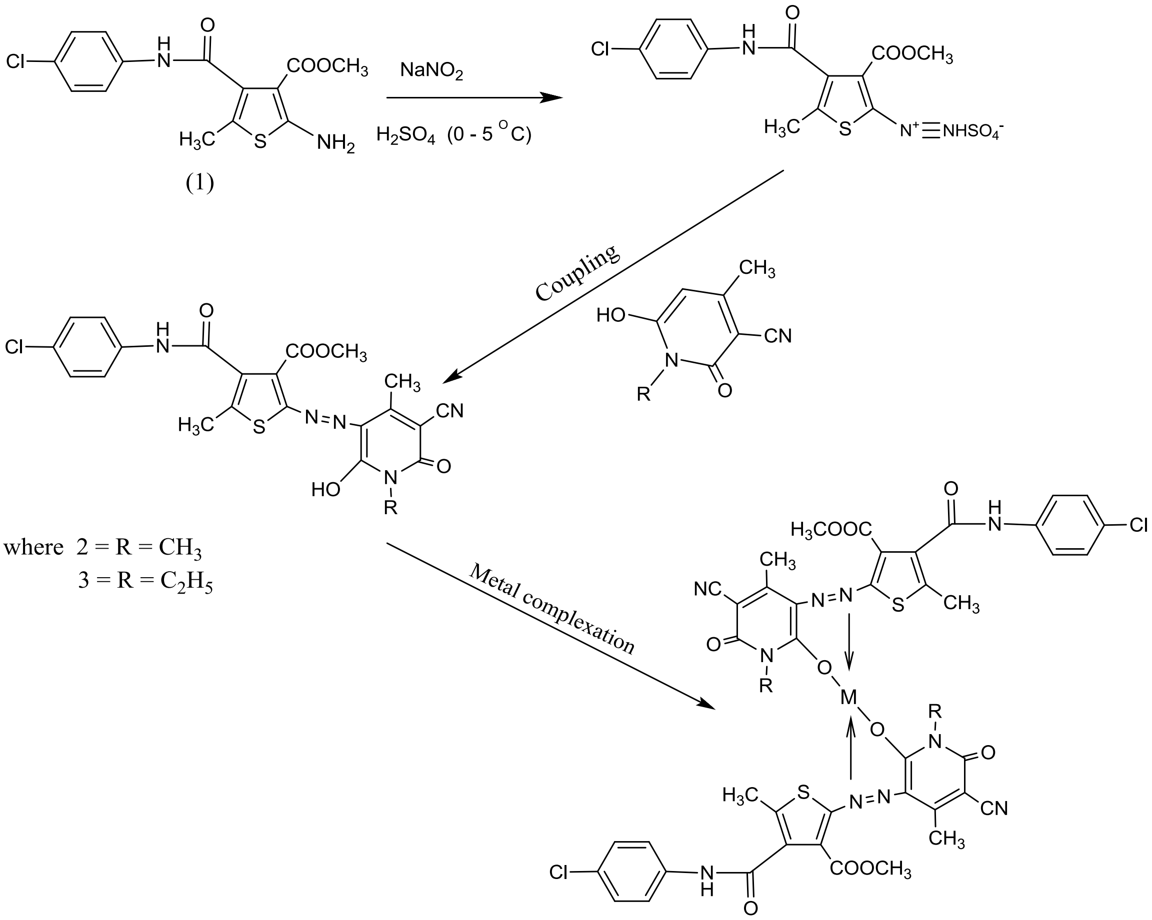
C-) thiophene 160.10 (-C=OO); 161.37 (CONH); 165.09 (C, C=O). IR (v cm^{-1}) 2989 (ArCH); 816 (ArCH bending); 2225 (CN); 2106 (R-N-C); 3474 (N-H str); 1491 (N-H bending); 678 (C-Cl); 3283 (OH); 1666 (C=O); 1245 (C-N); 1439 (N=N). λmax (472.00 nm), ε - (6.28 x 10^4 $Lmol^{-1}cm^{-1}$).

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 (Giles, 1974) and their fastness properties also determined according to the procedure described by the American Association of Textile Chemists and Colourists (AATCC) standard methods (AATCC, 1999). 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.

Table 1: Dyeing Properties of the Synthesized Dyes and their complexes on Polyester Fabrics

Dye/ Complex	Exhaustion (%)	Wash fastness	Light fastness	Perspiration (Acid)	Perspiration (Alkaline)	Sublimation
2	84	4	6	5	5	5
2a	86	5	6	5	5	5
2b	87	5	7	5	5	5
2c	85	5	6	5	5	5
3	90	5	6	5	5	5
3a	91	5	6	5	5	5
3b	89	5	5	5	5	5
3c	93	5	7	5	5	5



(1)

where 2 = R = CH_3
3 = R = C_2H_5

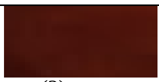
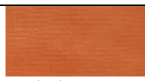
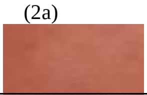
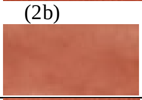
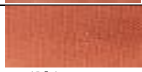
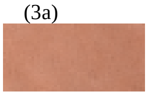
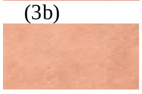
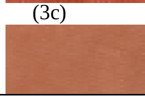
where a = M = Cu
b = M = Co
c = M = Zn

Scheme 1: Reaction scheme for the synthesis of intermediate, dyes and their complexes.

Table 2: Dyeing Properties of the Synthesized Dyes and their complexes on Nylon 6.6 Fabrics

Dye/ Complex	Exhaustion (%)	Wash Fastness	Light	Perspiration (Acid)	Perspiration (Alkaline)	Sublimation
2	85	4	5	5	5	5
2a	90	4	7	5	5	5
2b	88	4	6	5	5	5
2c	87	4	6	5	5	5
3	92	4	7	s5	5	5
3a	93	4	7	5	5	5
3b	90	4	6	5	5	5
3c	89	4	6	5	5	5

Table 3:Shade on Polyester and Nylon 6.6

NYLON 6.6	 (2)	 (2a)	 (2b)	 (2c)
POLYESTER				
NYLON 6.6	 (3)	 (3a)	 (3b)	 (3c)
POLYESTER				

IV. CONCLUSION

Disperse dyes and metal complexes derived from methyl 2-amino-4-[(4-chlorophenyl)carbamoyl]-5-methylthiophene-3-carboxylate were successful synthesized in good yields in this work. These dyes and their complexes were applied on polyester and nylon 6.6 and the were found to have a very good to excellent light fastness and wash fastness. The dyeing also showed excellent fastness to perspiration and sublimation.

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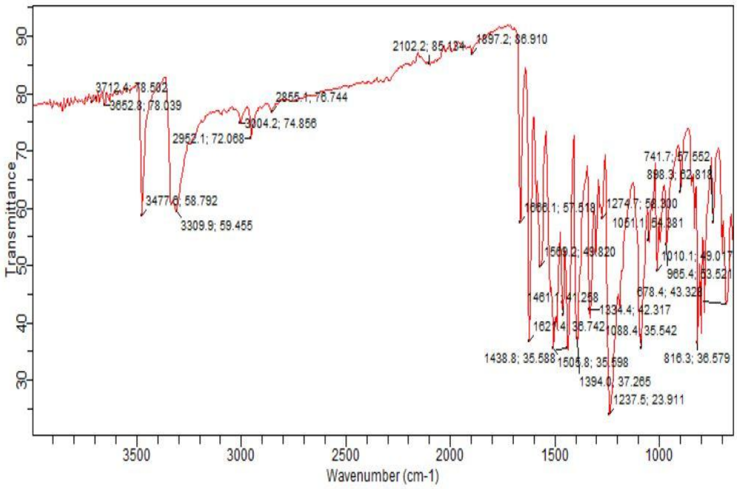
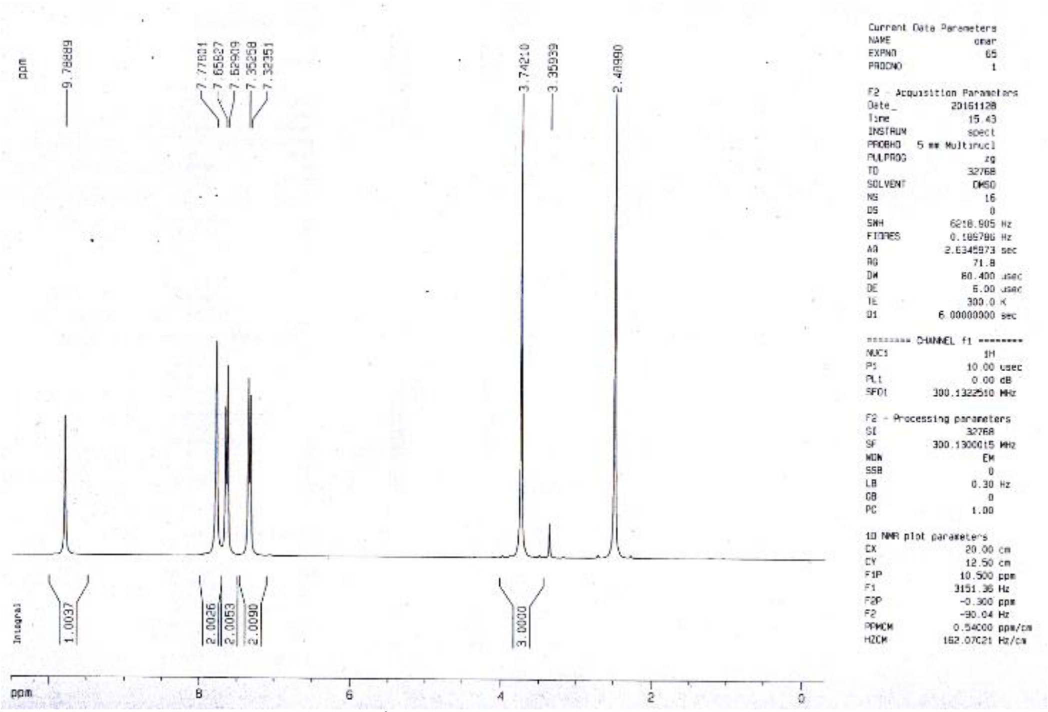
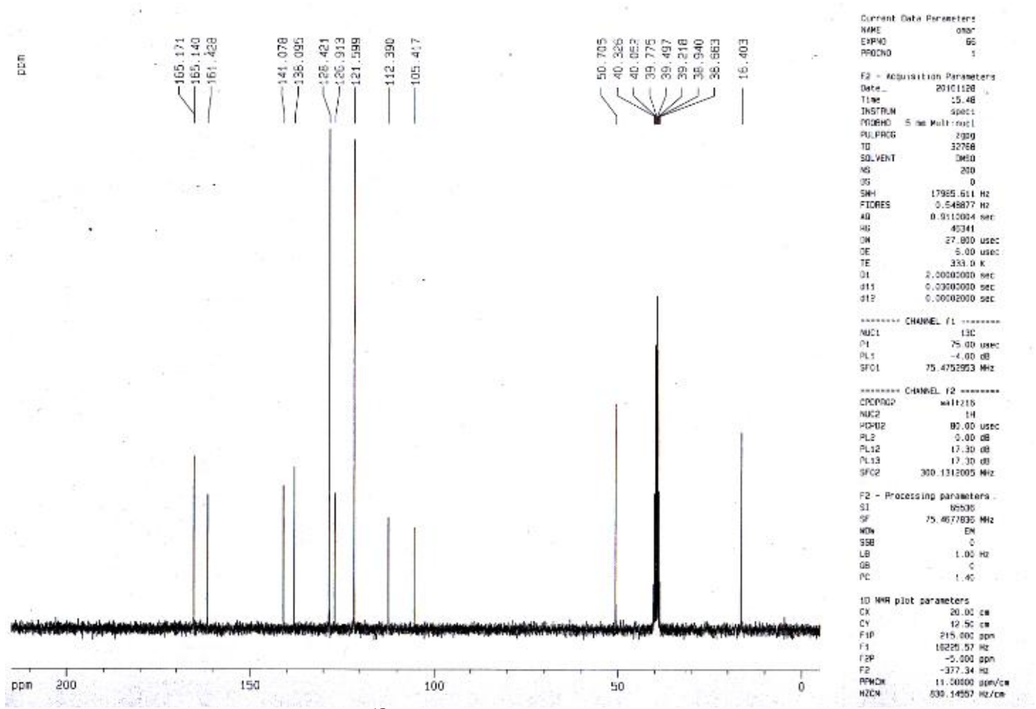


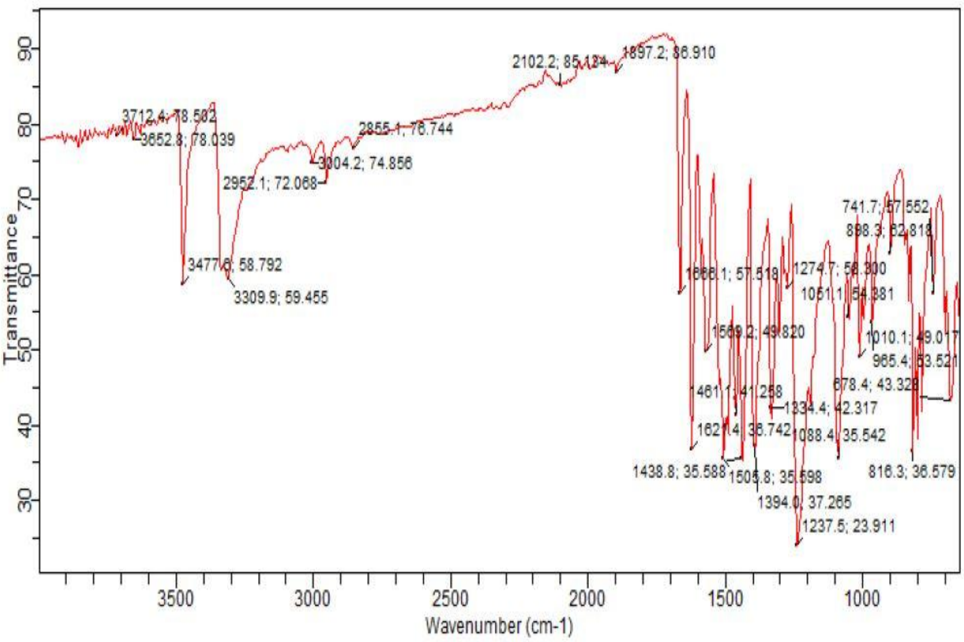
FTIR Spectrum of (1)



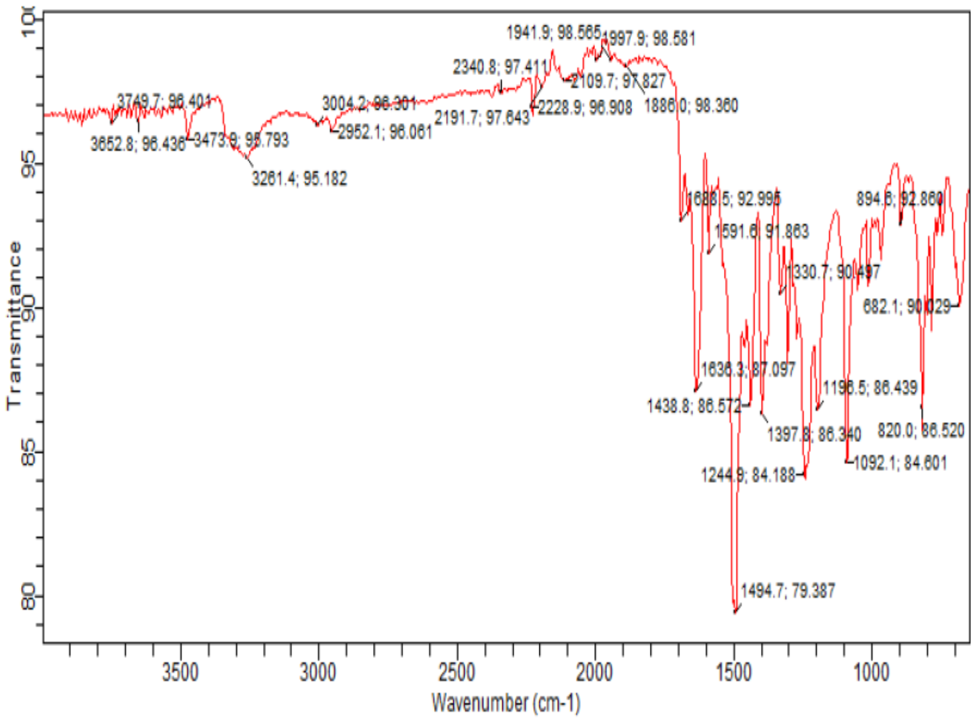
[1]H NMR Spectrum of (1)



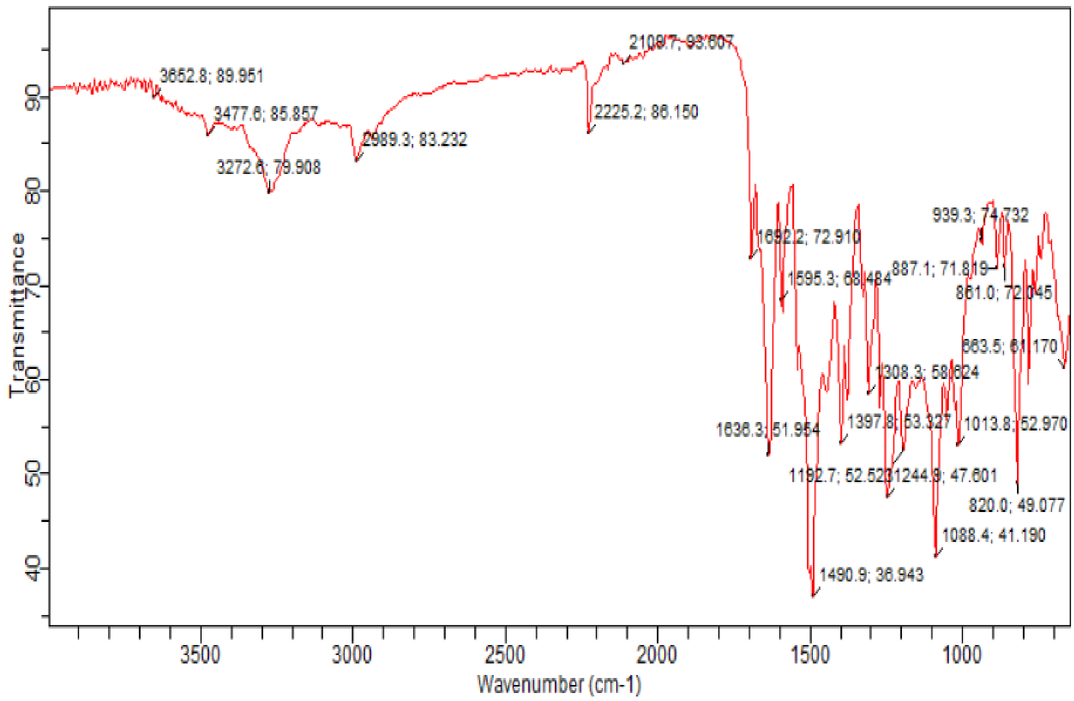
[13]C NMR Spectrum of (1)



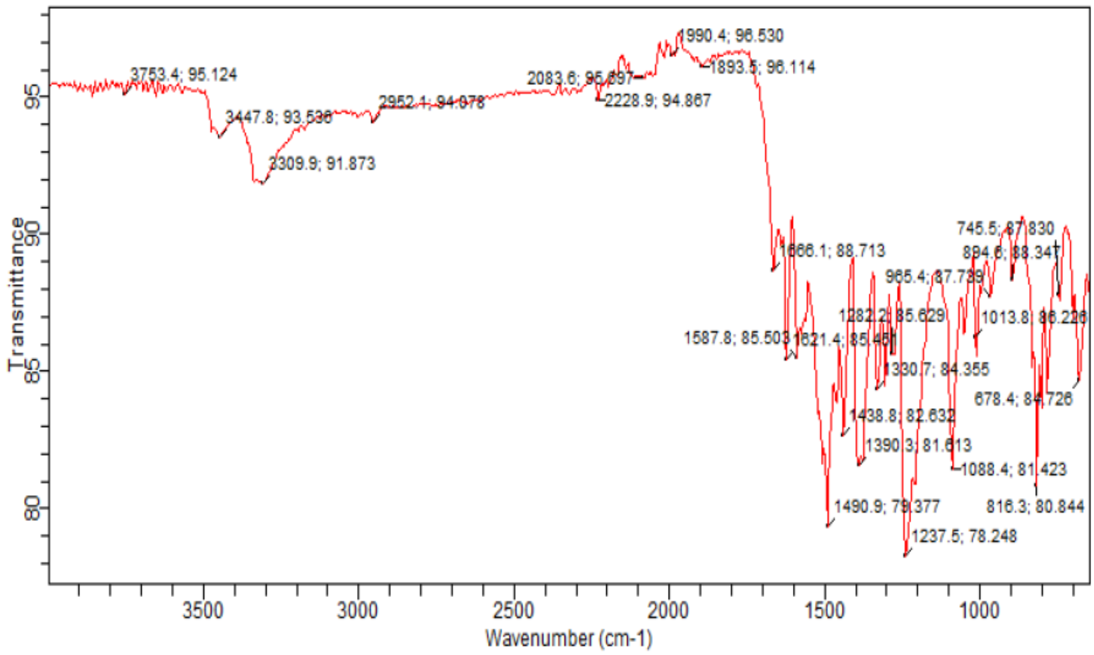
FTIR Spectrum of (2)



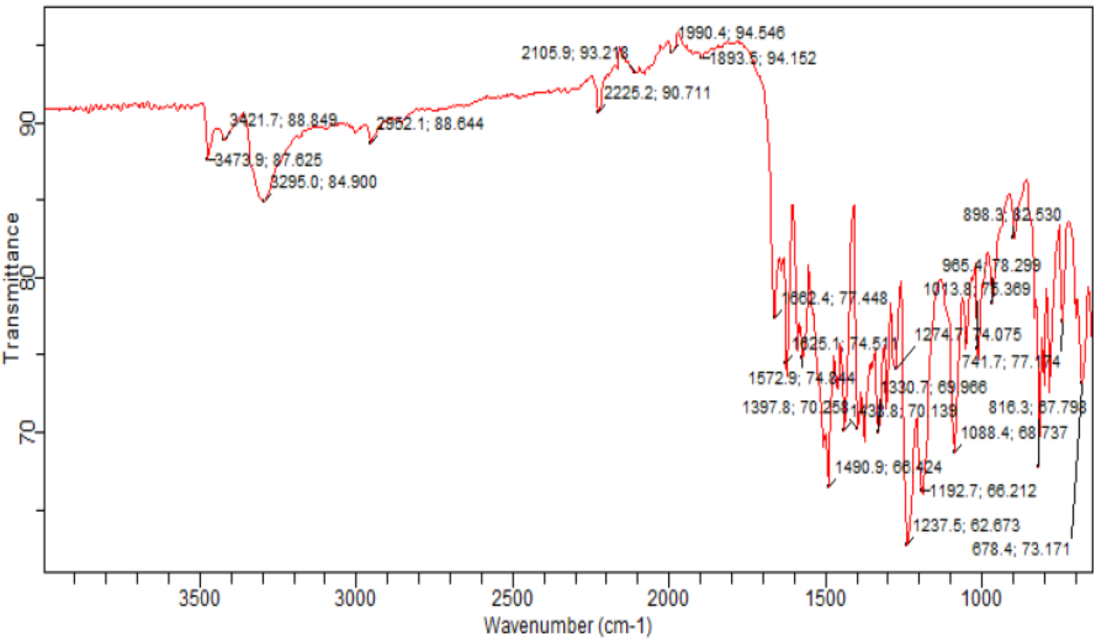
FTIR Spectrum of (2)



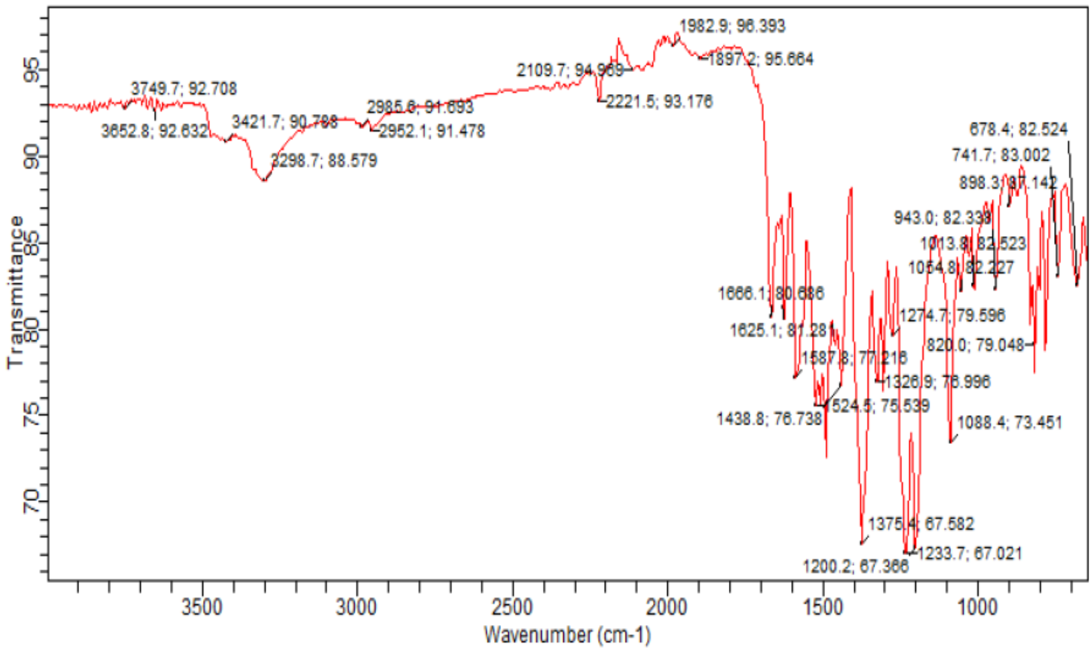
FTIR Spectrum of (3)



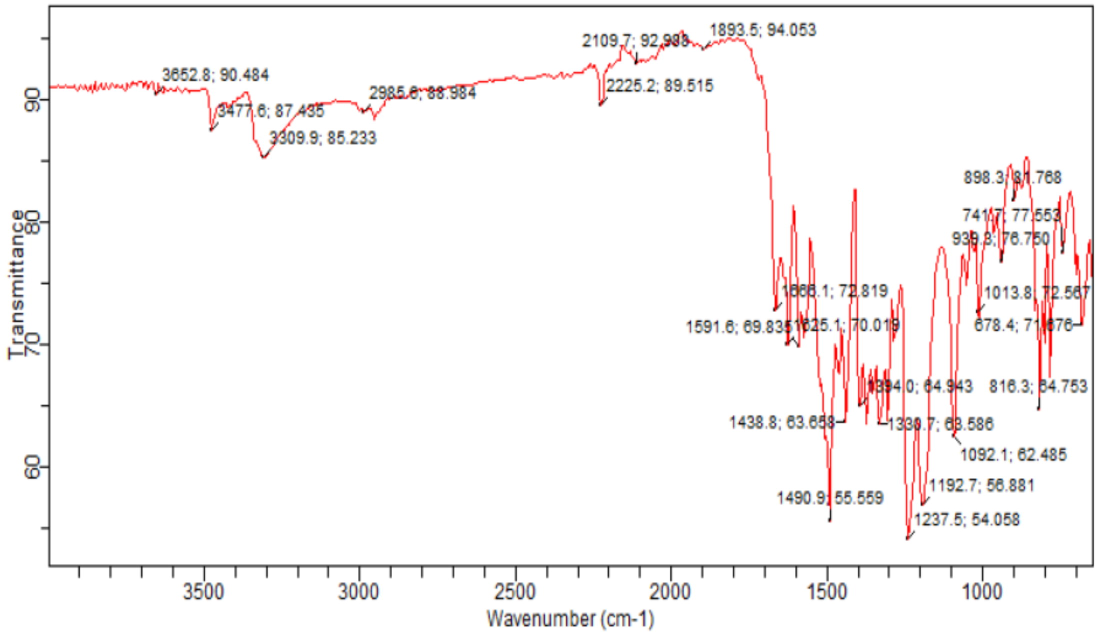
FTIR Spectrum of (2a)



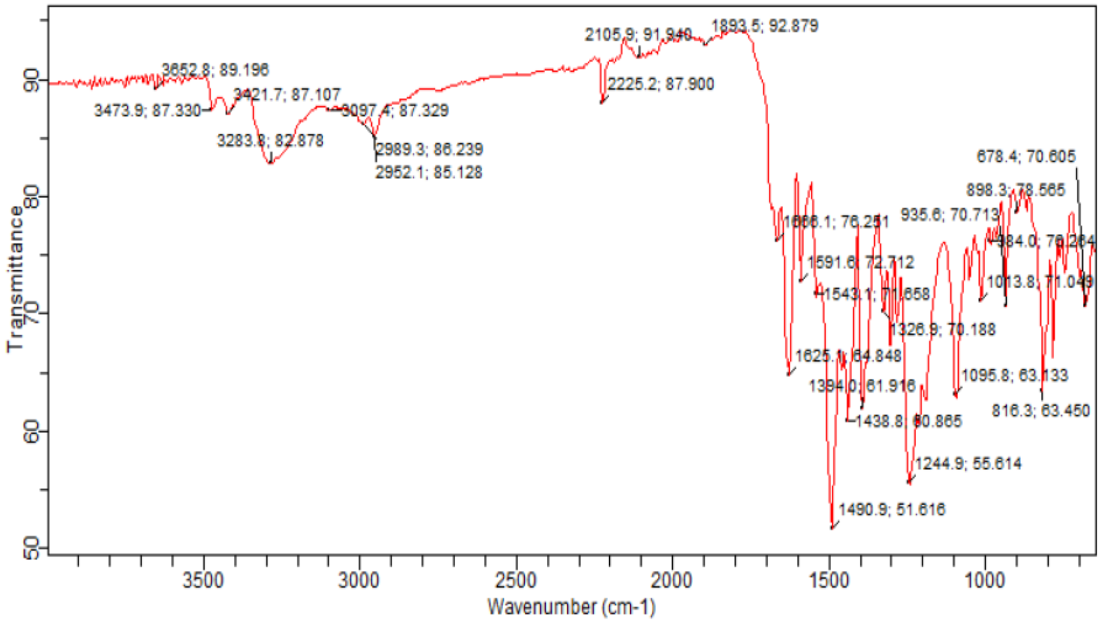
FTIR Spectrum of (2b)



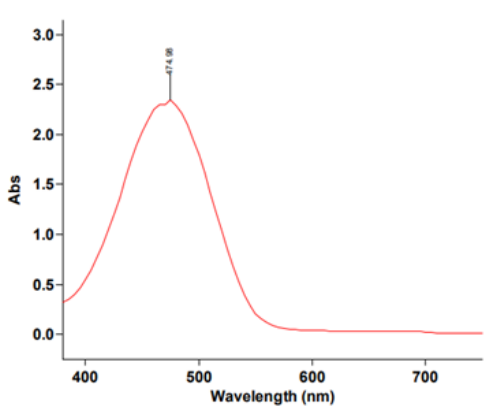
FTIR Spectrum of (3a)



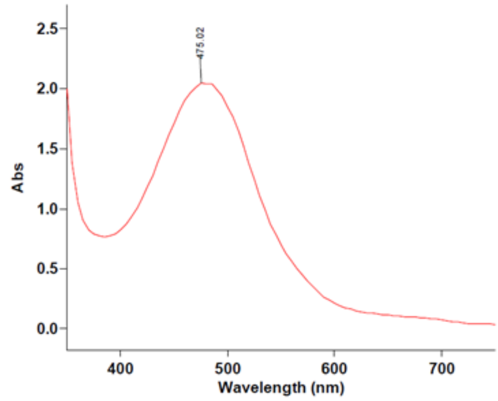
FTIR Spectrum of (3b)



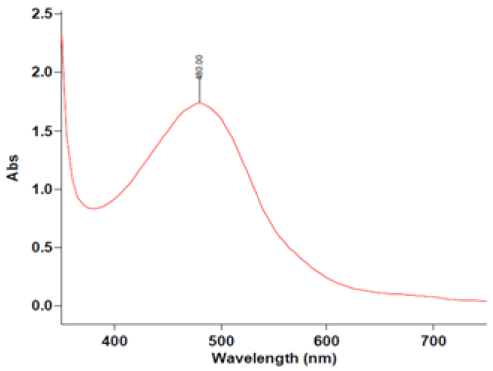
FTIR Spectrum of (3c)



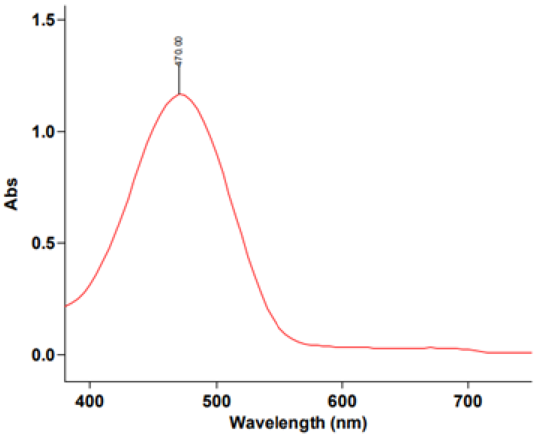
UV Spectrum of (2)



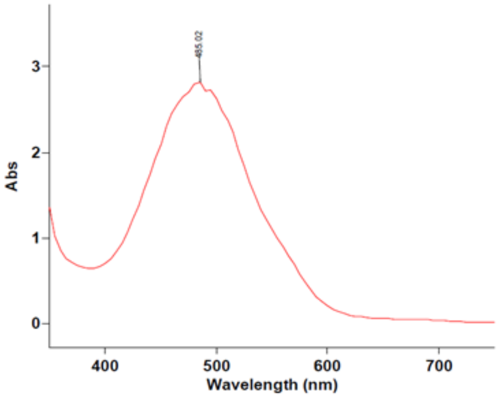
UV Spectrum of (2a)



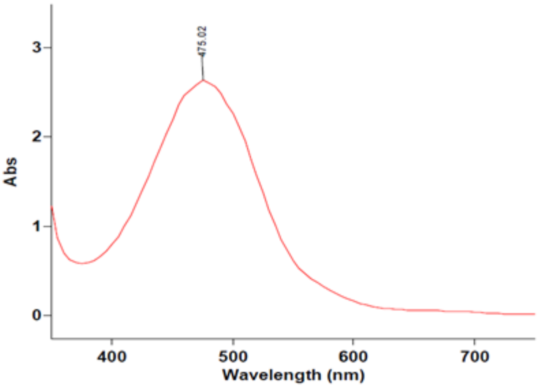
UV Spectrum of (2b)



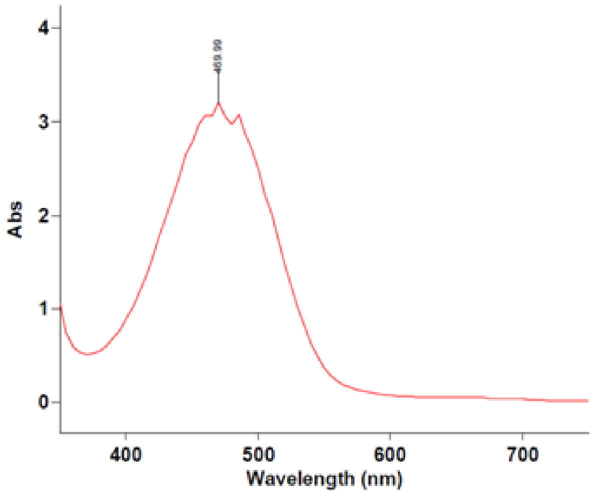
UV Spectrum of (3)



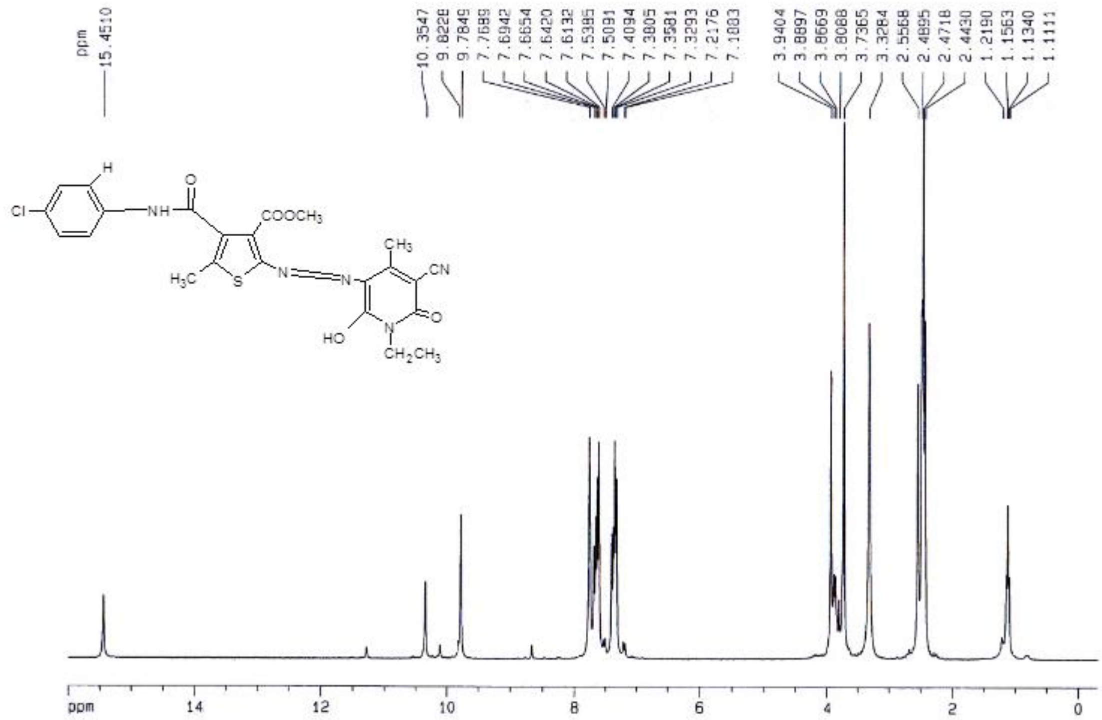
UV Spectrum of (3a)



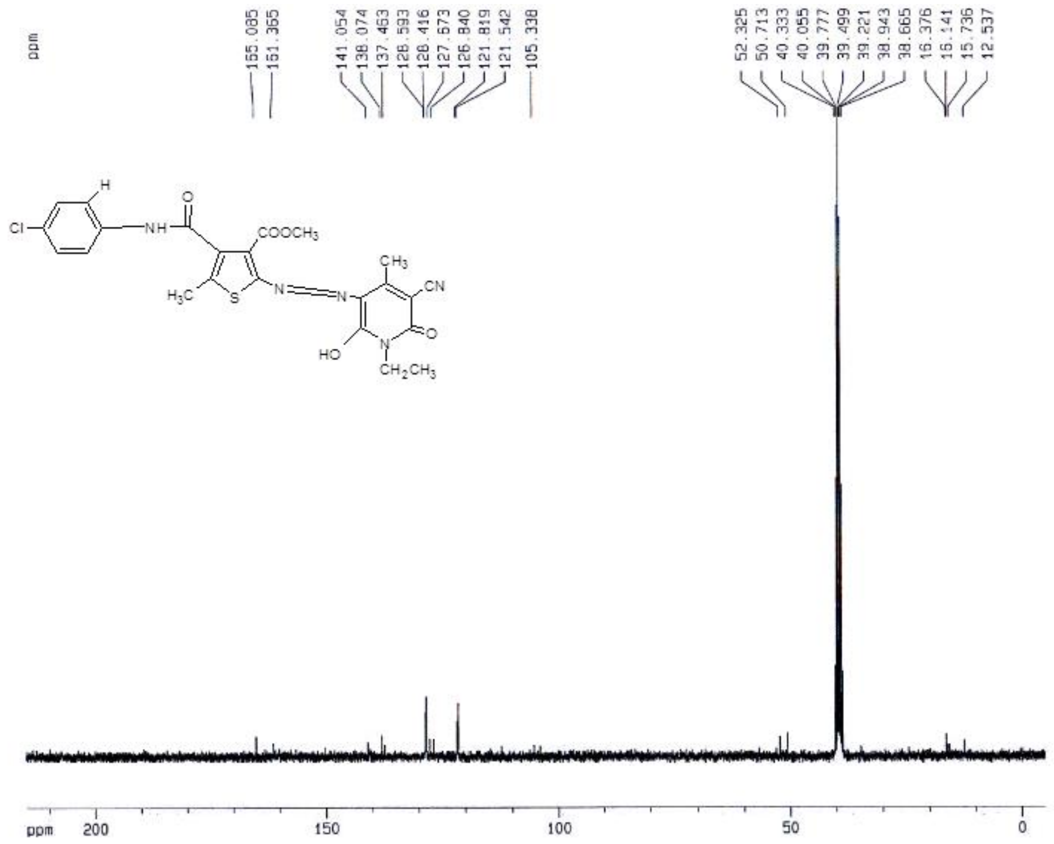
UV Spectrum of (3b)



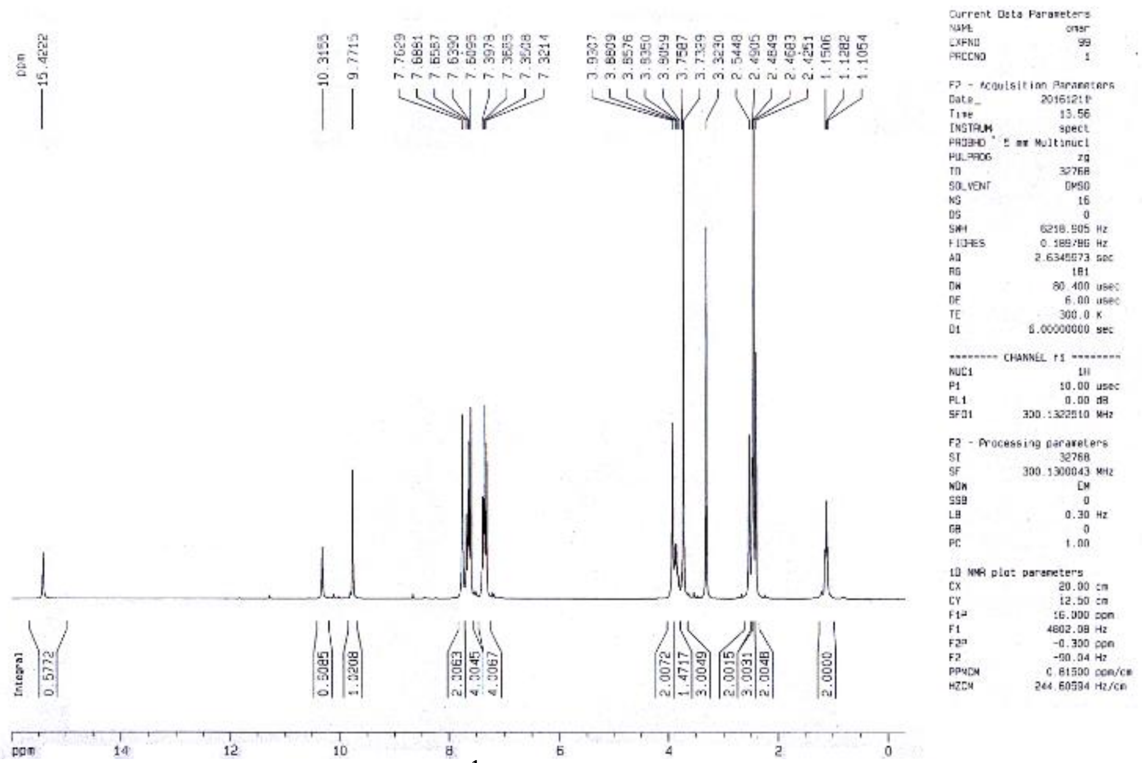
UV Spectrum of (3c)



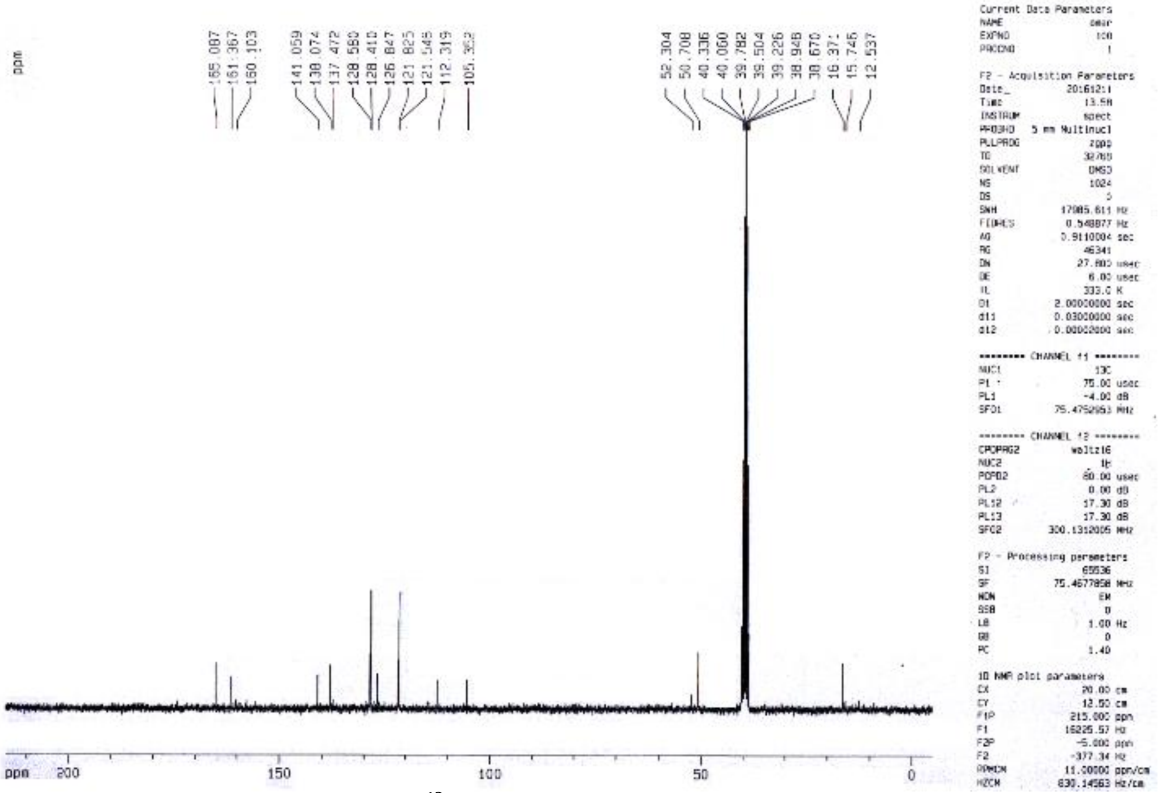
^{1}H NMR of (3)



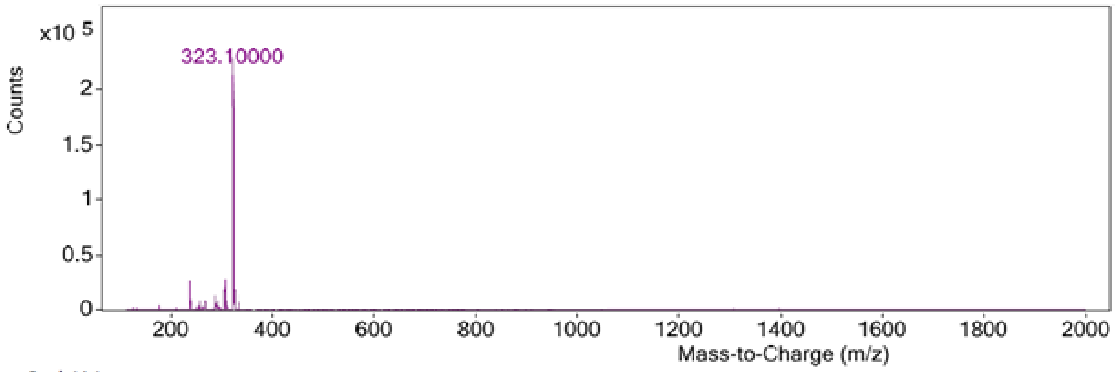
^{13}C NMR spectrum of (3)



^{1}H NMR of (3c)



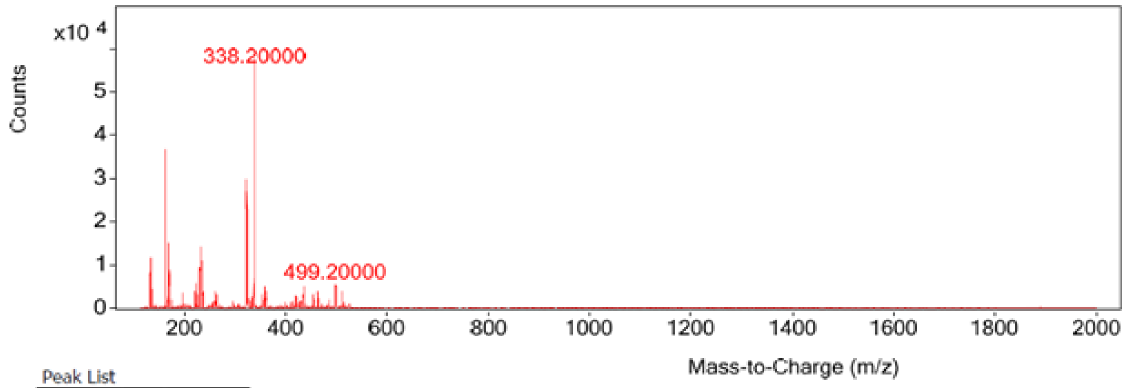
^{13}C NMR spectrum of (3c)



Peak List

m/z	z	Abund.
306.2		26974
323.1	1	228199
324.1	1	39649
325.1	1	110602

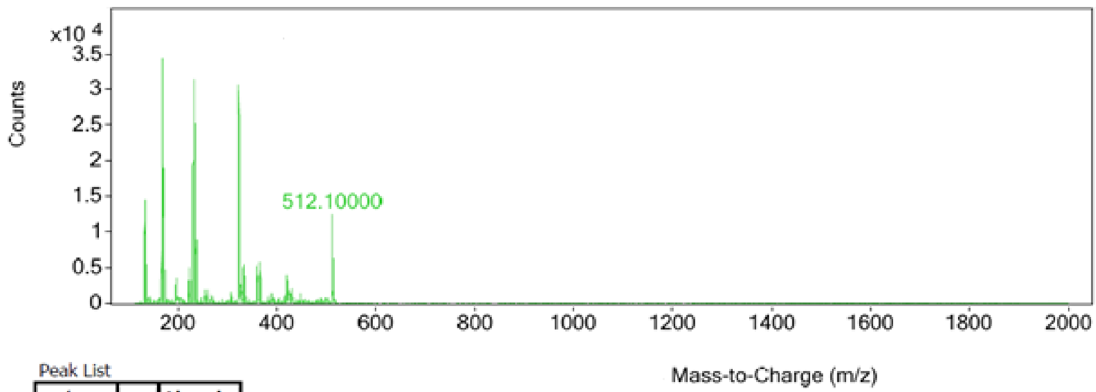
MS Spectrum of (1)



Peak List

m/z	z	Abund.
134.9		11679
163.1		36772
169.9		15135
230.8		9276
232.9		14128
234.8		10937
323.1	1	29629
325.1	1	12235
338.2	1	57916
339.2	1	14192

MS Spectrum of (2)



Peak List

m/z	z	Abund.
132.9		12547
134.9		14488
167.9		24276
169.9		34312
171.9		18990
230.9		20040
232.8		31358
234.9		25297
323.2		30732
512.1	1	12383

MS Spectrum of (3)