Supporting information

An efficient oxidation of alcohols using a new trinuclear copper complex as a reusable catalyst under solvent free condition

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General information

All the reagents used were chemically pure and were of analytical reagent grade. 4- nitro benzyl alcohol and 4-methoxy benzyl alcohol were purchased from Aldrich and the rest of the chemicals along with solvent were procured from local suppliers. The metalloligand [Cu(H2L)(H2O)] was synthesized by literature procedure using succinoyldihydrazine instead of oxaloyldihydrazine.\(^1\) The solvents were dried and distilled before use following the standard procedures.\(^2\)

Preparation of the catalyst \([\text{Cu}_3(\text{L})(\mu_2-\text{Cl})_2(\text{H}_2\text{O})_6]\) (I):

The precursor complex \([\text{Cu} (\text{H}_2\text{L}) (\text{H}_2\text{O})]\) (2.0 g; 4.43mmol) was suspended in methanol (30 mL) and stirred vigorously to get a homogeneous suspension. This suspension was added into copper chloride dihydrate solution maintaining \([\text{Cu} (\text{H}_2\text{L}) (\text{H}_2\text{O})]:\text{CuCl}_2.2\text{H}_2\text{O}\) molar ratio at 1:3. The mixture was refluxed for 3 h which precipitated a brown colored compound. The compound was suction filtered in hot condition and washed three times with methanol (30 mL each time). It was then dried in vacuum desiccator over fused calcium chloride.

Yield: 3.32 g, 75%, M.p.: >300 °C; Anal: Calc for C\(_{18}\)H\(_{26}\)Cl\(_2\)N\(_4\)O\(_{10}\)Cu\(_3\) (719.52 g mol\(^{-1}\)): Cu, 26.49; C, 30.02; H, 3.61; N, 7.78. Found: Cu, 26.19; C, 29.72; H, 3.58; N, 7.98. IR (KBr, cm\(^{-1}\)): 3431 m \(v_{(O-H)}\), 1622 s \(v_{(C=N)}\), 1598 s \(v_{(\text{Amide II}+\text{C-OPhenolic})}\), 1507 s \(v_{(\text{NCO})}\), 514 m \(v_{(\text{Cu-O Phenolic})}\), 473 m \(v_{(\text{Cu-O Carbonyl})}\). UV-Vis (DMSO, \(\lambda_{\text{max}}\), nm); \(\varepsilon\) (dm\(^3\)mol\(^{-1}\)cm\(^{-1}\)): 680(85), 384(4500), 303(6680), 316(5400). EPR: \(g\parallel = 2.244, g\perp = 2.084, g_{av} = 2.138, A_{\parallel} = 150\text{G, }g_{\parallel}/A_{\parallel} = 160.5\). Magnetic Moment: 1.13 BM per Copper (II) atoms. Molar Conductance (DMSO, \(\Omega^{-1}\text{cm}^{2}\text{mol}^{-1}\)): 1.2.

Characterization of catalyst \([\text{Cu}_3(\text{L})(\mu_2-\text{Cl})_2(\text{H}_2\text{O})_6]\) (I)

The complex shows loss of weight corresponding to six water molecules at 180 °C, when heated in an electronic oven for 4 hrs. This revealed the presence of six water molecules in coordination sphere of the complex.\(^3\)

The IR spectrum of ligand exhibits two strong bands at 1622 and 1609 cm\(^{-1}\), which are assigned to \(v_{\text{C-N}}\) vibration. As a result of coordination, these bands shift to lower wave number by \(~6\) cm\(^{-1}\) in the complex. The ligand band at 1659 cm\(^{-1}\) \(v_{\text{C=O}}\) in free dihydrazone is absent in the IR spectrum of the complex. This suggests enol form of ligand in complex.\(^4\) The band at 1269 cm\(^{-1}\) which is assigned to phenolic \(v_{\text{C-O}}\) in the free ligand, is shifted to higher wave number by 10 cm\(^{-1}\) in the complex suggesting the bonding of phenolic oxygen to copper ion. The absence of strong bands at 3199 and 1675 cm\(^{-1}\) in the complex due to \(v_{\text{N-H}}\) and \(v_{\text{C=O}}\)
indicates that the ligand undergoes tautomerization and subsequent coordination of the imidolate form to the metal centre. A new band at 1507 cm\(^{-1}\) due to \(\nu_{\text{NCO}}\) group confirms enolization of the ligand in the complex. The bands at 514 and 473 cm\(^{-1}\) in the complex are assigned to \(\nu_{\text{Cu-O}}\) (phenol) and \(\nu_{\text{Cu-O}}\) (enol), respectively, confirming coordination of phenolate and enolate oxygen atoms to the metal centre.\(^5\) The strong band at 3421 cm\(^{-1}\) in the complex is attributed to \(\nu_{\text{O-H}}\) of coordinated water molecules. The complex shows a weak band (sh) at 213 cm\(^{-1}\) attributed to \(\nu_{\text{Cu-Cl}}\) stretching frequency. The position of \(\nu_{\text{Cu-Cl}}\) stretching frequency is indicative of a tetragonally distorted octahedral stereochemistry of the complex and that the chloride group is involved in bridging and the complex is monomeric.\(^6\)

**Fig. S1.** FT-IR spectrum of [Cu\(_3\) (L)(µ\(_2\)-Cl)\(_2\)(H\(_2\)O)\(_6\)] (I)

The absorption spectrum of I in DMSO at room temperature (Fig. S2) shows four different bands, two of which (303 and 316 nm, \(\epsilon = 6680\) and 5400 dm\(^3\)mol\(^{-1}\)cm\(^{-1}\)) are assigned to ligand-based \(\pi-\pi^*\) and \(n-\pi^*\) transition (in reference to the free ligand). A third band at 384 nm is characteristic of salicylaldimine group of dihydrazone ligand. This may also have contribution from LMCT transition from the phenolate to the Cu\(^{II}\) metal centre (\(\epsilon = 4500\) dm\(^3\)mol\(^{-1}\)cm\(^{-1}\)). A fourth band at 680 nm (\(\epsilon = 85\) dm\(^3\)mol\(^{-1}\)cm\(^{-1}\)) is assigned to a metal-based d-d transition which is indicative of the distorted octahedral stereochemistry in of the metal centres in complex.\(^7\)
Electron Paramagnetic Resonance (EPR) spectroscopy is used to obtain the structural information about the ground state of Cu²⁺ in the complex. The trimetallic polycrystalline solid complex exhibits isotropic signal in solid state at RT with $g_{\text{av}}$ value 2.153. This indicates persistence of moderately strong interaction between adjacent metal ions in the structural unit of the complex. When the complex is cooled down to LNT in the solid state (Fig. S3), the coupling between adjacent spins is considerably reduced. This permits the appearance of hyperfine lines in the $g_{\parallel}$ region with hyperfine coupling constant $A_{\parallel}$ equal to 150 G. The $g_{\parallel}$ and $g_{\perp}$ values are 2.244 and 2.084, respectively. The magnetic parameters for complex fall in the order $g_{\parallel}>g_{\perp}>2.0023$. This shows that in complex, copper has $(d_{x^2-y^2})$ orbital as the ground state. The $g$-tensors suggest that the complex has distorted octahedral geometry. The quotients $g_{\parallel}/A_{\parallel}$ is equal to 160.5 for the complex. The value of 160.5 is very close to the range reported for square planar equatorial configuration (105-135). This suggests that in the complex, there is moderate distortion in the equatorial plane.
Fig. S3. X-band EPR spectrum of [Cu$_3$(L)(µ$_2$-Cl)$_2$(H$_2$O)$_6$](I) at LNT in polycrystalline phase at LNT. Field Set: 3000 G, Microwave frequency: 9.1 GHz, Scan range: 4000 G. The line below the derivative EPR signal is the spectrum recorded in the range 2000 G keeping the central field at 2000 G to see the forbidden transition around 1600 G corresponding to quartet state (S = 3/2).

The cyclic voltammetry (CV) of I in DMSO solution (0.1 TBAP) was performed to access the redox properties of copper centers (Figure S5). The uncoordinated ligand shows a redox couple at $E_{pc} = -0.74$ V and $E_{pa} = -0.62$ V, $\Delta E = 120$ mV and an irreversible reductive wave at -1.42 V, respectively. The complex shows three irreversible reductive waves and two oxidative waves, respectively, in its cyclic voltammogram recorded at 50 mV/s. The reductive waves at -0.67 and -1.11 V are close to reductive wave at -0.74 V and -1.42 V, respectively. Hence, the irreversible reductive waves at -0.67 V and -1.11 V are attributed to electron transfer reactions centered on the ligand. Excluding the irreversible reductive waves due to ligand centered electron transfer reactions, the additional reductive waves at -0.36 V and -0.08 V and the oxidative waves at -0.05 and +0.52 V, may be attributed to metal centered electron transfer reactions. The irreversible reductive wave at -0.36 V and the oxidative wave at +0.49 V do not have their counter parts in their oxidative and reductive scan respectively. This suggests that the metal-centered species corresponding to these reductive and oxidative waves are unstable and revert back to their corresponding original species. Hence, the reductive wave at -0.36 V may be attributed to the reduced species [(L)Cu$^1$Cu$^1$Cu$^1$] while the oxidative wave at +0.49 V may be attributed to oxidized species [(L)Cu$^{II}$Cu$^{II}$Cu$^{III}$]$^{3+}$. The absence of the wave corresponding to these species in the oxidative and reductive scan suggests that it is not possible to have [(L)Cu$^1$Cu$^1$Cu$^1$] and [(L)Cu$^{II}$Cu$^{II}$Cu$^{III}$] species in the solution. The reductive wave at -0.08 V corresponds to the oxidative wave at -0.05 V. The difference between these
waves is 30 mV. This is about half of the potential difference (60 mV) required for one electron transfer reaction. On comparing the earlier data with the observed data, it can be deduced that this redox couple is related to a reversible two electron transfer process controlled by diffusion.¹⁰

![Cyclic Voltammogram](image)

**Fig. S4.** Cyclic Voltammogram of ligand \((H_4L)\) at 100 mV/s in DMSO.
Fig. S5. Cyclic Voltammogram of [Cu₃ (L) (μ₂-Cl)₂(H₂O)₆] (I) at 100 mV/s in DMSO.

DFT was performed to optimize the structure of the prepared complex. Selected bond distances and angles are listed in Table TS1.

Table TS1: Selected bond lengths (Å), bond angles (°) and charge (e) for the complex (I)

<table>
<thead>
<tr>
<th>Bond lengths (A)</th>
<th>Bond angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu1-N38 = 1.79</td>
<td>O6-Cu1-Cl4 = 101.4°</td>
</tr>
<tr>
<td>Cu1-O6 = 1.92</td>
<td>N38-Cu1-Cl4 = 160.9°</td>
</tr>
<tr>
<td>Cu1-O35 = 2.04</td>
<td>N38-Cu1-O35 = 78.6°</td>
</tr>
<tr>
<td>Cu1-Cl4 = 2.41</td>
<td>O35-Cu2-O43 = 96.5°</td>
</tr>
<tr>
<td>Cu1-O53 = 3.08</td>
<td>Cl4-Cu2-Cl5 = 92.2°</td>
</tr>
<tr>
<td>Cu1-O56 = 2.30</td>
<td>O27-Cu3-N45 = 93.5°</td>
</tr>
<tr>
<td>Cu2-O23 = 2.03</td>
<td>O27-Cu3-Cl5 = 101.4°</td>
</tr>
<tr>
<td>Cu2-O43 = 2.0</td>
<td>N45-Cu3-Cl5 = 160.9°</td>
</tr>
<tr>
<td>Cu2-Cl4 = 2.39</td>
<td>Cu1-Cu2-Cu3 = 157.2°</td>
</tr>
<tr>
<td>Cu2-Cl5 = 2.43</td>
<td></td>
</tr>
<tr>
<td>Cu2-O50 = 2.61</td>
<td></td>
</tr>
<tr>
<td>Cu2-O47 = 2.29</td>
<td></td>
</tr>
<tr>
<td>Cu3-O43 = 2.02</td>
<td></td>
</tr>
<tr>
<td>Cu3-O27 = 1.91</td>
<td></td>
</tr>
</tbody>
</table>
Cu3-N45 = 1.96
Cu3-Cl5 = 2.42
Cu3-O59 = 3.26
Cu3-O10 = 2.37

Charge (e)

N30 = -0.352
Cu1 = 0.464
Cu2 = 0.273
Cu3 = 0.467
O6 = -0.639
O27 = -0.651
O35 = -0.609
O43 = -0.618
N45 = -0.355
Cl4 = -0.248
Cl5 = -0.284

Spectral data of compounds 1-17

1. Benzaldehyde$^{11}$ (1)

Ir (KBr): 2852, 2743, 1687 cm$^{-1}$. $^1$H (CDCl$_3$, 300 MHz): δ = 10.00 (s, 1H), 8.17 (d, $J = 7.5$ Hz, 1H), 7.88 (d, $J = 6.9$ Hz, 2H), 7.64-7.43(m, 2H).

2. 4-methoxy benzaldehyde$^{12}$ (2)

Ir (KBr): 2833, 2746, 1699 cm$^{-1}$. $^1$H (CDCl$_3$, 400 MHz): δ = 9.87 (s, 1H), 7.84 (d, $J = 8.8$ Hz, 2H), 7.01 (d, $J = 8.8$ Hz, 2H), 3.87 (s, 3H). $^{13}$C (CDCl$_3$, 100 MHz): δ = 190.9, 164.6, 131.9, 129.8, 114.3, 55.5.

3. 4-(N,N-Dimethylamino)benzaldehyde$^{12}$ (3)
Yellowish white powder; m.p.- 72-74°C; Ir (KBr): 2795, 2714, 1661 cm$^{-1}$. $^1$H (CDCl$_3$, 300 MHz): δ = 9.73 (s, 1H), 7.74 (d, $J = 8.7$ Hz, 2H), 6.71 (d, $J = 8.7$ Hz, 2H), 3.08 (s, 6H). $^{13}$C (CDCl$_3$, 75 MHz): δ = 189.6, 153.8, 131.4, 124.5, 110.5, 39.5.

4. 3,4-dimethoxy benzaldehyde$^{11}$ (4)

![3,4-dimethoxy benzaldehyde](image)

Peach Colored solid; m.p.- 39-41°C; Ir (KBr): 2839, 2762, 1680 cm$^{-1}$. $^1$H (CDCl$_3$, 300 MHz): δ = 9.84 (s, 1H), 7.46-7.32 (m, 2H), 6.99 (d, $J = 8.1$ Hz, 1H), 3.96 (s, 3H), 3.93 (s, 3H).

$^{13}$C (CDCl$_3$, 75 MHz): δ = 190.3, 154.0, 149.1, 129.7, 126.3, 110.0, 108.5, 55.7, 55.5.

5. 4-Nitro benzaldehyde$^{13}$ (5)

![4-Nitro benzaldehyde](image)

Yellow crystalline solid; m.p- 104-106°C; Ir (KBr): 2854, 2726, 1697 cm$^{-1}$. $^1$H (CDCl$_3$, 400 MHz): δ = 10.17 (s, 1H), 8.41 (d, $J = 8.8$ Hz, 2H), 8.10 (d, $J = 8.8$ Hz, 2H). $^{13}$C (CDCl$_3$, 100 MHz): δ = 190.3, 151.1, 140.0, 130.3, 124.3.

6. 2-Chloro benzaldehyde$^{13}$ (6)

![2-Chloro benzaldehyde](image)

Ir (KBr): 2896, 1689 cm$^{-1}$. $^1$H (CDCl$_3$, 300 MHz): δ = 10.47 (s, 1H), 7.92 (d, $J = 7.5$ Hz, 1H), 7.54-7.32 (m, 3H). $^{13}$C (CDCl$_3$, 75 MHz): δ = 189.6, 137.7, 134.9, 132.2, 130.4, 129.2, 127.1.

7. 2-Bromo Benzaldehyde$^{14}$ (7)

![2-Bromo benzaldehyde](image)

Colorless solid; m.p.- 18-20°C; Ir (KBr): 2864, 2750, 1697 cm$^{-1}$. $^1$H (CDCl$_3$, 300 MHz): δ = 10.34 (s, 1H), 7.91-7.87 (m, 1H), 7.68-7.61 (m, 1H), 7.46-7.39 (m, 2H). $^{13}$C (CDCl$_3$, 75 MHz): δ = 191.7, 135.2, 133.7, 133.3, 129.7, 127.7, 126.9.

8. Benzil$^{15}$ (8)
Yellow powder; m.p.- 95-97°C; Ir (KBr): 3224, 1666 cm\(^{-1}\). \(^1\)H (CDCl\(_3\), 400 MHz): \(\delta = 7.98\) (d, \(J = 8.0\) Hz, 4H), 7.68-7.49 (m, 6H). \(^{13}\)C (CDCl\(_3\), 100 MHz): \(\delta = 194.5, 134.9, 132.9, 129.9, 129.0\).

9. **Cinnamaldehyde\(^{11}\)** (9)

Ir (KBr): 2816, 2743, 1679 cm\(^{-1}\). \(^1\)H (CDCl\(_3\), 300 MHz): \(\delta = 9.71\) (d, \(J = 7.5\) Hz, 1H), 7.57-7.43 (m, 6H), 6.76-6.68 (m, 1H). \(^{13}\)C (CDCl\(_3\), 75 MHz): \(\delta = 193.7, 152.8, 146.4, 133.8, 130.5, 129.0, 128.4\).

10. **Acetophenone\(^{16}\)** (10)

Ir (KBr): 2928, 1686 cm\(^{-1}\). \(^1\)H (CDCl\(_3\), 300 MHz): \(\delta = 7.95\) (d, \(J = 7.2\) Hz, 2H), 7.56-7.41 (m, 3H), 2.58 (s, 3H). \(^{13}\)C (CDCl\(_3\), 75 MHz): \(\delta = 197.9, 136.9, 133.0, 128.2, 26.5\).

11. **4-Chloroacetophenone\(^{13}\)** (11)

Ir (KBr): 2926, 1687 cm\(^{-1}\). \(^1\)H (CDCl\(_3\), 300 MHz): \(\delta = 7.91\) (t, \(J = 9.0\) Hz, 2H), 7.44 (t, \(J = 9.1\) Hz, 2H), 2.57 (s, 3H). \(^{13}\)C (CDCl\(_3\), 75 MHz): \(\delta = 196.4, 139.2, 135.1, 129.4, 128.5, 26.2\).

12. **4-Methoxy acetophenone\(^{17}\)** (12)

White crystals; M.P.- 35-37°C; Ir (KBr): 2939, 1673 cm\(^{-1}\). \(^1\)H (CDCl\(_3\), 300 MHz): \(\delta = 7.92\) (d, \(J = 8.7\) Hz, 2H), 6.92 (d, \(J = 8.7\) Hz, 2H), 3.84 (s, 3H), 2.53 (s, 3H). \(^{13}\)C (CDCl\(_3\), 75 MHz): \(\delta = 196.4, 163.2, 130.3, 130.0, 113.4, 55.2, 26.0\).

13. **4-methyl acetophenone\(^{19}\)** (13)
14. 2-chloro-6-methyl quinoline-3-carbaldehyde\textsuperscript{18} (14)

White solid; m.p.- 122-124\degree C; Ir (KBr): 2872, 2723, 1688 cm\(^{-1}\). \(^1\)H (CDCl\(_3\), 300 MHz): \(\delta = 10.54\) (s, 1H), 8.66 (s, 1H), 7.97 (d, \(J = 8.4\) Hz, 1H), 7.72 (d, \(J = 9.0\) Hz, 2H), 2.56 (s, 3H). \(^{13}\)C (CDCl\(_3\), 75 MHz): \(\delta = 189.2, 149.1, 148.1, 139.4, 138.3, 135.8, 128.3, 128.1, 126.5, 126.2, 21.5\).

15. Thiophene-2-carbaldehyde\textsuperscript{17} (15)

Ir (KBr):2925, 2853, 1674 cm\(^{-1}\). \(^1\)H (CDCl\(_3\), 500 MHz): \(\delta = 9.86\) (d, \(J = 1.2\) Hz, 1H), 7.72-7.69 (m, 2H), 7.14 (t, \(J = 4.2\) Hz, 1H). \(^{13}\)C (CDCl\(_3\), 125 MHz): \(\delta = 183.1, 144.0\), 136.6, 135.2, 128.2

16. Propionaldehyde\textsuperscript{19} (16)

Ir (KBr): 2927, 2855, 1739 cm\(^{-1}\). \(^1\)H (CDCl\(_3\), 300 MHz): \(\delta = 9.43\) (s, 1H), 2.17-2.10 (q, \(J = 7.2\) Hz, 2H), 0.77 (t, \(J = 7.3\) Hz, 3H). \(^{13}\)C (CDCl\(_3\), 75 MHz): \(\delta = 201.8, 36.4, 5.1\).

17. Octanaldehyde\textsuperscript{20} (17)

Ir (KBr): 2927, 2857, 1717 cm\(^{-1}\). \(^1\)H (CDCl\(_3\), 300 MHz): \(\delta = 9.75\) (s, 1H), 2.44-2.31 (m, 2H), 1.65-1.58(m, 2H), 1.27 (s, 8H), 0.88 (s, 3H). \(^{13}\)C (CDCl\(_3\), 75 MHz): \(\delta = 202.9, 43.8, 31.5, 28.9, 24.6, 22.5, 22.0, 13.9\).

REFERENCES


$^1$H and $^{13}$C NMR spectra of compounds 1-17

1. Benzaldehyde (1)

Fig. 1. $^1$H NMR Spectra of Benzaldehyde
2. 4-methoxy benzaldehyde (2)

Fig. 2. $^1$H NMR Spectra of 4-methoxy benzaldehyde

3. 4-methoxy benzaldehyde (2)
Fig. 3. $^{13}$C NMR Spectra of 4-methoxy benzaldehyde

4. 4-(N,N-Dimethylamino)benzaldehyde (3)
Fig. 4. $^1$H NMR Spectra of 4-(N,N-Dimethylamino)benzaldehyde

5. 4-(N,N-Dimethylamino)benzaldehyde (3)
Fig. 5. $^{13}$C NMR Spectra of 4-(N,N-Dimethylamino)benzaldehyde

6. 3,4-dimethoxy benzaldehyde(4)
Fig. 6. $^1$H NMR Spectra of 3,4-dimethoxy benzaldehyde

7. 3,4-dimethoxy benzaldehyde (4)
Fig. 7. $^{13}$C NMR Spectra of 3,4-dimethoxy benzaldehyde

8. 4-nitro benzaldehyde (5)
Fig. 8. $^1$H NMR Spectra of 4-nitro benzaldehyde

9. 4-nitro benzaldehyde (5)
Fig. 9. $^{13}$C NMR Spectra of 4-nitro benzaldehyde

10. 2-chloro benzaldehyde (6)
Fig. 10. $^1$H NMR Spectra of 2-chloro benzaldehyde

11. 2-chloro benzaldehyde (6)
Fig. 11. $^{13}$C NMR Spectra of 2-chloro benzaldehyde

12. 2-bromo benzaldehyde (7)
Fig. 12. $^1$H NMR Spectra of 2-bromo benzaldehyde

13. 2-bromo benzaldehyde (7)
Fig. 13. $^{13}$C NMR Spectra of 2-bromo benzaldehyde

14. Benzil (8)
Fig. 14. $^1$H NMR Spectra of Benzil

15. Benzil (8)
Fig. 15. $^{13}$C NMR Spectra of Benzil

16. Cinnamaldehyde (9)
Fig. 16. $^1$H NMR Spectra of Cinnamaldehyde

17. Cinnamaldehyde (9)
Fig. 17. $^{13}$C NMR Spectra of Cinnamaldehyde

18. Acetophenone (10)
Fig. 18. $^1$H NMR Spectra of acetophenone

19. Acetophenone (10)
Fig. 19. $^{13}$C NMR Spectra of acetophenone

20. 4-chloro acetophenone (11)
Fig. 20. $^1$H NMR Spectra of 4-chloro acetophenone

21. 4-chloro acetophenone (11)
Fig. 21. $^{13}$C NMR Spectra of 4-chloro acetophenone

22. 4-methoxy acetophenone (12)
Fig. 22. $^1$H NMR Spectra of 4-methoxy acetophenone

23. 4-methoxy acetophenone (12)
Fig. 23. $^{13}$C NMR Spectra of 4-methoxy acetophenone

24. 4-methyl acetophenone(13)
Fig. 24. $^1$H NMR Spectra of 4-methyl acetophenone

25. 4-methyl acetophenone(13)
Fig. 25. $^{13}$C NMR Spectra of 4-methyl acetophenone

26. 2-chloro-6-methyl quinoline-3-carbaldehyde (14)
Fig. 26. $^1$H NMR Spectra of 2-chloro-6-methyl quinoline-3-carbaldehyde

27. 2-chloro-6-methyl quinoline-3-carbaldehyde (14)
Fig. 27. $^{13}$C NMR Spectra of 2-chloro-6-methyl quinoline-3-carbaldehyde

28. Thiophene-2-carbaldehyde (15)
Fig. 30. $^1$H NMR Spectra of Thiophene-2-carbaldehyde

29. Thiophene-2-carbaldehyde  (15)
Fig. 31. $^{13}$C NMR Spectra of Thiophene-2-carbaldehyde

30. Propionaldehyde(16)
Fig. 28. $^1$H NMR Spectra of Propionaldehyde

31. Propionaldehyde(16)
Fig. 29. $^{13}$C NMR Spectra of Propionaldehyde
32. Octanaldehyde(17)

Fig. 32. $^1$H NMR Spectra of Octanaldehyde
33. Octanaldehyde (17)

Fig. 33. $^{13}$C NMR Spectra of Octanaldehyde