Synthesis and characterization of a series of phenyl piperazine based ligands

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Abstract

Piperazine based compounds are gaining more attention in today’s research as the piperazine nucleus is found in many biologically active compounds. Substitution in nitrogen atom of piperazine with a suitable fragment containing donor atoms, make it unique for versatile binding possibilities with metal ion. Piperazine derived ligands and their metal complexes have shown applications in different fields like antimicrobial, antioxidant, antihistaminic, anticancer, DNA binding and protein binding, catalyst in ring opening polymerization (ROP), etc. Metal-organic framework derived from piperazine based ligands has also been reported in the literature. This paper presents the synthesis, and characterization of a series of piperazine based ligands. The asymmetrical ligands have been synthesized by cyclization of bis-chloroethyl amine with suitable amine. Some of the representative metal complexes are also synthesized and characterized.

Keywords: piperazine, phenylpiperazines, asymmetric ligands, metal complexes, TDDFT.
1. Introduction

Heterocycles compounds having nitrogen atoms in the ring have drawn considerable interest of the scientists from the last few decades, considering to their excellent therapeutic properties [1-4] Piperazine is a six membered heterocyclic compound containing two nitrogen atoms in the opposite side of the ring. It is a weak base [5] (pKb 3.97, 8.34) and freely soluble in aqueous and organic solvent. Piperazine with N as donor group as well as its derivatives containing suitable donor atom act as good ligands for formation of metal complexes. Substitution on both nitrogens results in symmetrically disubstituted derivatives as well as unsymmetrically mono and disubstituted compounds. This makes the piperazine based ligands unique as they can be easily modified for the desired application.

Piperazine ring is a common organizational motif in the field of drug design and development. With versatile binding properties it acts as a part of the molecular backbone of the ligand. It presents itself as a strong and selective binder and attaches to different biomolecules important from the perspective of medicinal chemistry. Based on this ‘privileged structure’ library of molecules are synthesized which target receptors for different therapeutic areas [6] such as antibacterial [7-10], antifungal [11-12], anticancer [13-15], antihistaminic [16], antipsycholytic [17,18]

N-substituted piperazines present themselves as interesting ligands [19] as they are mostly unaffected by acid-base chemistry but still bind either one [20]- or two-metal centres [21], in different conformations (Fig.1) [22-23]. This shows the potential of the piperazine based ligands to produce a diverse series of metal complexes.

![Figure 1: Possible binding modes of piperazine ring](image-url)
Different methodologies are used by various research groups to synthesize substituted piperazine based derivatives. Condensing bis-chloroethylamine with primary amine results in cyclization and form substituted phenylpiperazines [24] and this monosubstituted piperazine can be converted to corresponding disubstituted piperazine compounds by reacting with alkyl halides [25]. Substituted alkyl/aryl piperazine derivatives has also been synthesized by using monosubstituted piperazine as precursor and treating it with formaldehyde and benzotriazole and followed by suitable alkyl/aryl magnesium bromide [26]. Di substituted molecules with phenyl or pyridyl group attached to one nitrogen of the piperazine ring and nitro pyridyl group on the other nitrogen of the ring is easily prepared by simple condensation of the phenyl or pyridyl piperazine with chloronitropyridine under refluxing condition in an inert solvent like toluene [27]. More over from the ordinary refluxing method, solvent free synthesis of aryl-piperazine using palladium catalyst [28] and microwave assisted synthesis of 1-phenyl piperazine which is further used to prepare N-(4-phenylpiperazine-1-methyl) benzamine [29] has been reported. These substituted phenylpiperazine have been studied for their biological application such as anti-microbial activity [24,26], dopamine receptor [30], antioxidant activity [31], anthelmintic [28], anti-arrhythmia agents [32]. Pyridyl piperazine derived ligands with suitable organic linkers have been utilised in Metal-organic Framework (MOF) which describes the potential of piperazine derived ligands to bind with metal centre producing hybrid inorganic-organic material [33-36].

2. Experimental Section

Materials and Physical Measurements

All the chemicals were purchased commercially from external sources. All the chemicals and solvents were used without further purification. Bis-chloroethylamine was prepared by the standard method reported in the literature [24]. The ligands were characterized by various spectroscopy methods which includes UV-vis, FTIR, $^1$H NMR and Mass spectrometric analysis. Similarly, the complexes were characterized by UV-vis, FTIR and Mass spectrometric analysis. UV-visible absorption spectra were recorded on Shimadzu UV-1800 (200-800 nm). IR spectra were obtained on a Nicolet SHIMADZU FTIR 8400S spectrometer in the range of 4000-400 cm$^{-1}$. BRUCKER ADVANCE I.I 400 NMR Spectrometer has been used for recording $^1$H NMR spectra using d$^6$ – DMSO / CDCl$_3$ as solvents with TMS as the internal reference. XEVO G2-XS QTOF Mass Spectrometer has been used for recording
mass spectra using DMSO / Chloroform as solvent. The experiments were carried out at room temperature

2.1 Synthesis of 1-(2-pyridyl)-piperazine (LH1)

In 30ml of butanol, 3gm (21 mmol) of \textit{bis}-chboroethylamine and 2gm (21 mmol) of 2-aminopyridine was dissolve and refluxed on magnetic stirrer for 8 hours. The reaction mixture was cooled at room temperature and 3.03gm (25 mmol) of potassium carbonate was added in the mixture and refluxed for another 10 hours. The progress of the reaction was check by TLC. Upon completion, the reaction was cooled at room temperature and was filtered. The filtrate was cooled and the solvent volume was reduced slowly. The product was precipitated and collected after filtration and drying. Physical state \textit{solid}, colour \textit{white}, Yield 70%. \textit{FTIR (ATR,} \nu \textit{in cm}^{-1}) 3345 (N-H Stretch), 1498, 1504 (C=C Stretch) 1305 (Ar-N Stretch) 3104 (Ar-CH Stretch). $^1\text{H NMR (}\delta, \text{ppm})$ 2.49 (s, 1H, NH) 3.37 (t, 2H, CH$_2$) 3.55(t, 2H, CH$_2$) 6.40 (d, 1H, ArH) 7.98 (t, 1H, ArH) 6.81(t, 1H, ArH) 8.81(d, 1H, ArH).

![Figure 2: Preparation of 1-(2-pyridyl)-piperazine (LH1)](image1)

2.2 Synthesis of 1-(3-pyridyl)-piperazine (LH2)

Ligand LH2 was prepared by using same method as reported for ligand LH1. The ligand was obtained after complete removal of the solvent under vacuum. Physical state \textit{oily liquid}, colour \textit{brown}, Yield 72%. \textit{FTIR (ATR,} \nu \textit{in cm}^{-1}) 3447 (N-H Stretch), 1498, 1642 (C=C Stretch) 1341 (Ar-N Stretch) 2962 (Ar-CH Stretch). $^1\text{H NMR (}\delta, \text{ppm})$ 2.48 (s, 1H, NH) 3.50 (t, 2H, CH$_2$) 3.41 (t, 2H, CH$_2$) 6.89 (d, 1H, ArH) 7.56 (t, 1H, ArH) 7.58 (d, 1H, ArH) 8.18 (s, 1H, ArH).

![Figure 3: Preparation of 1-(3-pyridyl)-piperazine (LH2)](image2)

2.3 Synthesis of 1-(4-pyridyl)-piperazine (LH3)
Ligand LH3 was prepared by using same method as reported for ligand LH1. The ligand was obtained after complete removal of the solvent under vacuum. Physical state **oily liquid**, colour **white**, Yield 68%. **FTIR (ATR, ν in cm\(^{-1}\))** 3344 (N-H Stretch), 1498, 1550 (C=C Stretch) 1201 (Ar-N Stretch) 2947 (Ar.CH Stretch). **\(^1\)H NMR (δ, ppm)** 2.49 (s, 1H, NH) 3.33 (t, 2H, CH\(_2\)) 3.89 (t, 2H, CH\(_2\)) 6.84 (d, 1H, ArH) 8.52 (d, 1H, ArH) 8.52(d, 1H, ArH) 6.84 (d, 1H, ArH) **MS \([2M+H]^+\)** 327.

![Figure 4: Preparation of 1-(4-pyridyl)-piperazine (LH3)](image)

2.4 **Synthesis of 1-(phenyl)-piperazine (LH4)**

Ligand LH4 was prepared by using same method as reported for ligand LH1. Physical state **solid**, colour **white**, yield 80%. **FTIR (ATR, ν in cm\(^{-1}\))** 3344 (N-H Stretch), 1498, 1593 (C=C Stretch) 1321 (Ar-N Stretch) 2922 (Ar.CH Stretch). **\(^1\)H NMR (δ, ppm)** 3.38(s, 1H, NH) 2.59(t, 2H, CH\(_2\)) 3.1(t, 2H, CH\(_2\)) 7.11(d, 2H, ArH) 6.64(t, 2H, ArH) 6.61(t, 1H, ArH) **MS \([M+H]^+\)** 163.

![Figure 5: Preparation of 1-(phenyl)-piperazine (LH4)](image)

2.5 **Synthesis of 1-(4-chlorophenyl)-piperazine hydrochloride (LH5)**

Ligand LH5 was prepared by using same method as reported for ligand LH1. Physical state **solid**, colour **white**, yield 75%. **FTIR (ATR, ν in cm\(^{-1}\))** 3277 (N-H Stretch) 1510,14 (C=C Stretch) 1301 (Ar-N Stretch) 2926 (Ar.CH Stretch). **\(^1\)H NMR (δ, ppm)** 3.68(s, 1H, NH) 3.2(t, 2H, CH\(_2\)) 3.1(t, 2H, CH\(_2\)) 7.01(d, 2H, ArH) 7.25(t, 2H, ArH).

![Figure 6: Preparation of 1-(4-chlorophenyl)-piperazine hydrochloride (LH5)](image)

2.6 **Synthesis of 1-(2-methoxy phenyl)-piperazine (LH6)**
Ligand LH6 was prepared by using same method as reported for ligand LH1. Physical state solid, colour black, Yield 80%. **FTIR (ATR, \( \nu \) in cm\(^{-1} \))** 3277 (N-H Stretch) 1510,1497 (C=C Stretch) 1301 (Ar-N Stretch) 2926 (Ar.CH Stretch). **\(^1\)H NMR (\( \delta \), ppm)** 3.84 (s, 1H, NH) 3.14(t, 2H, CH\(_2\)) 3.25 (t, 2H, CH\(_2\)) 6.61 (d, 1H, ArH) 6.87 (t, 1H, ArH) 6.67 (t, 1H, ArH) 6.76 (d, 1H, ArH) 2.55 (s, 3H, CH\(_3\)) **MS [2M+H]**\(^+\) 385.

![Figure 7: Preparation of 1-(2-methoxy phenyl)-piperazine (LH6)]

**2.7 Synthesis of 1-(4-methoxy phenyl)-piperazine (LH7)**

Ligand LH7 was prepared by using same method as reported for ligand LH1. Physical state solid, colour dark violet, yield 70%. **FTIR (ATR, \( \nu \) in cm\(^{-1} \))** 3277 (N-H Stretch), 1510,1497 (C=C Stretch), 1301 (Ar-N Stretch), 2926 (Ar.CH Stretch). **\(^1\)H NMR (\( \delta \), ppm)** 3.7 (s, 1H, NH) 3.2 (t, 2H, CH\(_2\)) 3.40 (t, 2H, CH\(_2\)) 6.97 (d, 1H, ArH) 6.97 (d, 1H, ArH) 6.85 (d, 1H, ArH) 6.85 (d, 1H, ArH) 2.55 (s, 3H, CH\(_3\)).

![Figure 8: Preparation of 1-(4-methoxy phenyl)-piperazine (LH7)]

**2.8 Synthesis of 1-(3-hydroxyphenyl)-piperazine (LH8)**

Ligand LH8 was prepared by using same method as reported for ligand LH1. Physical state solid, colour black, yield 90%. **FTIR (ATR, \( \nu \) in cm\(^{-1} \))** 3232 (N-H Stretch), 1593,1498 (C=C Stretch), 1346 (Ar-N Stretch), 2956 (Ar.CH Stretch). **\(^1\)H NMR (\( \delta \), ppm)** 3.6 (s, 1H, NH) 3.41(s, 1H, OH) 3.14(t, 2H, CH\(_2\)) 3.25 (t, 2H, CH\(_2\)) 6.78 (d, 1H, ArH) 6.86 (t, 1H, ArH) 7.02(s, 1H, ArH) 6.98 (d, 1H, ArH) **MS [M+H]**\(^+\) 179.

![Figure 9: Preparation of 1-(3-hydroxyphenyl)-piperazine (LH8)]
2.9 Synthesis of 1-(4-hydroxyphenyl)-piperazine (LH9)

Ligand LH9 was prepared by using same method as reported for ligand LH1. Physical state solid, colour black, yield 80%. FTIR (ATR, ν in cm$^{-1}$) 3261 (N-H Stretch) 1599,1506 (C=C Stretch) 1357 (Ar-N Stretch) 2955 (Ar.CH Stretch).

$^1$H NMR (δ, ppm) 3.67 (s, 1H, NH) 3.41 (s, 1H, OH) 2.92 (t, 2H, CH$_2$) 3.40 (t, 2H, CH$_2$) 6.66 (d, 2H, ArH) 6.82 (t, 2H, ArH) MS [M+H]$^+$ 179.

Figure 10: Preparation of 1-(4-hydroxyphenyl)-piperazine (LH9)

2.10 Synthesis of 1-ethyl-4-(pyridin-2-yl)-piperazine (L10)

2.4 g (15 mmol) of 1-(2-pyridyl)-piperazine (LH1) was mixed with 1.6 g (15 mmol) of bromoethane in 30 ml of butanol and 2.6 g (19 mmol) of potassium carbonate was added to the above mixture and refluxed for four hours. The progress of the reaction was checked with the help of TLC. After refluxing for four hours, the solution was filtered and the filtrate were collected. Column chromatography was performed and the compound was eluted by a 9:1 mixture of chloroform and methanol. Physical state solid, colour white, yield 70%. FTIR (ATR, ν in cm$^{-1}$) 3344 (N-H Stretch), 1654 (C=C Stretch) 3000 (Ar.CH Stretch) 2915 (CH stretch).

$^1$H NMR (δ, ppm) 3.37 (t, 2H, CH$_2$) 3.47 (t, 2H, CH$_2$) 7.86 (d, 1H, ArH) 7.36 (t, 1H, ArH) 7.34 (d, 1H, ArH) 6.85 (d, 1H, ArH) 2.43 (t, 3H, CH$_3$) 1.28 (m, 2H, CH$_2$).

Figure 11: Preparation of 1-ethyl-4-(pyridin-2-yl)-piperazine (L10)

2.11 Synthesis of 1-ethyl-4-(pyridin-3-yl)-piperazine (L11)

Ligand L11 was prepared by using same method as reported for ligand L10. Physical state solid, colour dark brown, yield 68%. FTIR (ATR, ν in cm$^{-1}$) 3391 (N-H Stretch), 1577 (C=C Stretch), 2952 (Ar.CH Stretch), 2874 (CH stretch). $^1$HNMR (ppm) $^1$H NMR (δ, ppm) 3.33 (t, 2H, CH$_2$) 3.36 (t, 2H, CH$_2$) 6.30 (d, 1H, ArH) 7.45 (t, 1H, ArH) 7.89 (t, 1H, ArH) 8.30 (d, 1H, ArH) 1.34 (t, 3H, CH$_3$) 1.27 (m, 2H, CH$_2$).
2.12 1-ethyl-4-(pyridin-4-yl)-piperazine (L12)

Ligand L12 was prepared by using same method as reported for ligand L10. Physical state solid, colour yellowish white, yield 65%. FTIR (ATR, \( \nu \) in cm\(^{-1} \)) 3441 (N-H Stretch), 1651 (C=C Stretch) 3002 (Ar.CH Stretch) 2917 (CH stretch). \(^{1}\)HNMR (ppm) 3.35 (t, 2H, CH\(_2\)) 3.76 (t, 2H, CH\(_2\)) 6.76 (d, 2H, ArH) 8.07 (d, 2H, ArH) 1.37 (t, 3H, CH\(_3\)) 1.26 (m, 2H, CH\(_2\)).

![Figure 13: Preparation of 1-ethyl-4-(pyridin-4-yl)-piperazine (L12)](image)

Synthesis of metal complexes:

2.13 Metal complex of copper with 1-(2-pyridyl)-piperazine (CuL1)

0.24 g (1.28 mmol) of the cupric nitrate was added to a solution of 0.32 g (1.28 mmol) of ligand LH1 in 20 ml of methanol. The solution mixture was stirred for 10 minutes and was kept in a water bath to evaporate the solvent (methanol). The final product was dried in vacuum. yield 65% FTIR (ATR, \( \nu \) in cm\(^{-1} \)) 2998 (Ar.CH Stretch), 2913 (CH Stretch), 1657 (C=C Stretch), 702 (Cu-N Stretch) UV-vis (\( \lambda , \) nm) 300.

2.14 Metal complex of copper with 1-(3-pyridyl)-piperazine (CuL2)

CuL2 was prepared by following same method as for CuL1. yield 68%. FTIR (ATR, \( \nu \) in cm\(^{-1} \)) 3000 (Ar.CH Stretch), 2915 (CH Stretch), 1648 (C=C Stretch), 705 (Cu-N Stretch) UV-vis (\( \lambda , \) nm) 222, 297.

2.15 Metal complex of copper with 1-(4-pyridyl)-piperazine (CuL3)

CuL3 was prepared by following same method as for CuL1. yield 78%. FTIR (ATR, \( \nu \) in cm\(^{-1} \)) 3434 (Ar.CH Stretch), 2999 (CH Stretch), 1656 (C=C Stretch), 704 (Cu-N Stretch) UV-vis (\( \lambda , \) nm) 260, 304

3. Result and Discussion

3.1 UV-vis Spectroscopic study

The UV-vis spectroscopic results of ligands (LH1-LH3) and metal complexes (CuL1-CuL3) were recorded in the range of 200 to 800 nm at 1x10\(^{-3}\) M concentration using acetonitrile as
The wavelength ($\lambda_{\text{max}}$ in nm) and absorbance ($\varepsilon$ in Lmol cm$^{-1}$) is reported in the following table (Table 1).

**Table 1: UV-vis study of ligands (LH1-LH3) and their copper complexes**

| Sr. no. | Ligand | Wavelength (nm) | Absorption (Lmol$^{-1}$cm$^{-1}$) | Complex | Wavelength (nm) | Absorption (Lmol$^{-1}$cm$^{-1}$) |
|---------|--------|-----------------|-----------------------------------|---------|----------------|-----------------------------------|
| 1.      | LH1    | 258             | 1.4123                            | CuL1    | 300            | 1.187                             |
| 2.      | LH2    | 250, 330        | 2.412, 2.096                      | CuL2    | 254, 324       | 0.8481, 0.7383                    |
| 3.      | LH3    | 226, 299        | 3.063, 1.392                      | CuL3    | 260, 304       | 1.179, 0.510                      |

**Figure 14:** Experimental UV graph of free Ligands LH1-LH3
3.2 Computational chemistry of Ligands: Geometry optimization

Computational chemistry provides additional insight into experimental studies by providing information which cannot be otherwise generated experimentally like energy of a given geometry [33]. The optimized structures give detailed idea about the orientation of the ligating atoms in the ligands which are available for donation of electron pairs to the metals during complex formation [34]. It also gives a perspective difference of the ligands in terms of their ability to use the pyridyl nitrogen during network formation. The network formation is highly dependent on the axial coordination of the pyridyl nitrogen to the metal ion which is already bound to the piperazine nitrogen. All ligands (LH1-L12) were geometrically optimized using Orca 4.0.1.2 [35] to find the equilibrium structure of having lowest energy in the ground state. Hybrid functional method B3LYP was used for all the calculations using Pople Style basis set 6-31G(2d,2p). Frequency calculations of the optimized structure did not show any negative frequencies implying the obtained structures as global minima. Cartesian coordinates of all the optimised ligands (LH1-L12) have been provided in the supplementary file.
Figure 16: Optimized structure of Ligand LH1  
Figure 17: Optimised structure of ligand LH2  

Figure 18: Optimized structure of Ligand LH3  
Figure 19: Optimized structure of Ligand LH4
Figure 20: Optimized structure of Ligand LH5

Figure 21: Optimized structure of Ligand LH6

Figure 22: Optimized structure of Ligand LH7

Figure 23: Optimized structure of Ligand LH8
3.3 Theoretical UV spectroscopic study: TDDFT Calculation

Geometrically optimised Ligands LH1-LH3 were also analysed by TDDFT method [40-44] (nroots = 8) to calculate the energy of different excited states [45,46], orbital contributions and oscillator strength (f_{osc}) which are involved in the different type of electronic transition to give rise the UV-vis spectrum [38,47] of the ligands (Table 3). TDDFT calculations was done with method B3LYP/6-31G(2d,2p) basis set using ORCA computational package [35] without solvent effects (gas phase). Molecular orbitals (highest occupied molecular orbital
(HOMO), lowest unoccupied molecular orbital (LUMO) and frontier molecular orbital (FMO)) that are involved in these most important transitions are sketched and plotted with the help of Avogadro [48]. UV graph were plotted for individual ligand LH1-LH3 for both experimental data and theoretically calculated values. Ligands absorption wavelength($\lambda_{\text{max}}$) and their absorbance are compared to the theoretically calculated $\lambda_{\text{max}}$ and absorbance (calculated from theoretical UV graph) for ligands LH1-LH3(Table 2).

**Table 2: Compared results of experimental and theoretical calculation**

| Ligand | Experimental Observation | TDDFT/ B3LYP Calculation |
|--------|--------------------------|---------------------------|
|        | $\lambda_{\text{max}}$(nm) | Absorbance | $\lambda_{\text{max}}$(nm) | Absorbance |
| LH1    | 258                      | 1.4123          | 270                      | 1.0385     |
| LH2    | 250                      | 1.4476          | 250                      | 1.4476     |
| LH3    | 299                      | 0.6435          | 304                      | 0.4720     |

**Figure 28:** Experimental and calculated UV graph of Ligand LH1
Figure 29: Molecular orbital diagram (with isosurface value 0.02) of the FMOs and nearby orbitals involved in the electronic transition for LH1
Figure 30: Experimental and calculated UV graph of Ligand LH2
**Figure 31:** Molecular orbital diagram (with isosurface value 0.02) of the FMOs and nearby orbitals involved in the electronic transition for LH2
Figure 32: Experimental and calculated UV graph of Ligand LH3

LUMO (45)  

LUMO +1(46)
Table: 3 Transition state, orbital contributions, oscillator strength ($f_{osc}$) and transition energies (in eV) calculated with TDDFT/B3LYP.

| Ligand | Transition state | Molecular orbital involved* | Oscillator strength($f_{osc}$)*\(^\#\) | Energy of Transition(eV) |
|--------|------------------|-----------------------------|--------------------------------------|-------------------------|
| LH1    | State 1          | 44 $\rightarrow$ 45        | 0.982795                             | 0.802                   |
|        | State 2          | 43 $\rightarrow$ 45        | 0.985712                             | 2.064                   |
|        | State 3          | 43 $\rightarrow$ 45        | 0.926135                             | 3.553                   |
|        | State 4          | 42 $\rightarrow$ 45        | 0.997181                             | 3.648                   |

Figure 33: Molecular orbital diagram (with isosurface value 0.02) of the FMOs and nearby orbitals involved in the electronic transition for LH3.
| State | Transition | Energy | Intensity |
|-------|------------|--------|-----------|
| State 5 | 42 → 47 | 0.830541 | 3.922 |
| State 6 | 41 → 45 | 0.994964 | 4.094 |
| State 7 | 43 → 46 | 0.835273 | 4.781 |
| State 8 | 43 → 47 | 0.858147 | 4.888 |
| LH2 | State 1 | 44 → 45 | 0.985601 | 1.102 |
| State 2 | 43 → 45 | 0.395800 | 1.911 |
| | 43 → 44 | 0.460925 | 1.911 |
| State 3 | 44 → 45 | 0.887956 | 1.945 |
| State 4 | 44 → 47 | 0.532879 | 2.681 |
| State 5 | 43 → 45 | 0.503156 | 2.786 |
| | 43 → 44 | 0.421735 | 2.786 |
| State 6 | 42 → 46 | 0.153408 | 3.654 |
| | 42 → 44 | 0.202370 | 3.654 |
| | 43 → 45 | 0.108468 | 3.654 |
| State 7 | 43 → 45 | 0.677848 | 3.777 |
| State 8 | 42 → 44 | 0.486137 | 3.812 |
| | 43 → 45 | 0.138568 | 3.812 |
| LH3 | State 1 | 43 → 45 | 0.202422 | 1.771 |
| | 44 → 45 | 0.787911 | 1.771 |
| State 2 | 43 → 45 | 0.787135 | 2.589 |
| | 44 → 45 | 0.207074 | 2.589 |
| State 3 | 42 → 45 | 0.994640 | 3.511 |
| State 4 | 41 → 45 | 0.997697 | 3.843 |
| State 5 | 44 → 46 | 0.896518 | 4.707 |
| State 6 | 42 → 46 | 0.879932 | 4.858 |
| State 7 | 43 → 47 | 0.178097 | 5.062 |

*(Molecular orbitals involved in the transition are added to +1 from their calculated value as ORCA counts the orbitals from zero)*
**4. Conclusion**

This paper reports the synthesis of twelve ligands based on substituted phenyl or heterocycle containing piperazine as core structure. Six pyridyl piperazine ligands namely 1-(2-pyridyl)-piperazine (LH1), 1-(3-pyridyl)-piperazine (LH2), and 1-(4-pyridyl)-piperazine (LH3) and their ethylated derivatives 1-ethyl-4-(pyridine-2-yl)piperazine (L10), 1-ethyl-4-(pyridine-3-yl)piperazine (L11), and 1-ethyl-4-(pyridine-4-yl)piperazine (L12) and other ligands containing phenyl ring with suitable functional group such as chloro, hydroxy and methoxy group (LH4-LH9) and characterized by various spectroscopic techniques such as IR, NMR and MS. Complexation of synthesized ligands (LH1-LH3) were done with copper metal. From the UV data it is established that the ligands are binding with copper as was observed by the change in the absorption pattern of the metal complex from the ligand itself. In general, IR peaks for metal-nitrogen appear near 660-760 cm\(^{-1}\). In the above-mentioned complexes peaks appear in this range which confirms the binding of ligand with the metal ions.

The ligands were also theoretically analysed by computational studies. With the help of computational studies, we investigated different piperazine based ligands to calculate energy of a given optimised geometry. Geometrical optimization also provides the knowledge of orientation of piperazine ring in different conformations with different substitution in the phenyl ring. Piperazine ring mostly follow the more stable chair conformation in the ligands LH3, LH5, LH7 and LH9 having substitution in para position of phenyl ring which favours the less steric repulsion in these ligands but partial chair conformations are also observed in case of ligands (LH1, LH2, LH4). Ligands L10-L12 follow partial boat conformations owing to the both side substitution of the piperazine ring. TDDFT (time-dependent density functional theory) calculation of optimized ligands were performed and the UV-vis spectrum were compared of the ligand LH1-LH3 to that of experimental observation. Ligand LH1-LH3 have shown absorption maxima at wavelength due transitions between different molecular orbitals. Pictorial representation of these molecular orbitals shows the variation in the electron densities in the orbital contribution of the three ligands LH1-LH3 which have systematic variation in the position of pyridyl nitrogen. The UV-vis absorption wavelength maxima obtained at TDDFT/B3LYP/6-31G(2d,2p) level has been compared with the experimental results, and a good agreement between the theoretical and experimental data is
observed. Thus, these results have shown that a large variety of calculations can be done by computational studies for predicting spectroscopic results of the experimental work.

5. References

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**Supplementary File**

**Synthesis and characterization of a series of phenyl piperazine based ligands**

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**IR of 1-(2-pyridyl)-piperazine (LH1)**
Figure 1: IR Spectrum of 1-(2-pyridyl)-piperazine (LH1)

NMR of 1-(2-pyridyl)-piperazine (LH1)
Figure 2: NMR spectrum of 1-(2-pyridyl)-piperazine (LH1)

IR of 1-(3-pyridyl)-piperazine (LH2)
Figure 3: IR Spectrum of 1-(3-pyridyl)-piperazine (LH2)

NMR of 1-(3-pyridyl)-piperazine (LH2)
Figure 4: NMR spectrum of 1-(3-pyridyl)-piperazine (LH2)

IR of 1-(4-pyridyl)-piperazine (LH3)
Figure 5: Spectrum of 1-(4-pyridyl)-piperazine (LH3)
Figure 6: NMR spectrum of 1-(4-pyridyl)-piperazine (LH3)

MS of 1-(4-pyridyl)-piperazine (LH3)
Figure 7: Mass spectrum of 1-(4-pyridyl)-piperazine (LH3)

IR of 1-(phenyl)-piperazine (LH4)
Figure 8: IR Spectrum of 1-(phenyl)-piperazine (LH4)

NMR of 1-(phenyl)-piperazine (LH4)
Figure 9: NMR spectrum of 1-(phenyl)-piperazine (LH4)

MS of 1-(phenyl)-piperazine (LH4)
Figure 10: Mass spectrum of 1-(phenyl)-piperazine (LH4)

NMR of 1-(4-chlorophenyl)-piperazine hydrochloride (LH5)
**Figure 11**: NMR spectrum of 1-(4-chlorophenyl)-piperazine (LH5)

IR of 1-(2-methoxy phenyl)-piperazine (LH6)
Figure 12: IR spectrum of 1-(2-methoxy phenyl)-piperazine (LH6)

NMR of 1-(2-methoxy phenyl)-piperazine (LH6)
Figure 13: NMR spectrum of 1-(2-hydroxy phenyl)-piperazine (LH6)

MS of 1-(2-methoxy phenyl)-piperazine(LH6)
Figure 14: Mass spectrum of 1-(2-methoxy phenyl)-piperazine (LH6)

NMR of 1-(4-methoxy phenyl)-piperazine(LH7)
Figure 15: NMR spectrum of 1-(4-methoxy phenyl)-piperazine (LH7)

IR of 1-(3-hydroxyphenyl)-piperazine (LH8)
Figure 16: IR spectrum of 1-(3-hydroxyphenyl)-piperazine (LH8)

NMR of 1-(3-hydroxyphenyl)-piperazine (LH8)
Figure 17: NMR spectrum of 1-(3-hydroxyphenyl)-piperazine (LH8)

MS of 1-(3-hydroxyphenyl)-piperazine (LH8)
Figure 18: Mass spectrum of 1-(3-hydroxyphenyl)-piperazine (LH8)

IR of 1-(4-hydroxyphenyl)-piperazine (LH9)
Figure 19: IR spectrum of 1-(3-hydroxyphenyl)-piperazine (LH9)

NMR of 1-(4-hydroxyphenyl)-piperazine (LH9)
Figure 20: NMR spectrum of 1-(4-hydroxyphenyl)-piperazine (LH9)

MS of 1-(4-hydroxyphenyl)-piperazine (LH9)
Figure 21: Mass spectrum of 1-(4-hydroxyphenyl)-piperazine (LH9)

IR spectrum of 1-ethyl-2-(pyridine-2-yl)-piperazine (L10)
Figure 22: IR spectrum of 1-ethyl-2-(pyridine-2-yl)-piperazine (L10)

NMR spectrum of 1-ethyl-2-(pyridine-2-yl)-piperazine (L10)
Figure 23: NMR spectrum of 1-ethyl-2-(pyridin-2-yl)-piperazine (L10)

IR spectrum of 1-ethyl-2-(pyridine-3-yl)-piperazine (L11)
Figure 24: IR spectrum of 1-ethyl-2-(pyridine-3-yl)-piperazine (L11)

NMR spectrum of 1-ethyl-2-(pyridine-3-yl)-piperazine (L11)
Figure 25: NMR spectrum of 1-ethyl-2-(pyridin-3-yl)-piperazine (L11)

IR spectrum of 1-ethyl-2-(pyridine-4-yl)-piperazine (L12)
**Figure 26:** IR spectrum of 1-ethyl-2-(pyridine-4-yl)-piperazine (L12)

**NMR spectrum of 1-ethyl-2-(pyridine-4-yl)-piperazine (L12)**
Figure 27: NMR spectrum of 1-ethyl-2-(pyridine-4-yl)piperazine (L12)
Synthesis and characterization of a series of phenyl piperazine based ligands

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Table 1: Coordinates of geometry optimized Ligand LH1

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| N    | 1.193186| -0.50539| -0.07215|
| C    | 0.289268| -0.46863| -1.08136|
| H    | -0.48234| 0.271462| -0.86355|
| H    | 0.796636| -0.18992| -2.00619|
| C    | -0.39098| -1.85002| -1.27653|
| H    | -1.09627| -2.0146 | -0.46126|
| H    | -0.98293| -1.88018| -2.1913 |
| N    | 0.477986| -2.88805| -1.27866|
| H    | 0.014612| -4.24864| -1.78812|
| C    | 1.907616| -1.6232 | 0.220207 |
| H    | 2.968203| -1.3793 | 0.302444 |
| H    | 1.563862| -2.01203| 1.179462 |
| C    | 1.752492| -2.73997| -0.85002 |
| H    | 2.353513| -2.44612| -1.71147 |
| H    | 2.137454| -3.69752| -0.4993 |
| C    | 1.63686 | 0.666089| 0.407722 |
| C    | 2.715708| 1.425802| -0.37942 |
| H    | 3.123879| 1.033544| -1.31111 |
| N    | 1.111448| 1.122576| 1.562025 |
| C    | 1.47799 | 2.284669| 2.138723 |
| C    | 3.193176| 2.753779| 0.198459 |
| C    | 2.545527| 3.195837| 1.509215 |
| H    | 1.006225| 2.585828| 3.073943 |
| H    | 2.832428| 4.132876| 1.986261 |
| H    | 3.955375| 3.354913| -0.2971 |

Table 2: Coordinates of geometry optimized Ligand LH2
| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| N    | -0.36321 | -0.17645 | -0.33624 |
| C    | -1.25927 | 0.794635 | -0.6683 |
| H    | -1.11454 | 1.026933 | -1.72453 |
| H    | -1.03629 | 1.712017 | -0.12274 |
| C    | -2.75003 | 0.419829 | -0.45508 |
| H    | -3.41425 | 1.145853 | -0.92395 |
| H    | -2.90549 | 0.420839 | 0.625062 |
| C    | -0.76414 | -1.47441 | -0.27997 |
| H    | -0.0561 | -2.29232 | -0.1705 |
| C    | 0.953362 | 0.141534 | -0.21249 |
| C    | 1.474549 | 1.530286 | -0.62085 |
| H    | 0.829655 | 2.303652 | -1.03728 |
| C    | 1.990963 | -0.85849 | 0.356238 |
| H    | 1.683659 | -1.84281 | 0.703749 |
| N    | 3.292911 | -0.53386 | 0.481377 |
| C    | 2.966576 | 1.783127 | -0.43891 |
| H    | 3.409627 | 2.740404 | -0.71321 |
| C    | 3.82775 | 0.652815 | 0.13678 |
| H    | 4.896776 | 0.814918 | 0.274093 |
| C    | -2.26305 | -1.83326 | -0.42462 |
| H    | -2.42004 | -2.7898 | -0.92296 |
| H    | -2.60177 | -1.99801 | 0.598943 |
| N    | -2.99431 | -0.81875 | -0.92257 |
| H    | -4.27039 | -1.10525 | -1.70677 |

Table 3: Coordinates of geometry optimized Ligand LH3
| Atom | X    | Y    | Z    |
|------|------|------|------|
| C    | -1.79263 | 1.959887 | 0.845792 |
| C    | -0.31095 | 1.721119 | 1.238718 |
| H    | 0.328702  | 2.141601  | 0.462464  |
| H    | -0.09276  | 2.292949  | 2.142052  |
| H    | -1.84779  | 1.782142  | -0.22943  |
| H    | -2.10164  | 2.983122  | 1.059471  |
| N    | -2.60319  | 1.084348  | 1.464171  |
| H    | -3.96998  | 1.525155  | 1.977067  |
| C    | -2.33165  | -0.21915  | 1.282182  |
| H    | -3.04676  | -0.83763  | 1.824641  |
| H    | -2.39756  | -0.44038  | 0.215672  |
| C    | -0.872    | -0.54701  | 1.692948  |
| H    | -0.85366  | -0.78313  | 2.758087  |
| H    | -0.56216  | -1.4598   | 1.183702  |
| N    | 0.054316  | 0.427158  | 1.465071  |
| C    | 1.360114  | 0.159065  | 1.739294  |
| C    | 2.453859  | 1.238037  | 1.663824  |
| H    | 2.233493  | 2.26845   | 1.387353  |
| C    | 3.896931  | 0.834024  | 1.997059  |
| H    | 4.683197  | 1.58722   | 1.947983  |
| N    | 4.21735   | -0.42534  | 2.350346  |
| C    | 3.335017  | -1.43759  | 2.451978  |
| H    | 3.69114   | -2.42329  | 2.751137  |
| C    | 1.840831  | -1.24021  | 2.160125  |
| H    | 1.157192  | -2.08263  | 2.258716  |
### Table 4: Coordinates of geometry optimized Ligand LH4

| Atom | X      | Y      | Z     |
|------|--------|--------|-------|
| C    | 2.83358| 0.401912| -0.08468 |
| C    | 1.351353| 0.859691| -0.09655 |
| H    | 1.148036| 1.362723| -1.04324 |
| H    | 1.218877| 1.619953| 0.673668 |
| H    | 3.471016| 1.101764| -0.6251 |
| H    | 3.129902| 0.37972| 0.965292 |
| N    | 0.406633| -0.10937| 0.076276 |
| C    | 0.719325| -1.43417| -0.01612 |
| H    | 0.270349| -1.82276| -0.93155 |
| H    | 0.230385| -1.96762| 0.799449 |
| C    | 2.227028| -1.79948| -0.00749 |
| H    | 2.406881| -2.76038| -0.48966 |
| H    | 2.511763| -1.8637| 1.043962 |
| N    | 2.961512| -0.83663| -0.58878 |
| H    | 4.162836| -1.19804| -1.45578 |
| C    | -0.90793| 0.254236| 0.116263 |
| C    | -1.31754| 1.745095| 0.089351 |
| H    | -0.57137| 2.536686| 0.036079 |
| C    | -2.79315| 2.146053| 0.132949 |
| H    | -3.06944| 3.200219| 0.114085 |
| C    | -3.88106| 1.076393| 0.201032 |
| H    | -4.93117| 1.366796| 0.231297 |
| C    | -3.49496| -0.40105| 0.222233 |
| H    | -4.27194| -1.16409| 0.267067 |
| C    | -2.023| -0.81527| 0.179102 |
| H    | -1.78793| -1.87868| 0.190849 |

### Table 5: Coordinates of geometry optimized Ligand LH5
| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| C    | 0.931305 | -2.3467 | 10.18042 |
| C    | 2.310267 | -2.33389 | 10.83229 |
| H    | 2.189385 | -2.26253 | 11.92651 |
| H    | 2.862798 | -1.4545  | 10.50089 |
| H    | 1.058327 | -2.28218 | 9.084227 |
| H    | 0.369128 | -1.46649 | 10.50911 |
| N    | 3.058142 | -3.54694 | 10.47802 |
| N    | 0.21985  | -3.55195 | 10.59825 |
| H    | -0.71811 | -3.55621 | 10.21221 |
| C    | 0.943785 | -4.74619 | 10.17171 |
| H    | 1.072924 | -4.79912 | 9.075315 |
| H    | 0.388562 | -5.63463 | 10.48971 |
| C    | 2.327331 | -4.76329 | 10.82011 |
| H    | 2.884115 | -5.62486 | 10.44335 |
| H    | 2.211513 | -4.87869 | 11.91207 |
| C    | 4.448882 | -3.53192 | 10.69331 |
| C    | 5.227773 | -2.47183 | 10.18919 |
| H    | 4.752288 | -1.66915 | 9.637625 |
| C    | 6.605723 | -2.44437 | 10.34962 |
| H    | 7.186643 | -1.6226  | 9.947899 |
| C    | 7.244206 | -3.49076 | 11.01171 |
| C    | 5.121353 | -4.5688  | 11.36186 |
| H    | 4.567854 | -5.39471 | 11.7892 |
| C    | 6.507019 | -4.55394 | 11.51337 |
| H    | 7.006218 | -5.3634  | 12.03324 |
| Cl   | 8.992016 | -3.46282 | 11.2074 |

**Table 6: Coordinates of geometry optimized Ligand LH6**
| Atom | X    | Y    | Z    |
|------|------|------|------|
| C    | 1.214616 | -1.75749 | 10.73787 |
| C    | 2.306211 | -2.84148 | 10.98715 |
| H    | 2.773389 | -2.63881 | 11.94869 |
| H    | 1.776668 | -3.79494 | 11.01841 |
| H    | 1.70341  | -0.79506 | 10.89692 |
| H    | 0.3885   | -1.85056 | 11.44284 |
| N    | 3.196797 | -2.87669 | 9.957053 |
| C    | 2.671744 | -2.97039 | 8.705427 |
| H    | 3.425616 | -2.9864  | 7.919338 |
| H    | 2.07429  | -3.88243 | 8.653782 |
| C    | 1.663619 | -1.81388 | 8.47059 |
| H    | 1.173597 | -1.89435 | 7.500301 |
| H    | 2.243074 | -0.88974 | 8.503526 |
| N    | 0.753064 | -1.78913 | 9.467805 |
| H    | -0.70722 | -1.46605 | 9.170111 |
| C    | 4.517435 | -2.61952 | 10.1511 |
| C    | 5.258825 | -1.75794 | 9.109698 |
| H    | 4.731449 | -1.34752 | 8.248928 |
| C    | 6.734823 | -1.41635 | 9.294573 |
| H    | 7.245647 | -0.7919  | 8.561728 |
| C    | 7.491975 | -1.94065 | 10.50979 |
| H    | 8.546472 | -1.69749 | 10.6396 |
| C    | 6.781441 | -2.82135 | 11.53607 |
| H    | 7.357675 | -3.20174 | 12.3794 |
| C    | 5.286581 | -3.18513 | 11.37675 |
| O    | 4.711246 | -3.9602  | 12.16069 |
| C    | 5.248318 | -4.46875 | 13.15126 |
| H    | 5.62204  | -3.68906 | 13.81742 |
| H    | 6.098553 | -5.07949 | 12.84259 |
| H    | 4.52347  | -5.0888  | 13.67866 |

Table 7: Coordinates of geometry optimized Ligand LH7
### Table 8: Coordinates of geometry optimized Ligand LH8

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| C    | -3.32417 | 1.170631 | -1.09132 |
| C    | -1.83592 | 1.272239 | -0.66534 |
| H    | -1.29084 | 1.81041 | -1.44127 |
| H    | -1.76916 | 1.896816 | 0.226866 |
| H    | -3.31446 | 1.003851 | -2.16967 |
| H    | -3.86476 | 2.091689 | -0.8732 |
| N    | -3.92492 | 0.122263 | -0.50439 |
| H    | -5.36935 | 0.226934 | -0.02673 |
| C    | -3.35696 | -1.07967 | -0.69739 |
| H    | -3.34796 | -1.28941 | -1.76822 |
| H    | -3.92224 | -1.85622 | -0.18204 |
| C    | -1.87005 | -1.07259 | -0.25498 |
| H    | -1.34428 | -1.85737 | -0.79948 |
| H    | -1.81646 | -1.35881 | 0.796588 |
| N    | -1.18841 | 0.099421 | -0.40719 |
| C    | 0.133611 | 0.138871 | -0.07188 |
| C    | 0.918221 | 1.468535 | -0.10091 |
| H    | 0.43741 | 2.403141 | -0.38645 |
| C    | 2.399367 | 1.506687 | 0.277381 |
| H    | 2.934105 | 2.456264 | 0.249116 |
| C    | 3.140205 | 0.235562 | 0.695557 |
| C    | 0.880349 | -1.14331 | 0.356247 |
| H    | 0.371385 | -2.10507 | 0.402478 |
| C    | 2.361857 | -1.09467 | 0.732799 |
| H    | 2.857528 | -2.01897 | 1.029517 |
| O    | 4.341769 | 0.336511 | 0.990127 |
| C    | 5.03829 | -0.62234 | 1.342216 |
| H    | 6.053196 | -0.2797 | 1.543799 |
| H    | 5.054126 | -1.38154 | 0.558098 |
| H    | 4.618534 | -1.08022 | 2.239778 |
| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| C    | 1.421447 | 1.071796 | -0.8945 |
| C    | 2.842343 | 1.055594 | -1.01669 |
| C    | 3.604485 | 0.039747 | -0.36777 |
| C    | 2.937746 | -0.95094 | 0.397618 |
| C    | 1.523778 | -0.94666 | 0.527695 |
| C    | 0.772186 | 0.069709 | -0.12254 |
| H    | 0.835513 | 1.829842 | -1.37701 |
| H    | 3.338481 | 1.808594 | -1.59741 |
| H    | 4.67373  | 0.012313 | -0.44861 |
| H    | 1.03058  | -1.70041 | 1.109132 |
| N    | -0.5648  | 0.070397 | 0.003094 |
| C    | -1.30109 | -0.3649  | -1.04877 |
| H    | -0.78445 | -1.16057 | -1.58811 |
| H    | -1.44521 | 0.470391 | -1.73624 |
| C    | -2.71434 | -0.81854 | -0.58676 |
| H    | -2.56624 | -1.74279 | -0.02602 |
| H    | -3.3709  | -1.01566 | -1.4342  |
| N    | -3.26789 | 0.097626 | 0.238819 |
| H    | -4.76012 | 0.402598 | 0.163372 |
| C    | -2.53671 | 0.516347 | 1.295891 |
| H    | -2.37854 | -0.33227 | 1.963303 |
| H    | -3.06231 | 1.303444 | 1.836549 |
| C    | -1.12259 | 0.976581 | 0.843168 |
| H    | -0.47429 | 1.170397 | 1.699339 |
| H    | -1.25314 | 1.913937 | 0.299656 |
| O    | 3.550747 | -1.84736 | 0.975967 |
| H    | 5.071605 | -1.92921 | 0.891031 |

**Table 9: Coordinates of geometry optimized Ligand LH9**
| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| C    | 1.558663 | 0.746308 | 0.810855 |
| C    | 2.973214 | 0.77603  | 0.625422 |
| C    | 3.555515 | 0.035843 | -0.43556  |
| C    | 2.751308 | -0.73365 | -1.31524  |
| C    | 1.336627 | -0.76396 | -1.13056  |
| C    | 0.749931 | -0.02423 | -0.06935  |
| H    | 1.10051  | 1.299419 | 1.607268  |
| H    | 3.600655 | 1.350898 | 1.277911  |
| H    | 0.711669 | -1.33959 | -1.78499  |
| N    | -0.58272 | -0.06182 | 0.092614  |
| C    | -1.30051 | 1.017029 | -0.30608  |
| H    | -0.85146 | 1.485807 | -1.18329  |
| H    | -1.30062 | 1.74809  | 0.50425   |
| C    | -2.78368 | 0.631229 | -0.56664  |
| H    | -3.40614 | 1.511292 | -0.72822  |
| H    | -2.78249 | 0.022378 | -1.47213  |
| N    | -3.2723  | -0.11512 | 0.449004  |
| H    | -4.70947 | 0.073031 | 0.922929  |
| C    | -2.56203 | -1.19952 | 0.832278  |
| H    | -3.02107 | -1.66931 | 1.702146  |
| H    | -2.54828 | -1.9121  | 0.006053  |
| C    | -1.07778 | -0.82265 | 1.09966   |
| H    | -0.46443 | -1.71099 | 1.259463  |
| H    | -1.06094 | -0.23156 | 2.016954  |
| O    | 4.77453  | 0.062156 | -0.59541  |
| H    | 5.4027   | 1.123957 | -1.49176  |
| H    | 3.208389 | -1.29897 | -2.1279   |

**Table 10: Coordinates of geometry optimized Ligand L10**
| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| C    | -2.7744 | 1.607251 | -0.06664 |
| C    | -1.25334 | 1.641156 | -0.37446 |
| H    | -1.13286 | 1.937908 | -1.41754 |
| H    | -0.76499 | 2.407275 | 0.229107 |
| H    | -2.90462 | 1.54241 | 1.014102 |
| H    | -3.27084 | 2.528323 | -0.37207 |
| N    | -3.41091 | 0.548288 | -0.61359 |
| H    | -4.92958 | 0.576376 | -0.74897 |
| C    | -2.72662 | -0.53135 | -1.04917 |
| H    | -2.51584 | -0.37811 | -2.10822 |
| H    | -3.35112 | -1.42185 | -0.9778 |
| C    | -1.36597 | -0.71187 | -0.32481 |
| H    | -1.57856 | -1.06018 | 0.686811 |
| H    | -0.78382 | -1.49335 | -0.8141 |
| N    | -0.63842 | 0.435279 | -0.21761 |
| C    | 0.720594 | 0.390413 | -0.08079 |
| C    | 1.542039 | 1.610056 | -0.56046 |
| H    | 1.052597 | 2.475582 | -1.00582 |
| C    | 3.064522 | 1.621497 | -0.46342 |
| H    | 3.626431 | 2.485262 | -0.81855 |
| C    | 3.79977 | 0.423498 | 0.121271 |
| H    | 4.88743 | 0.432922 | 0.190945 |
| C    | 3.014131 | -0.78448 | 0.622887 |
| H    | 3.570599 | -1.61656 | 1.053998 |
| C    | 1.469219 | -0.82998 | 0.541488 |
| O    | 0.826983 | -1.7897 | 1.00275 |
| C    | 1.338109 | -2.7889 | 1.521287 |
| H    | 0.553102 | -3.48149 | 1.824764 |
| H    | 1.927845 | -2.49754 | 2.392179 |
| H    | 2.008496 | -3.27815 | 0.812424 |

**Table 11: Coordinates of geometry optimized Ligand L11**
| Atom | X    | Y    | Z    |
|------|------|------|------|
| C    | -1.42362 | 0.821484 | -1.00259 |
| C    | 0.055908  | 1.078397  | -0.61447  |
| H    | 0.092632  | 1.917751  | 0.081753   |
| H    | 0.593246  | 1.412507  | -1.50227   |
| H    | -1.39135  | 0.360891  | -1.99138   |
| H    | -1.97815  | 1.759079  | -1.0639    |
| N    | -1.99818  | -0.05353  | -0.15144   |
| C    | -1.39021  | -1.24709  | 0.009008   |
| H    | -1.35006  | -1.74119  | -0.96319   |
| H    | -1.92202  | -1.88786  | 0.71394    |
| C    | 0.08693   | -1.05682  | 0.440646   |
| H    | 0.127551  | -1.00735  | 1.529921   |
| H    | 0.645493  | -1.95266  | 0.168545   |
| N    | 0.734442  | 0.037636  | -0.05221   |
| C    | 2.051689  | 0.206256  | 0.252126   |
| C    | 2.821046  | 1.493169  | -0.14301   |
| N    | 4.123032  | 1.663271  | 0.159514   |
| C    | 4.883164  | 0.769152  | 0.819372   |
| H    | 5.929573  | 1.002226  | 1.015931   |
| C    | 2.84325   | -0.86916  | 1.017916   |
| H    | 2.399185  | -1.80619  | 1.352013   |
| C    | 4.309415  | -0.56702  | 1.305019   |
| H    | 4.93302   | -1.28158  | 1.842069   |
| C    | -3.27823  | 0.116058  | 0.237877   |
| H    | -3.51271  | 1.174891  | 0.35644    |
| H    | -3.48637  | -0.4464   | 1.14919    |
| C    | -4.19016  | -0.43773  | -0.86439   |
| H    | -4.01831  | 0.100427  | -1.79731   |
| H    | -5.23022  | -0.30886  | -0.56481   |
| H    | -3.99144  | -1.49938  | -1.01579   |
| H    | 2.317437  | 2.299004  | -0.67515   |

Table 12: Coordinates of geometry optimized Ligand L12
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | -1.30126| 0.915804| -1.25676|
| C    | 0.011812| 1.151957| -0.46694|
| H    | 0.634365| 1.851072| -1.02561|
| H    | -0.23169| 1.658579| 0.468283|
| H    | -1.01933| 0.854976| -2.30932|
| H    | -1.98524| 1.756419| -1.12862|
| N    | -1.87783| -0.25358| -0.90764|
| C    | -1.11131| -1.35941| -1.01409|
| H    | -0.82481| -1.47501| -2.06081|
| H    | -1.65033| -2.25505| -0.70078|
| C    | 0.208701| -1.20632| -0.21542|
| H    | 0.947128| -1.89519| -0.62609|
| H    | 0.035271| -1.53874| 0.809282|
| N    | 0.745505| 0.044981| -0.16182|
| C    | 1.941305| 0.211818| 0.466368|
| C    | 2.552183| 1.601551| 0.715023|
| H    | 2.0551  | 2.518152| 0.399603|
| C    | 3.904492| 1.682051| 1.43715|
| H    | 4.350285| 2.659581| 1.620527|
| N    | 4.553915| 0.577715| 1.852031|
| C    | 4.101712| -0.68022| 1.68908|
| H    | 4.698467| -1.51103| 2.065322|
| C    | 2.767356| -0.9756 | 0.98985 |
| H    | 2.432898| -2.00675| 0.882135|
| C    | -3.21535| -0.37818| -1.02896|
| H    | -3.49614| -1.35331| -1.43088|
| H    | -3.64516| 0.4316  | -1.62123|
| C    | -3.7896 | -0.27517| 0.386551|
| H    | -4.87448| -0.3706 | 0.341026|
| H    | -3.53265| 0.691317| 0.822261|
| H    | -3.38531| -1.07343| 1.01047|