CHAPTER III
SYNTHESIS OF LIGANDS AND THEIR COPPER COMPLEXES

3.1 Introduction

Design and development of synthesized molecules that can mimic the biological system are of prime importance because of their potential application in therapeutic fields [1-7]. The design of metal–ligand complexes is of particular interest in the medicinal research. It is well known that metal ions present in the complexes are not only accelerating the drug action but also increase the effectiveness of the organic ligands [8]. The medicinal properties of metal complexes depend on the nature of the metal ions and the ligands also [9]. The immune interest in the preparation of new metal complexes other than platinum complexes has focused the study on interaction of metal complexes with DNA and protein for their potential applications in biotechnology and medicine.

The clinical success of cisplatin and related platinum-based drugs, as anticancer agents that bind covalently to DNA, is severely affected by the serious side effects, toxicity, and acquired drug resistance [10-13]. This is an impetus to synthetic inorganic chemists to adopt innovative strategies for the preparation of more effective, less toxic, target specific, and preferably noncovalently bound therapeutic agents. Copper is one of the most interesting biometals [14, 15] due to its bio-essential activity and oxidative nature has attracted numerous researchers to address Cu(II) complexes with clinical applications [16–19]. Copper(II) is known to play a significant role in naturally occurring biological systems as well as a pharmacological agent [20]. The therapeutic efficiencies of copper complexes may be altered is due to the fact that by changing the ligand environment one can tune the DNA binding and pharmacological profiles and leads to effective therapeutic agents.

Flavones constitute one of the major classes of naturally occurring components. Synthesis of flavones and their derivatives has attracted considerable attention is due to their significant biochemical, pharmaceutical and antioxidant activities. It has been
observed that the presence of hydroxyl groups at position 3 or 5 is frequently required for higher biological activities.

Flavonoids are best known as radical scavengers. The valuable effects are due to their abilities to accept free radicals, complexation properties with copper ions have also been recognized to contribute to the whole biological activity [21]. The experimental and theoretical studies showed that the idea of complexation site for flavonoids involves the hydroxyl group on carbon 3 or 5 and the adjacent 4- carbonyl group.

This chapter has been devoted to synthesis of structurally modified ligands which may tune the biochemical properties of copper complexes. The synthesis of ligands derived from different hydroxyflavone derivatives and their copper complexes were discussed. This chapter is divided into four sub sections provide the different structurally modified flavone derivatives and their copper complexes towards therapeutics.

Section: 1

Flavone skeleton is chosen in the present work as active pharmacophore. Some structural modifications are made on the above compounds and designed to explore their antioxidant activities. Schiff-bases are multifunctional groups and they are able to improve various biological and pharmacological activities of a pharmacophore, such as antitumor, antioxidation and antibacterial activities. It is known that flavone and its derivatives exhibit extensively biological and pharmacological activities. In the present research work, there is considerable efforts have been devoted to design and synthesize functional flavone derivatives. Therefore, well-designed functional groups would enable a fine-tuning of special properties of a pharmacophore.

This section was aimed to design some ligands by incorporating substituted alkyl amine in O- replacement at ring “C” in the flavone nucleus. The literature evidences of N-alkyl derivatives of aromatic nucleus exhibited higher therapeutic efficiencies than N-substituted alkyl derivatives in the side chain of aromatic nucleus. The biochemical
action of copper both as an essential trace metal bound to several proteins and as a constituent of exogenously administered compounds in humans, mainly in the form of complexes than can interact with biomolecules is well known. Current interest in copper complexes focuses among others on their potential use as antimicrobial, antiviral, anti-inflammatory and antitumor agents, however, the copper-based compounds tested so far are almost exclusively copper(II) complexes.

Knowledge gained from literature evidences allows replacing some structural changes with a systematic tailor made approach in the search for new antioxidant substances that may be mimic natural antioxidant systems. 3-/5-Hydroxyflavone containing compounds form an important class among heterocyclic pharmaceuticals and represent an attractive scaffold for designing antituberculosis agents. 5-Hydroxyflavone is synthesized from 2, 6-dihydroxyacetophenone according to the literature method [9] and identified by elemental analysis, melting point, IR and UV spectrum.
Scheme 1  The schematic outline of synthesis of ligands

CuCl₂ + L → [CuL(Cl)(H₂O)] except ligands having R⁵ = Cl, NO₂

Reagents and conditions: (a) n-propyl amine/n-pentyl amine, toluene, 110 °C, reflux;
(b) reflux in ethanolic medium, 60 °C.

The carbon representation of ligand system is given below
General Procedure

The synthesis of compounds 2a–2h was prepared by refluxing 1a-1d (different hydroxyflavone(s)) with n-propyl amine/n-pentyl amine in toluene at 120 °C whose intermediates were condensed with different aromatic amines \([o\text{-chloroaniline (a)/ o\text{-aminobenzenethiol (b)/ o\text{-aminophenol (c)/ o\text{-nitroaniline (d)/ o\text{-aminobenzoic acid (e)}}]}\) in ethanolic medium is depicted in scheme 1. The synthesised ligands were purified using column chromatographic technique. The complexes were obtained by refluxing the equimolar solutions of copper chloride and ligand(s). The copper complexes were obtained as solids in different yields (scheme 2).

The purity of synthesized compounds was confirmed by TLC and elemental analysis. C, N and H analysis were carried out micro analytically. Magnetic moments were determined at room temperature. They are insoluble in acetone, ethanol, benzene and chloroform, but their considerable solubility has been noticed in DMF and DMSO. The complexes are stable at room temperature. They are non-hygroscopic and can be stored for a long length of period without decomposition.

\(L^{2a}\): Yield: 70%. Anal.Calcd for \(C_{18}H_{17}NO_{2}\). C, 77.40; H, 6.13; N, 5.01. Found: C, 77.42; H, 6.14; N, 4.99. FAB mass spectrometry (FAB-MS): \(m/z\) 280 [M+1]. \(^1\)H-NMR (300 MHz, CDCl\(_3\), δ, ppm): 8.59 (1H, s, -OH, D\(_2\)O exchangeable), 6.67-7.71 (9H, m, Ar-H), 4.12 (2H, t, CH\(_2\)), 1.70 (2H, m, CH\(_2\)), 1.02 (3H, t, CH\(_3\)). \(^{13}\)C-NMR (300 MHz, CDCl\(_3\), ppm): 162.2 (C-2), 97.2 (C-3), 182.1 (C-4), 162.6 (C-5), 106.6 (C-6), 136.7 (C-7), 100.7 (C-8), 145.3 (C-9), 119.3 (C-10), 134.2 (C-11), 128.3 (C-12), 128.6 (C-13), 127.9 (C-14), 128.6 (C-15), 128.3 (C-16), 48.7 (C-17), 21.4 (C-18), 11.9 (C-19). IR (KBr, cm\(^{-1}\)): 3500-3700, bs (OH); 1750, (C=O)st; 1332, (-C(9)-N-C(2))st.

\(L^{2b}\): Yield: 56%. Anal.Calcd for \(C_{18}H_{17}NO_{3}\). C, 73.20; H, 5.80; N, 4.74. Found: C, 73.21; H, 5.79; N, 4.73. FAB mass spectrometry (FAB-MS): \(m/z\) 296 [M+1]. \(^1\)H-NMR (300 MHz, CDCl\(_3\), δ, ppm): 9.51 (1H, s, -OH, D\(_2\)O exchangeable), 8.32 (1H, s, -OH, D\(_2\)O exchangeable), 6.24-7.49 (8H, m, Ar-H), 4.09 (2H, t, CH\(_2\)), 1.72 (2H, m, CH\(_2\)), 1.01 (3H,
$^{13}$C-NMR (300 MHz, CDCl$_3$, ppm): 162.2 (C-2), 97.2 (C-3), 182.1 (C-4), 162.6 (C-5), 106.6 (C-6), 136.7 (C-7), 100.7 (C-8), 145.3 (C-9), 119.3 (C-10), 126.8 (C-11), 130.1 (C-12), 115.8 (C-13), 157.7 (C-14), 115.8 (C-15), 130.1 (C-16), 48.7 (C-17), 21.4 (C-18), 11.9 (C-19). IR (KBr, cm$^{-1}$): 3500-3700, bs (OH); 1739, (C=O)st; 1290, (-C(9)-N-C(2))st.

L$^2c$: Yield: 65%. Anal.Calc'd for C$_{18}$H$_{17}$NO$_3$. C, 73.20; H, 5.80; N, 4.74. Found: C, 73.21; H, 5.79; N, 4.73. FAB mass spectrometry (FAB-MS): m/z 296 [M+1]. $^1$H-NMR (300 MHz, CDCl$_3$, δ, ppm): 11.12 (1H, s, -OH, D$_2$O exchangeable), 9.56 (1H, s, -OH, D$_2$O exchangeable), 6.68-7.81 (8H, m, Ar-H), 4.09 (2H, t, CH$_2$), 1.72 (2H, m, CH$_2$), 1.01 (3H, t, CH$_3$). $^{13}$C-NMR (300 MHz, CDCl$_3$, ppm): 123.9 (C-2), 146.0 (C-3), 178.2 (C-4), 126.3 (C-5), 122.7 (C-6), 135.3 (C-7), 108.2 (C-8), 143.9 (C-9), 127.1 (C-10), 126.8 (C-11), 130.1 (C-12), 115.8 (C-13), 157.7 (C-14), 115.8 (C-15), 130.1 (C-16), 48.7 (C-17), 21.4 (C-18), 11.9 (C-19). IR (KBr, cm$^{-1}$): 3500-3700, bs (OH); 1724, (C=O)st; 1286, (-C(9)-N-C(2))st.

L$^2d$: Yield: 76%. Anal.Calc'd for C$_{18}$H$_{17}$NO$_2$. C, 77.40; H, 6.13; N, 5.01. Found: C, 77.42; H, 6.14; N, 4.99. FAB mass spectrometry (FAB-MS): m/z 280 [M+1]. $^1$H-NMR (300 MHz, CDCl$_3$, δ, ppm): 11.73 (1H, s, -OH, D$_2$O exchangeable), 6.67-7.71 (9H, m, Ar-H), 4.12 (2H, t, CH$_2$), 1.70 (2H, m, CH$_2$), 1.02 (3H, t, CH$_3$). $^{13}$C-NMR (300 MHz, CDCl$_3$, ppm): 123.8 (C-2), 146.2 (C-3), 178.2 (C-4), 126.3 (C-5), 122.7 (C-6), 135.3 (C-7), 108.2 (C-8), 143.9 (C-9), 127.1 (C-10), 128.6 (C-12), 134.2 (C-11), 128.3 (C-15), 128.3 (C-16), 48.7 (C-17), 21.4 (C-18), 11.9 (C-19). IR (KBr, cm$^{-1}$): 3500-3700, bs (OH); 1737, (C=O)st; 1290, (-C(9)-N-C(2))st.

L$^2e$: Yield: 64%. Anal.Calc'd for C$_{20}$H$_{21}$NO$_2$. C, 78.15; H, 6.89; N, 4.56. Found: C, 78.16; H, 6.86; N, 4.57. FAB mass spectrometry (FAB-MS): m/z 308 [M+1]. $^1$H-NMR (300 MHz, CDCl$_3$, δ, ppm): 8.62 (1H, s, -OH, D$_2$O exchangeable), 6.67-7.71 (9H, m, Ar-H), 4.12 (2H, t, CH$_2$), 1.46 (2H, m, CH$_2$), 1.31 (2H, m, CH$_2$), 1.24 (2H, m, CH$_2$), 1.02 (3H, t, CH$_3$). $^{13}$C-NMR (300 MHz, CDCl$_3$, ppm): 162.2 (C-2), 97.2 (C-3), 182.1 (C-4), 162.6 (C-5), 106.6 (C-6), 136.7 (C-7), 100.7 (C-8), 145.3 (C-9), 119.3 (C-10), 134.2 (C-11),
128.3 (C-12), 128.6 (C-13), 127.9 (C-14), 128.6 (C-15), 128.3 (C-16), 46.7 (C-17), 28.2 (C-18), 29.6 (C-19), 22.3 (C-20), 14.2 (C-21). IR (KBr, cm$^{-1}$): 3500-3700, bs (OH); 1749, (C=O)st; 1298, (-C(9)-N-C(2))st.

$L^2f$: Yield: 55%. Anal.Calcd for C$_{20}$H$_{21}$NO$_3$. C, 74.28; H, 6.55; N, 4.33. Found: C, 74.26; H, 6.53; N, 4.35. FAB mass spectrometry (FAB-MS): m/z 324 [M+1]. $^1$H-NMR (300 MHz, CDCl$_3$, δ, ppm): 9.56 (1H, s, -OH, D$_2$O exchangeable), 8.43 (1H, s, -OH, D$_2$O exchangeable), 6.44-7.49 (8H, m, Ar-H), 4.12 (2H, t, CH$_2$), 1.46 (2H, m, CH$_2$), 1.31 (2H, m, CH$_2$), 1.24 (2H, m, CH$_2$), 1.01 (3H, t, CH$_3$). $^{13}$C-NMR (300 MHz, CDCl$_3$, ppm): 162.2 (C-2), 97.2 (C-3), 182.1 (C-4), 162.6 (C-5), 106.6 (C-6), 136.7 (C-7), 100.7 (C-8), 145.3 (C-9), 119.3 (C-10), 126.8 (C-11), 130.1 (C-12), 115.8 (C-13), 157.7 (C-14), 115.8 (C-15), 130.1 (C-16), 46.7 (C-17), 28.2 (C-18), 29.6 (C-19), 22.3 (C-20), 14.2 C-21). IR (KBr, cm$^{-1}$): 3500-3700, bs (OH); 1723, (C=O)st; 1302, (-C(9)-N-C(2))st.

$L^2g$: Yield: 60%. Anal.Calcd for C$_{20}$H$_{21}$NO$_3$. C, 74.28; H, 6.55; N, 4.33. Found: C, 74.26; H, 6.53; N, 4.35. FAB mass spectrometry (FAB-MS): m/z 324 [M+1]. $^1$H-NMR (300 MHz, CDCl$_3$, δ, ppm): 11.9 (1H, s, -OH, D$_2$O exchangeable), 9.81 (1H, s, -OH, D$_2$O exchangeable), 6.68-7.81 (8H, m, Ar-H), 4.12 (2H, t, CH$_2$), 1.46 (2H, m, CH$_2$), 1.31 (2H, m, CH$_2$), 1.24 (2H, m, CH$_2$), 1.01 (3H, t, CH$_3$). $^{13}$C-NMR (300 MHz, CDCl$_3$, ppm): 123.9 (C-2), 146.0 (C-3), 178.2 (C-4), 126.3 (C-5), 122.7 (C-6), 135.3 (C-7), 108.2 (C-8), 143.9 (C-9), 127.1 (C-10), 126.8 (C-11), 130.1 (C-12), 115.8 (C-13), 157.7 (C-14), 115.8 (C-15), 130.1 (C-16), 46.7 (C-17), 28.2 (C-18), 29.6 (C-19), 22.3 (C-20), 14.2 C-21). IR (KBr, cm$^{-1}$): 3500-3700, bs (OH); 1723, (C=O)st; 1302, (-C(9)-N-C(2))st.

$L^2h$: Yield: 62%. Anal.Calcd for C$_{20}$H$_{21}$NO$_2$. C, 78.15; H, 6.89; N, 4.56. Found: C, 78.16; H, 6.86; N, 4.57. FAB mass spectrometry (FAB-MS): m/z 308 [M+1]. $^1$H-NMR (300 MHz, CDCl$_3$, δ, ppm): 11.9 (1H, s, -OH, D$_2$O exchangeable), 6.67-7.71 (9H, m, Ar-H), 4.12 (2H, t, CH$_2$), 1.46 (2H, m, CH$_2$), 1.31 (2H, m, CH$_2$), 1.24 (2H, m, CH$_2$), 1.02 (3H, t, CH$_3$). $^{13}$C-NMR (300 MHz, CDCl$_3$, ppm): 123.8 (C-2), 146.2 (C-3), 178.2 (C-4), 126.3 (C-5), 122.7 (C-6), 135.3 (C-7), 108.2 (C-8), 143.9 (C-9), 127.1 (C-10), 134.2 (C-11), 128.3 (C-12), 128.6 (C-13), 127.9 (C-14), 128.6 (C-15), 128.3 (C-16), 46.7 (C-17), 28.2
(C-18), 29.6 (C-19), 22.3 (C-20), 14.2 (C-21). IR (KBr, cm$^{-1}$): 3500-3700, bs (OH); 1744, (C=O)st; 1342, (-C(9)-N-C(2))st.

**L$^3$**: Yield: 70%. Anal. Calcd for C$_{24}$H$_{21}$ClN$_2$O. C, 74.12; H, 5.44; N, 7.2. Found C, 74.15; H, 5.58; N, 7.23. FAB mass spectrometry (FAB-MS): m/z 390 [M+1]. $^1$H-NMR (300 MHz, CDCl$_3$, $\delta$, ppm): 8.59 (1H, s, -OH, D$_2$O exchangeable), 6.63-7.75 (13H, m, Ar-H), 4.12 (2H, t, CH$_2$), 1.70 (2H, m, CH$_2$), 1.02 (3H, t, CH$_3$). $^{13}$C-NMR (300 MHz, CDCl$_3$, ppm): 155.3 (C-2), 101.8 (C-3), 164.5 (C-4), 161.7 (C-5), 106.2 (C-6), 133.7 (C-7), 100.4 (C-8), 144.8 (C-9), 102.2 (C-10), 134.4 (C-11), 128.3 (C-12), 128.4 (C-13), 127.8 (C-14), 128.4 (C-15), 128.3 (C-16), 48.7 (C-17), 21.4 (C-18), 11.9 (C-19), 143.3 (C-21), 127.6 (C-22), 130.3 (C-23), 128.4 (C-24), 118.7 (C-26). IR (KBr, cm$^{-1}$): 3500-3700, bs (OH); 1628 (-C=N)st; 1334, (-C(9)-N-C(2))st.

**L$^4$**: Yield: 65%. Anal. Calcd for C$_{24}$H$_{22}$N$_2$OS. C, 74.58; H, 5.74; N, 7.25. Found C, 74.57; H, 5.72; N, 7.24. FAB mass spectrometry (FAB-MS): m/z 387 [M+1]. $^1$H-NMR (300 MHz, CDCl$_3$, $\delta$, ppm): 8.59 (1H, s, -OH, D$_2$O exchangeable), 6.65-7.71 (13H, m, Ar-H), 4.12 (2H, t, CH$_2$), 1.70 (2H, m, CH$_2$), 1.02 (3H, t, CH$_3$). $^{13}$C-NMR (300 MHz, CDCl$_3$, ppm): 155.3 (C-2), 101.8 (C-3), 164.5 (C-4), 161.7 (C-5), 106.2 (C-6), 133.7 (C-7), 100.4 (C-8), 144.8 (C-9), 102.2 (C-10), 134.4 (C-11), 128.3 (C-12), 128.4 (C-13), 127.8 (C-14), 128.4 (C-15), 128.3 (C-16), 48.7 (C-17), 21.4 (C-18), 11.9 (C-19), 158.1 (C-21), 126.1 (C-22), 130.7 (C-23), 127.6 (C-24), 138.3 (C-25), 117.3 (C-26). IR (KBr, cm$^{-1}$): 3500-3700, bs (OH); 2561 (SH)st; 1632 (-C=N)st; 1354, (-C(9)-N-C(2))st.

**L$^5$**: Yield: 72%. Anal. Calcd for C$_{24}$H$_{22}$N$_2$O$_2$. C, 77.81; H, 5.99; N, 7.56. Found C, 77.83; H, 5.98; N, 7.58. FAB mass spectrometry (FAB-MS): m/z 371 [M+1]. $^1$H-NMR (300 MHz, CDCl$_3$, $\delta$, ppm): 8.59 (1H, s, -OH, D$_2$O exchangeable), 8.2 (1H, s, -OH, D$_2$O exchangeable), 6.42-7.71 (13H, m, Ar-H), 4.09 (2H, t, CH$_2$), 1.70 (2H, m, CH$_2$), 1.13 (3H, t, CH$_3$). $^{13}$C-NMR (300 MHz, CDCl$_3$, ppm): 155.3 (C-2), 101.8 (C-3), 164.5 (C-4), 161.7 (C-5), 106.2 (C-6), 133.7 (C-7), 100.4 (C-8), 144.8 (C-9), 102.2 (C-10), 134.4 (C-11), 128.3 (C-12), 128.4 (C-13), 127.8 (C-14), 128.3 (C-15), 128.3 (C-16), 48.7 (C-17), 21.4 (C-18), 11.9 (C-19), 141.4 (C-21), 151.6 (C-22), 119.7 (C-23), 128.4 (C-24), 118.7 (C-25).
122.5 (C-25), 115.6 (C-26). IR (KBr, cm$^{-1}$): 3500-3700, bs (OH); 1624 (-C=N)st; 1308, (-C(9)-N-C(2))st.

$L^6$: Yield: 89%. Anal.Calcd for C$_{24}$H$_{21}$N$_3$O$_3$. C, 72.16; H, 5.3; N, 10.52. Found C, 72.15; H, 5.32; N, 10.5. FAB mass spectrometry (FAB-MS): $m/z$ 400 [M+1]. $^1$H-NMR (300 MHz, CDCl$_3$, δ, ppm): 8.59 (1H, s, -OH, D$_2$O exchangeable), 6.42-7.71 (13H, m, Ar-H), 4.09 (2H, t, CH$_2$), 1.70 (2H, m, CH$_2$), 1.13 (3H, t, CH$_3$). $^{13}$C-NMR (300 MHz, CDCl$_3$, ppm): 155.3 (C-2), 101.8 (C-3), 164.5 (C-4), 161.7 (C-5), 106.2 (C-6), 133.7 (C-7), 100.4 (C-8), 144.8 (C-9), 102.2 (C-10), 134.4 (C-11), 128.3 (C-12), 128.4 (C-13), 127.8 (C-14), 128.4 (C-15), 128.3 (C-16), 48.7 (C-17), 21.4 (C-18), 11.9 (C-19), 146.3 (C-21), 145.3 (C-22), 125.1 (C-23), 128.4 (C-24), 131.4 (C-25), 129.9 (C-26). IR (KBr, cm$^{-1}$): 3500-3700, bs (OH); 1628 (-C=N)st; 1308, (-C(9)-N-C(2))st.

$L^7$: Yield: 78%. Anal.Calcd for C$_{25}$H$_{22}$N$_2$O$_3$. C, 75.36; H, 5.57; N, 7.03. Found C, 75.30; H, 5.59; N, 7.07. FAB mass spectrometry (FAB-MS): $m/z$ 399 [M+1]. $^1$H-NMR (300 MHz, CDCl$_3$, δ, ppm): 8.59 (1H, s, -OH, D$_2$O exchangeable), 10.7 (1H, s, -COOH, D$_2$O exchangeable), 6.42-7.71 (13H, m, Ar-H), 4.09 (2H, t, CH$_2$), 1.70 (2H, m, CH$_2$), 1.13 (3H, t, CH$_3$). $^{13}$C-NMR (300 MHz, CDCl$_3$, ppm): 155.3 (C-2), 101.8 (C-3), 164.5 (C-4), 161.7 (C-5), 106.2 (C-6), 133.7 (C-7), 100.4 (C-8), 144.8 (C-9), 102.2 (C-10), 134.4 (C-11), 128.3 (C-12), 128.4 (C-13), 127.8 (C-14), 128.4 (C-15), 128.3 (C-16), 48.7 (C-17), 21.4 (C-18), 11.9 (C-19), 146.3 (C-21), 145.3 (C-22), 125.1 (C-23), 128.4 (C-24), 131.4 (C-25), 129.9 (C-26). IR (KBr, cm$^{-1}$): 3500-3700, bs (OH); 1580 & 1385, (COOH)st; 1684 (-C=N)st; 1322, (-C(9)-N-C(2))st.

$L^8$: Yield: 70%. Anal.Calcd for C$_{24}$H$_{21}$ClN$_2$O$_2$. C, 71.19; H, 5.23; N, 6.9. Found C, 71.21; H, 5.25; N, 6.91. FAB mass spectrometry (FAB-MS): $m/z$ 406 [M+1]. $^1$H-NMR (300 MHz, CDCl$_3$, δ, ppm): 9.51 (1H, s, -OH, D$_2$O exchangeable), 8.32 (1H, s, -OH, D$_2$O exchangeable), 6.63-7.75 (12H, m, Ar-H), 4.12 (2H, t, CH$_2$), 1.70 (2H, m, CH$_2$), 1.02 (3H, t, CH$_3$). $^{13}$C-NMR (300 MHz, CDCl$_3$, ppm): 155.2 (C-2), 101.8 (C-3), 164.5 (C-4), 161.7 (C-5), 106.4 (C-6), 133.2 (C-7), 100.4 (C-8), 144.7 (C-9), 102.3 (C-10), 126.7 (C-11), 130.3 (C-12), 115.6 (C-13), 157.5 (C-14), 115.6 (C-15), 130.3 (C-16), 48.7
(C-17), 21.4 (C-18), 11.9 (C-19), 143.3 (C-21), 127.6 (C-22), 130.3 (C-23), 128.4 (C-24), 128.0 (C-25), 118.7 (C-26). IR (KBr, cm$^{-1}$): 3500-3700, bs (OH); 1694 (-C=N)st; 1308, (-C(9)-N-C(2))st.

**L**$^9$: Yield: 60%. Anal.Calcd for C$_{24}$H$_{22}$N$_2$O$_2$S. C, 71.62; H, 5.51; N, 6.96. Found C, 71.65; H, 5.50; N, 6.98. FAB mass spectrometry (FAB-MS): m/z 403 [M+1]. $^1$H-NMR (300 MHz, CDCl$_3$, δ, ppm): 9.51 (1H, s, -OH, D$_2$O exchangeable), 8.32 (1H, s, -OH, D$_2$O exchangeable), 6.65-7.71 (12H, m, Ar-H), 4.12 (2H, t, CH$_2$), 1.70 (2H, m, CH$_2$), 1.02 (3H, t, CH$_3$). $^{13}$C-NMR (300 MHz, CDCl$_3$, ppm): 155.2 (C-2), 101.8 (C-3), 164.5 (C-4), 161.7 (C-5), 106.4 (C-6), 133.2 (C-7), 100.4 (C-8), 144.7 (C-9), 102.3 (C-10), 126.7 (C-11), 130.3 (C-12), 115.6 (C-13), 157.5 (C-14), 115.6 (C-15), 130.3 (C-16), 48.7 (C-17), 21.4 (C-18), 11.9 (C-19), 158.1 (C-21), 126.1 (C-22), 130.7 (C-23), 127.6 (C-24), 138.3 (C-25), 117.3 (C-26). IR (KBr, cm$^{-1}$): 3500-3700, bs (OH); 2556 (SH)st; 1620 (-C-N)st; 1260 (-C=N)st; 1284, (-C(9)-N-C(2))st.

**L**$^{10}$: Yield: 65%. Anal.Calcd for C$_{24}$H$_{22}$N$_2$O$_3$. C, 74.59; H, 5.74; N, 7.25. Found C, 74.57; H, 5.73; N, 7.26. FAB mass spectrometry (FAB-MS): m/z 387 [M+1]. $^1$H-NMR (300 MHz, CDCl$_3$, δ, ppm): 9.51 (1H, s, -OH, D$_2$O exchangeable), 8.32 (1H, s, -OH, D$_2$O exchangeable), 6.42-7.1 (12H, m, Ar-H), 4.09 (2H, t, CH$_2$), 1.70 (2H, m, CH$_2$), 1.13 (3H, t, CH$_3$). $^{13}$C-NMR (300 MHz, CDCl$_3$, ppm): 155.2 (C-2), 101.8 (C-3), 164.5 (C-4), 161.7 (C-5), 106.4 (C-6), 133.2 (C-7), 100.4 (C-8), 144.7 (C-9), 102.3 (C-10), 126.7 (C-11), 130.3 (C-12), 115.6 (C-13), 157.5 (C-14), 115.6 (C-15), 130.3 (C-16), 48.7 (C-17), 21.4 (C-18), 11.9 (C-19), 158.1 (C-21), 126.1 (C-22), 130.7 (C-23), 127.6 (C-24), 138.3 (C-25), 117.3 (C-26). IR (KBr, cm$^{-1}$): 3500-3700, bs (OH); 2556 (SH)st; 1620 (-C-N)st; 1284, (-C(9)-N-C(2))st.

**L**$^{11}$: Yield: 56%. Anal.Calcd for C$_{24}$H$_{21}$N$_3$O$_4$. C, 69.39; H, 5.1; N, 10.11. Found C, 69.37; H, 5.11; N, 10.1. FAB mass spectrometry (FAB-MS): m/z 416 [M+1]. $^1$H-NMR (300 MHz, CDCl$_3$, δ, ppm): 9.51 (1H, s, -OH, D$_2$O exchangeable), 8.32 (1H, s, -OH, D$_2$O exchangeable), 6.92-7.71 (12H, m, Ar-H), 4.12 (2H, t, CH$_2$), 1.70 (2H, m, CH$_2$), 1.02 (3H, t, CH$_3$). $^{13}$C-NMR (300 MHz, CDCl$_3$, ppm): 155.2 (C-2), 101.8 (C-3), 164.5 (C-4),...
161.7 (C-5), 106.4 (C-6), 133.2 (C-7), 100.4 (C-8), 144.7 (C-9), 102.3 (C-10), 126.7 (C-11), 130.3 (C-12), 115.6 (C-13), 157.5 (C-14), 115.6 (C-15), 130.3 (C-16), 48.7 (C-17), 21.4 (C-18), 11.9 (C-19), 146.3 (C-21), 145.3 (C-22), 125.1 (C-23), 128.4 (C-24), 131.4 (C-25), 129.9 (C-26). IR (KBr, cm\(^{-1}\)): 3500-3700, bs (OH); 1626 (-C=N)\text{st}; 1288, (-C(9)-N-C(2))\text{st}.

\(\text{L}^12\): Yield: 62%. Anal.Calcd for C\(_{25}\)H\(_{22}\)N\(_2\)O\(_4\). C, 72.45; H, 5.35; N, 6.76. Found C, 72.44; H, 5.32; N, 6.77. FAB mass spectrometry (FAB-MS): \(m/z\) 415 [M+1]. \(^1\)H-NMR (300 MHz, CDCl\(_3\), \(\delta\), ppm): 10.7 (1H, s, -COOH, D\(_2\)O exchangeable), 9.51 (1H, s, -OH, D\(_2\)O exchangeable), 8.32 (1H, s, -OH, D\(_2\)O exchangeable), 6.42-7.71 (12H, m, Ar-H), 4.09 (2H, t, CH\(_2\)), 1.70 (2H, t, CH\(_2\)), 1.13 (3H, t, CH\(_3\)). \(^13\)C-NMR (300 MHz, CDCl\(_3\), ppm): 155.2 (C-2), 101.8 (C-3), 164.5 (C-4), 161.7 (C-5), 106.4 (C-6), 133.2 (C-7), 100.4 (C-8), 144.7 (C-9), 102.3 (C-10), 126.7 (C-11), 130.3 (C-12), 115.6 (C-13), 157.5 (C-14), 115.6 (C-15), 130.3 (C-16), 48.7 (C-17), 21.4 (C-18), 11.9 (C-19), 153.5 (C-21), 116.2 (C-22), 166.3 (-COOH), 128.3 (C-23), 124.3 (C-24), 135.4 (C-25), 126.8 (C-26). IR (KBr, cm\(^{-1}\)): 3500-3700, bs (OH); 1633 (-C=N)\text{st}; 1304, (-C(9)-N-C(2))\text{st}.

\(\text{L}^13\): Yield: 58%. Anal.Calcd for C\(_{24}\)H\(_{21}\)ClN\(_2\)O\(_2\). C, 71.19; H, 5.23; N, 6.92. Found C, 71.21; H, 5.25; N, 6.91. FAB mass spectrometry (FAB-MS): \(m/z\) 406 [M+1]. \(^1\)H-NMR (300 MHz, CDCl\(_3\), \(\delta\), ppm): 11.12 (1H, s, -OH, D\(_2\)O exchangeable), 9.56 (1H, s, -OH, D\(_2\)O exchangeable), 6.63-7.75 (12H, m, Ar-H), 4.12 (2H, t, CH\(_2\)), 1.70 (2H, m, CH\(_2\)), 1.02 (3H, t, CH\(_3\)). \(^13\)C-NMR (300 MHz, CDCl\(_3\), ppm): 114.8 (C-2), 127.3 (C-3), 147.2 (C-4), 130.2 (C-5), 117.2 (C-6), 131.7 (C-7), 107.6 (C-8), 143.5 (C-9), 115.3 (C-10), 126.7 (C-11), 130.3 (C-12), 115.6 (C-13), 157.5 (C-14), 130.3 (C-16), 48.7 (C-17), 21.4 (C-18), 11.9 (C-19), 143.3 (C-21), 127.6 (C-22), 130.3 (C-23), 128.4 (C-24), 128.4 (C-25), 118.7 (C-26). IR (KBr, cm\(^{-1}\)): 3500-3700, bs (OH); 1633 (-C=N)\text{st}; 1304, (-C(9)-N-C(2))\text{st}.

\(\text{L}^14\): Yield: 60%. Anal.Calcd for C\(_{24}\)H\(_{22}\)N\(_2\)O\(_2\)S. C, 71.62; H, 5.5; N, 6.96. Found C, 71.65; H, 5.50; N, 6.98. FAB mass spectrometry (FAB-MS): \(m/z\) 403 [M+1]. \(^1\)H-NMR (300 MHz, CDCl\(_3\), \(\delta\), ppm): 11.12 (1H, s, -OH, D\(_2\)O exchangeable), 9.56 (1H, s, -OH, D\(_2\)O exchangeable), 6.63-7.75 (12H, m, Ar-H), 4.12 (2H, t, CH\(_2\)), 1.70 (2H, m, CH\(_2\)), 1.02 (3H, t, CH\(_3\)).
exchangeable), 6.65-7.71 (12H, m, Ar-H), 4.12 (2H, t, CH₂), 1.70 (2H, m, CH₂), 1.02 (3H, t, CH₃). ¹³C-NMR (300 MHz, CDCl₃, ppm): 114.8 (C-2), 127.3 (C-3), 147.2 (C-4), 130.2 (C-5), 117.2 (C-6), 131.7 (C-7), 107.6 (C-8), 143.5 (C-9), 115.3 (C-10), 126.7 (C-11), 130.3 (C-12), 115.6 (C-13), 157.5 (C-14), 115.6 (C-15), 130.3 (C-16), 48.7 (C-17), 21.4 (C-18), 11.9 (C-19), 158.1 (C-21), 126.1 (C-22), 130.7 (C-23), 127.6 (C-24), 138.3 (C-25), 117.3 (C-26). IR (KBr, cm⁻¹): 3500-3700, bs (OH); 2558 (SH)st; 1642 (-C=N)st; 1312, (-C(9)-N-C(2))st.

L¹⁵: Yield: 65%. Anal.Calcd for C₂₄H₂₂N₂O₃. C, 74.59; H, 5.74; N, 7.25. Found C, 74.57; H, 5.73; N, 7.26. FAB mass spectrometry (FAB-MS): m/z 387 [M+1]. ¹H-NMR (300 MHz, CDCl₃, δ, ppm): 11.12 (1H, s, -OH, D₂O exchangeable), 9.56 (1H, s, -OH, D₂O exchangeable), 8.2 (1H, s, -OH, D₂O exchangeable), 6.42-7.71 (12H, m, Ar-H), 4.09 (2H, t, CH₂), 1.70 (2H, m, CH₂), 1.13 (3H, t, CH₃). ¹³C-NMR (300 MHz, CDCl₃, ppm): 114.8 (C-2), 127.3 (C-3), 147.2 (C-4), 130.2 (C-5), 117.2 (C-6), 131.7 (C-7), 107.6 (C-8), 143.5 (C-9), 115.3 (C-10), 126.7 (C-11), 130.3 (C-12), 115.6 (C-13), 157.5 (C-14), 115.6 (C-15), 130.3 (C-16), 48.7 (C-17), 21.4 (C-18), 11.9 (C-19), 158.1 (C-21), 126.1 (C-22), 130.7 (C-23), 127.6 (C-24), 138.3 (C-25), 117.3 (C-26). IR (KBr, cm⁻¹): 3500-3700, bs (OH); 2558 (SH)st; 1642 (-C=N)st; 1312, (-C(9)-N-C(2))st.

L¹⁶: Yield: 60%. Anal.Calcd for C₂₄H₂₁N₃O₄. C, 69.39; H, 5.1; N, 10.11. Found C, 69.37; H, 5.11; N, 10.1. FAB mass spectrometry (FAB-MS): m/z 416 [M+1]. ¹H-NMR (300 MHz, CDCl₃, δ, ppm): 11.12 (1H, s, -OH, D₂O exchangeable), 9.56 (1H, s, -OH, D₂O exchangeable), 6.92-7.71 (12H, m, Ar-H), 4.12 (2H, t, CH₂), 1.70 (2H, m, CH₂), 1.02 (3H, t, CH₃). ¹³C-NMR (300 MHz, CDCl₃, ppm): 114.8 (C-2), 127.3 (C-3), 147.2 (C-4), 130.2 (C-5), 117.2 (C-6), 131.7 (C-7), 107.6 (C-8), 143.5 (C-9), 115.3 (C-10), 126.7 (C-11), 130.3 (C-12), 115.6 (C-13), 157.5 (C-14), 115.6 (C-15), 130.3 (C-16), 48.7 (C-17), 21.4 (C-18), 11.9 (C-19), 146.3 (C-21), 145.3 (C-22), 125.1 (C-23), 128.4 (C-24), 131.4 (C-25), 129.9 (C-26). IR (KBr, cm⁻¹): 3500-3700, bs (OH); 1632 (-C=N)st; 1312, (-C(9)-N-C(2))st.
L<sup>17</sup>: Yield: 72%. Anal. Calcd for C<sub>25</sub>H<sub>22</sub>N<sub>2</sub>O<sub>4</sub>. C, 72.45; H, 5.35; N, 6.76. Found C, 72.44; H, 5.32; N, 6.77. FAB mass spectrometry (FAB-MS): m/z 415 [M+1]. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, δ, ppm): 11.12 (1H, s, -OH, D<sub>2</sub>O exchangeable), 10.7 (1H, s, -COOH, D<sub>2</sub>O exchangeable), 9.56 (1H, s, -OH, D<sub>2</sub>O exchangeable), 6.42-7.71 (12H, m, Ar-H), 4.09 (2H, t, CH<sub>2</sub>), 1.70 (2H, m, CH<sub>2</sub>), 1.13 (3H, t, CH<sub>3</sub>). <sup>13</sup>C-NMR (300 MHz, CDCl<sub>3</sub>, ppm): 114.8 (C-2), 127.3 (C-3), 147.2 (C-4), 130.2 (C-5), 117.2 (C-6), 131.7 (C-7), 107.6 (C-8), 143.5 (C-9), 115.3 (C-10), 126.7 (C-11), 130.3 (C-12), 115.6 (C-13), 157.5 (C-14), 115.6 (C-15), 130.3 (C-16), 48.7 (C-17), 21.4 (C-18), 11.9 (C-19), 153.5 (C-21), 116.2 (C-22), 166.3 (-COOH), 128.3 (C-23), 124.3 (C-24), 135.4 (C-25), 126.8 (C-26). IR (KBr, cm<sup>-1</sup>): 3500-3700, bs (OH); 1571 & 1379, (COOH)st; 1624 (-C=)=st; 1296, (-C(9)-N-C(2))st.

L<sup>18</sup>: Yield: 58%. Anal. Calcd for C<sub>24</sub>H<sub>21</sub>ClN<sub>2</sub>O. C, 74.12; H, 5.44; N, 7.2. Found C, 74.14; H, 5.40; N, 7.18. FAB mass spectrometry (FAB-MS): m/z 390 [M+1]. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, δ, ppm): 11.73 (1H, s, -OH, D<sub>2</sub>O exchangeable), 6.63-7.75 (13H, m, Ar-H), 4.12 (2H, t, CH<sub>2</sub>), 1.70 (2H, m, CH<sub>2</sub>), 1.02 (3H, t, CH<sub>3</sub>). <sup>13</sup>C-NMR (300 MHz, CDCl<sub>3</sub>, ppm): 114.8 (C-2), 127.3 (C-3), 147.2 (C-4), 130.2 (C-5), 117.2 (C-6), 131.7 (C-7), 107.6 (C-8), 143.5 (C-9), 115.3 (C-10), 134.4 (C-11), 128.3 (C-12), 128.4 (C-13), 127.8 (C-14), 128.4 (C-15), 128.3 (C-16), 48.7 (C-17), 21.4 (C-18), 11.9 (C-19), 143.3 (C-21), 127.6 (C-22), 130.3 (C-23), 128.4 (C-24), 128.4 (C-25), 118.7 (C-26). IR (KBr, cm<sup>-1</sup>): 3500-3700, bs (OH); 1645 (-C=)=st; 1324, (-C(9)-N-C(2))st.

L<sup>19</sup>: Yield: 82%. Anal. Calcd for C<sub>24</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>S. C, 74.58; H, 5.74; N, 7.25. Found C, 74.57; H, 5.72; N, 7.24. FAB mass spectrometry (FAB-MS): m/z 387 [M+1]. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, δ, ppm): 11.73 (1H, s, -OH, D<sub>2</sub>O exchangeable), 6.65-7.71 (13H, m, Ar-H), 4.12 (2H, t, CH<sub>2</sub>), 1.70 (2H, m, CH<sub>2</sub>), 1.02 (3H, t, CH<sub>3</sub>). <sup>13</sup>C-NMR (300 MHz, CDCl<sub>3</sub>, ppm): 114.8 (C-2), 127.3 (C-3), 147.2 (C-4), 130.2 (C-5), 117.2 (C-6), 131.7 (C-7), 107.6 (C-8), 143.5 (C-9), 115.3 (C-10), 134.4 (C-11), 128.3 (C-12), 128.4 (C-13), 127.8 (C-14), 128.4 (C-15), 128.3 (C-16), 48.7 (C-17), 21.4 (C-18), 11.9 (C-19), 143.3 (C-21), 127.6 (C-22), 130.3 (C-23), 128.4 (C-24), 128.4 (C-25), 118.7 (C-26). IR (KBr, cm<sup>-1</sup>): 3500-3700, bs (OH); 1615 (-C=)=st; 1320, (-C(9)-N-C(2))st.
\( \text{L}^{20} \): Yield: 80\%. Anal. Caled for \( \text{C}_{24}\text{H}_{22}\text{N}_{2}\text{O}_{2} \). C, 77.81; H, 5.99; N, 7.56. Found C, 77.83; H, 5.98; N, 7.58. FAB mass spectrometry (FAB-MS): \( m/z \) 371 [M+1]. \(^1\)H-NMR (300 MHz, CDCl\(_3\), \( \delta \), ppm): 11.73 (1H, s, -OH, D\(_2\)O exchangeable), 8.2 (1H, s, -OH, D\(_2\)O exchangeable), 6.48-7.84 (13H, m, Ar-H), 4.09 (2H, t, CH\(_2\)), 1.70 (2H, m, CH\(_2\)), 1.13 (3H, t, CH\(_3\)). \(^{13}\)C-NMR (300 MHz, CDCl\(_3\), ppm): 114.8 (C-2), 127.3 (C-3), 147.2 (C-4), 130.2 (C-5), 117.2 (C-6), 131.7 (C-7), 107.6 (C-8), 143.5 (C-9), 115.3 (C-10), 134.4 (C-11), 128.3 (C-12), 128.4 (C-13), 127.8 (C-14), 128.4 (C-15), 128.3 (C-16), 48.7 (C-17), 21.4 (C-18), 11.9 (C-19), 141.4 (C-21), 151.6 (C-22), 119.7 (C-23), 128.4 (C-24), 122.5 (C-25), 115.6 (C-26). IR (KBr, cm\(^{-1}\)): 3500-3700, bs (OH); 1621 (-C=N)st; 1318, (-C(9)-N-C(2))st.

\( \text{L}^{21} \): Yield: 72\%. Anal. Caled for \( \text{C}_{24}\text{H}_{21}\text{N}_{3}\text{O}_{3} \). C, 72.16; H, 5.3; N, 10.52. Found C, 72.15; H, 5.32; N, 10.5. FAB mass spectrometry (FAB-MS): \( m/z \) 400 [M+1]. \(^1\)H-NMR (300 MHz, CDCl\(_3\), \( \delta \), ppm): 11.73 (1H, s, -OH, D\(_2\)O exchangeable), 6.92-7.71 (13H, m, Ar-H), 4.12 (2H, t, CH\(_2\)), 1.70 (2H, m, CH\(_2\)), 1.02 (3H, t, CH\(_3\)). \(^{13}\)C-NMR (300 MHz, CDCl\(_3\), ppm): 114.8 (C-2), 127.3 (C-3), 147.2 (C-4), 130.2 (C-5), 117.2 (C-6), 131.7 (C-7), 107.6 (C-8), 143.5 (C-9), 115.3 (C-10), 134.4 (C-11), 128.3 (C-12), 48.7 (C-17), 21.4 (C-18), 11.9 (C-19), 141.4 (C-21), 151.6 (C-22), 119.7 (C-23), 128.4 (C-24), 122.5 (C-25), 115.6 (C-26). IR (KBr, cm\(^{-1}\)): 3500-3700, bs (OH); 1621 (-C=N)st; 1318, (-C(9)-N-C(2))st.

\( \text{L}^{22} \): Yield: 60\%. Anal. Caled for \( \text{C}_{25}\text{H}_{22}\text{N}_{2}\text{O}_{3} \). C, 75.36; H, 5.57; N, 7.03. Found C, 75.37; H, 5.54; N, 7.05. FAB mass spectrometry (FAB-MS): \( m/z \) 399 [M+1]. \(^1\)H-NMR (300 MHz, CDCl\(_3\), \( \delta \), ppm): 11.73 (1H, s, -OH, D\(_2\)O exchangeable), 10.7 (1H, s, -COOH, D\(_2\)O exchangeable), 6.42-7.71 (13H, m, Ar-H), 4.09 (2H, t, CH\(_2\)), 1.70 (2H, m, CH\(_2\)), 1.13 (3H, t, CH\(_3\)). \(^{13}\)C-NMR (300 MHz, CDCl\(_3\), ppm): 114.8 (C-2), 127.3 (C-3), 147.2 (C-4), 130.2 (C-5), 117.2 (C-6), 131.7 (C-7), 107.6 (C-8), 143.5 (C-9), 115.3 (C-10), 134.4 (C-11), 128.3 (C-12), 128.4 (C-13), 127.8 (C-14), 128.4 (C-15), 128.4 (C-16), 48.7 (C-17), 21.4 (C-18), 11.9 (C-19), 153.5 (C-21), 146.3 (C-22), 125.1 (C-23), 128.4 (C-24), 131.4 (C-25), 125.9 (C-26). IR (KBr, cm\(^{-1}\)): 3500-3700, bs (OH); 1613 (-C=N)st; 1288, (-C(9)-N-C(2))st.
L\textsuperscript{23}: Yield: 82%. Anal.Calcd for C\textsubscript{26}H\textsubscript{25}ClN\textsubscript{2}O. C, 74.9; H, 6.04; N, 6.72. Found: C, 74.92; H, 6.03; N, 6.70. FAB mass spectrometry (FAB-MS): m/z 418 [M+1]. 

\textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}, \delta, ppm): 8.62 (1H, s, -OH, D\textsubscript{2}O exchangeable), 6.95-7.84 (13H, m, Ar-H), 4.12 (2H, t, CH\textsubscript{2}), 1.46 (2H, m, CH\textsubscript{2}), 1.31 (2H, m, CH\textsubscript{2}), 1.24 (2H, m, CH\textsubscript{2}), 1.02 (3H, t, CH\textsubscript{3}). \textsuperscript{13}C-NMR (300 MHz, CDCl\textsubscript{3}, ppm): 155.2 (C-2), 101.7 (C-3), 164.3 (C-4), 161.6 (C-5), 106.4 (C-6), 133.1 (C-7), 100.3 (C-8), 144.7 (C-9), 102.2 (C-10), 134.2 (C-11), 128.3 (C-12), 128.6 (C-13), 127.9 (C-14), 128.6 (C-15), 128.3 (C-16), 46.7 (C-17), 28.2 (C-18), 29.6 (C-19), 22.3 (C-20), 14.2 (C-21), 143.1 (C-23), 127.7 (C-24), 130.3 (C-25), 128.5 (C-26), 128.4 (C-27), 118.7 (C-28). IR (KBr, cm\textsuperscript{-1}): 3500-3700, bs (OH); 1610 (-C=N)st; 1322, (-C(9)-N-C(2))st.

L\textsuperscript{24}: Yield: 73%. Anal.Calcd for C\textsubscript{26}H\textsubscript{26}N\textsubscript{2}OS. C, 75.33; H, 6.32; N, 6.76. Found: C, 75.34; H, 6.35; N, 6.74. FAB mass spectrometry (FAB-MS): m/z 415 [M+1]. 

\textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}, \delta, ppm): 8.62 (1H, s, -OH, D\textsubscript{2}O exchangeable), 6.67-7.71 (13H, m, Ar-H), 4.12 (2H, t, CH\textsubscript{2}), 1.46 (2H, m, CH\textsubscript{2}), 1.31 (2H, m, CH\textsubscript{2}), 1.24 (2H, m, CH\textsubscript{2}), 1.02 (3H, t, CH\textsubscript{3}). \textsuperscript{13}C-NMR (300 MHz, CDCl\textsubscript{3}, ppm): 155.2 (C-2), 101.7 (C-3), 164.3 (C-4), 161.6 (C-5), 106.4 (C-6), 133.1 (C-7), 100.3 (C-8), 144.7 (C-9), 102.2 (C-10), 134.2 (C-11), 128.3 (C-12), 128.6 (C-13), 127.9 (C-14), 128.6 (C-15), 128.3 (C-16), 46.7 (C-17), 28.2 (C-18), 29.6 (C-19), 22.3 (C-20), 14.2 (C-21), 143.1 (C-23), 127.7 (C-24), 130.3 (C-25), 128.5 (C-26), 128.4 (C-27), 118.7 (C-28). IR (KBr, cm\textsuperscript{-1}): 3500-3700, bs (OH); 2562 (SH)st; 1629 (-C=N)st; 1295, (-C(9)-N-C(2))st.

L\textsuperscript{25}: Yield: 85%. Anal.Calcd for C\textsubscript{26}H\textsubscript{26}N\textsubscript{2}O\textsubscript{2}. C, 78.36; H, 6.58; N, 7.03. Found: C, 78.35; H, 6.59; N, 7.05. FAB mass spectrometry (FAB-MS): m/z 399 [M+1]. 

\textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}, \delta, ppm): 8.62 (1H, s, -OH, D\textsubscript{2}O exchangeable), 8.2 (1H, s, -OH, D\textsubscript{2}O exchangeable), 6.91-7.77 (13H, m, Ar-H), 4.12 (2H, t, CH\textsubscript{2}), 1.46 (2H, m, CH\textsubscript{2}), 1.31 (2H, m, CH\textsubscript{2}), 1.24 (2H, m, CH\textsubscript{2}), 1.02 (3H, t, CH\textsubscript{3}). \textsuperscript{13}C-NMR (300 MHz, CDCl\textsubscript{3}, ppm): 155.2 (C-2), 101.7 (C-3), 164.3 (C-4), 161.6 (C-5), 106.4 (C-6), 133.1 (C-7), 100.3 (C-8), 144.7 (C-9), 102.2 (C-10), 134.2 (C-11), 128.3 (C-12), 128.6 (C-13), 127.9 (C-14), 128.6 (C-15), 128.3 (C-16), 46.7 (C-17), 28.2 (C-18), 29.6 (C-19), 22.3 (C-20), 14.2 (C-21), 143.1 (C-23), 127.7 (C-24), 130.3 (C-25), 128.5 (C-26), 128.4 (C-27), 118.7 (C-28). IR (KBr, cm\textsuperscript{-1}): 3500-3700, bs (OH); 2562 (SH)st; 1629 (-C=N)st; 1295, (-C(9)-N-C(2))st.
141.3 (C-23), 151.5 (C-24), 119.8 (C-25), 128.6 (C-26), 122.5 (C-27), 115.7 (C-28). IR (KBr, cm⁻¹): 3500-3700, bs (OH); 1632 (-C=N)st; 1284, (-C(9)-N-C(2))st.

L²⁶: Yield: 79%. Anal. Calcd for C₂₆H₂₅N₃O₃. C, 73.05; H, 5.89; N, 9.83. Found C, 73.07; H, 5.91; N, 9.8. FAB mass spectrometry (FAB-MS): m/z 428 [M+1]. ¹H-NMR (300 MHz, CDCl₃, δ, ppm): 8.62 (1H, s, -OH, D₂O exchangeable), 6.95-7.75 (13H, m, Ar-H), 4.12 (2H, t, CH₂), 1.46 (2H, m, CH₂), 1.31 (2H, m, CH₂), 1.24 (2H, m, CH₂), 1.02 (3H, t, CH₃). ¹³C-NMR (300 MHz, CDCl₃, ppm): 155.2 (C-2), 101.7 (C-3), 164.3 (C-4), 161.6 (C-5), 106.4 (C-6), 133.1 (C-7), 100.3 (C-8), 144.7 (C-9), 102.2 (C-10), 134.2 (C-11), 128.3 (C-12), 128.6 (C-13), 127.9 (C-14), 128.6 (C-15), 128.3 (C-16), 46.7 (C-17), 28.2 (C-18), 29.6 (C-19), 22.3 (C-20), 14.2 (C-21), 146.3 (C-23), 145.3 (C-24), 125.1 (C-25), 128.4 (C-26), 131.4 (C-27), 129.9 (C-28). IR (KBr, cm⁻¹): 3500-3700, bs (OH); 1637 (-C=N)st; 1284, (-C(9)-N-C(2))st.

L²⁷: Yield: 85%. Anal. Calcd for C₂₇H₂₆N₂O₃. C, 76.03; H, 6.14; N, 6.57. Found: C, 76.01; H, 6.12; N, 6.59. FAB mass spectrometry (FAB-MS): m/z 427 [M+1]. ¹H-NMR (300 MHz, CDCl₃, δ, ppm): 10.7 (1H, s, -COOH, D₂O exchangeable), 8.62 (1H, s, -OH, D₂O exchangeable), 6.95-7.85 (13H, m, Ar-H), 4.12 (2H, t, CH₂), 1.46 (2H, m, CH₂), 1.31 (2H, m, CH₂), 1.24 (2H, m, CH₂), 1.02 (3H, t, CH₃). ¹³C-NMR (300 MHz, CDCl₃, ppm): 155.2 (C-2), 101.7 (C-3), 164.3 (C-4), 161.6 (C-5), 106.4 (C-6), 133.1 (C-7), 100.3 (C-8), 144.7 (C-9), 102.2 (C-10), 134.2 (C-11), 128.3 (C-12), 128.6 (C-13), 127.9 (C-14), 128.6 (C-15), 128.3 (C-16), 46.7 (C-17), 28.2 (C-18), 29.6 (C-19), 22.3 (C-20), 14.2 (C-21), 146.3 (C-23), 145.3 (C-24), 125.1 (C-25), 128.4 (C-26), 131.4 (C-27), 129.9 (C-28). IR (KBr, cm⁻¹): 3500-3700, bs (OH); 1637 (-C=N)st; 1284, (-C(9)-N-C(2))st.

L²⁸: Yield: 82%. Anal. Calcd for C₂₆H₂₅ClN₂O₂. C, 72.13; H, 5.82; N, 6.47. Found: C, 72.15; H, 5.84; N, 6.46. FAB mass spectrometry (FAB-MS): m/z 434 [M+1]. ¹H-NMR (300 MHz, CDCl₃, δ, ppm): 9.56 (1H, s, -OH, D₂O exchangeable), 8.43 (1H, s, -OH, D₂O exchangeable), 6.91-7.85 (12H, m, Ar-H), 4.12 (2H, t, CH₂), 1.46 (2H, m, CH₂), 1.31 (2H, m, CH₂), 1.24 (2H, m, CH₂), 1.02 (3H, t, CH₃). ¹³C-NMR (300 MHz, CDCl₃, ppm):
155.2 (C-2), 101.7 (C-3), 164.3 (C-4), 161.6 (C-5), 106.4 (C-6), 133.1 (C-7), 100.3 (C-8),
144.7 (C-9), 102.2 (C-10), 126.8 (C-11), 130.2 (C-12), 115.8 (C-13), 157.6 (C-14), 115.8
(C-15), 130.2 (C-16), 46.7 (C-17), 28.2 (C-18), 29.6 (C-19), 22.3 (C-20), 14.2 (C-21),
143.1 (C-23), 127.7 (C-24), 130.3 (C-25), 128.5 (C-26), 128.4 (C-27), 118.7 (C-28).
IR (KBr, cm$^{-1}$): 3500-3700, bs (OH); 1621 (-C=N)st; 1311, (-C(9)-N-C(2))st.

L$^{29}$: Yield: 66%. Anal. Calcd for C$_{26}$H$_{26}$N$_2$O$_2$S. C, 72.53; H, 6.09; N, 6.51. Found: C, 72.51; H, 6.07; N, 6.52. FAB mass spectrometry (FAB-MS): m/z 431 [M+1]. $^1$H-NMR
(300 MHz, CDCl$_3$, $\delta$, ppm): 9.56 (1H, s, -OH, D$_2$O exchangeable), 8.43 (1H, s, -OH, D$_2$O exchangeable), 6.92-7.84 (12H, m, Ar-H), 4.12 (2H, t, CH$_2$), 1.46 (2H, m, CH$_2$), 1.31
(2H, m, CH$_2$), 1.24 (2H, m, CH$_2$), 1.02 (3H, t, CH$_3$). $^{13}$C-NMR (300 MHz, CDCl$_3$, ppm):
155.2 (C-2), 101.7 (C-3), 164.3 (C-4), 161.6 (C-5), 106.4 (C-6), 133.1 (C-7), 100.3 (C-8),
144.7 (C-9), 102.2 (C-10), 126.8 (C-11), 130.2 (C-12), 115.8 (C-13), 157.6 (C-14), 115.8
(C-15), 130.2 (C-16), 46.7 (C-17), 28.2 (C-18), 29.6 (C-19), 22.3 (C-20), 14.2 (C-21),
143.1 (C-23), 127.7 (C-24), 130.3 (C-25), 128.5 (C-26), 128.4 (C-27), 118.7 (C-28).
IR (KBr, cm$^{-1}$): 3500-3700, bs (OH); 2555 (SH)st; 1621 (-C=N)st; 1311, (-C(9)-N-C(2))st.

L$^{30}$: Yield: 70%. Anal. Calcd for C$_{26}$H$_{26}$N$_2$O$_3$. C, 75.34; H, 6.32; N, 6.76. Found: C, 75.36; H, 6.33; N, 6.75. FAB mass spectrometry (FAB-MS): m/z 415 [M+1]. $^1$H-NMR
(300 MHz, CDCl$_3$, $\delta$, ppm): 9.56 (1H, s, -OH, D$_2$O exchangeable), 8.43 (1H, s, -OH, D$_2$O exchangeable), 8.2 (1H, s, -OH, D$_2$O exchangeable), 8.2 (1H, s, -OH, D$_2$O exchangeable), 6.85-7.86 (12H, m, Ar-H), 4.12 (2H, t, CH$_2$), 1.46 (2H, m, CH$_2$), 1.31 (2H, m, CH$_2$), 1.24 (2H, m, CH$_2$), 1.02 (3H, t, CH$_3$). $^{13}$C-NMR (300 MHz, CDCl$_3$, ppm):
155.2 (C-2), 101.7 (C-3), 164.3 (C-4), 161.6 (C-5), 106.4 (C-6), 133.1 (C-7), 100.3 (C-8), 144.7
(C-9), 102.2 (C-10), 126.8 (C-11), 130.2 (C-12), 115.8 (C-13), 157.6 (C-14), 115.8 (C-15), 130.2
(C-16), 46.7 (C-17), 28.2 (C-18), 29.6 (C-19), 22.3 (C-20), 14.2 (C-21), 143.1 (C-23), 127.7
(C-24), 130.3 (C-25), 128.5 (C-26), 128.4 (C-27), 118.7 (C-28). IR (KBr, cm$^{-1}$): 3500-3700, bs (OH); 1634, (-C=N)st; 1316, (-C(9)-N-C(2))st.
**L**: Yield: 82%. Anal. Calcd for C_{26}H_{25}N_{3}O_{4}. C, 70.41; H, 5.68; N, 9.47. Found C, 70.40; H, 5.64; N, 9.49. FAB mass spectrometry (FAB-MS): m/z 444 [M+1]. ^1^H-NMR (300 MHz, CDCl\textsubscript{3}, δ, ppm): 9.56 (1H, s, -OH, D\textsubscript{2}O exchangeable), 8.43 (1H, s, -OH, D\textsubscript{2}O exchangeable), 7.12–7.89 (12H, m, Ar-H), 4.12 (2H, t, CH\textsubscript{2}), 1.46 (2H, m, CH\textsubscript{2}), 1.31 (2H, m, CH\textsubscript{2}), 1.24 (2H, m, CH\textsubscript{2}), 1.02 (3H, t, CH\textsubscript{3}). ^1^3^C-NMR (300 MHz, CDCl\textsubscript{3}, ppm): 155.2 (C-2), 101.7 (C-3), 164.3 (C-4), 161.6 (C-5), 106.4 (C-6), 133.1 (C-7), 100.3 (C-8), 144.7 (C-9), 102.2 (C-10), 126.8 (C-11), 130.2 (C-12), 115.8 (C-13), 157.6 (C-14), 115.8 (C-15), 130.2 (C-16), 46.7 (C-17), 28.2 (C-18), 29.6 (C-19), 22.3 (C-20), 14.2 (C-21), 146.3 (C-23), 145.3 (C-24), 125.1 (C-25), 128.4 (C-26), 131.4 (C-27), 129.9 (C-28). IR (KBr, cm\textsuperscript{-1}): 3500–3700, bs (OH); 1604, (-C=N)\textsuperscript{st}; 1285, (-C(9)-N-C(2))\textsuperscript{st}.

**L**: Yield: 75 %. Anal. Calcd for C_{27}H_{26}N_{2}O_{4}. C, 73.28; H, 5.92; N, 6.33. Found: C, 73.25; H, 5.93; N, 6.35. FAB mass spectrometry (FAB-MS): m/z 443 [M+1]. ^1^H-NMR (300 MHz, CDCl\textsubscript{3}, δ, ppm): 10.7 (1H, s, -COOH, D\textsubscript{2}O exchangeable), 9.56 (1H, s, -OH, D\textsubscript{2}O exchangeable), 8.43 (1H, s, -OH, D\textsubscript{2}O exchangeable), 7.17–7.83 (12H, m, Ar-H), 4.12 (2H, t, CH\textsubscript{2}), 1.46 (2H, m, CH\textsubscript{2}), 1.31 (2H, m, CH\textsubscript{2}), 1.24 (2H, m, CH\textsubscript{2}), 1.02 (3H, t, CH\textsubscript{3}). ^1^3^C-NMR (300 MHz, CDCl\textsubscript{3}, ppm): 155.2 (C-2), 101.7 (C-3), 164.3 (C-4), 161.6 (C-5), 106.4 (C-6), 133.1 (C-7), 100.3 (C-8), 144.7 (C-9), 102.2 (C-10), 126.8 (C-11), 130.2 (C-12), 115.8 (C-13), 157.6 (C-14), 115.8 (C-15), 130.2 (C-16), 46.7 (C-17), 28.2 (C-18), 29.6 (C-19), 22.3 (C-20), 14.2 (C-21), 146.3 (C-23), 145.3 (C-24), 125.1 (C-25), 128.4 (C-26), 131.4 (C-27), 129.9 (C-28). IR (KBr, cm\textsuperscript{-1}): 3500–3700, bs (OH); 1604 (-C=N)\textsuperscript{st}; 1285, (-C(9)-N-C(2))\textsuperscript{st}.

**L**: Yield: 75%. Anal. Calcd for C_{26}H_{25}ClN_{2}O_{2}. C, 72.13; H, 5.82; N, 6.47. Found: C, 72.15; H, 5.84; N, 6.46. FAB mass spectrometry (FAB-MS): m/z 434 [M+1]. ^1^H-NMR (300 MHz, CDCl\textsubscript{3}, δ, ppm): 11.9 (1H, s, -OH, D\textsubscript{2}O exchangeable), 9.81 (1H, s, -OH, D\textsubscript{2}O exchangeable), 6.84–7.72 (12H, m, Ar-H), 4.12 (2H, t, CH\textsubscript{2}), 1.46 (2H, m, CH\textsubscript{2}), 1.31 (2H, m, CH\textsubscript{2}), 1.24 (2H, m, CH\textsubscript{2}), 1.02 (3H, t, CH\textsubscript{3}). ^1^3^C-NMR (300 MHz, CDCl\textsubscript{3}, ppm): 114.9 (C-2), 127.2 (C-3), 147.2 (C-4), 130.2 (C-5), 117.2 (C-6), 131.6 (C-7), 107.6 (C-8), 143.2 (C-9), 115.2 (C-10), 126.8 (C-11), 130.2 (C-12), 115.8 (C-13), 157.6 (C-14), 115.8 (C-15), 130.2 (C-16), 46.7 (C-17), 28.2 (C-18), 29.6 (C-19), 22.3 (C-20), 14.2 (C-21),
143.1 (C-23), 127.7 (C-24), 130.3 (C-25), 128.5 (C-26), 128.4 (C-27), 118.7 (C-28).
IR (KBr, cm\(^{-1}\)): 3500-3700, bs (OH); 1622 (-C=N)st; 1318, (-C(9)-N-C(2))st.

\( \text{L}^{34} \): Yield: 68%. Anal. Calcd for C\(_{26}\)H\(_{26}\)N\(_2\)O\(_2\)S. C, 72.53; H, 6.09; N, 6.51; S, 7.45.
Found: C, 72.51; H, 6.07; N, 6.52; S, 7.47. FAB mass spectrometry (FAB-MS): \( m/z \) 431 [M+1]. \(^1\)H-NMR (300 MHz, CDCl\(_3\), \( \delta \), ppm) : 11.9 (1H, s, -OH, D\(_2\)O exchangeable), 9.81 (1H, s, -OH, D\(_2\)O exchangeable), 7.12-7.78 (12H, m, Ar-H), 4.12 (2H, t, CH\(_2\)), 1.46 (2H, m, CH\(_2\)), 1.31 (2H, m, CH\(_2\)), 1.24 (2H, m, CH\(_2\)), 1.02 (3H, t, CH\(_3\)). \(^{13}\)C-NMR (300 MHz, CDCl\(_3\), ppm): 114.9 (C-2), 127.2 (C-3), 147.2 (C-4), 130.2 (C-5), 117.2 (C-6), 131.6 (C-7), 107.6 (C-8), 143.2 (C-9), 115.2 (C-10), 126.8 (C-11), 130.2 (C-12), 115.8 (C-13), 157.6 (C-14), 115.8 (C-15), 130.2 (C-16), 46.7 (C-17), 28.2 (C-18), 29.6 (C-19), 22.3 (C-20), 14.2 (C-21), 143.1 (C-23), 127.7 (C-24), 130.3 (C-25), 128.5 (C-26), 128.4 (C-27), 118.7 (C-28). IR (KBr, cm\(^{-1}\)): 3500-3700, bs (OH); 2559 (SH)st; 1268 (-C=N)st; 1308, (-C(9)-N-C(2))st.

\( \text{L}^{35} \) : Yield: 60%. Anal. Calcd for C\(_{26}\)H\(_{26}\)N\(_2\)O\(_3\). C, 75.34; H, 6.32; N, 6.76. Found: C, 75.36; H, 6.33; N, 6.75. FAB mass spectrometry (FAB-MS): \( m/z \) 415 [M+1]. \(^1\)H-NMR (300 MHz, CDCl\(_3\), \( \delta \), ppm) : 11.9 (1H, s, -OH, D\(_2\)O exchangeable), 9.81 (1H, s, -OH, D\(_2\)O exchangeable), 6.94-7.64 (13H, m, Ar-H), 4.12 (2H, t, CH\(_2\)), 1.46 (2H, m, CH\(_2\)), 1.31 (2H, m, CH\(_2\)), 1.24 (2H, m, CH\(_2\)), 1.02 (3H, t, CH\(_3\)). \(^{13}\)C-NMR (300 MHz, CDCl\(_3\), ppm): 114.9 (C-2), 127.2 (C-3), 147.2 (C-4), 130.2 (C-5), 117.2 (C-6), 131.6 (C-7), 107.6 (C-8), 143.2 (C-9), 115.2 (C-10), 126.8 (C-11), 130.2 (C-12), 115.8 (C-13), 157.6 (C-14), 115.8 (C-15), 130.2 (C-16), 46.7 (C-17), 28.2 (C-18), 29.6 (C-19), 22.3 (C-20), 14.2 (C-21), 143.1 (C-23), 127.7 (C-24), 130.3 (C-25), 128.5 (C-26), 128.4 (C-27), 118.7 (C-28). IR (KBr, cm\(^{-1}\)): 3500-3700, bs (OH); 2559 (SH)st; 1605 (-C=N)st; 1292, (-C(9)-N-C(2))st.

\( \text{L}^{36} \) : Yield: 79%. Anal. Calcd for C\(_{26}\)H\(_{25}\)N\(_3\)O\(_4\). C, 70.41; H, 5.68; N, 9.47. Found C, 70.40; H, 5.64; N, 9.49. FAB mass spectrometry (FAB-MS): \( m/z \) 444 [M+1]. \(^1\)H-NMR (300 MHz, CDCl\(_3\), \( \delta \), ppm) : 11.9 (1H, s, -OH, D\(_2\)O exchangeable), 9.81 (1H, s, -OH, D\(_2\)O exchangeable), 6.92-7.84 (12H, m, Ar-H), 4.12 (2H, t, CH\(_2\)), 1.46 (2H, m, CH\(_2\)), 1.31
(2H, m, CH₂), 1.24 (2H, m, CH₂), 1.02 (3H, t, CH₃). ¹³C-NMR (300 MHz, CDCl₃, ppm):
114.9 (C-2), 127.2 (C-3), 147.2 (C-4), 130.2 (C-5), 117.2 (C-6), 131.6 (C-7), 107.6 (C-8),
143.2 (C-9), 115.2 (C-10), 126.8 (C-11), 130.2 (C-12), 115.8 (C-13), 157.6 (C-14), 115.8
(C-15), 130.2 (C-16), 46.7 (C-17), 28.2 (C-18), 29.6 (C-19), 22.3 (C-20), 14.2 (C-21), 146.3
(C-23), 145.3 (C-24), 125.1 (C-25), 128.4 (C-26), 131.4 (C-27), 129.9 (C-28).
IR (KBr, cm⁻¹): 3500-3700, bs (OH); 1610 (-C=N)st; 1295, (-C(9)-N-C(2))st.

L³⁷: Yield: 62%. Anal.Calcd for C₂₇H₂₆N₂O₄. C, 73.28; H, 5.92; N, 6.33. Found:
C, 73.25; H, 5.93; N, 6.35. FAB mass spectrometry (FAB-MS): m/z 443 [M+1]. ¹H-NMR
(300 MHz, CDCl₃, δ, ppm): 11.9 (1H, s, -OH, D₂O exchangeable), 10.7 (1H, s, -COOH,
D₂O exchangeable), 9.81 (1H, s, -OH, D₂O exchangeable), 6.97-7.62 (12H, m, Ar-H),
4.12 (2H, t, CH₂), 1.46 (2H, m, CH₂), 1.31 (2H, m, CH₂), 1.24 (2H, m, CH₂), 1.02 (3H, t,
CH₃). ¹³C-NMR (300 MHz, CDCl₃, ppm): 114.9 (C-2), 127.2 (C-3), 147.2 (C-4),
130.2 (C-5), 117.2 (C-6), 131.6 (C-7), 107.6 (C-8), 143.2 (C-9), 115.2 (C-10), 126.8 (C-11),
130.2 (C-12), 115.8 (C-13), 157.6 (C-14), 115.8 (C-15), 130.2 (C-16), 46.7 (C-17), 28.2
(C-18), 29.6 (C-19), 22.3 (C-20), 14.2 (C-21), 153.5 (C-23), 127.7 (C-24), 166.3
(COOH), 128.3 (C-25), 124.3 (C-26), 135.4 (C-27), 126.8 (C-28). IR (KBr, cm⁻¹):
3500-3700, bs (OH); 1572 & 1377, (COOH)st; 1612 (-C=N)st; 1302, (-C(9)-N-C(2))st.

L³⁸: Yield: 65%. Anal.Calcd for C₂₆H₂₅ClN₂O. C, 74.90; H, 6.04; N, 6.72. Found:
C, 74.92; H, 6.03; N, 6.70. FAB mass spectrometry (FAB-MS): m/z 418 [M+1]. ¹H-NMR
(300 MHz, CDCl₃, δ, ppm): 11.9 (1H, s, -OH, D₂O exchangeable), 6.84-7.26 (13H, m,
Ar-H), 4.12 (2H, t, CH₂), 1.46 (2H, m, CH₂), 1.31 (2H, m, CH₂), 1.24 (2H, m, CH₂), 1.02
(3H, t, CH₃). ¹³C-NMR (300 MHz, CDCl₃, ppm): 114.9 (C-2), 127.1 (C-3), 147.2 (C-4),
130.1 (C-5), 117.3 (C-6), 131.6 (C-7), 107.5 (C-8), 143.5 (C-9), 115.1 (C-10), 134.2
(C-11), 128.3 (C-12), 128.6 (C-13), 127.9 (C-14), 128.6 (C-15), 128.3 (C-16), 46.7
(C-17), 28.2 (C-18), 29.6 (C-19), 22.3 (C-20), 14.2 (C-21), 143.1 (C-23), 127.7 (C-24),
130.3 (C-25), 128.5 (C-26), 128.4 (C-27), 118.7 (C-28). IR (KBr, cm⁻¹): 3500-3700, bs
(OH); 1617 (-C=N)st; 1312, (-C(9)-N-C(2))st.
L\textsuperscript{39}: Yield: 72\%. Anal.Calcd for C\textsubscript{26}H\textsubscript{26}N\textsubscript{2}O\textsubscript{2}. C, 75.33; H, 6.32; N, 6.76. Found: C, 75.34; H, 6.35; N, 6.74. FAB mass spectrometry (FAB-MS): \(m/z\) 415 [M+1]. \(^1\)H-NMR (300 MHz, CDCl\textsubscript{3}, \(\delta\, ppm\)): 11.9 (1H, s, -OH, D\textsubscript{2}O exchangeable), 7.72-7.81 (13H, m, Ar-H), 4.12 (2H, t, CH\textsubscript{2}), 1.46 (2H, m, CH\textsubscript{2}), 1.31 (2H, m, CH\textsubscript{2}), 1.24 (2H, m, CH\textsubscript{2}), 1.02 (3H, t, CH\textsubscript{3}). \(^{13}\)C-NMR (300 MHz, CDCl\textsubscript{3}, ppm): 114.9 (C-2), 127.1 (C-3), 147.2 (C-4), 130.1 (C-5), 117.3 (C-6), 131.6 (C-7), 107.5 (C-8), 143.5 (C-9), 115.1 (C-10), 134.2 (C-11), 128.3 (C-12), 128.6 (C-13), 127.9 (C-14), 128.6 (C-15), 128.3 (C-16), 46.7 (C-17), 28.2 (C-18), 29.6 (C-19), 22.3 (C-20), 14.2 (C-21), 143.1 (C-23), 127.7 (C-24), 130.3 (C-25), 128.5 (C-26), 128.4 (C-27), 118.7 (C-28). IR (KBr, cm\textsuperscript{-1}): 3500-3700, bs (OH); 1622 (-C=N)st; 1324, (-C(9)-N-C(2))st.

L\textsuperscript{40}: Yield: 70\%. Anal.Calcd for C\textsubscript{26}H\textsubscript{26}N\textsubscript{2}O\textsubscript{2}. C, 78.36; H, 6.58; N, 7.03. Found: C, 78.35; H, 6.59; N, 7.05. FAB mass spectrometry (FAB-MS): \(m/z\) 399 [M+1]. \(^1\)H-NMR (300 MHz, CDCl\textsubscript{3}, \(\delta\, ppm\)): 11.9 (1H, s, -OH, D\textsubscript{2}O exchangeable), 8.2 (1H, s, -OH, D\textsubscript{2}O exchangeable), 6.67-7.71 (13H, m, Ar-H), 4.12 (2H, t, CH\textsubscript{2}), 1.46 (2H, m, CH\textsubscript{2}), 1.31 (2H, m, CH\textsubscript{2}), 1.24 (2H, m, CH\textsubscript{2}), 1.02 (3H, t, CH\textsubscript{3}). \(^{13}\)C-NMR (300 MHz, CDCl\textsubscript{3}, ppm): 114.9 (C-2), 127.1 (C-3), 147.2 (C-4), 130.1 (C-5), 117.3 (C-6), 131.6 (C-7), 107.5 (C-8), 143.5 (C-9), 115.1 (C-10), 134.2 (C-11), 128.3 (C-12), 128.6 (C-13), 127.9 (C-14), 128.6 (C-15), 128.3 (C-16), 46.7 (C-17), 28.2 (C-18), 29.6 (C-19), 22.3 (C-20), 14.2 (C-21), 143.1 (C-23), 127.7 (C-24), 130.3 (C-25), 128.5 (C-26), 128.4 (C-27), 118.7 (C-28). IR (KBr, cm\textsuperscript{-1}): 3500-3700, bs (OH); 1622 (-C=N)st; 1324, (-C(9)-N-C(2))st.

L\textsuperscript{41}: Yield: 60\%. Anal.Calcd for C\textsubscript{26}H\textsubscript{25}N\textsubscript{3}O\textsubscript{3}. C, 73.05; H, 5.89; N, 9.83. Found C, 73.07; H, 5.91; N, 9.8. FAB mass spectrometry (FAB-MS): \(m/z\) 428 [M+1]. \(^1\)H-NMR (300 MHz, CDCl\textsubscript{3}, \(\delta\, ppm\)): 11.9 (1H, s, -OH, D\textsubscript{2}O exchangeable), 6.87-7.75 (13H, m, Ar-H), 4.12 (2H, t, CH\textsubscript{2}), 1.46 (2H, m, CH\textsubscript{2}), 1.31 (2H, m, CH\textsubscript{2}), 1.24 (2H, m, CH\textsubscript{2}), 1.02 (3H, t, CH\textsubscript{3}). \(^{13}\)C-NMR (300 MHz, CDCl\textsubscript{3}, ppm): 114.9 (C-2), 127.1 (C-3), 147.2 (C-4), 130.1 (C-5), 117.3 (C-6), 131.6 (C-7), 107.5 (C-8), 143.5 (C-9), 115.1 (C-10), 134.2 (C-11), 128.3 (C-12), 128.6 (C-13), 127.9 (C-14), 128.6 (C-15), 128.3 (C-16), 46.7 (C-17), 28.2 (C-18), 29.6 (C-19), 22.3 (C-20), 14.2 (C-21), 141.3 (C-23), 151.5 (C-24), 119.8 (C-25), 128.6 (C-26), 122.5 (C-27), 115.7 (C-28). IR (KBr, cm\textsuperscript{-1}): 3500-3700, bs (OH); 1622 (-C=N)st; 1324, (-C(9)-N-C(2))st.
128.4 (C-26), 131.4 (C-27), 129.9 (C-28). IR (KBr, cm$^{-1}$): 3500-3700, bs (OH); 1629 (-C=N)st; 1336, (-C(9)-N-C(2))st.

**L$^4$**: Yield: 70%. Anal.Calcd for C$_{27}$H$_{26}$N$_2$O$_3$. C, 76.03; H, 6.14; N, 6.57. Found: C, 76.01; H, 6.12; N, 6.59. FAB mass spectrometry (FAB-MS): $m/z$ 427 [M+1].$^1$H-NMR (300 MHz, CDCl$_3$, δ, ppm): 11.9 (1H, s, -OH, D$_2$O exchangeable), 10.7 (1H, s, -COOH, D$_2$O exchangeable), 6.93-7.86 (13H, m, Ar-H), 4.12 (2H, t, CH$_2$), 1.46 (2H, m, CH$_2$), 1.31 (2H, m, CH$_2$), 1.24 (2H, m, CH$_2$), 1.02 (3H, t, CH$_3$).$^{13}$C-NMR (300 MHz, CDCl$_3$, ppm): 114.9 (C-2), 127.1 (C-3), 147.2 (C-4), 130.1 (C-5), 117.3 (C-6), 131.6 (C-7), 107.5 (C-8), 143.5 (C-9), 115.1 (C-10), 134.2 (C-11), 128.3 (C-12), 128.6 (C-13), 127.9 (C-14), 128.6 (C-15), 128.3 (C-16), 46.7 (C-17), 28.2 (C-18), 29.6 (C-19), 22.3 (C-20), 14.2 (C-21), 153.5 (C-23), 116.2 (C-24), 166.3 ( -COOH), 128.3 (C-25), 124.3 (C-26), 135.4 (C-27), 126.8 (C-28). IR (KBr, cm$^{-1}$): 3500-3700, bs (OH); 1576 & 1383 (COOH)st; 1632 (-C=N)st; 1336, (-C(9)-N-C(2))st.

**Preparation of copper complexes of Ligands (3-42)**

The ligand (s) (0.05 mM) and copper chloride (0.05 mM) were dissolved in ethanol (20 mL). A drop of triethylamine was added to the mixture with caution. Heat the solution for 7 hr at string condition, then poured it into water. The precipitate obtained was dissolved in DMC (dichloromethane), washed with water, dried over sodium sulphate and purified by column chromatography in chloroform : methanol medium.

**Complex of L$^3$**: Yield: 65%. Anal.Calcd for C$_{24}$H$_{22}$Cl$_2$CuN$_2$O$_2$: C, 57.09; H, 4.39; Cu, 12.59; N, 5.55. Found C, 57.08; H, 4.37; Cu, 12.61; N, 5.56. FAB mass spectrometry (FAB-MS): $m/z$ 506 [M+1]. $\mu_{\text{eff}}$ (BM) = 1.92; $\Lambda_m$ (mho$^{-1}$cm$^2$ mol$^{-1}$) = 18.

**Complex of L$^4$**: Yield: 72%. Anal.Calcd for C$_{24}$H$_{22}$CuN$_2$O$_2$S: C, 61.85; H, 4.76; Cu, 13.63; N, 6.01. Found C, 61.81; H, 4.78; Cu, 13.64; N, 6.0. FAB mass spectrometry (FAB-MS): $m/z$ 467 [M+1]. $\mu_{\text{eff}}$ (BM) = 1.85; $\Lambda_m$ (mho$^{-1}$cm$^2$ mol$^{-1}$) = 15.
Complex of \( L^5 \): Yield: 68%. Anal. Calcd for \( C_{24}H_{22}CuN_2O_3 \): C, 64.06; H, 4.93; Cu, 14.12; N, 6.23. Found C, 64.09; H, 4.92; Cu, 14.14; N, 6.22. FAB mass spectrometry (FAB-MS): \( m/z \ 451 \ [M+1] \). \( \mu_{\text{eff}} \) (BM) = 1.72; \( \Lambda_m \) (mho\(^{-1}\)cm\(^2\) mol\(^{-1}\)) = 17.

Complex of \( L^6 \): Yield: 85%. Anal. Calcd for \( C_{24}H_{22}ClCuN_3O_4 \): C, 55.92; H, 4.30; Cu, 12.33; N, 8.15. Found C, 55.9; H, 4.31; Cu, 12.31; N, 8.17. FAB mass spectrometry (FAB-MS): \( m/z \ 516 \ [M+1] \). \( \mu_{\text{eff}} \) (BM) = 1.96; \( \Lambda_m \) (mho\(^{-1}\)cm\(^2\) mol\(^{-1}\)) = 11.

Complex of \( L^7 \): Yield: 82%. Anal. Calcd for \( C_{25}H_{22}CuN_2O_3 \): C, 62.82; H, 4.64; Cu, 13.29; N, 5.86. Found C, 62.85; H, 4.68; Cu, 13.27; N, 5.84. FAB mass spectrometry (FAB-MS): \( m/z \ 479 \ [M+1] \). \( \mu_{\text{eff}} \) (BM) = 1.78; \( \Lambda_m \) (mho\(^{-1}\)cm\(^2\) mol\(^{-1}\)) = 8.

Complex of \( L^8 \): Yield: 62%. Anal. Calcd for \( C_{24}H_{22}ClCuN_3O_4 \): C, 55.34; H, 4.26; Cu, 12.20; N, 5.38. Found C, 55.36; H, 4.29; Cu, 12.18; N, 5.35. FAB mass spectrometry (FAB-MS): \( m/z \ 522 \ [M+1] \). \( \mu_{\text{eff}} \) (BM) = 1.80; \( \Lambda_m \) (mho\(^{-1}\)cm\(^2\) mol\(^{-1}\)) = 17.

Complex of \( L^9 \): Yield: 74%. Anal. Calcd for \( C_{24}H_{22}CuN_2O_3S \): C, 59.80; H, 4.60; Cu, 13.18; N, 5.81. Found C, 59.76; H, 4.62; Cu, 13.15; N, 5.82. FAB mass spectrometry (FAB-MS): \( m/z \ 483 \ [M+1] \). \( \mu_{\text{eff}} \) (BM) = 1.83; \( \Lambda_m \) (mho\(^{-1}\)cm\(^2\) mol\(^{-1}\)) = 18.

Complex of \( L^{10} \): Yield: 82%. Anal. Calcd for \( C_{24}H_{22}CuN_2O_4 \): C, 61.86; H, 4.76; Cu, 13.64; N, 6.01. Found C, 61.88; H, 4.78; Cu, 13.65; N, 6.0. FAB mass spectrometry (FAB-MS): \( m/z \ 467 \ [M+1] \). \( \mu_{\text{eff}} \) (BM) = 1.81; \( \Lambda_m \) (mho\(^{-1}\)cm\(^2\) mol\(^{-1}\)) = 15.

Complex of \( L^{11} \): Yield: 79%. Anal. Calcd for \( C_{24}H_{22}ClCuN_3O_5 \): C, 54.24; H, 4.17; Cu, 11.96; N, 7.91. Found C, 54.23; H, 4.13; Cu, 11.94; N, 7.93. FAB mass spectrometry (FAB-MS): \( m/z \ 532 \ [M+1] \). \( \mu_{\text{eff}} \) (BM) = 1.72; \( \Lambda_m \) (mho\(^{-1}\)cm\(^2\) mol\(^{-1}\)) = 8.

Complex of \( L^{12} \): Yield: 92%. Anal. Calcd for \( C_{25}H_{22}CuN_2O_5 \): C, 60.78; H, 4.49; Cu, 12.86; N, 5.67. Found C, 60.82; H, 4.53; Cu, 12.83; N, 5.65. FAB mass spectrometry (FAB-MS): \( m/z \ 495 \ [M+1] \). \( \mu_{\text{eff}} \) (BM) = 1.94; \( \Lambda_m \) (mho\(^{-1}\)cm\(^2\) mol\(^{-1}\)) = 6.
Complex of L\textsuperscript{13}: Yield: 76%. Anal. Calcd for C\textsubscript{24}H\textsubscript{22}Cl\textsubscript{2}CuN\textsubscript{2}O\textsubscript{3}: C, 55.34; H, 4.26; Cu, 12.20; N, 5.38. Found C, 55.36; H, 4.29; Cu, 12.18; N, 5.35. FAB mass spectrometry (FAB-MS): m/z 522 [M+1]. \(\mu_{\text{eff}}\) (BM) = 1.78; \(\Lambda_m\) (mho\(^{-1}\)cm\(^2\) mol\(^{-1}\)) = 9.

Complex of L\textsuperscript{14}: Yield: 78%. Anal. Calcd for C\textsubscript{24}H\textsubscript{22}CuN\textsubscript{2}O\textsubscript{3}S: C, 59.80; H, 4.60; Cu, 13.18; N, 5.81. Found C, 59.76; H, 4.62; Cu, 13.15; N, 5.82. FAB mass spectrometry (FAB-MS): m/z 483 [M+1]. \(\mu_{\text{eff}}\) (BM) = 1.83; \(\Lambda_m\) (mho\(^{-1}\)cm\(^2\) mol\(^{-1}\)) = 13.

Complex of L\textsuperscript{15}: Yield: 85%. Anal. Calcd for C\textsubscript{24}H\textsubscript{22}CuN\textsubscript{2}O\textsubscript{4}: C, 61.86; H, 4.76; Cu, 13.64; N, 6.01. Found C, 61.88; H, 4.78; Cu, 13.65; N, 6.0. FAB mass spectrometry (FAB-MS): m/z 467 [M+1]. \(\mu_{\text{eff}}\) (BM) = 1.81; \(\Lambda_m\) (mho\(^{-1}\)cm\(^2\) mol\(^{-1}\)) = 11.

Complex of L\textsuperscript{16}: Yield: 93%. Anal. Calcd for C\textsubscript{24}H\textsubscript{22}ClCuN\textsubscript{3}O\textsubscript{5}: C, 54.24; H, 4.17; Cu, 11.96; N, 7.91. Found C, 54.23; H, 4.13; Cu, 11.94; N, 7.93. FAB mass spectrometry (FAB-MS): m/z 532 [M+1]. \(\mu_{\text{eff}}\) (BM) = 1.72; \(\Lambda_m\) (mho\(^{-1}\)cm\(^2\) mol\(^{-1}\)) = 16.

Complex of L\textsuperscript{17}: Yield: 91%. Anal. Calcd for C\textsubscript{25}H\textsubscript{22}CuN\textsubscript{2}O\textsubscript{5}: C, 60.78; H, 4.49; Cu, 12.86; N, 5.67. Found C, 60.82; H, 4.53; Cu, 12.83; N, 5.65. FAB mass spectrometry (FAB-MS): m/z 495 [M+1]. \(\mu_{\text{eff}}\) (BM) = 1.94; \(\Lambda_m\) (mho\(^{-1}\)cm\(^2\) mol\(^{-1}\)) = 19.

Complex of L\textsuperscript{18}: Yield: 65%. Anal. Calcd for C\textsubscript{24}H\textsubscript{22}Cl\textsubscript{2}CuN\textsubscript{2}O\textsubscript{2}: C, 57.09; H, 4.39; Cu, 12.59; N, 5.55. Found C, 57.08; H, 4.37; Cu, 12.61; N, 5.56. FAB mass spectrometry (FAB-MS): m/z 506 [M+4]. \(\mu_{\text{eff}}\) (BM) = 1.92; \(\Lambda_m\) (mho\(^{-1}\)cm\(^2\) mol\(^{-1}\)) = 12.

Complex of L\textsuperscript{19}: Yield: 72%. Anal. Calcd for C\textsubscript{24}H\textsubscript{22}CuN\textsubscript{2}O\textsubscript{2}S: C, 61.85; H, 4.76; Cu, 13.63; N, 6.01. Found C, 61.81; H, 4.78; Cu, 13.64; N, 6.0. FAB mass spectrometry (FAB-MS): m/z 467 [M+1]. \(\mu_{\text{eff}}\) (BM) = 1.85; \(\Lambda_m\) (mho\(^{-1}\)cm\(^2\) mol\(^{-1}\)) = 16.

Complex of L\textsuperscript{20}: Yield: 69%. Anal. Calcd for C\textsubscript{24}H\textsubscript{22}CuN\textsubscript{2}O\textsubscript{3}: C, 64.06; H, 4.93; Cu, 14.12; N, 6.23. Found C, 64.09; H, 4.92; Cu, 14.14; N, 6.22. FAB mass spectrometry (FAB-MS): m/z 451 [M+1]. \(\mu_{\text{eff}}\) (BM) = 1.72; \(\Lambda_m\) (mho\(^{-1}\)cm\(^2\) mol\(^{-1}\)) = 17.
Complex of $L^{21}$: Yield: 86%. Anal. Calcd for C$_{24}$H$_{22}$ClCuN$_3$O$_4$: C, 55.92; H, 4.30; Cu, 12.33; N, 8.15. Found C, 55.9; H, 4.31; Cu, 12.31; N, 8.17. FAB mass spectrometry (FAB-MS): $m/z$ 516 [M+2]. $\mu_{\text{eff}}$(BM) = 1.96; $\Lambda_m$(mho$^{-1}$cm$^2$ mol$^{-1}$) = 19.

Complex of $L^{22}$: Yield: 87%. Anal. Calcd for C$_{25}$H$_{22}$CuN$_2$O$_4$: C, 62.82; H, 4.64; Cu, 13.29; N, 5.86. Found C, 62.85; H, 4.68; Cu, 13.27; N, 5.84. FAB mass spectrometry (FAB-MS): $m/z$ 479 [M+1]. $\mu_{\text{eff}}$(BM) = 1.78; $\Lambda_m$(mho$^{-1}$cm$^2$ mol$^{-1}$) = 8.

Complex of $L^{23}$: Yield: 73%. Anal. Calcd for C$_{26}$H$_{26}$Cl$_2$CuN$_3$O$_2$: C, 58.59; H, 4.92; Cu, 11.92; N, 5.26. Found C, 58.61; H, 4.93; Cu, 11.90; N, 5.25. FAB mass spectrometry (FAB-MS): $m/z$ 534 [M+1]. $\mu_{\text{eff}}$(BM) = 1.72; $\Lambda_m$(mho$^{-1}$cm$^2$ mol$^{-1}$) = 13.

Complex of $L^{24}$: Yield: 62%. Anal. Calcd for C$_{26}$H$_{26}$CuN$_2$O$_2$S: C, 63.20; H, 5.30; Cu, 12.86; N, 5.67. Found C, 63.22; H, 5.33; Cu, 12.85; N, 5.66. FAB mass spectrometry (FAB-MS): $m/z$ 495 [M+1]. $\mu_{\text{eff}}$(BM) = 1.88; $\Lambda_m$(mho$^{-1}$cm$^2$ mol$^{-1}$) = 18.

Complex of $L^{25}$: Yield: 88%. Anal. Calcd for C$_{26}$H$_{26}$CuN$_2$O$_3$: C, 65.32; H, 5.48; Cu, 13.29; N, 5.86. Found C, 65.35; H, 5.47; Cu, 13.26; N, 5.85. FAB mass spectrometry (FAB-MS): $m/z$ 479 [M+1]. $\mu_{\text{eff}}$(BM) = 1.81; $\Lambda_m$(mho$^{-1}$cm$^2$ mol$^{-1}$) = 11.

Complex of $L^{26}$: Yield: 83%. Anal. Calcd for C$_{26}$H$_{26}$ClCuN$_3$O$_4$: C, 57.46; H, 4.82; Cu, 11.69; N, 7.73. Found C, 57.45; H, 4.80; Cu, 11.67; N, 7.74. FAB mass spectrometry (FAB-MS): $m/z$ 544 [M+1]. $\mu_{\text{eff}}$(BM) = 1.93; $\Lambda_m$(mho$^{-1}$cm$^2$ mol$^{-1}$) = 8.

Complex of $L^{27}$: Yield: 90%. Anal. Calcd for C$_{27}$H$_{26}$CuN$_2$O$_4$: C, 64.08; H, 5.18; Cu, 12.56; N, 5.54. Found C, 64.06; H, 5.15; Cu, 12.57; N, 5.56. FAB mass spectrometry (FAB-MS): $m/z$ 507 [M+1]. $\mu_{\text{eff}}$(BM) = 1.78; $\Lambda_m$(mho$^{-1}$cm$^2$ mol$^{-1}$) = 12.

Complex of $L^{28}$: Yield: 72%. Anal. Calcd for C$_{27}$H$_{26}$Cl$_2$CuN$_2$O$_3$: C, 56.89; H, 4.77; Cu, 11.58; N, 5.10. Found C, 56.91; H, 4.80; Cu, 11.59; N, 5.09. FAB mass spectrometry (FAB-MS): $m/z$ 550 [M+1]. $\mu_{\text{eff}}$(BM) = 1.81; $\Lambda_m$(mho$^{-1}$cm$^2$ mol$^{-1}$) = 18.
Complex of L\textsuperscript{30}: Yield: 88%. Anal. Calcd for C\textsubscript{26}H\textsubscript{26}CuN\textsubscript{2}O\textsubscript{3}S: C, 61.22; H, 5.14; Cu, 12.46; N, 5.49. Found C, 61.19; H, 5.11; Cu, 12.47; N, 5.47. FAB mass spectrometry (FAB-MS): \( m/z 511 \ [M+1] \). \( \mu_{\text{eff}} \) (BM) = 1.78; \( \Lambda_m \) (mho\textsuperscript{-1}cm\textsuperscript{2}mol\textsuperscript{-1}) = 13.

Complex of L\textsuperscript{30}: Yield: 83%. Anal. Calcd for C\textsubscript{26}H\textsubscript{26}CuN\textsubscript{2}O\textsubscript{4}: C, 63.21; H, 5.30; Cu, 12.86; N, 5.67. Found C, 63.17; H, 5.31; Cu, 12.84; N, 5.69. FAB mass spectrometry (FAB-MS): \( m/z 495 \ [M+1] \). \( \mu_{\text{eff}} \) (BM) = 1.86; \( \Lambda_m \) (mho\textsuperscript{-1}cm\textsuperscript{2}mol\textsuperscript{-1}) = 15.

Complex of L\textsuperscript{31}: Yield: 79%. Anal. Calcd for C\textsubscript{26}H\textsubscript{26}ClCuN\textsubscript{3}O\textsubscript{5}: C, 55.81; H, 4.68; Cu, 11.36; N, 7.51. Found C, 55.84; H, 4.69; Cu, 11.39; N, 7.50. FAB mass spectrometry (FAB-MS): \( m/z 560 \ [M+1] \). \( \mu_{\text{eff}} \) (BM) = 1.94; \( \Lambda_m \) (mho\textsuperscript{-1}cm\textsuperscript{2}mol\textsuperscript{-1}) = 12.

Complex of L\textsuperscript{32}: Yield: 85%. Anal. Calcd for C\textsubscript{27}H\textsubscript{26}CuN\textsubscript{2}O\textsubscript{5}: C, 62.12; H, 5.02; Cu, 12.17; N, 5.37. Found C, 62.16; H, 5.03; Cu, 12.15; N, 5.38. FAB mass spectrometry (FAB-MS): \( m/z 523 \ [M+1] \). \( \mu_{\text{eff}} \) (BM) = 1.96; \( \Lambda_m \) (mho\textsuperscript{-1}cm\textsuperscript{2}mol\textsuperscript{-1}) = 20.

Complex of L\textsuperscript{33}: Yield: 80%. Anal. Calcd for C\textsubscript{26}H\textsubscript{26}Cl\textsubscript{2}CuN\textsubscript{3}O\textsubscript{5}: C, 56.89; H, 4.77; Cu, 11.58; N, 5.10. Found C, 56.91; H, 4.80; Cu, 11.59; N, 5.09. FAB mass spectrometry (FAB-MS): \( m/z 550 \ [M+1] \). \( \mu_{\text{eff}} \) (BM) = 1.81; \( \Lambda_m \) (mho\textsuperscript{-1}cm\textsuperscript{2}mol\textsuperscript{-1}) = 19.

Complex of L\textsuperscript{34}: Yield: 85%. Anal. Calcd for C\textsubscript{26}H\textsubscript{26}CuN\textsubscript{2}O\textsubscript{3}S: C, 61.22; H, 5.14; Cu, 12.46; N, 5.49. Found C, 61.19; H, 5.11; Cu, 12.47; N, 5.47. FAB mass spectrometry (FAB-MS): \( m/z 511 \ [M+1] \). \( \mu_{\text{eff}} \) (BM) = 1.78; \( \Lambda_m \) (mho\textsuperscript{-1}cm\textsuperscript{2}mol\textsuperscript{-1}) = 14.

Complex of L\textsuperscript{35}: Yield: 83%. Anal. Calcd for C\textsubscript{26}H\textsubscript{26}CuN\textsubscript{2}O\textsubscript{4}: C, 63.21; H, 5.30; Cu, 12.86; N, 5.67. Found C, 63.17; H, 5.31; Cu, 12.84; N, 5.69. FAB mass spectrometry (FAB-MS): \( m/z 495 \ [M+1] \). \( \mu_{\text{eff}} \) (BM) = 1.86; \( \Lambda_m \) (mho\textsuperscript{-1}cm\textsuperscript{2}mol\textsuperscript{-1}) = 16.

Complex of L\textsuperscript{36}: Yield: 79%. Anal. Calcd for C\textsubscript{26}H\textsubscript{26}ClCuN\textsubscript{3}O\textsubscript{5}: C, 55.81; H, 4.68; Cu, 11.36; N, 7.51. Found C, 55.84; H, 4.69; Cu, 11.39; N, 7.50. FAB mass spectrometry (FAB-MS): \( m/z 560 \ [M+1] \). \( \mu_{\text{eff}} \) (BM) = 1.94; \( \Lambda_m \) (mho\textsuperscript{-1}cm\textsuperscript{2}mol\textsuperscript{-1}) = 12.
Complex of $L^{37}$: Yield: 90%. Anal.Calcd for $C_{27}H_{26}CuN_2O_5$: C, 62.12; H, 5.02; Cu, 12.17; N, 5.37. Found C, 62.16; H, 5.03; Cu, 12.15; N, 5.38. FAB mass spectrometry (FAB-MS): $m/z$ 523 [M+1]. $\mu_{\text{eff}}$ (BM) = 1.96; $\Lambda_m$ (mho$^{-1}$cm$^2$ mol$^{-1}$) = 18.

Complex of $L^{38}$: Yield: 74%. Anal.Calcd for $C_{26}H_{26}Cl_2CuN_2O_2$: C, 58.59; H, 4.92; Cu, 11.92; N, 5.26. Found C, 58.61; H, 4.93; Cu, 11.90; N, 5.25. FAB mass spectrometry (FAB-MS): $m/z$ 534 [M+1]. $\mu_{\text{eff}}$ (BM) = 1.72; $\Lambda_m$ (mho$^{-1}$cm$^2$ mol$^{-1}$) = 13.

Complex of $L^{39}$: Yield: 65%. Anal.Calcd for $C_{26}H_{26}CuN_2S$: C, 63.20; H, 5.30; Cu, 12.86; N, 5.67. Found C, 63.22; H, 5.33; Cu, 12.85; N, 5.66. FAB mass spectrometry (FAB-MS): $m/z$ 495 [M+1]. $\mu_{\text{eff}}$ (BM) = 1.88; $\Lambda_m$ (mho$^{-1}$cm$^2$ mol$^{-1}$) = 18.

Complex of $L^{40}$: Yield: 85%. Anal.Calcd for $C_{26}H_{26}CuN_2O_3$: C, 65.32; H, 5.48; Cu, 13.29; N, 5.86. Found C, 65.35; H, 5.47; Cu, 13.26; N, 5.85. FAB mass spectrometry (FAB-MS): $m/z$ 479 [M+1]. $\mu_{\text{eff}}$ (BM) = 1.81; $\Lambda_m$ (mho$^{-1}$cm$^2$ mol$^{-1}$) = 11.

Complex of $L^{41}$: Yield: 86%. Anal.Calcd for $C_{26}H_{26}ClCuN_3O_4$: C, 57.46; H, 4.82; Cu, 11.69; N, 7.73. Found C, 57.45; H, 4.80; Cu, 11.67; N, 7.74. FAB mass spectrometry (FAB-MS): $m/z$ 544 [M+1]. $\mu_{\text{eff}}$ (BM) = 1.93; $\Lambda_m$ (mho$^{-1}$cm$^2$ mol$^{-1}$) = 8.

Complex of $L^{42}$: Yield: 94%. Anal.Calcd for $C_{27}H_{26}CuN_2O_4$: C, 64.08; H, 5.18; Cu, 12.56; N, 5.54. Found C, 64.06; H, 5.15; Cu, 12.57; N, 5.56. FAB mass spectrometry (FAB-MS): $m/z$ 507 [M+1]. $\mu_{\text{eff}}$ (BM) = 1.78; $\Lambda_m$ (mho$^{-1}$cm$^2$ mol$^{-1}$) = 12.
Section-2

There is considerable interest in developing novel antimicrobials due to growing concern over rise in rate of infection by antibiotic-resistant microorganisms. The enormous significance of flavone based therapeutic agents caught our attention for the synthesis of structurally modified flavone derivatives to modulate electrochemical behavior that are associated with their pharmacological properties. Flavone (both natural and synthetic) are the key components of many bioactive compounds. The flavone scaffold is a useful structural motif for the development of effective therapeutic agents. There is a continuing interest in metal complexes of Schiff bases includes the presence of both hard nitrogen or oxygen and soft sulphur donor atoms in the backbones of these ligands. The structural properties of copper proteins are an intense absorption band near 600 nm and relatively high copper(II)/copper(I) reduction potentials. In this section, the hydroxyflavone scaffold was modified with different aromatic amines. The proposed system of copper complexes of 5-hydroxyflavone derivatives may be mimic natural proteins. The detailed synthetic strategy is outlined in the Scheme 2. Synthesis of flavones and their derivatives have attracted considerable attention due to their significant biocidal, pharmaceutical and antioxidant activities. It has been observed that the presence of hydroxyl groups at C-5 is required for higher biological activities. In this section, the structurally modified 5-hydroxyflavone derivatives (L\textsuperscript{43-51}) are synthesized from 5-hydroxyflavone with 4-aminoantipyrine (L\textsuperscript{43}), o-aminophenol (L\textsuperscript{44}), o-aminobenzoic acid (L\textsuperscript{45}), o-aminothiazole (L\textsuperscript{46}), thiosemicarbazide (L\textsuperscript{47}), 4-aminoantipyrine-o-aminophenol (L\textsuperscript{48}), 4-aminoantipyrine-o-aminobenzoic acid (L\textsuperscript{49}), 4-aminoantipyrine-o-aminothiazole (L\textsuperscript{50}) and 4-aminoantipyrine-thiosemicarbazide (L\textsuperscript{51}), respectively. The corresponding Cu(II) complexes are also prepared.
a - o-aminophenol
b - o-aminobenzoyl acid
c - 4-aminocarbazol
4-aminothiazole
e - thiosalicilic acid
f - copper chloride
The Carbon skeleton representation of ligands ($L^{43}$-$L^{51}$)
Preparation of Ligand (L\textsuperscript{43}-L\textsuperscript{47})

5-Hydroxyflavone was synthesized from 2,6-dihydroxyacetophenone according to the method of Looker \textit{et al.}, [22] and identified by elemental analysis, IR and UV spectrum.

Equimolar amount of 5-hydroxyflavone and o-aminophenol (a)/ o-aminobenzoic acid (b)/ 4-aminoantipyrine(c)/ o-aminothiazole (d)/ thiosemicarbazide (e) were dissolved in ethanol (40 mL). Acetic acid (1.0 mL) was added to this solution. The solution was stirred for 3 hr and precipitates formed (scheme 3). The precipitate was filtered and washed with water and dried.

L\textsuperscript{43}: Yield: 60%. Anal.Calcd for C\textsubscript{21}H\textsubscript{15}NO\textsubscript{3}: C, 76.58; H, 4.59; N, 4.25. Found: C, 76.50; H, 4.52; N, 4.18. FAB mass spectrometry (FAB-MS): \(m/z\) 330 [M+1]. \(^1\)H-NMR (300 MHz, CDCl\textsubscript{3}, \(\delta\), ppm): 11.2 (1H, s, -OH, D\textsubscript{2}O exchangeable), 8.1 (1H, s, -OH, D\textsubscript{2}O exchangeable), 6.6-7.8 (13H, m, Ar-H). \(^{13}\)C-NMR (300 MHz, CDCl\textsubscript{3}, \(\delta\), ppm): 154.6 (C-2), 86.4 (C-3), 167.6 (C-4), 163.3 (C-5), 114.6 (C-6), 134.4 (C-7), 110.9 (C-8), 154.6 (C-9), 108.8 (C-10), 131.6 (C-11), 126.3 (C-12), 127.5 (C-13), 126.4 (C-14), 127.5 (C-15), 129.3 (C-16), 142.6 (C-18), 152.2 (C-19), 120.6 (C-20), 129.2 (C-21), 124.2 (C-22), 116.8 (C-23).

L\textsuperscript{44}: Yield: 65%. Anal.Calcd for C\textsubscript{22}H\textsubscript{15}NO\textsubscript{4}: C, 73.94; H, 4.23; N, 3.91. Found: C, 73.88; H, 4.16; N, 3.88. FAB mass spectrometry (FAB-MS): \(m/z\) 358 [M+1]. \(^1\)H-NMR (300 MHz, CDCl\textsubscript{3}, \(\delta\), ppm): 11.2 (1H, s, -OH, D\textsubscript{2}O exchangeable) 8.1 (1H, s, -OH, D\textsubscript{2}O exchangeable), 6.6-7.8 (13H, m, Ar-H). \(^{13}\)C-NMR (300 MHz, CDCl\textsubscript{3}, \(\delta\), ppm): 150.6 (C-2), 86.4 (C-3), 167.6 (C-4), 163.3 (C-5), 114.6 (C-6), 134.4 (C-7), 110.9 (C-8), 154.6 (C-9), 108.8 (C-10), 131.6 (C-11), 126.3 (C-12), 127.5 (C-13), 126.4 (C-14), 127.5 (C-15), 129.3 (C-16), 154.6 (C-18), 115.5 (C-19), 129.7 (C-20), 125.6 (C-21), 136.6 (C-22), 127.4 (C-23), 167.8 (C-24).
L$^{45}$: Yield: 76%. Anal. Calcd for C$_{26}$H$_{21}$N$_{3}$O$_{3}$: C, 73.74; H, 4.99; N, 9.9. Found: C, 73.68; H, 4.91; N, 9.82. FAB mass spectrometry (FAB-MS): $m/z$ 424 [M$^+$1]. $^1$H-NMR (300 MHz, CDCl$_3$, $\delta$, ppm): 11.5 (1H, s, -OH, D$_2$O exchangeable), 6.4-7.5 (14H, m, Ar-H), 1.8 (3H, s, H$_3$C-N), 1.5 (3H, s, H$_3$C-C). $^{13}$C-NMR (300 MHz, CDCl$_3$, $\delta$, ppm): 150.6 (C-2), 86.4 (C-3), 167.6 (C-4), 163.3 (C-5), 114.6 (C-6), 134.4 (C-7), 110.9 (C-8), 154.6 (C-9), 108.8 (C-10), 131.6 (C-11), 126.3 (C-12), 127.5 (C-13), 126.4 (C-14), 127.5 (C-15), 129.3 (C-16), 110.3 (C-18), 161.3 (C-19), 150.7 (C-22), 13.6 (C-23), 35.9 (C-24), 136.5 (C-25), 124.7 (C-26), 130.6 (C-27), 122.3 (C-28) 130.6 (C-29), 124.7 (C-30).

L$^{46}$: Yield: 62%. Anal. Calcd for C$_{18}$H$_{12}$N$_{2}$O$_{2}$S: C, 67.49; H, 3.78; N, 8.75. Found: C, 67.42; H, 3.72; N, 8.69. FAB mass spectrometry (FAB-MS): $m/z$ 321 [M$^+$1]. $^1$H-NMR (300 MHz, CDCl$_3$, $\delta$, ppm): 11.6 (1H, s, -OH, D$_2$O exchangeable), 5.98-7.92 (11H, m, Ar-H). $^{13}$C-NMR (300 MHz, CDCl$_3$, $\delta$, ppm): 150.6 (C-2), 86.4 (C-3), 167.6 (C-4), 163.3 (C-5), 114.6 (C-6), 134.4 (C-7), 110.9 (C-8), 154.6 (C-9), 108.8 (C-10), 131.6 (C-11), 126.3 (C-12), 127.5 (C-13), 126.4 (C-14), 127.5 (C-15), 129.3 (C-16), 172.6 (C-18), 141.5 (C-20), 115.9 (C-21).

L$^{47}$: Yield: 70%. Anal. Calcd for C$_{16}$H$_{13}$N$_{3}$O$_{2}$S: C, 61.72; H, 4.2; N, 13.49. Found: C, 61.65; H, 4.15; N, 13.4. FAB mass spectrometry (FAB-MS): $m/z$ 312 [M$^+$1]. $^1$H-NMR (300 MHz, CDCl$_3$, $\delta$, ppm): 11.8 (1H, s, -NH), 11.3 (1H, s, -OH, D$_2$O exchangeable), 8.0 (1H, s, br, HN of –NH$_2$), 7.5 (1H, s, br, HN of –NH$_2$), 6.9-7.8 (9H, m, Ar-H). $^{13}$C-NMR (300 MHz, CDCl$_3$, $\delta$, ppm): 150.6 (C-2), 86.4 (C-3), 167.6 (C-4), 163.3 (C-5), 114.6 (C-6), 134.4 (C-7), 110.9 (C-8), 154.6 (C-9), 108.8 (C-10), 131.6 (C-11), 126.3 (C-12), 127.5 (C-13), 126.4 (C-14), 127.5 (C-15), 129.3 (C-16), 182.3 (C-19).

**Preparation of Ligand (L$^{48}$-L$^{51}$)**

5-hydroxyflavone and 4-aminoantipyrine-o-aminophenol (a) / o-aminobenzoic acid (b) / o-aminothiazole (d) / thiosemicarbazide (e) were dissolved in ethanol (40 mL) in equimolar volume. Acetic acid (1.0 mL) was added to this solution. The solution was
refluxed for 6 hr with stirring and a yellow precipitate formed (Scheme 4). The precipitate was filtered and washed with water and ethanol.

**L48**: Yield: 65%. Anal.Calcd for C_{32}H_{26}N_{4}O_{3}: C, 74.69; H, 5.09; N, 10.88. Found: C, 74.62; H, 5.1; N, 10.82. FAB mass spectrometry (FAB-MS): m/z 515 [M+1]. \(^1\)H-NMR (300 MHz, CDCl₃, δ, ppm): 11.5 (1H, s, -OH, D₂O exchangeable), 8.7 (1H, s, -OH, D₂O exchangeable), 6.7-7.91 (18H, m, Ar-H), 1.94 (3H, s, H₃C-N), 1.7 (3H, s, H₃C-C).

\(^{13}\)C-NMR (300 MHz, CDCl₃, δ, ppm): 150.6(C-2), 86.4 (C-3), 167.6 (C-4), 163.3 (C-5), 114.6 (C-6), 134.4 (C-7), 110.9 (C-8), 154.6 (C-9), 108.8 (C-10), 131.6 (C-11), 126.3 (C-12), 127.5 (C-13), 126.4 (C-14), 127.5 (C-15), 129.3 (C-16), 110.3 (C-18), 152.9 (C-19), 150.7 (C-22), 13.6 (C-23), 35.9 (C-24), 136.5 (C-25), 124.7 (C-26), 130.6 (C-27), 122.3 (C-28) 130.6 (C-29), 124.7 (C-30), 135.6 (C-32), 150.7 (C-33), 118.3 (C-34), 127.9 (C-35), 123.5 (C-36), 113.9 (C-37).

**L49**: Yield: 69%. Anal.Calcd for C_{33}H_{26}N_{4}O_{4}: C, 73.04; H, 4.83; N, 10.32. Found: C, 72.95; H, 4.75; N, 10.3. FAB mass spectrometry (FAB-MS): m/z 543 [M+1]. \(^1\)H-NMR (300 MHz, CDCl₃, δ, ppm): 11.5 (1H, s, -OH, D₂O exchangeable), 10.7 (1H, s, -COOH, D₂O exchangeable), 6.5-7.68 (18H, m, Ar-H), 1.94 (3H, s, H₃C-N), 1.7 (3H, s, H₃C-C).

\(^{13}\)C-NMR (300 MHz, CDCl₃, δ, ppm): 150.6(C-2), 86.4 (C-3), 167.6 (C-4), 163.3 (C-5), 114.6 (C-6), 134.4 (C-7), 110.9 (C-8), 154.6 (C-9), 108.8 (C-10), 131.6 (C-11), 126.3 (C-12), 127.5 (C-13), 126.4 (C-14), 127.5 (C-15), 129.3 (C-16), 110.3 (C-18), 152.9 (C-19), 150.7 (C-22), 13.6 (C-23), 35.9 (C-24), 136.5 (C-25), 124.7 (C-26), 130.6 (C-27), 122.3 (C-28) 130.6 (C-29), 124.7 (C-30), 147.9 (C-32), 116.7 (C-33), 128.8 (C-34), 124.7 (C-35), 136.1 (C-36), 127.7 (C-37), 166.7 (C-38).

**L50**: Yield: 60%. Anal.Calcd for C_{29}H_{23}N_{5}O_{2}S: C, 68.89; H, 4.58; N, 13.85. Found: C, 68.9; H, 4.52; N, 13.78. FAB mass spectrometry (FAB-MS): m/z 506 [M+1]. \(^1\)H-NMR (300 MHz, CDCl₃, δ, ppm): 11.5 (1H, s, -OH, D₂O exchangeable), 6.4-7.5 (16H, m, Ar-H), 1.94 (3H, s, H₃C-N), 1.7 (3H, s, H₃C-C). \(^{13}\)C-NMR (300 MHz, CDCl₃, δ, ppm): 150.6 (C-2), 86.4 (C-3), 167.6 (C-4), 163.3 (C-5), 114.6 (C-6), 134.4 (C-7), 108.8 (C-10), 126.3 (C-12), 127.5 (C-13), 126.4 (C-14), 127.5 (C-15), 129.3 (C-16), 110.9 (C-8), 154.6 (C-9), 108.8 (C-10), 131.6 (C-11), 126.3 (C-12), 127.5 (C-13), 126.4 (C-14), 127.5 (C-15), 129.3 (C-16), 110.9 (C-8), 154.6 (C-9), 108.8 (C-10), 131.6 (C-11), 126.3 (C-12), 127.5 (C-13), 126.4 (C-14), 127.5 (C-15).
(C-15), 129.3 (C-16), 110.3 (C-18), 151.3 (C-19), 150.7 (C-22), 13.6 (C-23), 35.9 (C-24),
136.5 (C-25), 124.7 (C-26), 130.6 (C-27), 122.3 (C-28), 130.6 (C-29), 124.7 (C-30), 172.7
(C-32), 139.1 (C-34), 118.2 (C-35).

\[ \text{L}^{51}: \text{Yield: 56\%. Anal.Calcd for } C_{27}H_{24}N_6O_2S: \text{ C, 65.3; H, 4.87; N, 16.92. Found: C, 65.24; H, 4.83; N, 16.86. FAB mass spectrometry (FAB-MS): } m/z \text{ 497 [M+1].} \]

\[ ^1H-\text{NMR (300 MHz, CDCl}_3, \text{ } \delta, \text{ ppm): 12.1 (1H, s, -NH), 11.5 (1H, s, -OH, D}_2\text{O exchangeable), 8.6 (1H, s, br, HN of } -\text{NH}_2, 7.95 (1H, s, br, HN of } -\text{NH}_2), 6.92-7.71 (14H, m, Ar-H), 1.94 (3H, s, H}_3\text{C-N), 1.7 (3H, s, H}_3\text{C-C).} \]

\[ ^{13}\text{C-NMR (300 MHz, CDCl}_3, \text{ } \delta, \text{ ppm): } 150.6 (C-2), 86.4 (C-3), 167.6 (C-4), 163.3 (C-5), 114.6 (C-6), 134.4 (C-7), 110.9 (C-8), 154.6 (C-9), 108.8 (C-10), 131.6 (C-11), 126.3 (C-12), 127.5 (C-13), 126.4 (C-14), 127.5 (C-15), 129.3 (C-16), 110.3 (C-18), 143.1 (C-19), 150.7 (C-22), 13.6 (C-23), 35.9 (C-24), 136.5 (C-25), 124.7 (C-26), 130.6 (C-27), 122.3 (C-28) 130.6 (C-29), 124.7 (C-30), 180.3 (C-33). \]

**Preparation of copper complexes of Ligands (L^{43}-L^{51})**

The ligand (s) (0.05 mM) and copper acetate (0.05 mM) were dissolved in acetone (20 mL). A drop of triethylamine was added to the mixture with caution. After stirring for 4 hr at room temperature, the precipitate was separated by suction filtration, purified by washing several times with acetone and dried in vaccum.

**Complex of L^{43}:** Yield: 74%. Anal.Calcd for CuC\(_{21}\)H\(_{15}\)NO\(_4\): C, 61.68; H, 3.70; Cu, 15.54; N, 3.43. Found: C, 61.64; H, 3.64; Cu, 15.59; N, 3.45. FAB mass spectrometry (FAB-MS): \( m/z \text{ 410 [M+1]. } \mu_{\text{eff}} \text{(BM) = 1.92; } \Lambda_m \text{ (mho}^{-1}\text{cm}^2\text{mol}^{-1}) = 24. \)

**Complex of L^{44}:** Yield: 79%. Anal.Calcd for CuC\(_{22}\)H\(_{15}\)NO\(_5\): C, 60.48; H, 3.46; Cu, 14.54; N, 3.21. Found: C, 60.43; H, 3.48; Cu, 14.51; N, 3.24. FAB mass spectrometry (FAB-MS): \( m/z \text{ 438 [M+1]. } \mu_{\text{eff}} \text{(BM) = 2.06; } \Lambda_m \text{ (mho}^{-1}\text{cm}^2\text{mol}^{-1}) = 22. \)
Complex of $\text{L}^{45}$: Yield: 62%. Anal. Calcd for CuC$_{28}$H$_{33}$N$_3$O$_5$: C, 61.68; H, 4.25; Cu, 11.67; N, 7.71. Found: C, 61.72; H, 4.21; Cu, 11.72; N, 7.7. FAB mass spectrometry (FAB-MS): $m/z$ 546 [M+1]. $\mu_{\text{eff}}$ (BM) = 2.06; $\Lambda_{m}$ (mho cm$^{-2}$ mol$^{-1}$) = 18.

Complex of $\text{L}^{46}$: Yield: 76%. Anal. Calcd for CuC$_{20}$H$_{16}$N$_2$O$_5$S: C, 52.22; H, 3.5; Cu, 13.83; N, 6.09. Found: 52.2; H, 3.51; Cu, 13.8; N, 6.14. FAB mass spectrometry (FAB-MS): $m/z$ 437 [M+1]. $\mu_{\text{eff}}$ (BM) = 1.98; $\Lambda_{m}$ (mho$^{-1}$ cm$^2$ mol$^{-1}$) = 16.

Complex of $\text{L}^{47}$: Yield: 60%. Anal. Calcd for CuC$_{16}$H$_{13}$N$_3$O$_3$: C, 49.16; H, 3.35; Cu, 16.26; N, 10.75. Found: C, 49.14; H, 3.32; Cu, 16.3; N, 10.79. FAB mass spectrometry (FAB-MS): $m/z$ 392 [M+1]. $\mu_{\text{eff}}$ (BM) = 2.06; $\Lambda_{m}$ (mho$^{-1}$ cm$^2$ mol$^{-1}$) = 29.

Complex of $\text{L}^{48}$: Yield: 66%. Anal. Calcd for CuC$_{32}$H$_{24}$N$_4$O$_3$: C, 66.71; H, 4.20; Cu, 11.03; N, 9.73. Found: C, 66.68 H, 4.24; Cu, 11.06; N, 9.69. FAB mass spectrometry (FAB-MS): $m/z$ 577 [M+1]. $\mu_{\text{eff}}$ (BM) = 1.99; $\Lambda_{m}$ (mho$^{-1}$ cm$^2$ mol$^{-1}$) = 14.

Complex of $\text{L}^{49}$: Yield: 58%. Anal. Calcd for CuC$_{33}$H$_{24}$N$_4$O$_4$: C, 65.61; H, 4.00; Cu, 10.52; N, 9.27. Found: C, 65.64; H, 4.03; Cu, 10.48; N, 9.23. FAB mass spectrometry (FAB-MS): $m/z$ 605 [M+1]. $\mu_{\text{eff}}$ (BM) = 1.88; $\Lambda_{m}$ (mho$^{-1}$ cm$^2$ mol$^{-1}$) = 20.

Complex of $\text{L}^{50}$: Yield: 76%. Anal. Calcd for CuC$_{31}$H$_{25}$N$_5$O$_4$: C, 59.36; H, 4.02; Cu, 10.13; N, 11.17. Found: C, 59.39; H, 4.0; Cu, 10.17; N, 11.2. FAB mass spectrometry (FAB-MS): $m/z$ 603 [M+1]. $\mu_{\text{eff}}$ (BM) = 1.98; $\Lambda_{m}$ (mho$^{-1}$ cm$^2$ mol$^{-1}$) = 58.

Complex of $\text{L}^{51}$: Yield: 80%. Anal. Calcd for CuC$_{27}$H$_{22}$N$_6$O$_2$: C, 58.10; H, 3.97; Cu, 11.39; N, 15.06. Found: C, 58.13; H, 3.95; Cu, 11.33; N, 15.01. FAB mass spectrometry (FAB-MS): $m/z$ 559 [M+1]. $\mu_{\text{eff}}$ (BM) = 1.90; $\Lambda_{m}$ (mho$^{-1}$ cm$^2$ mol$^{-1}$) = 10.
Section-3

Several classes of antimicrobial compounds are presently available; microorganism’s resistance to these drugs constantly emerges. In order to prevent this serious medical problem, the elaboration of new types of antibacterial agents or the expansion of bioactivity of the naturally known biosensitive compounds is a very interesting research problem. The synthesis and characterization of metal complexes with organic bioactive ligands is one of the promising fields for the search, in particular, of copper complexes with derivatives of hydroxyflavone. Metal complexes of S-, N-, and O-chelating ligands have attracted the considerable attention because of their interesting physico-chemical properties, pronounced biological activities, and as models of metalloenzyme active sites. The structural modifications of promising lead compounds are still a major line of approach to develop new therapeutic agents. It involves an intensive effort to condense the different pharmacophoric groups of bioactive active moieties into one compound, and it may behave as chemotherapeutic agents. Due to the diversified nature, hydroxyflavone derivatives are a useful substance in medicinal research. In the present study, we report the synthesis and biochemical activities of copper complexes with hydroxyflavone derivatives.

Metal complexes derived from flavone derivatives have been extensively investigated due to the high physiological activities of the free ligands and the presence of a chelatophore group of different donor atoms in the coordination sphere. In this chapter, the proposed system of ligands contains different coordinating groups like –OH, -SH, -COOH etc and also possessed a highly conjugated aromatic system. 3-hydroxyflavone is chosen in the present work as active pharmacy core and some structural modifications are designed to explore their antioxidant activities. Schiff-bases are able to improve various biological and pharmacological activities of a pharmacy core such as antitumor, antioxidation and antibacterial activities. The structural modifications of 3-hydroxyflavone with 4-aminoantipyrine (L$^{52}$) / o-aminophenol (L$^{53}$) / o-aminobenzoic acid (L$^{54}$) / o-aminobenzenethiol (L$^{55}$) / thiosemicarbazide (L$^{56}$) are carried out in ethanol. Their corresponding Cu(II) complexes are also prepared. The experimental results are given in this chapter.
a \textit{o}-aminophenol \\
b \textit{o}-aminobenzoic acid \\
c 4-aminoantipyrine \\
e thiosemicarbazide \\
f copper chloride \\
g \textit{o}-aminothiol
Preparation of Ligand (L°52-L°56)

Equimolar amount of 3-hydroxyflavone and o-aminophenol (a)/ o-aminobenzoic acid (b)/ 4-aminoantipyrine (c)/ o-aminothiazole (g)/ thiosemicarbazide (d) were dissolved in ethanol (40 mL). Acetic acid (1.0 mL) was added to this solution. The solution was stirred for 7 hr and poured into cold ice, precipitate formed. The precipitate was dissolved in DMC. The organic layer was separated and washed the water layer with DMC. The compound was purified using column chromatography technique.

L°52: Yield: 60%. Anal.Calcd for C21H15NO3: C, 76.58; H, 4.59; N, 4.25. Found: C, 76.50; H, 4.52; N, 4.18. FAB mass spectrometry (FAB-MS): m/z 330 [M+1]. 1H-NMR (300 MHz, CDCl3, δ, ppm): 8.59 (1H, s, -OH, D2O exchangeable), 8.1 (1H, s, -OH, D2O exchangeable), 6.78-7.97 (13H, m, Ar-H). 13C-NMR (300 MHz, CDCl3, δ, ppm): 153.8 (C-2), 129.8 (C-3), 147.9 (C-4), 128.3 (C-5), 122.7 (C-6), 132.4 (C-7), 114.9 (C-8), 155.1 (C-9), 118.8 (C-10), 131.6 (C-11), 126.3 (C-12), 127.5 (C-13), 126.4 (C-14), 127.5 (C-15), 129.3 (C-16), 142.6 (C-18), 152.2 (C-19), 120.6 (C-20), 129.2 (C-21), 124.2 (C-22), 116.8 (C-23).

L°53: Yield: 65%. Anal.Calcd for C22H15NO4: C, 73.94; H, 4.23; N, 3.91. Found: C, 73.88; H, 4.16; N, 3.88. FAB mass spectrometry (FAB-MS): m/z 358 [M+1]. 1H-NMR (300 MHz, CDCl3, δ, ppm): 8.59 (1H, s, -OH, D2O exchangeable) 10.7 (1H, s, -OH, D2O exchangeable), 6.6-7.8 (13H, m, Ar-H). 13C-NMR (300 MHz, CDCl3, δ, ppm): 153.8 (C-2), 129.8 (C-3), 147.9 (C-4), 128.3 (C-5), 122.7 (C-6), 132.4 (C-7), 114.9 (C-8), 155.1 (C-9), 118.8 (C-10), 131.6 (C-11), 126.3 (C-12), 127.5 (C-13), 126.4 (C-14), 127.5 (C-15), 129.3 (C-16), 154.6 (C-18), 155.5 (C-19), 129.7 (C-20), 125.6 (C-21), 136.6 (C-22), 127.4 (C-23), 167.8 (C-24).

L°54: Yield: 76%. Anal.Calcd for C26H21N3O3: C, 73.74; H, 4.99; N, 9.9. Found: C, 73.68; H, 4.91; N, 9.82. FAB mass spectrometry (FAB-MS): m/z 424 [M+1]. 1H-NMR (300 MHz, CDCl3, δ, ppm): 8.59 (1H, s, -OH, D2O exchangeable), 6.4-7.5 (14H, m, Ar-H), 1.4 (3H, s, H3C-N), 1.62 (3H, s, H3C-C). 13C-NMR (300 MHz, CDCl3, δ, ppm): 153.8 (C-2), 129.8 (C-3), 147.9 (C-4), 128.3 (C-5), 122.7 (C-6), 132.4 (C-7), 114.9 (C-8), 155.1 (C-9),
118.8 (C-10), 131.6 (C-11), 126.3 (C-12), 127.5 (C-13), 126.4 (C-14), 127.5 (C-15), 129.3 (C-16), 110.3 (C-18), 161.3 (C-19), 150.7 (C-22), 13.6 (C-23), 35.9 (C-24), 136.5 (C-25), 124.7 (C-26), 130.6 (C-27), 122.3 (C-28) 130.6 (C-29), 124.7 (C-30).

L$^{55}$: Yield: 68%. Anal. Calcd for C$_{21}$H$_{15}$NO$_2$: C, 73.03; H, 4.38; N, 4.06. Found: C, 73.0; H, 4.4; N, 3.99. FAB mass spectrometry (FAB-MS): $m/z$ 345 [M+1]. $^1$H-NMR (300 MHz, CDCl$_3$, $\delta$, ppm): 8.59 (1H, s, -OH, D$_2$O exchangeable), 6.78-7.97 (13H, m, Ar-H). $^{13}$C-NMR (300 MHz, CDCl$_3$, $\delta$, ppm): 153.8 (C-2), 129.8 (C-3), 147.9 (C-4), 128.3 (C-5), 122.7 (C-6), 132.4 (C-7), 114.9 (C-8), 155.1 (C-9), 118.8 (C-10), 131.6 (C-11), 126.3 (C-12), 127.5 (C-13), 126.4 (C-14), 127.5 (C-15), 129.3 (C-16), 157.3 (C-18), 125.2 (C-19), 132.2 (C-20), 128.2 (C-21), 137.5 (C-22), 116.8 (C-23).

L$^{56}$: Yield: 70%. Anal. Calcd for C$_{16}$H$_{13}$N$_3$O$_2$: C, 61.72; H, 4.2; N, 13.49. Found: C, 61.65; H, 4.15; N, 13.4. FAB mass spectrometry (FAB-MS): $m/z$ 312 [M+1]. $^1$H-NMR (300 MHz, CDCl$_3$, $\delta$, ppm): 11.8 (1H, s, -NH), 11.3 (1H, s, -OH, D$_2$O exchangeable), 8.0 (1H, s, br, HN of –NH$_2$), 7.5 (1H, s, br, HN of –NH$_2$), 6.9-7.8 (9H, m, Ar-H). $^{13}$C-NMR (300 MHz, CDCl$_3$, $\delta$, ppm): 153.8 (C-2), 129.8 (C-3), 147.9 (C-4), 128.3 (C-5), 122.7 (C-6), 132.4 (C-7), 114.9 (C-8), 155.1 (C-9), 118.8 (C-10), 131.6 (C-11), 126.3 (C-12), 127.5 (C-13), 126.4 (C-14), 127.5 (C-15), 129.3 (C-16), 182.3(C-19).

**Preparation of copper complexes of Ligands (L$^{52}$-L$^{56}$)**

The ligand (s) (0.05 mM) and copper chloride (0.05 mM) were dissolved in ethanol (20 mL). A drop of triethylamine was dropped to the mixture with caution. After stirring for 4 hr at room temperature, the precipitate was separated by suction filtration, purified by washing several times with acetone and dried in vaccum.

**Complex of L$^{52}$**: Yield: 74%. Anal. Calcd for CuC$_{21}$H$_{15}$NO$_4$: C, 61.68; H, 3.70; Cu, 15.54; N, 3.43. Found: C, 61.64; H, 3.64; Cu, 15.59; N, 3.45. FAB mass spectrometry (FAB-MS): $m/z$ 410 [M+1]. $\mu_{\text{eff}}$(BM) = 1.92; $\Lambda_m$ (mho$^{-1}$cm$^2$ mol$^{-1}$) = 24.
Complex of L\textsuperscript{53}: Yield: 79%. Anal.Calcd for CuC\textsubscript{22}H\textsubscript{15}NO\textsubscript{5}: C, 60.48; H, 3.46; Cu, 14.54; N, 3.21. Found: C, 60.43; H, 3.48; Cu, 14.51; N, 3.24. FAB mass spectrometry (FAB-MS): \(m/z\) 438 [M+1]. \(\mu_{\text{eff}}\) (BM) = 2.06; \(\Lambda_{m}\) (mho\(^{-1}\)cm\(^2\) mol\(^{-1}\)) = 22.

Complex of L\textsuperscript{54}: Yield: 62%. Anal.Calcd for CuC\textsubscript{28}H\textsubscript{23}N\textsubscript{3}O\textsubscript{5}: C, 61.68; H, 4.25; Cu, 11.67; N, 7.71. Found: C, 61.72; H, 4.21; Cu, 11.72; N, 7.7. FAB mass spectrometry (FAB-MS): \(m/z\) 546 [M+1]. \(\mu_{\text{eff}}\) (BM) = 2.06; \(\Lambda_{m}\) (mho\(^{-1}\)cm\(^2\) mol\(^{-1}\)) = 18.

Complex of L\textsuperscript{55}: Yield: 76%. Anal.Calcd for CuC\textsubscript{21}H\textsubscript{15}NO\textsubscript{3}S: C, 59.35; H, 3.56 Cu, 14.95; N, 3.3. Found: C, 59.32; H, 3.58; Cu, 14.91; N, 3.36. FAB mass spectrometry (FAB-MS): \(m/z\) 424 [M+1]. \(\mu_{\text{eff}}\) (BM) = 1.98; \(\Lambda_{m}\) (mho\(^{-1}\)cm\(^2\) mol\(^{-1}\)) = 16.

Complex of L\textsuperscript{56}: Yield: 60%. Anal.Calcd for CuC\textsubscript{16}H\textsubscript{13}N\textsubscript{3}O\textsubscript{3}S: C, 49.16; H, 3.35; Cu, 16.26; N, 10.75. Found: C, 49.14; H, 3.32; Cu, 16.3; N, 10.79. FAB mass spectrometry (FAB-MS): \(m/z\) 392 [M+1]. \(\mu_{\text{eff}}\) (BM) = 2.06; \(\Lambda_{m}\) (mho\(^{-1}\)cm\(^2\) mol\(^{-1}\)) = 29.
Due to their importance in biological processes, Cu(II) complexes synthesis and activity studies have been the focus from different perspectives. Flavonoids constitute a group of organic compounds that have been extensively studied due to their properties and applications. Furthermore, different hydroxyflavone derivatives have the potential to form different types of coordination compounds due to the several electron-rich donor centers. The flexibility and conformational freedom of hydroxyflavone derived ligands give rise to a variety of interesting structural motifs.

The less rigid molecule of o-phenylenediamine, which possesses a hydrophilic skeleton, can also be used as a linker of pharmacophoric elements via attachment on adjacent free amino groups. Metal ions contained within well-designed molecules already constitute a great boon for the medicinal pharmacopoeia. In the search for potential chemotherapeutic agents, considerable effort has been focused on the development of anticancer agents that contain heterocyclic structures (3/5-hydroxyflavone) as their main structural motif. In this chapter, a highly conjugated heteroaromatic compounds were synthesized using o-phenylene diamine / m-phenylene diamine. In order to ascertain the structural properties of Schiff base ligands by the substitutions of o-phenylene diamine / m-phenylene diamine at different positions of hydroxyl group at flavone nucleus. Flavonoids exhibit several biological activities and also have free radical scavenging abilities. The presence of a double bond between the C-2 and C-3 together with the keto group at C-4, also appear to be a significant factor of good antioxidant activity. This section is devoted to the design/ modifications of 3-/5-hydroxyflavone and o-phenylenediamine/m-phenylenediamine dissolved in ethanol. The ligands (L^{57-60}) and their Cu(II) complexes were prepared. The experimental data are also presented.
(1a) \( R_1^1 \) H, \( R_2^2 \) OH, \( R_3^3 \) H
(1d) \( R_1^1 \) OH, \( R_2^2 \) H, \( R_3^3 \) H

h  \( \alpha \)-phenylene diammine
i  \( m \)-phenylene diammine
5-Hydroxyflavone was synthesized from 2,6-dihydroxyacetophenone according to the method of Looker et al. [11] and identified by elemental analysis, melting point, IR and UV spectrum. Equimolar amount of 5-hydroxyflavone and o-phenylenediamine/ m-phenylenediamine were dissolved in ethanol (40 mL). Acetic acid (1.0 mL) was added to this solution. The solution was stirred and refluxed for 5 h and precipitates formed. The precipitate was dissolved in DMC. The organic layer was separated and washed the water layer with DMC. The compound was purified using column chromatography.

L\textsuperscript{57}: Yield: 65%. Anal.Calcd for C\textsubscript{36}H\textsubscript{24}N\textsubscript{2}O\textsubscript{4}: C, 78.82; H, 4.41; N, 5.5. Found: C, 78.98; H, 4.56; N, 5.58. FAB mass spectrometry (FAB-MS): m/z 424 [M+1]. \textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}, \(\delta\), ppm): 8.59 (1H, s, -OH, D\textsubscript{2}O exchangeable), 6.4-7.5 (14H, m, Ar-H). \textsuperscript{13}C-NMR (300 MHz, CDCl\textsubscript{3}, \(\delta\), ppm): 153.8 (C-2), 129.8 (C-3), 147.9 (C-4), 128.3 (C-5), 122.7 (C-6), 132.4 (C-7), 114.9 (C-8), 155.1 (C-9), 118.8 (C-10), 131.6 (C-11), 126.3 (C-12), 127.5 (C-13), 126.4 (C-14), 127.5 (C-15), 129.3 (C-16), 144.5 (C-18), 131.3 (C-19), 123.5 (C-20).

L\textsuperscript{58}: Yield: 62%. Anal.Calcd for C\textsubscript{36}H\textsubscript{24}N\textsubscript{2}O\textsubscript{4}: C, 78.82; H, 4.41; N, 5.5. Found: C, 78.98; H, 4.56; N, 5.58. FAB mass spectrometry (FAB-MS): m/z 424 [M+1]. \textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}, \(\delta\), ppm): 8.59 (1H, s, -OH, D\textsubscript{2}O exchangeable), 6.4-7.5 (14H, m, Ar-H). \textsuperscript{13}C-NMR (300 MHz, CDCl\textsubscript{3}, \(\delta\), ppm): 153.8 (C-2), 129.8 (C-3), 147.9 (C-4), 128.3 (C-5), 122.7 (C-6), 132.4 (C-7), 114.9 (C-8), 155.1 (C-9), 118.8 (C-10), 131.6 (C-11), 126.3 (C-12), 127.5 (C-13), 126.4 (C-14), 127.5 (C-15), 129.3 (C-16), 154.9 (C-18), 119.6 (C-19), 132.5 (C-20), 115.6(C-23).

L\textsuperscript{59}: Yield: 76%. Anal.Calcd for C\textsubscript{36}H\textsubscript{24}N\textsubscript{2}O\textsubscript{4}: C, 78.82; H, 4.41; N, 5.5. Found: C, 78.98; H, 4.56; N, 5.58. FAB mass spectrometry (FAB-MS): m/z 424 [M+1]. \textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}, \(\delta\), ppm): 11.23 (1H, s, -OH, D\textsubscript{2}O exchangeable), 6.4-7.5 (14H, m, Ar-H). \textsuperscript{13}C-NMR (300 MHz, CDCl\textsubscript{3}, \(\delta\), ppm): 154.6 (C-2), 86.4 (C-3), 167.6 (C-4), 163.3 (C-5), 114.6 (C-6), 134.4 (C-7), 110.9 (C-8), 154.6 (C-9), 108.8 (C-10), 131.6 (C-11), 126.3
(C-12), 127.5 (C-13), 126.4 (C-14), 127.5 (C-15), 129.3 (C-16), 144.5 (C-18), 131.3 (C-19), 123.5 (C-20).

**L**$^{60}$: Yield: 73%. Anal.Calcd for C$_{36}$H$_{24}$N$_2$O$_4$: C, 78.82; H, 4.41; N, 5.5. Found: C, 78.98; H, 4.56; N, 5.58. FAB mass spectrometry (FAB-MS): m/z 424 [M+1]. $^1$H-NMR (300 MHz, CDCl$_3$, δ, ppm): 11.23 (1H, s, -OH, D$_2$O exchangeable), 6.4-7.5 (14H, m, Ar-H). $^{13}$C-NMR (300 MHz, CDCl$_3$, δ, ppm): 154.6 (C-2), 86.4 (C-3), 167.6 (C-4), 163.3 (C-5), 114.6 (C-6), 134.4 (C-7), 110.9 (C-8), 154.6 (C-9), 108.8 (C-10), 131.6 (C-11), 126.3 (C-12), 127.5 (C-13), 126.4 (C-14), 127.5 (C-15), 129.3 (C-16), 154.9 (C-18), 119.6 (C-19), 132.5 (C-20), 115.6(C-23).

**Preparation of Copper Complexes of Ligands (L$^{57-60}$)**

The ligand(s) (0.05 mM) and copper acetate (0.05 mM) were dissolved in acetone (20 mL). Under stirring, triethylamine (0.075 mM) was then dropped to the mixture with caution. After stirring for 4 h at room temperature, the precipitate was separated by suction filtration, purified by washing several times with acetone and dried in vacuum.

**Complex of L$^{57}$**: Yield: 69%. Anal Calcd for CuC$_{36}$H$_{22}$N$_2$O$_4$: C, 70.87; H, 3.63; Cu, 10.42; N, 4.59. Found: C, 70.84; H, 3.66; Cu, 10.4; N, 4.53. FAB-MS, m/z 611 [M+1]. $\mu_{\text{eff}}$(BM)=1.96; $\Lambda_m$ (mho$^{-1}$cm$^2$ mol$^{-1}$) = 20.

**Complex of L$^{58}$**: Yield: 75%. Anal. Calcd for CuC$_{36}$H$_{24}$N$_2$O$_4$: C, 70.87; H, 3.63; Cu, 10.42; N, 4.59. Found: C, 70.84; H, 3.66; Cu, 10.4; N, 4.53. FAB-MS, m/z 611 [M+1]. $\mu_{\text{eff}}$(BM)=1.98; $\Lambda_m$ (mho$^{-1}$cm$^2$ mol$^{-1}$) = 16.

**Complex of L$^{59}$**: Yield: 65%. Anal. Calcd for CuC$_{36}$H$_{24}$N$_2$O$_4$: C, 70.87; H, 3.63; Cu, 10.42; N, 4.59. Found: C, 70.84; H, 3.66; Cu, 10.4; N, 4.53. FAB-MS, m/z 611 [M+1]. $\mu_{\text{eff}}$(BM)=2.04; $\Lambda_m$ (mho$^{-1}$cm$^2$ mol$^{-1}$) = 10.
**Complex of L₆⁰:** Yield: 78%. Anal. Calcd for CuC₃₆H₂₄N₂O₄: C, 70.87; H, 3.63; Cu, 10.42; N, 4.59. Found: C, 70.84; H, 3.66; Cu, 10.4; N, 4.53. FAB-MS, m/z 611 [M+1]. $\mu_{\text{eff}}(\text{BM})=1.93$; $\Lambda_m$ (mho$^{-1}$cm$^2$mol$^{-1}$) = 22.
Reference


