New Journal of Chemistry

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Cite this: DOI: 10.1039/c0xx00000x

ARTICLE TYPE

www.rsc.org/xxxxxx

Bi-functionalized PEG_{1000} ionic liquid [Imim-PEG_{1000}-TEMPO][$CuCl_2^-$]: An efficient and reusable catalytic system for solvent-free aerobic oxidation of alcohols

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Experimental Section

All starting materials were purchased from commercial sources and used without further treatment. Analytical thin layer chromatography (TLC) was performed on precoated silica plates. Yields of the products refer to purification by silica-gel column chromatography. IR spectrum analysis was recorded on Nicolet IS-10 fourier transform infrared spectroscopy. ^{1}HNMR were recorded on a Bruker Advance III (500MHz) spectrometer with tetramethylsilane (TMS) as an internal standard. High performance liquid chromatography experiments were performed on a liquid chromatograph (Shimazhu LC-20AT, Japan).

Synthesis of bi-functionalized PEG_{1000} ionic liquid [Imim-PEG_{1000}-TEMPO][$CuCl_2^-$]

To a solution of PEG-1000 (0.06 mol, 60 g) in toluene (150 mL), pyridine(0.12 mol, 9.6 mL) was added, followed by the addition of thionyl chloride (0.12 mol, 8.7 mL) within 30 min under N_2 atmosphere at 0 ^{o}C. The resulting slurry was stirred for 24 h at room temperature and filtered. The toluene was then removed by rotator evaporation under reduced pressure to give intermediate **1** as a gray viscous liquid. In the next step, 4-hydroxy-TEMPO (8.6 g, 0.05mol) was added to a suspension of Na (1.15 g, 0.05 mol) in benzene (100 mL) and the resulting slurry was stirred for 8

h at room temperature. Intermediate **1** (0.025 mol) was then added and stirring resumed for 24 h at room temperature. The suspension was then filtered and the filtrate concentrated under reduced pressure. This solution was then added to ether (100 mL) that was stirred vigorously and the precipitate collected by filtration, washed twice with ether (50 mL), and dried under vacuum. The product **2** was obtained as orange red viscous solid. Then, intermediate **2** (0.025 mol) was added to N-methylimidazole (2.05 g, 0.025 mol) solution which was dissolved in toluene, and the mixture was stirred at 70 °C for 20 h. The reaction was determined by HPLC and evaporated under reduced pressure to give intermediate **3** as an orange red oil with a yield of 98.3% . In the last step, the intermediate 3 was mixed with anhydrous CuCl together under N_2 atmosphere with a mechanical stirring at room temperature. The obtained red brown liquid were washed with ether, evaporated by reduced pressure and dried in vacuum successively. Then, the ionic liquid ([Imim-PEG_{1000}-TEMPO][$CuCl_2^-$]) was thus obtained.

General procedure for soxidation of alcohols

To a 10 mL round-bottom flask containing the [Imim-PEG_{1000}-TEMPO][$CuCl_2^-$] (0.5 mmol), benzyl alcohol (10 mmol) was successively added under a constant vigorous stiring. The reaction was proceed under temperature of 60 ^oC and monitored by TLC. Upon completion, the reaction mixture was cooled to room temperature and extracted three times by adding ether. The organic phase was dried over anhydrous $MgSO_4$, evaporated under reduced pressure and to give benaldehyde (96% yield) with spectral data consistent with the assigned structures for the products. The next run was performed under identical reaction conditions.

Characterization of aldehyde products

Benzaldehyde (Table 2, entry 1)

Colorless liquid; ^{1}HNMR (500MHz, DMSO-d_6): δ10.00 (s, 1H, -CHO), 7.91-7.89(d, 2H, Ar-H), 7.70-7.69(t, 1H, Ar-H), 7.61-7.58(t, 2H, Ar-H). Elemental analysis % Calcd for C_7H_6O: C 79.22; H 5.70; O 15.08. Found: C 79.28; H 5.68; O 15.04.

4-Methyl benzaldehyde (Table 2, entry 2)

Colorless liquid; ^{1}H NMR (DMSO-d_6, 500 MHz): δ9.93 (s, 1H, -CHO), 7.76-7.75(s, 2H, Ar-H), 7.34(s, 2H, Ar-H), 2.35-2.33(s, 3H, -CH_3). Elemental analysis % Calcd for C_8H_8O: C 79.97; H 6.71; O 13.32. Found: C 79.92; H 6.73; O 13.35.

2-Methoxybezaldehyde (Table 2, entry 3)

Colorless solid; m.p. 38-40℃; ^{1}H NMR (DMSO-d_6, 500 MHz): δ9.95 (s, 1H, -CHO), 7.47 (s, 2H, Ar-H), 7.38(s, H, Ar-H), 7.22-7.20(s, H, Ar-H), 3.79(s, 3H, -CH_3). Elemental analysis % Calcd for $C_8H_8O_2$: C 70.57; H 5.93; O 23.50. Found: C 70.50; H 5.94; O 23.56.

3-Methoxybezaldehyde (Table 2, entry 4)

Colorless liquid; ^{1}H NMR (DMSO-d_6, 500 MHz): δ9.92 (s, 1H, -CHO), 7.46(d, 2H, Ar-H), 7.36-7.35(d, H, Ar-H), 7.22-7.20(m, H, Ar-H), 3.79(s, 3H, -CH_3). Elemental analysis % Calcd for $C_8H_8O_2$: C 70.57; H 5.93; O 23.50. Found: C 70.52; H 5.95; O 23.53.

4-Methoxybezaldehyde (Table 2, entry 5)

Colorless liquid; ^{1}H NMR (DMSO-d_6, 500 MHz): δ9.85 (s, 1H, -CHO), 7.81-7.79(m, 2H, Ar-H), 7.01-6.99(m, 2H, Ar-H), 3.79(s, 3H, -CH_3). Elemental analysis % Calcd for $C_8H_8O_2$: C 70.57; H 5.93; O 23.50. Found: C 70.53; H 5.94; O 23.53.

4-Nitrobenzaldehyde (Table 2, entry 6)

Light yellow acicular crystals; m.p. 103-106℃; ^{1}H NMR (DMSO-d_6, 500 MHz): δ10.17 (s, 1H, -CHO), 8.43-8.41(t, 2H, Ar-H), 8.17-8.16 (t, 2H, Ar-H). Elemental analysis % Calcd for $C_7H_5NO_3$: C

55.63; H 3.34; O 31.76 ; N 9.27; Found: C 55.71; H 3.33; O 31.71 ; N 9.25;

4-Chlorobenzaldehyde (Table 2, entry 7)

White solid; m.p. 46-47℃; ^{1}H NMR (DMSO-d_6, 500 MHz): δ9.98 (s, 1H, -CHO), 7.91-7.89(t, 1H, Ar-H), 7.64-7.62 (s, 2H, Ar-H). Elemental analysis % Calcd for C_7H_5ClO: C 59.81; H 3.59; O 11.38; Cl 25.22. Found: C 59.90; H 3.58; O 11.35; Cl 25.17.

Phenylacetaldehyde (Table 2, entry 8)

Colorless liquid; ^{1}H NMR (DMSO-d_6, 500 MHz): δ9.72 (s, 1H, -CHO), 7.73-7.72(d, 2H, Ar-H), 7.59-7.58(t, 1H, Ar-H), 7.29-7.27(t, 2H, Ar-H). Elemental analysis % Calcd for C_8H_8O: C 79.97; H 6.71; O 13.32. Found: C 79.93; H 6.73; O 13.34.

Cinnamaldehyde (Table 2, entry 9)

Light yellow liquid; ^{1}H NMR (DMSO-d_6, 500MHz) δ9.69 (s, 1H, -CHO), 7.76-7.73(d, 2H, Ar-H), 7.49-7.47(d, 3H, Ar-H), 6.89-6.84(m, 2H, -CH). Elemental analysis % Calcd for C_9H_8O: C 81.79; H 6.10; O 12.11. Found: $C_{13}H_9N_3O_2$: C 81.85; H 6.08; O 12.07.

Acetophenone (Table 2, entry 10)

Colorless liquid; ^{1}HNMR(DMSO-d_6, 500MHz): δ7.95-7.93 (s, 1H, Ar-H),7.71-7.69(m, 2H, Ar-H), 7.34-7.28(m, 2H, Ar-H), 2.55(s, 3H, -CH_3). Elemental analysis % Calcd for C_8H_8O: C 79.97; H 6.71; O 13.32. Found: C 79.80; H 6.69; O 13.31.

Benzophenone (Table 2, entry 11)

White crystals; m.p. 48-49℃; ^{1}HNMR(500MHz, DMSO-d_6): δ7.75 (d, 2H, Ar-H), 7.74-7.73(t, 2H, Ar-H), 7.59-7.57(t, 4H, Ar-H). Elemental analysis % Calcd for $C_{13}H_{10}O$: C85.69; H 5.53; O 8.78. Found: C 85.65; H 5.54; O 8.81.

Cyclohexanone (Table 2, entry 12)

Colorless liquid; ^{1}HNMR(500MHz, DMSO-d_6): δ2.24-2.23 (t, 2H, -CH_2), 1.77-1.74(s, 2H, -CH_2),1.67-1.65(s, 2H, -CH_2), Elemental analysis % Calcd for $C_6H_{10}O$: C 73.43; H 10.27; O 16.30. Found: C 73.39; H 10.28; O 16.33.

2-Furaldehyde (Table 2, entry 13)

Colorless liquid; ^{1}HNMR(500MHz, DMSO-d_6): δ9.07-9.06 (s, H, -CHO), 7.55(s, 2H, -CH),7.00(s, 1H, -CH) ,6.24(s, 1H, -CH), Elemental analysis % Calcd for $C_6H_{10}O$: C 62.50; H 4.20; O 33.30. Found: C C 62.58; H 4.18; O 33.24.

2-Pyridinecarboxaldehyde (Table 2, entry 14)

Colorless liquid; ^{1}HNMR(500MHz, DMSO-d_6): δ9.96 (s, 1H, -CHO), 8.82-8.79(s, 1H, -CH),8.02-8.00(s, 1H, -CH), 7.89 (s, 1H, -CH) , 7.67-7.66 (s, 1H, -CH). Elemental analysis % Calcd for C_6H_5NO: C 67.28; H 4.71; O 14.94; N 13.07. Found: C 67.26; H 4.69; O 14.95; N 13.10.

Dodecyl aldehyde (Table 2, entry 15)

Colorless liquid; ^{1}HNMR(500MHz, DMSO-d_6): δ9.65 (s, 1H, -CHO), 1.52-1.49(s, 20H, -CH_2), 0.85(s, 3H, -CH_3). Elemental analysis % Calcd for $C_{12}H_{24}O$: C 78.19; H 13.13; O 8.68. Found: C 78.23; H 13.12; O 8.65

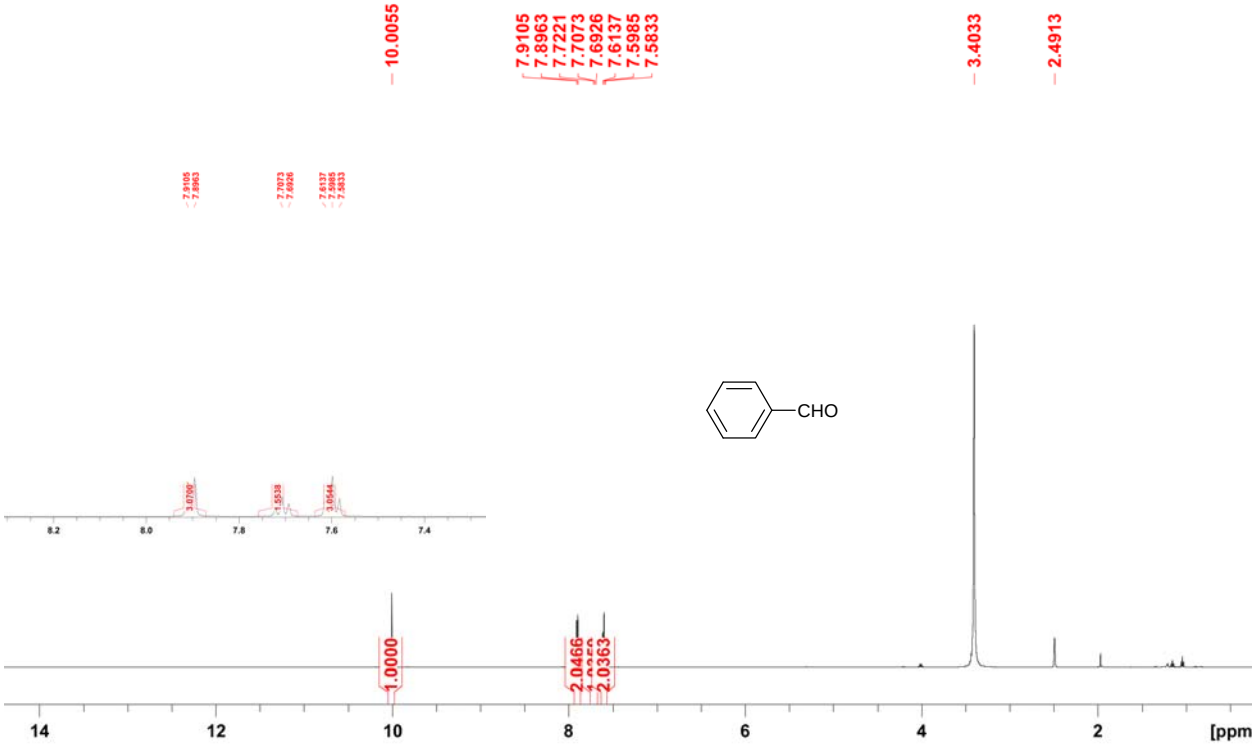

Fig 1. [1]HNMR of benzaldehyde

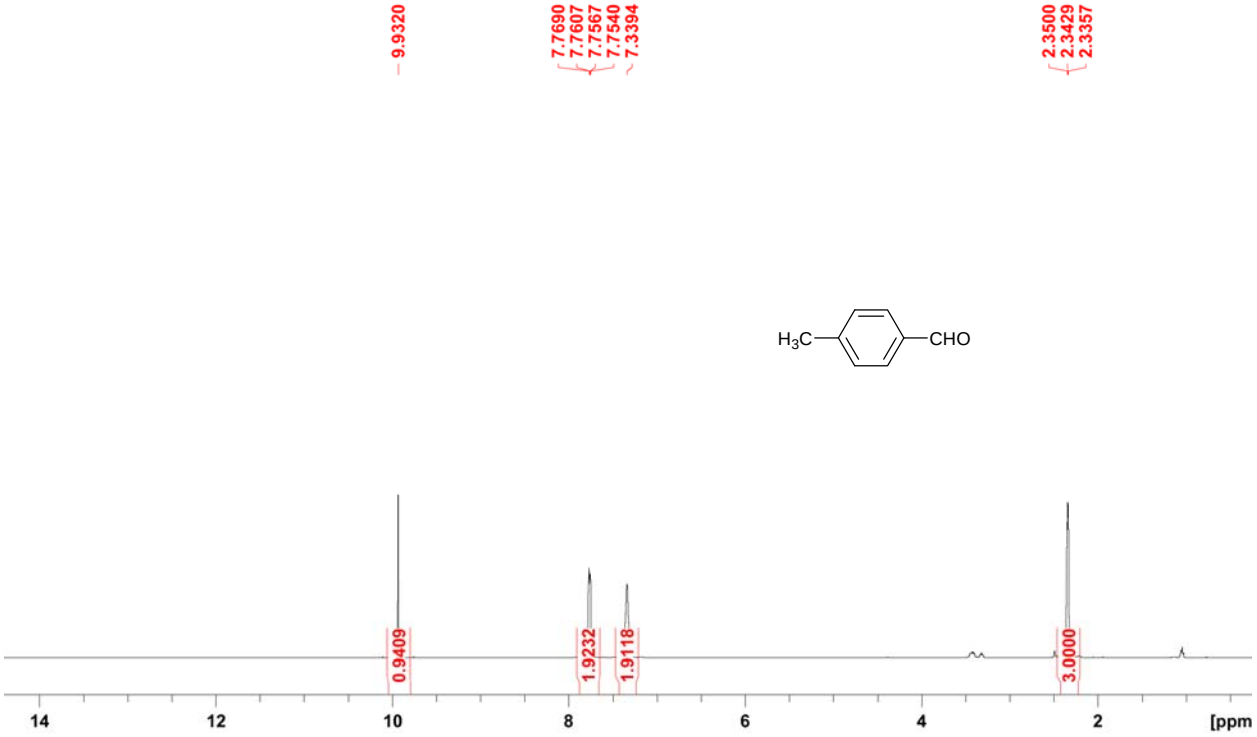

Fig 2. [1]HNMR of 4-methyl benzaldehyde

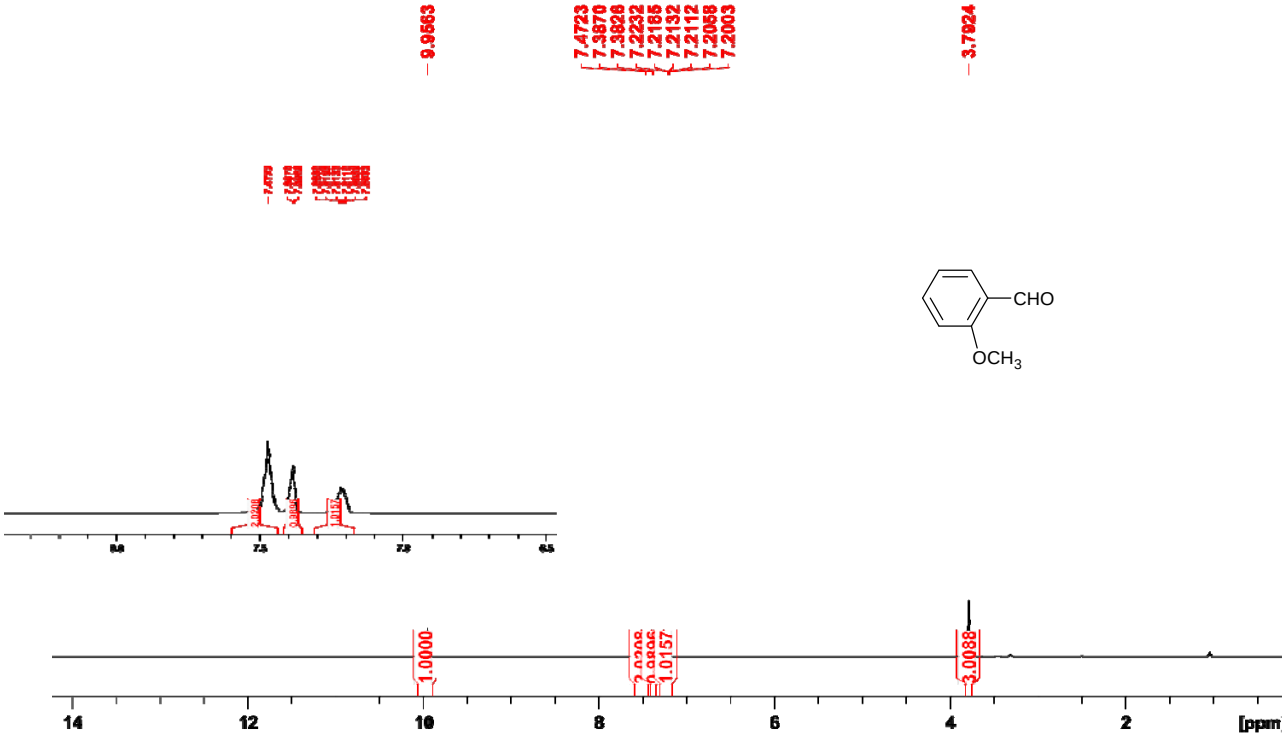

Fig 3. [1]HNMR of 2-methoxybezaldehyde

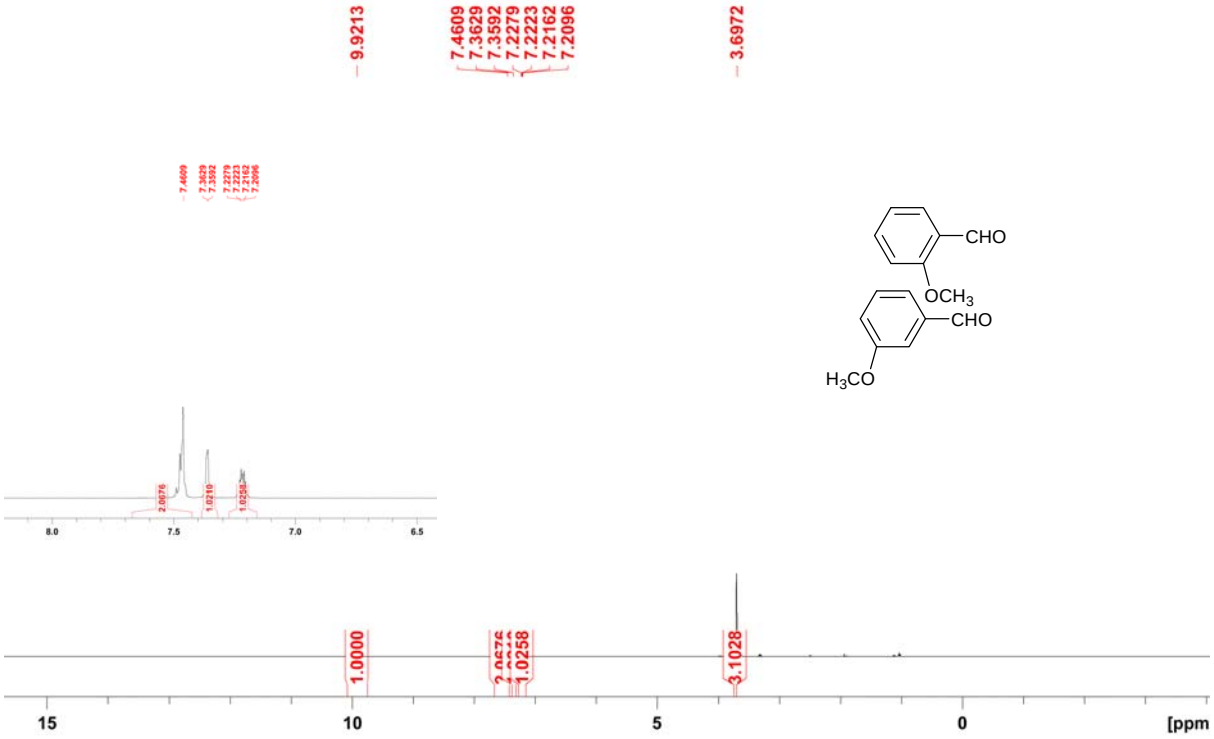

Fig 4. [1]HNMR of 3-methoxybezaldehyde

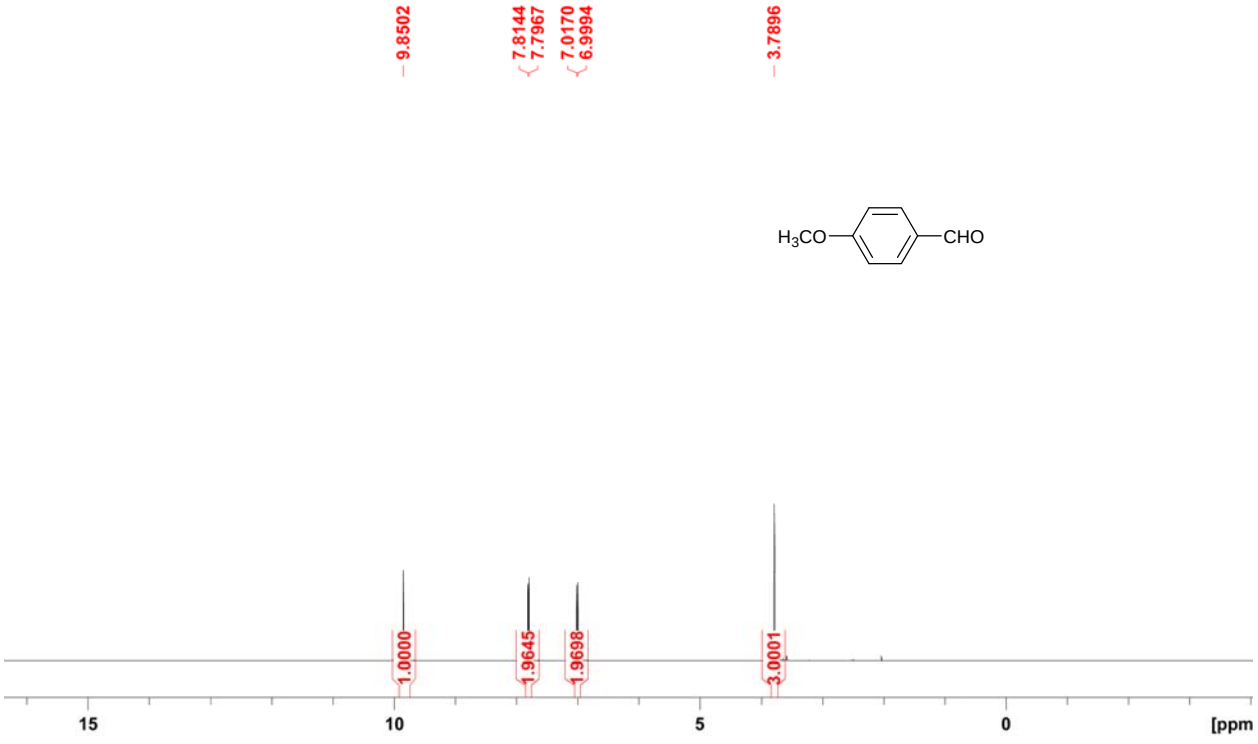

Fig 5. [1]HNMR of 4-methoxybezaldehyde

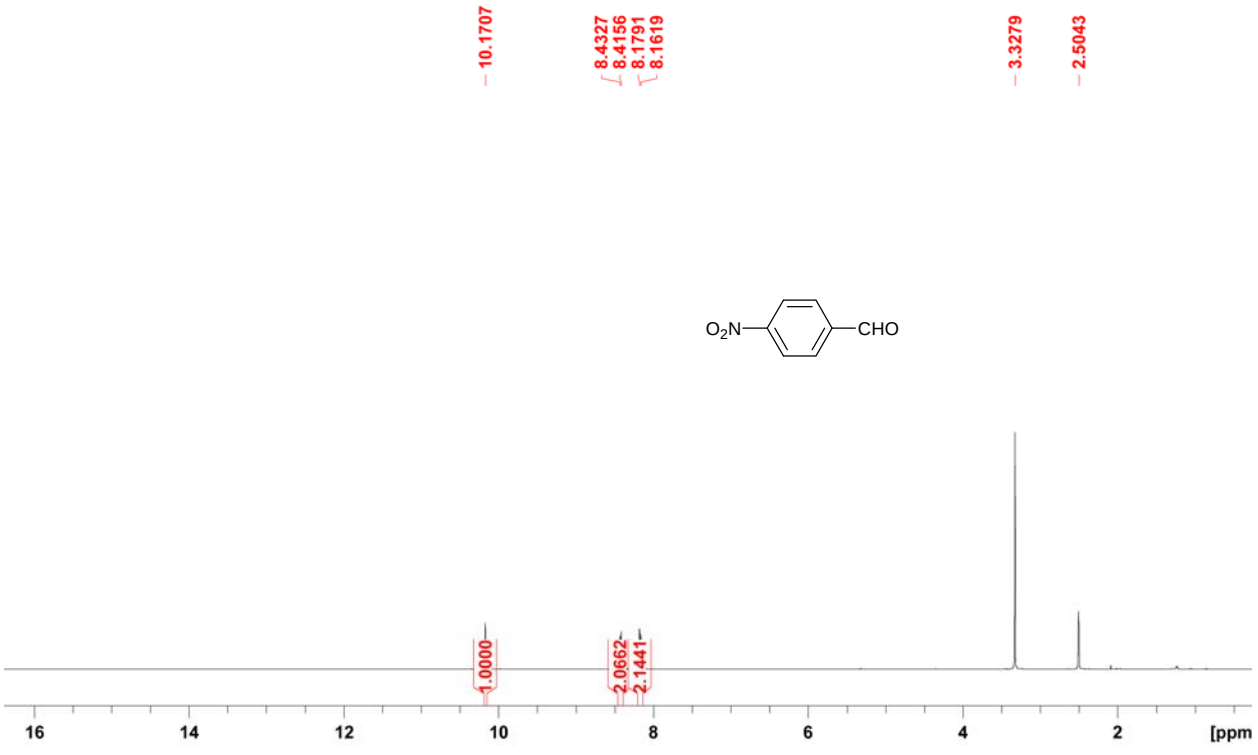

Fig 6. [1]HNMR of 4-nitrobenzaldehyde

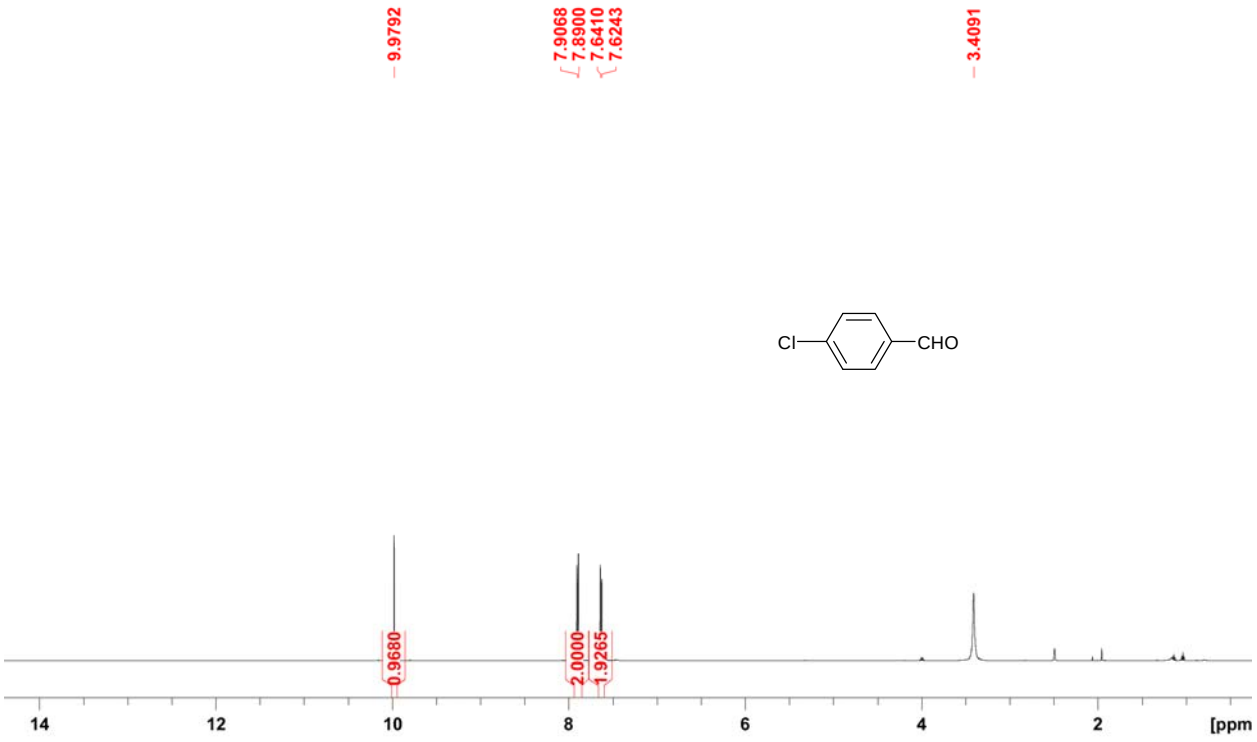

Fig 7. ^{1}HNMR of 4-chlorobenzaldehyde

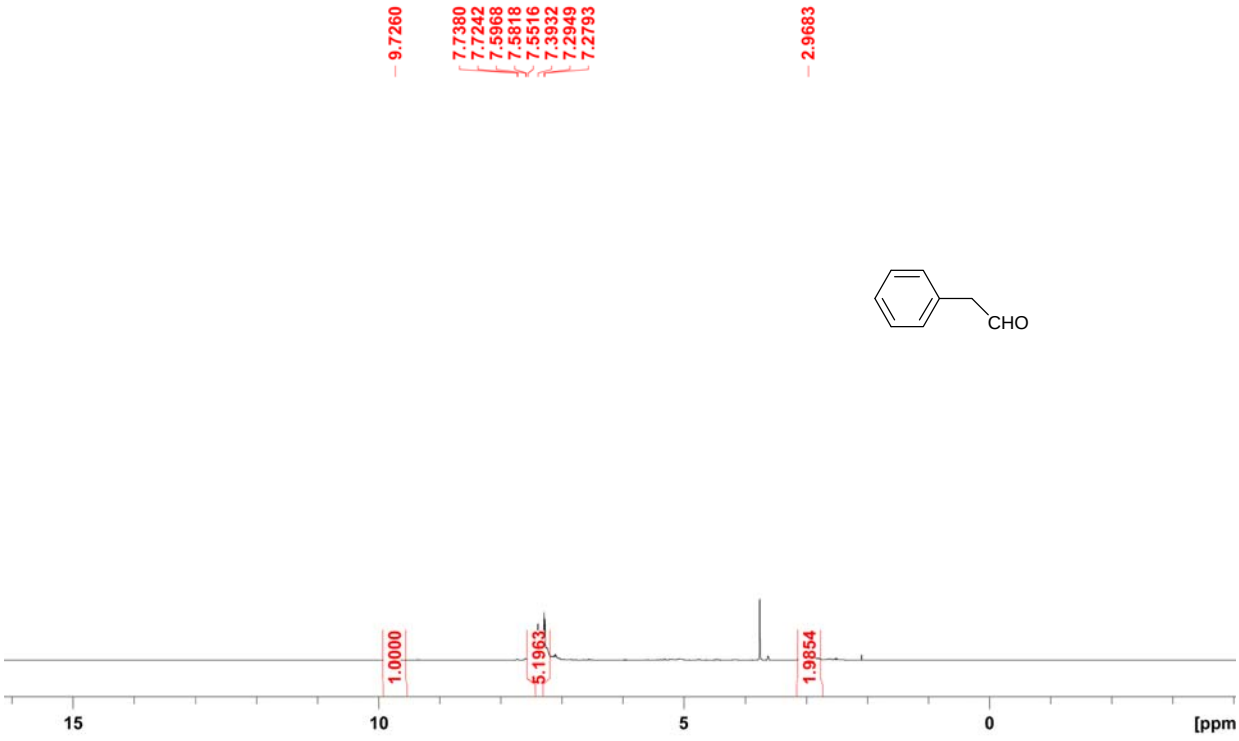

Fig 8. ^{1}HNMR of phenylacetaldehyde

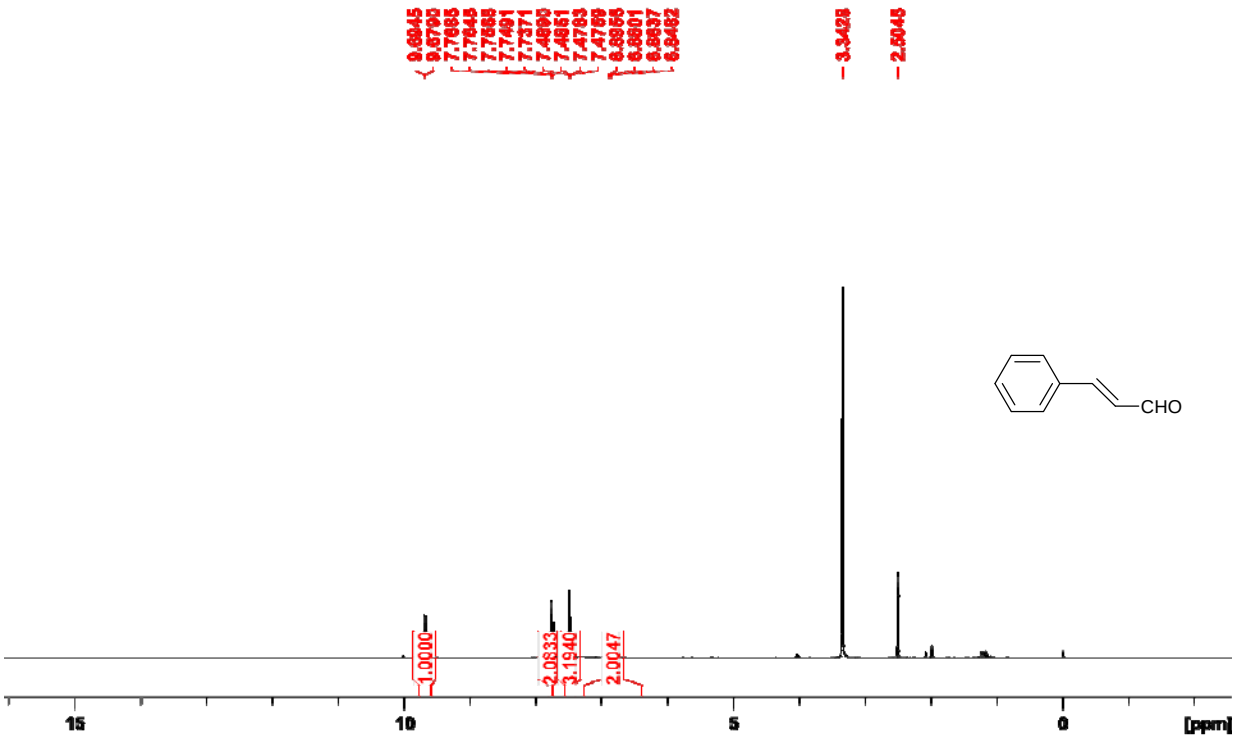

Fig 9. [1]HNMR of cinnamaldehyde

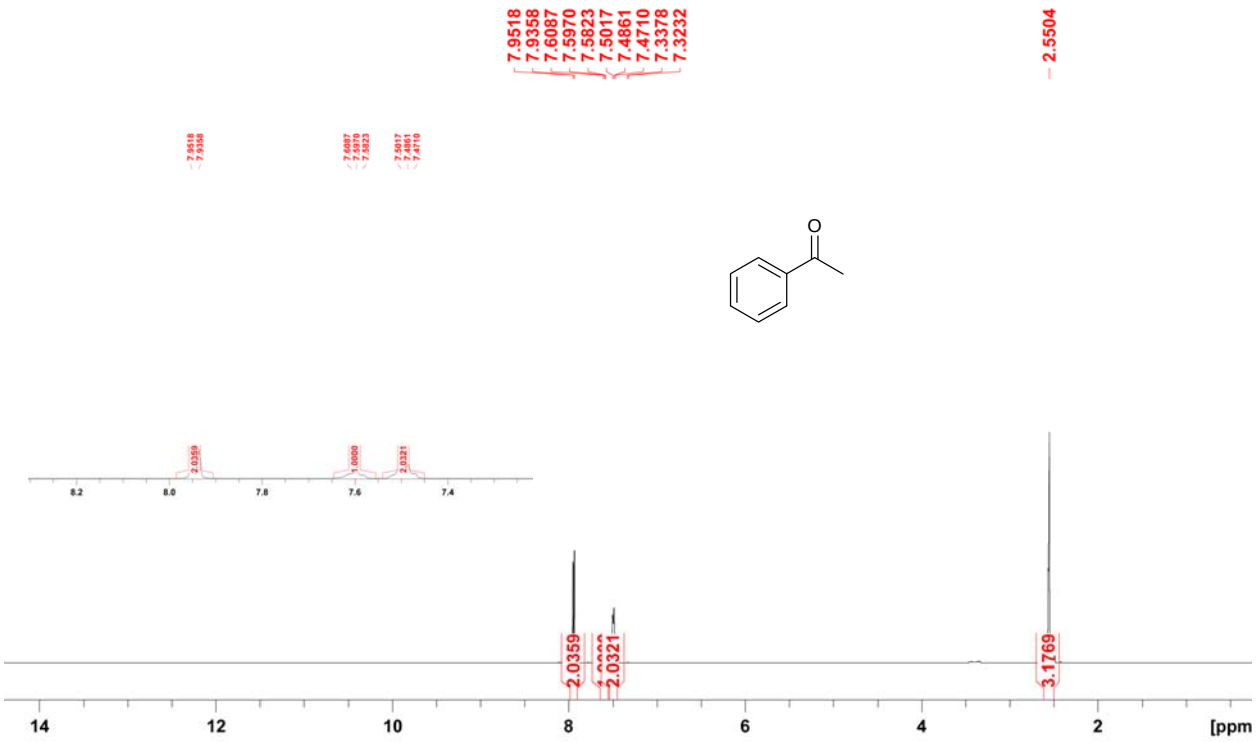

Fig 10. [1]HNMR of acetophenone

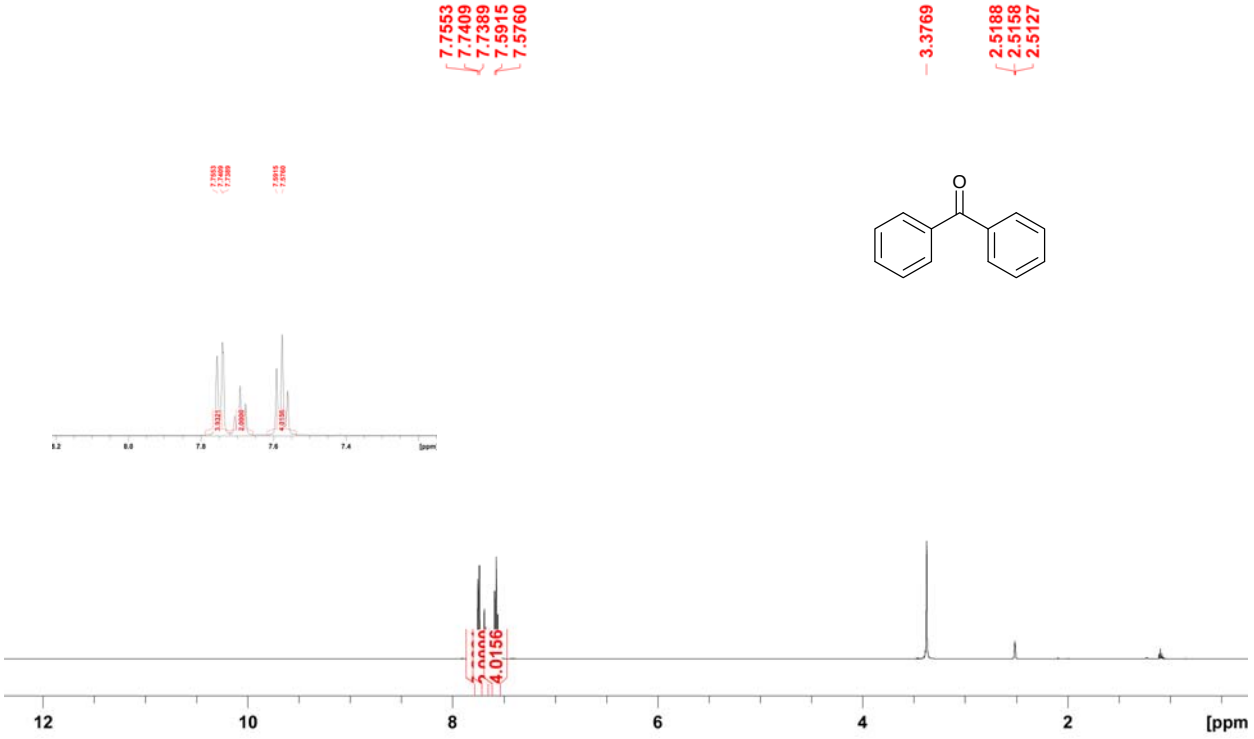

Fig 11. [1]HNMR of benzophenone

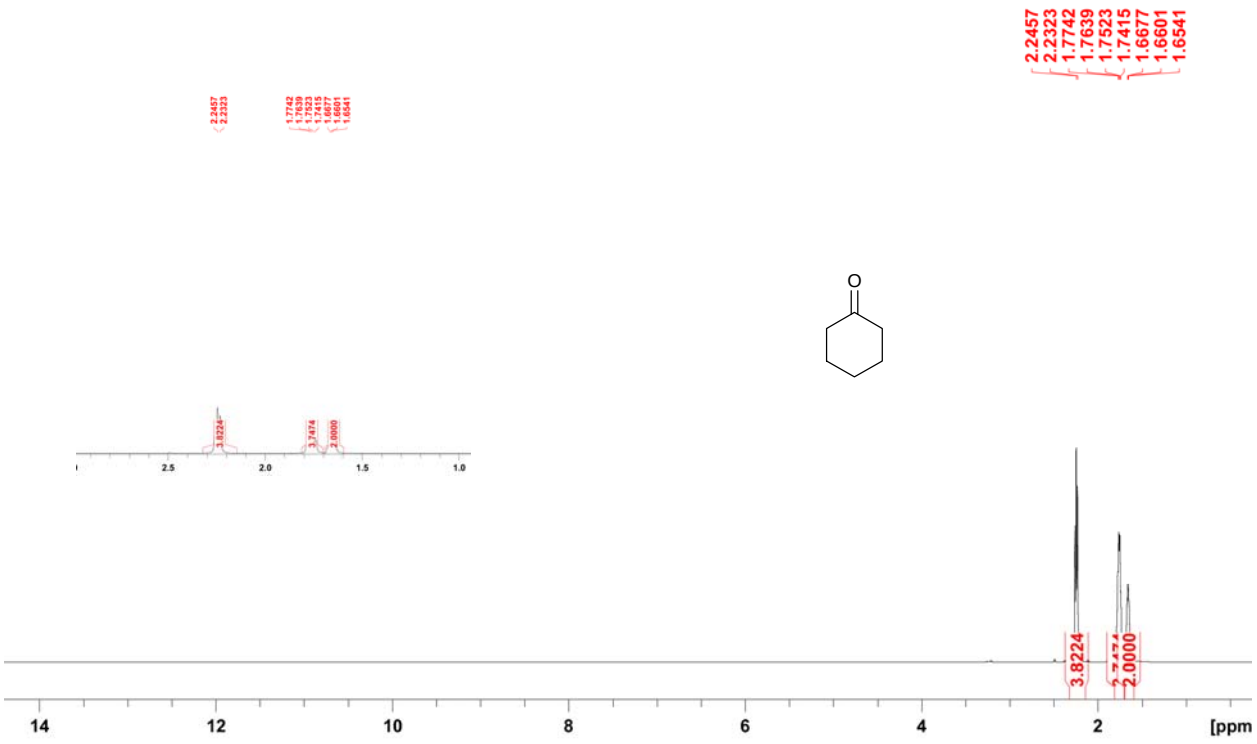

Fig 12. [1]HNMR of cyclohexanone

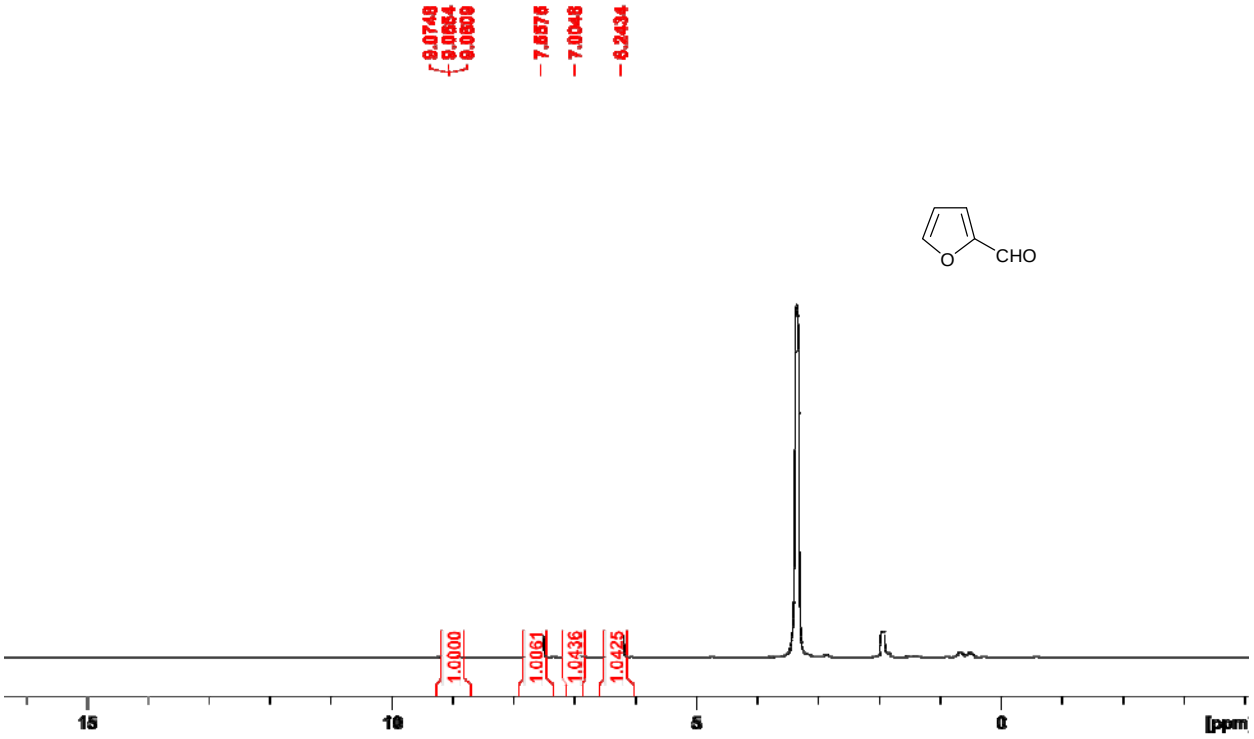

Fig 13. [1]HNMR of 2-furaldehyde

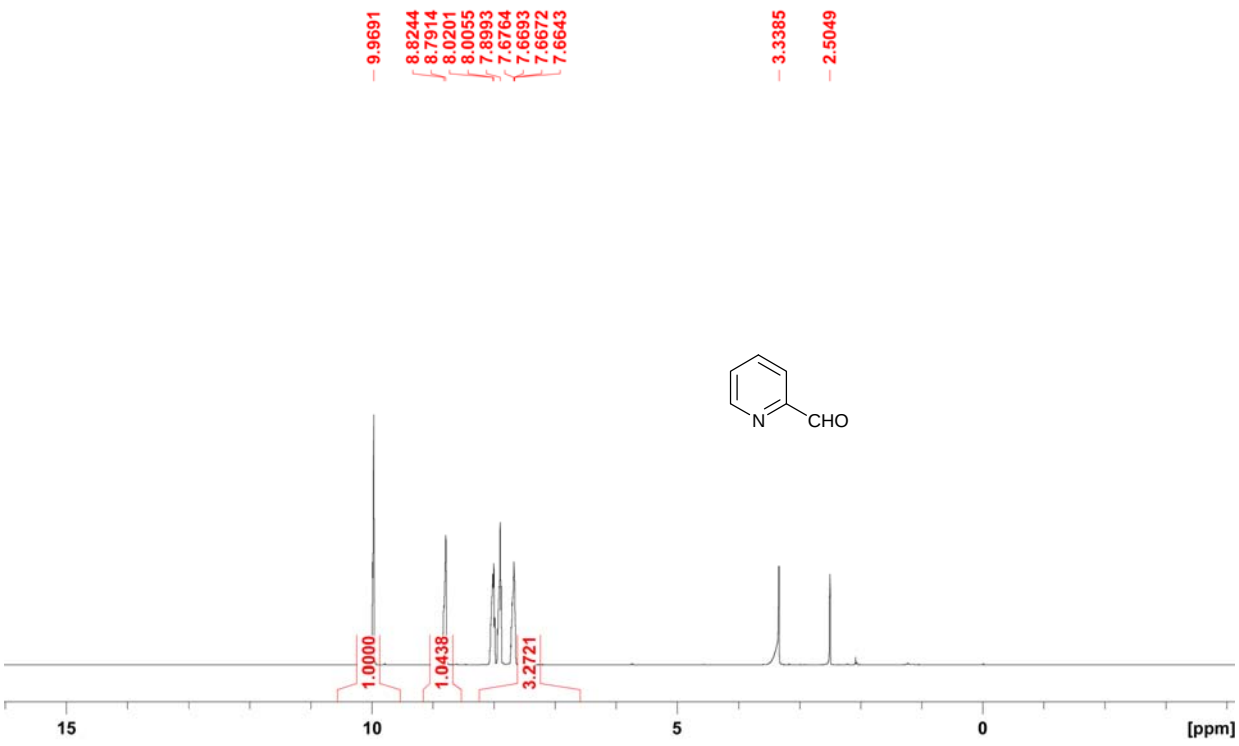

Fig 14. [1]HNMR of 2-pyridinecarboxaldehyde

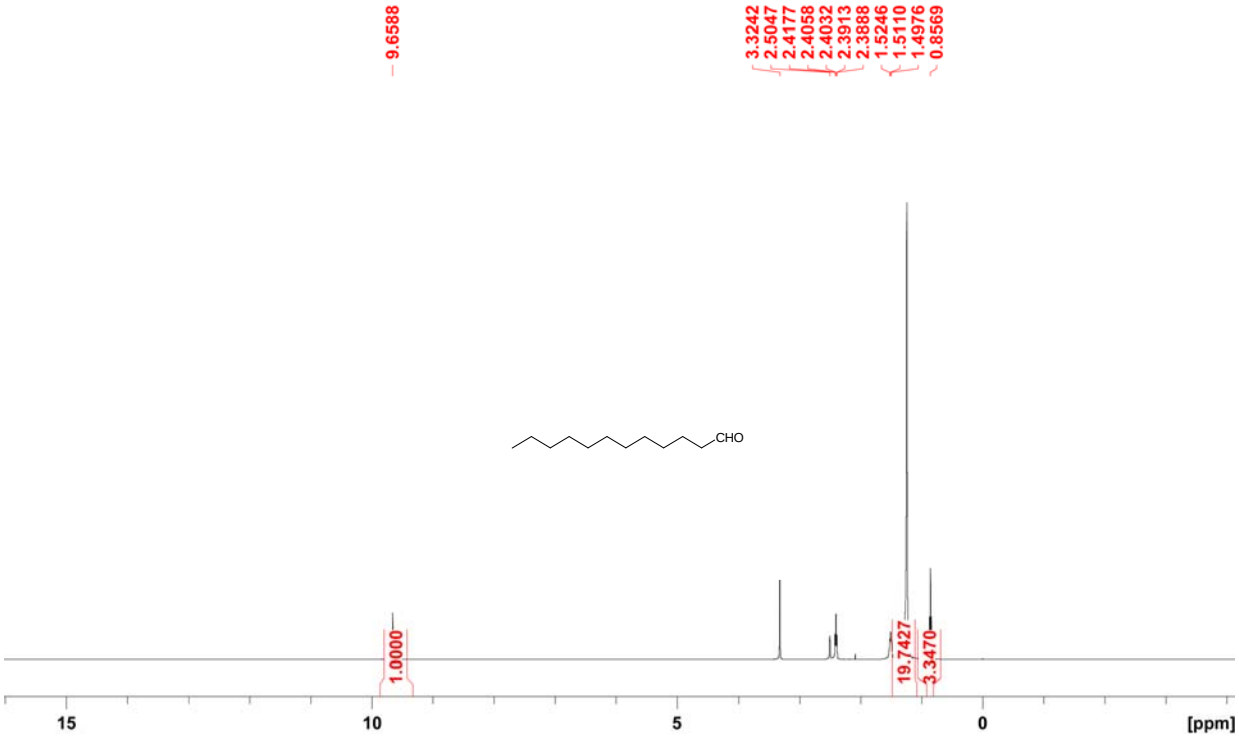

Fig 15. ^{1}HNMR of dodecyl aldehyde