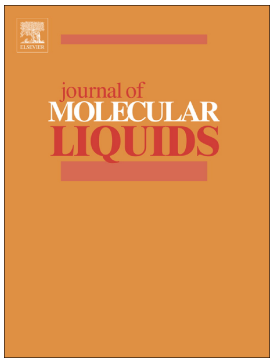


Polymer supported Zn-salen complexes: An effective one-pot oxidative esterification of aldehydes to carboxylic esters

Kamlesh Rudreshwar Balinge, Avinash Ganesh Khiratkar, Pundlik Rambhau Bhagat

PII: S0167-7322(17)33348-2
DOI: doi: 10.1016/j.molliq.2017.07.105
Reference: MOLLIQ 7684

To appear in: *Journal of Molecular Liquids*

Received date: 27 May 2017
Revised date: 25 June 2017
Accepted date: 7 July 2017

Please cite this article as: Kamlesh Rudreshwar Balinge, Avinash Ganesh Khiratkar, Pundlik Rambhau Bhagat , Polymer supported Zn-salen complexes: An effective one-pot oxidative esterification of aldehydes to carboxylic esters, *Journal of Molecular Liquids* (2017), doi: 10.1016/j.molliq.2017.07.105

Polymer supported Zn-salen complexes: An effective one-pot oxidative esterification of aldehydes to carboxylic esters

Kamlesh Rudreshwar Balinge, Avinash Ganesh Khiratkar, Pundlik Rambhau Bhagat*

Department of Chemistry, School of Advanced Sciences,

VIT University, Vellore 632 014, India.

*Corresponding author. Tel.: +91 9047289073; Fax: +91 416 2240411.

E-mail address: drprbhagat111@gmail.com (P.R. Bhagat).

Abstract

Polymer-supported Zn-salen (PS-Zn-salen) complexes were synthesized, characterized and used as a catalyst for one-pot oxidative esterification of aldehydes with alcohols. The PS-Zn-salen heterogeneous catalyst exhibited a high-performance for the oxidative esterification of aldehydes to the corresponding methyl/ethyl esters using hydrogen peroxide as a green oxidant. Due to the synergistic effect of polymer support, the heterogeneous catalyst presented superior catalytic activity and afford 100% conversion of 3,4,5-trimethoxybenzaldehyde and 4-chlorobenzaldehyde to corresponding esters under optimized conditions. The different alcohol substrates study (viz. methyl alcohol, ethyl alcohol, allyl alcohol and benzyl alcohol) showed reasonable selectivity for esters, indicating the scope of the catalysts. Significantly, the synthesized complexes possess good hydrophobic/heterogeneous properties, which permit facile reclamation of the catalyst by using mere filtration. Moreover, the effect of counter anions of complex also studied which indicated that there is no appreciable influence on the conversion of product. The catalyst was reused up to 5th successive run with the average conversion of ester

87.4%. Mechanistic studies have recognized that this “one pot” direct oxidative esterification proceeds through acid formation, proven by a GC-MS. The catalyst is also found to be very stable, up to 280 $^{\circ}$C, confirmed by the thermo gravimetric study.

Keyword: PS-Zn-salen; Oxidative esterification; One pot reaction; Methyl benzoates; Ethyl benzoates.

1. Introduction

Carboxylic esters are the most essential and abundant functional groups in nature but also serve effectively as versatile building blocks for the synthesis of natural products, polymeric materials and fine chemicals, etc. [1] Esters are valuable reagent and they have extensive industrial applications such as in the flavoring agent, diluents and solvent extractants [2]. The traditional esterification process based on nucleophilic substitution of carboxylic acid derivatives such as carboxylic halides, anhydrides and activated esters with alcohols [3]. While benzyl esters are normally prepared by way of nucleophilic displacement of a carboxylate ion on benzyl chloride [4]. However, a number of procedures have been developed, the investigation for the new, facile, economical, and environmentally friendly processes that avoid the use of a large excess of chemicals and expensive activators [5]. For the one-pot oxidative esterification reactions, various metal catalysts were used such as Palladium [6-8], Vanadium [9, 10], Copper [11, 12], Iron [13], Ruthenium [14, 15], Calcium, Magnesium [16], Cerium and Lithium [17]. A number of metal free catalysts like N-heterocyclic carbene (NHC) [18-20], metal based M-NHCs complex [21-23] and Ionic liquid as a catalyst [24]. Nanoparticle such as gold nanoparticles [25], Gold-Nickel oxide nanoparticle [26], Silica-encapsulated iron oxide nanoparticles [27], Graphene oxide nanoparticles [28], Cesium salt with Ni substituted [2, 29]. Reagents such as oxone [30], Sodium bromide [31], Iodine [32-34], $ZnBr_2$ [35], KI-TBHP [36], Indium(III)Triflate

[37], $TsNBr_2$ [38], Imidazolium perrhenate [39], functionalized pyrrolizidines [40] and N-iodo saccharine [41] were also reported. Despite exhaustive efforts into the oxidative esterification of aldehydes, the development of a more effective, mild and eco-friendly method still remains a challenge. So far, these methods suffer from few substrate scopes, use of stoichiometric quantities of harmful and risky heavy metal oxidants [42], dry reaction conditions, longer reaction time, inferior yields as well as low reaction efficacy. The improvement of a one-pot oxidative esterification of aldehydes under heterogeneous catalytic conditions that reduce perilous wastes is extremely required for both commercial and environmental points of view. Amongst the reported schemes heterogeneous catalysts are favored due to their simplistic reclamation, less contagion of the product and effective reusability. On the contrary, most of the reported heterogeneous catalysts like Pd/styrene-divinyl benzene copolymer catalyst [43], Titanium superoxide [1], phosphotungstate anchored to MCM-41 and ZrO_2 [44] are based on the expensive metals and involve the monotonous multi-step synthetic processes. Applications of polymer-supported reagents in organic synthesis have grown up over the years due to the convenience in handling, easy workup procedures, and reusability of the reagents. It is well known that hydrophilic catalysts suffer deactivation by water due to capillary condensation and slow water desorption. However, the problem may be avoided by the use of a hydrophobic catalyst [43]. Additionally, there are many reports involving the application of hydrophobic styrene-divinyl benzene copolymer (SDB) used in the reaction involving water as bye-product [45-49].

Previously, we have tested a novel method for the preparation of (PS-Zn-salen) complex and its catalytic activities toward the synthesis of hydantoins, thiohydantoins and Schiff bases. To the best of our knowledge, PS-Zn-salen complexes catalyzed the one-pot esterification of

aldehydes with alcohols under heterogeneous conditions have not explored. In this context, we wish to report oxidative esterification of aldehydes catalyzed by PS-Zn-salen complexes using H_2O_2 oxidant.

2. Experimental

2.1. Materials

All chemicals were used reagent grade with the utmost purity available. $ZnCl_2$, $LiN(CF_3SO_2)_2$, $LiClO_4$, 4-Vinylbenzyl chloride (used by washing with dil. NaOH), DMSO-*d6*, $CDCl_3$, $NaBF_4$, KPF_6, were purchased from Sigma Aldrich (India), ethylene diamine, Azobisisobutyronitrile (AIBN), 4-hydroxybenzaldehyde, formaldehyde and other aldehydes, H_2O_2 were acquired from SDFCL and Avra Synthesis Pvt. Ltd., ethanol from Changshu Yangyuan chemical China, chloroform, acetonitrile, benzimidazole, THF procured from Spectrochem Pvt. Ltd. and used as received unless otherwise it is stated.

2.2. Characterization techniques

FT-IR spectra were obtained from IR affinity 1 Shimadzu FT-IR spectrophotometer using KBr pellet method. NMR spectra were recorded in DMSO-d6 and $CDCl_3$ on Bruker spectrometer operating at 400 MHz and chemical shifts are given in ppm downfield from TMS ($\delta = 0.00$). Surface morphology and the elemental composition of the complex were investigated by scanning electron microscope (SEM) along with energy dispersive X-ray (EDX) spectroscopy (Carl Zeiss EVO/18SH, UK). An accelerating voltage of 10 kV was applied to obtain SEM images. Thermal stability of PSBIL was confirmed using TG/DTA thermoanalyser SII, 7200 (Seiko, Japan).

2.3. Synthesis and characterization of PS-Zn-salen complexes.

2.3.1. Synthesis of polyvinyl benzyl chloride (PVBC) **1a**, poly 1-(4-sec-butyl)benzyl)-1H-benzo[d]imidazole **1b** and *5-(chloromethyl)-2-hydroxybenzaldehyde* **1c**.

The compounds **1a**, **1b** were synthesized according to literature [50] while **1c** was obtained as the Supplementary Information of literature [51] and the characterization data of the corresponding compounds match with literature report.

(yield 70 %) **1a** ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.08 (Ar-H, br), 6.5 (Ar-H, br), 4.56 (CH_2-Cl, br), 1.71 (br), 1.60 (br), 1.42 (br), 0.95 (br). ^{13}C NMR (100 MHz, $CDCl_3$) 145.56, 134.97, 128.57, 46.37, 40.36, 31.60, 25.28. FT-IR (KBr) in cm^{-1} : 3024, 2922, 2848, 1610, 1510, 1442, 1221, 1265, 1109, 1018, 912, 823, 707, 669, 559.

(yield: 74 %) **1b** ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (NCHN, br), 7.7 (Bim-H, br), 7.19 (Bim-H, br), 6.6 (Ar-H, br), 6.17 (Ar-H, br), 4.95 (Bim-CH_2-Ar, br), 1.84 (br), 1.48 (br), 1.25 (br), 0.84 (br). ^{13}C NMR (100MHz, $CDCl_3$) 143.85, 143.09, 133.95, 128.03, 127.27, 122.97, 122.35, 120.37, 110.06, 67.99, 48.33, 29.71, 25.62. FT-IR (KBr) in cm^{-1} : 2918, 1492, 1363, 1330, 1259, 1197, 1178, 844, 817, 738, 634, 574.

(Yield: 58 %) **1c** ^{1}H NMR (400 MHz, $CDCl_3$) δ = 11.08 (s, Ph-CHO, 1H) 9.90 (s, Ph-OH, 1H), 7.6-7.55 (m, CH arom, 2H), 7.02-7.00 (d, J = 8.89Hz, CH arom, 1H), 4.6 (s, 2H, -CH_2-). ^{13}C NMR (100 MHz, $CDCl_3$) 196.19, 161.64, 137.64, 133.64, 118.33, 45.24. FT-IR (KBr) in cm^{-1} : 3203, 3243, 2875, 1647, 1579, 1481, 1379, 1259, 1186, 1145, 1080, 991, 876, 766, 717, 667, 572, 497.

*2.3.2. Synthesis of 1-(4-(sec-butyl)benzyl)-3-(3-formyl-4-hydroxybenzyl)-1H-benzo[d]imidazol-3-ium chloride (IL).***1d**

The mixture of poly 1-(4-sec-butyl)benzyl)-1H-benzo[d]imidazole (20 mmol) and 5-(chloromethyl)-2-hydroxybenz-aldehyde (20 mmol) charged to a 100 mL round bottom flask in acetonitrile medium. The reaction mixture was kept at room temperature with controlled stirring for 24 h. The precipitated compound was then washed with diethyl ether to obtained white powder of **1d**. Yield: 68 %.

^{1}H NMR (400 MHz, DMSO-d_6) δ = 10.25 (CH=O, s), 8.4 (C-NH-C, s), 8.1-7.5 (Bim H, br), 7.2-6.2 (Ar, br), 5.8, (CH_2, br), 5.5 (CH_2, br), 2, 1.23, 1.09, 0.85 (aliphatic proton). FT-IR (KBr) in cm^{-1} : 3396, 2926, 1614, 1556, 1487, 1442, 1371, 1282, 1249, 1188, 744, 632.

*2.3.3. Synthesis of 3,3'-((((1E,1'E)-(ethane-1,2- dylbis(azanylylidene)) bis(methanylylidene)) bis(4-hydroxy-3,1-phenylene))bis(methylene))bis(1-(4-(sec-butyl)benzyl)-1H-benzo[d]imidazol-3-ium) chloride ie. [PS-salen ligand].***1e***

The salen ligand was prepared by the stirring solution of 1, 2-diethyl amine (7.5 mmol) in ethanol and IL (**1d)** (15 mmol) for 30 min at room temperature followed by refluxing for 2 h. The ligand was isolated and purified by repeated washing with ethanol to remove unreacted amine. The product was then dried under vacuum to acquire the yellow powder of salen ligand **1e**. Yield: 80 %.

^{1}H NMR (400 MHz, DMSO-d_6) δ = 13.18 (OH, br), 10.26 (CH=O, s), 8.5 (C-NH-C, s), 8.4-7.5 (Bim H, br), 7.2-6.8 (Ar, br), 5.6, (CH_2, br), 5.5 (CH_2, br), 3.5, 2, 1.23, 1.09, 0.85 (aliphatic proton). FT-IR (KBr) in cm^{-1} : 3354, 3053, 3024, 2968, 2920, 2850, 1631, 1558, 1494, 1423, 1369, 1334, 1284, 1188, 742, 634, 574.

*2.3.4. Synthesis of Zn-salen complex (PS-Zn-salen complex).***1f**

The PS-Zn-salen complex was successfully synthesized and characterized by the altering method from reported in the literature [52], salen ligand **1e** (1 mmol) in 10 mL ethanol and $ZnCl_2$ (1

mmol) was added to a 100 mL and the mixture was stirred for 1h at room temperature. The mixture was then refluxed at 75-80 °C for 2 h. The product was easily separated after the reaction by recurrent washing with ethanol and dried in oven at 80 °C for 2 h, get yellow fine powder of PS-Zn-salen complex **1f** (Scheme 1). Yield: 83 %.

*2.3.5. Synthesis of catalysts **1g-1j**.*

The syntheses of catalysts **1g**-**1j** were carried out according to the literature [53]. The PS-Zn-salen complex (1 equivalent) was suspended in distilled water and 2.2 equivalent aqueous solutions of $NaBF_4$ or KPF_6 or $LiN(CF_3SO_2)_2$ or $LiClO_4$ were added drop wise with constant stirring for 15 min at room temp. The reaction mixture was allowed to stir for 5 h, after which the solids **1g, 1h, 1i** and **1j** respectively were collected by filtration and washed with distilled water repeatedly over filter paper, till negative silver nitrate test. The negative silver nitrate test ensures the complete conversion of chloride to tetrafluoro borate, hexafluorophosphate, bis (tri-fluoromethane) sulphonimide and perchlorate. The resulted catalysts were finally dried in an oven at 80 °C for 2 h (Scheme 2).

*2.4. General procedure for one pot oxidative esterification of aldehydes to corresponding methyl esters with PS-Zn-salen complex **(1f)** and H_2O_2.*

The reaction of 3,4,5-trimethoxybenzaldehyde (0.01 mol) with H_2O_2 (0.04 mol) and methanol was carried out in 100 mL round bottom flask. The reaction mixture was reflux for 24 h. After completion of the reaction, the reaction mixture pour in distilled water; the aqueous solution was the extracted with ethyl acetate (3×20 mL) and brine solution to get clear ethyl acetate layer. The organic layer was dried with anhydrous sodium sulfate. It was filtered and vaporized to dryness at reduced pressure to obtained corresponding methyl etster.

2a) methyl 3,4,5-trimethoxybenzoate (Yield = 100%); GC-MS m/z: calcd. for $C_{11}H_{14}O_5$: 226.0841, found 226.2370. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31 (s, 2H), 3.92 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) 191.08, 166.73, 152.94, 142.19, 125.14, 106.83, 60.91, 56.29, 56.23, 52.22. FT-IR (KBr) in cm^{-1} : 2949, 2839, 1712, 1587, 1504, 1409, 1327, 1224, 1176, 1124, 989, 864, 761, 732, 534, 435.

2b) methyl 4-methoxybenzoate (Yield = 70%); GC-MS m/z: calcd. for $C_9H_{10}O_3$: 166.0630, found 166.2266. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.80 (d, 4H), 3.91 (s, 3H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) 167.18, 163.41, 153.69, 149.64, 132.14, 122.50, 115.01, 114.38, 55.61, 51.97. FT-IR (KBr) in cm^{-1} : 2951, 1720, 1600, 1435, 1273, 1176, 1109, 1026, 964, 823, 707, 686, 545.

2c) methyl benzoate (Yield = 92%); GC-MS m/z: calcd. for $C_8H_8O_2$: 136.0524, found 136.2046. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.07-8.59 (d, J = 7.42 Hz, 2H), 7.92-7.87 (t, J = 7.86 Hz, 1H), 7.48-7.44 (t, J = 7.85 Hz, 2H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) 171.09, 167.21, 133.72, 132.93, 130.20, 129.58, 128.37, 52.12. FT-IR (KBr) in cm^{-1} : 2953, 2835, 1691, 1602, 1506, 1436, 1290, 1213, 1166, 1101, 1028, 825, 771, 731, 609, 514.

2d) methyl 4-chlorobenzoate (Yield = 94%); GC-MS m/z: calcd. for $C_8H_7ClO_2$: 170.0135, found 170.1256. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.97-7.95 (d, J = 8.72 Hz, 2H), 7.41-7.39 (d, J = 8.28 Hz, 2H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) 165.1, 131.56, 128.91, 128.73, 128.60, 128.39, 52.29.

2e) methyl 2-nitrobenzoate (Yield = 75%); GC-MS m/z: calcd. for $C_8H_7NO_4$: 181.0375, found 181.1664. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.15-8.12 (d, J = 7.82 Hz, 1H), 7.9-7.86 (t, J = 8.72, 3h), 3.94 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) 165.95, 148.50, 134.08, 131.78, 129.95, 128.79,

124.35, 53.30. FT-IR (KBr) in cm^{-1} : 2954, 1730, 1525, 1438, 1290, 1255, 1126, 1072, 954, 856, 786, 734, 696, 640.

2f) methyl 4-fluorobenzoate (Yield = 47%); GC-MS m/z: calcd. for $C_8H_7FO_2$: 154.0430, found 154.1607.^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00-7.96 (q, J = 5.67 Hz, 2H), 7.05-6.97 (m, 2H), 3.84 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) 167.03, 166.26, 132.17, 132.07, 126.38, 115.04, 115.20, 52.21. FT-IR (KBr) in cm^{-1} : 2954, 1720, 1600, 1508, 1436, 1273, 1230, 1153, 1111, 1012, 964, 850, 765, 686, 605, 505.

2g) methyl 4-methylbenzoate (Yield = 91%); GC-MS m/z: calcd. for $C_9H_{10}O_2$: 150.0681, found 150.1919.^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.96-7.94 (d, J = 8.06 Hz, 2H), 7.26-7.24 (d, J = 8.73 Hz, 2H), 9.62 (s, 3H), 2.4 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) 167.45, 143.66, 129.62, 129.10, 126.93, 52.03, 21.65. FT-IR (KBr) in cm^{-1} : 2951, 1718, 1610, 1514, 1435, 1276, 1176, 1107, 1020, 964, 839, 754, 690, 605, 468.

2h) methyl 3-hydroxy-4-methoxybenzoate (Yield = 89%); GC-MS m/z: calcd. for $C_9H_{10}O_4$: 182.0579, found 182.2102. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.53 (m, 1H), 7.19, (s, 1H), 6.8-6.7 (d, J = 8.39, 1H), 5.56 (s, 1H), 3.88 (s, 3H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) 166.83, 150.38, 145.25, 123.44, 122.80, 115.59, 109.83, 56.04, 51.97. FT-IR (KBr) in cm^{-1} : 3410, 2953, 2845, 1699, 1612, 1510, 1436, 1532, 1276, 1211, 1126, 1020, 985, 889, 628, 532, 447.

2i) methyl 4-hydroxybenzoate (Yield = 67%); GC-MS m/z: calcd. for $C_8H_8O_3$: 152.0473, found 152.2112. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38 (d, J = 8.66 Hz, 2H), 7.10 (d, J = 8.72 Hz, 2H), 5.9 (s, 1H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) 171.27, 167.16, 154.94, 136.62, 120.86, 56.82. FT-IR (KBr) in cm^{-1} :3336, 3132, 3028, 2954, 2709, 1678, 1606, 1510, 1456, 1357, 1284, 1188, 1093, 829, 758, 698, 617, 522, 482.

2j) methyl 4-bromobenzoate (Yield = 100%); GC-MS m/z: calcd. for $C_8H_7BrO_2$: 213.9629, found 214.0043. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91-7.89 (d, J = 8.70 Hz, 2H), 7.59-7.57 (d, J = 8.74 Hz, 2H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) 166.42, 131.72, 131.12, 129.08, 128.69, 52.32. FT-IR (KBr) in cm^{-1} : 3091, 2949, 2848, 2555, 1710, 1587, 1435, 1273, 1172, 1109, 1006, 954, 848, 754, 682, 547, 470.

2k) ethyl 3,4,5-trimethoxybenzoate (Yield = 83%); GC-MS m/z: calcd. for $C_{12}H_{16}O_5$: 240.0998, found 240.1572. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.3 (s, 2H), 4.41-4.36 (q, J = 5.8 Hz, 2H), 3.9 (s, 9H), 1.43-1.39 (t, J = 7.19 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) 166.30, 152.90, 142.08, 125.53, 106.76, 61.17, 60.92, 56.24, 14.40. FT-IR (KBr) in cm^{-1} : 2972, 2941, 2839, 1710, 1587, 1458, 1413, 1328, 1220, 1222, 999, 948, 864, 763, 727, 626, 536.

2l) ethyl 4-methoxybenzoate (Yield = 72%); GC-MS m/z: calcd. for $C_{10}H_{12}O_3$: 180.0786, found 180.1891.^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.9 (d, J = 8.74 Hz, 2H), 7.4 (d, J = 8.64 Hz, 2H), 4.4 (q, J = 5.67 Hz, 2H), 9.9 (s, 3H), 1.4 (t, J = 7.41 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) 166.86, 153.63, 149.65, 116.08, 114.87, 60.90, 55.83, 14.35. FT-IR (KBr) in cm^{-1} : 2939, 2835, 1680, 1600, 1506, 1440, 1367, 1213, 1101, 1028, 825, 771, 731, 605, 514.

2m) ethyl benzoate (Yield = 83%); GC-MS m/z: calcd. for $C_9H_{10}O_2$: 150.0681, found 150.1821. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.15-8.01 (m, 2H), 7.65-7.46 (m, 2H), 4.43-4.38 (q, J = 5.9 Hz, 2H), 1.44-1.40 (t, J = 7.38 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) 166.85, 132.86, 130.20, 129.55, 128.33, 61.05, 14.31. FT-IR (KBr) in cm^{-1} : 3064, 2983, 1695, 1600, 1450, 1367, 1273, 1105, 1026, 935, 850, 707, 646, 532.

2n) ethyl 4-chlorobenzoate (Yield = 90%); GC-MS m/z: calcd. for $C_9H_9ClO_2$: 184.0291, found 184.1560. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92-7.89 (d, J = 9.01 Hz, 2H), 7.34-7.32 (d, J = 9.01, 2H), 4.33-4.27 (q, J = 5.7 Hz, 2H), 1.34-1.30 (t, J = 7.37 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$)

165.79, 139.25, 131.55, 130.95, 128.66, 61.22, 14.29. FT-IR (KBr) in cm^{-1} : 2983, 1716, 1593, 1487, 1002, 1269, 1770, 1089, 1014, 848, 758, 684, 526, 474.

2o) ethyl 2-nitrobenzoate (Yield = 66%); GC-MS m/z: calcd. for $C_9H_9NO_4$: 195.0532, found 195.0810. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.98-7.62 (m, 4H), 4.9 (q, J = 5.6, 2H), 1.37 (t, J = 7.42, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) 165.5, 134.41, 133.3, 131.8, 129.5, 124.01, 102.7, 62.9, 13.7. FT-IR (KBr) in cm^{-1} : 2980, 2899, 1728, 1525, 1348, 1290, 1255, 1128, 1070, 1010, 958, 856, 785, 734, 638.

2p) ethyl 4-fluorobenzoate (Yield = 84%); GC-MS m/z: calcd. for $C_9H_9FO_2$: 168.0587, found 168.1471. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.93-7.91 (d, J = 7.64 Hz, 2H), 7.60-7.58 (d, J = 7.68 Hz, 2H), 4.41-4.36 (q, J = 5.67 Hz, 2H), 1.29-1.26 (t, J = 7.38 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) 169.01, 166.31, 131.87, 126.38, 115.20, 60.45, 14.19.

2q) ethyl 4-methylbenzoate (Yield = 86%); GC-MS m/z: calcd. for $C_{10}H_{12}O_2$: 164.0837, found 164.1788. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94-792 (d, J = 7.46 Hz, 2H), 7.21-7.19 (d, J = 8.24 Hz, 2H), 4.31-4.26 (q, J = 5.67 Hz, 2H), 2.36 (s, 3H), 1.33-1.29 (t, 7.58 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) 165.99, 143.10, 129.32, 129.08, 125.99, 61.11, 14.35.

2r) ethyl 3-hydroxy-4-methoxybenzoate (Yield = 83%); GC-MS m/z: calcd. for $C_{10}H_{12}O_4$: 196.0736, found 196.1943. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65 (d, J = 8.51 Hz, 1H), 6.90 (d, J = 8.9 Hz, 1H), 6.7 (s, 1H), 5.6 (s, 1H), 4.98-4.33 (q, J = 5.56 Hz, 2H), 3.97 (s, 3H), 1.41-1.38 (t, J = 7.58 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) 167.10, 153.10, 145.66, 123.39, 123.00, 116.10, 122.17, 61.33, 13.99.

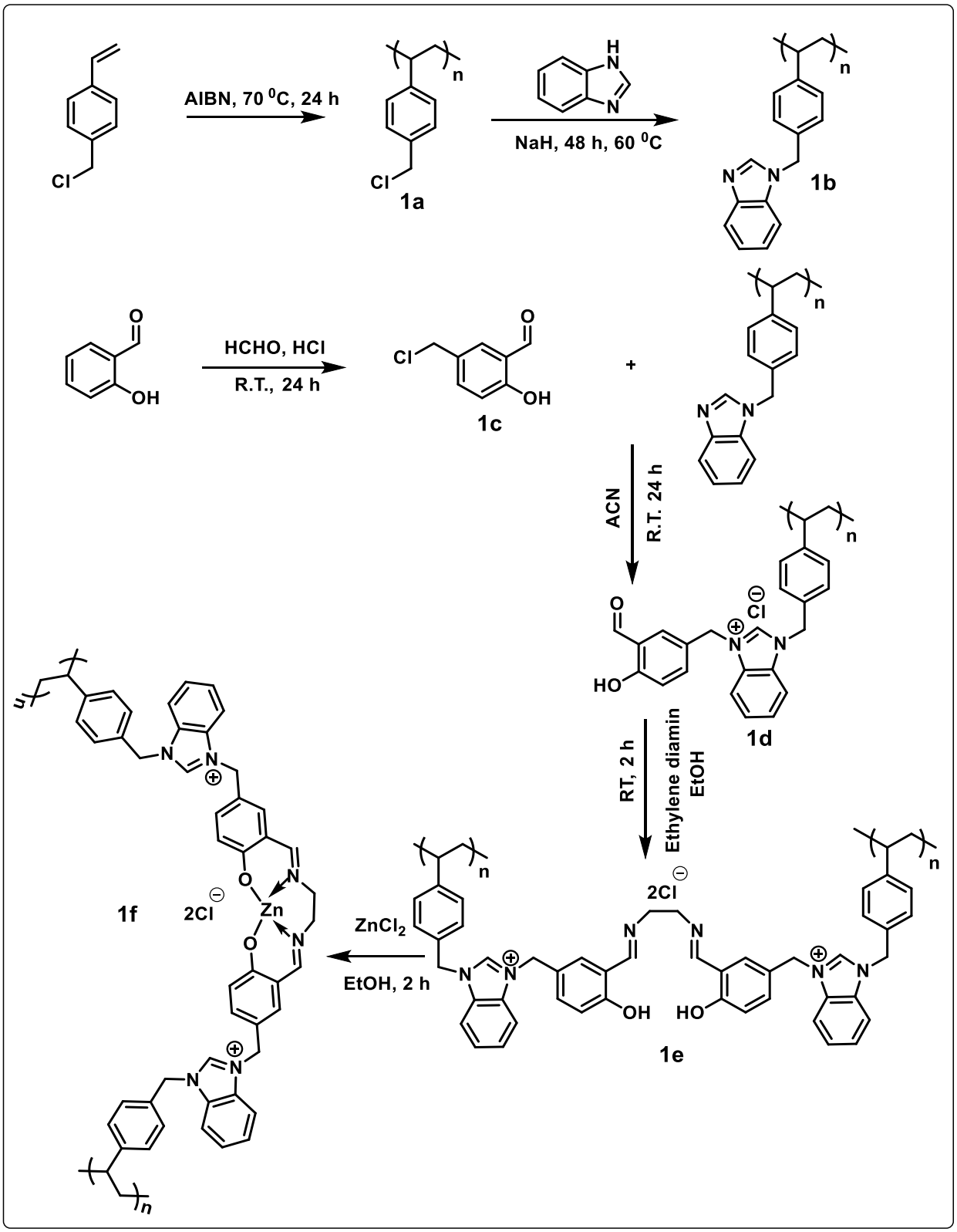
2s) ethyl 4-hydroxybenzoate (Yield = 29%); GC-MS m/z: calcd. for $C_9H_{10}O_3$: 166.0630, found 166.1979. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.4 (d, J = 8.01 Hz, 2H), 7.21 (d, J = 8.12 Hz, 2H),

4.51 (q, J = 5.24 Hz, 2H), 1.40 (t, 14.64 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) 170.19, 167.366, 155.19, 136.13, 120.96, 61.47, 14.56.

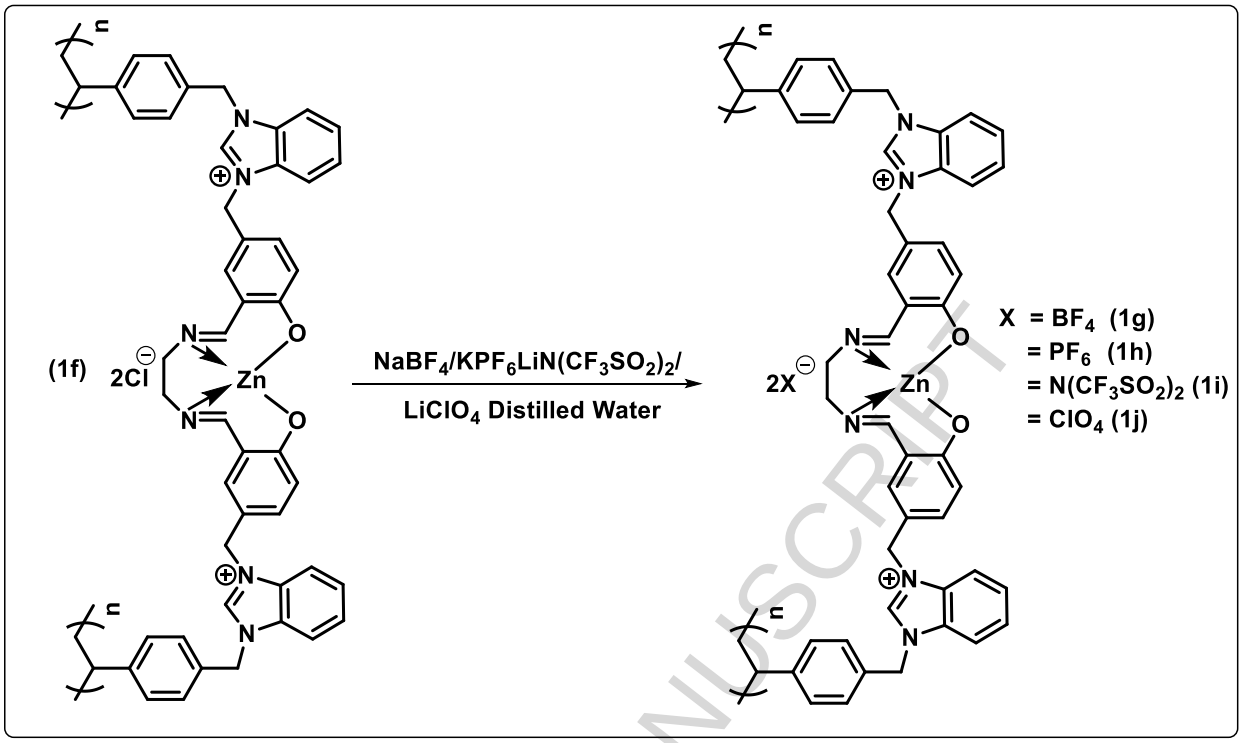
2t) ethyl 4-bromobenzoate (Yield = 79%); GC-MS m/z: calcd. for $C_9H_9BrO_2$: 227.9786, found 228.0552. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.93-7.91 (d, J = 7.53 Hz, 2H), 7.60-7.58 (d, J = 7.53 Hz, 2H), 4.41-4.36 (q, J = 5.68 Hz, 2H), 1.36-1.32 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) 165.95. 131.66, 130.99, 129.37, 127.92, 61.27, 14.28.

2u) allyl 4-chlorobenzoate (Yield = 56%); GC-MS m/z: calcd. for $C_{10}H_9ClO_2$: 196.0291, found 196.0551. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.90 (d, J = 8.2 Hz, 2H), 7.61 (d, J = 8.3 Hz, 2H), 6.0 (m, 1H), 5.42 (dd, 2H), 4.8 (d, J = 7.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) 165.5, 138.8, 132.8, 130.1, 128.5, 128.5, 118.1, 167.1.

2v) benzyl 4-chlorobenzoate (Yield = 15%); GC-MS m/z: calcd. for $C_{14}H_{11}ClO_2$: 246.0448, found 245.9993. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.09 (d, J = 8.3 Hz, 2H), 7.52 (d, J = 8.1 Hz, 2H), 7.5 (m, 5H), 5.31 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) 166.8, 135.9,131, 129.5, 127.9, 128.1, 128.4, 128.9, 66.5.



Scheme 1. Preparation of polymer supported Zinc-centered salen complex (PS-Zn-salen) complex **(1f)**.



Scheme 2. Preparation of catalyst **1g, 1h, 1i** and **1j**.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. Fourier transform infrared (FT-IR) spectroscopy

The FT-IR spectra of the PS-Zn-salen complex (Fig. 1) to define the coordination sites that may be involved in chelation. The most significant IR spectral bands in the ligand for (O-H) appeared at 3396 cm^{-1}. Correspondingly, stretching bands observed at 1631 cm^{-1} for (C=N) in the ligand. The formation of Schiff base Zn(II)-complex is evidenced by the disappearance of (O-H) stretching band in salen ligand. Certain evidence of the bonding is also shown by the appearance of the new band in the region (532 cm^{-1} and 416 cm^{-1}) in the spectrum of the complex due to (Zn-O) and (Zn-N) stretching vibrations. For the Schiff base, the (C=N-) stretching of salen ligand is observed as a strong band at 1631 cm^{-1} is slightly shifted to the lower

region at 1622 cm^{-1} which revealed that azomethine nitrogen is involved in coordination to the metal [54, 55].

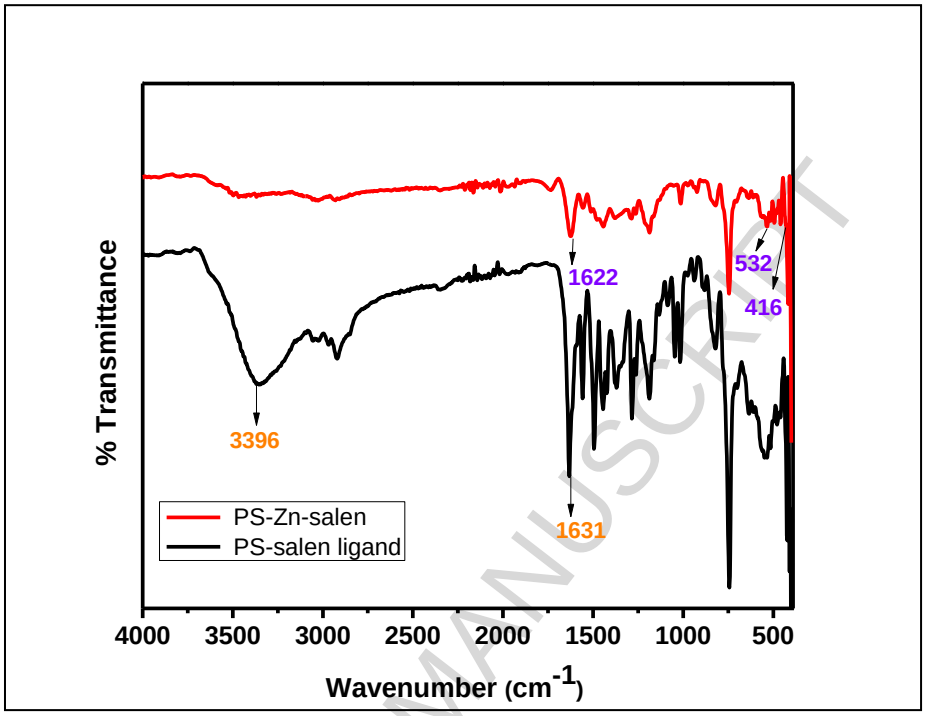


Fig. 1. The FT-IR spectrum of PS-salen ligand (1e) and PS-Zn-salne complex (1f).

3.1.2. Scanning electron microscopy (SEM) images and Energy Dispersive X-Ray Analysis (EDX)

The surface morphology and elemental analysis of polymer supported Zn-salen complex was characterized by SEM/EDX (Fig. 2). The scanning electron micrograph (SEM) images were reported for PS-salen ligand (A) and PS-Zn-salen complex (C) which clearly indicate the formation of the desired complex. The surface of PS-Zn-salen complex expose micron sized particles deposited over the surface (Fig. 2C). The comparative spectrum of energy-dispersive X-ray spectroscopy, ligand (B) and a metal complex (D) support the presence of Zn in the metal complex (D).

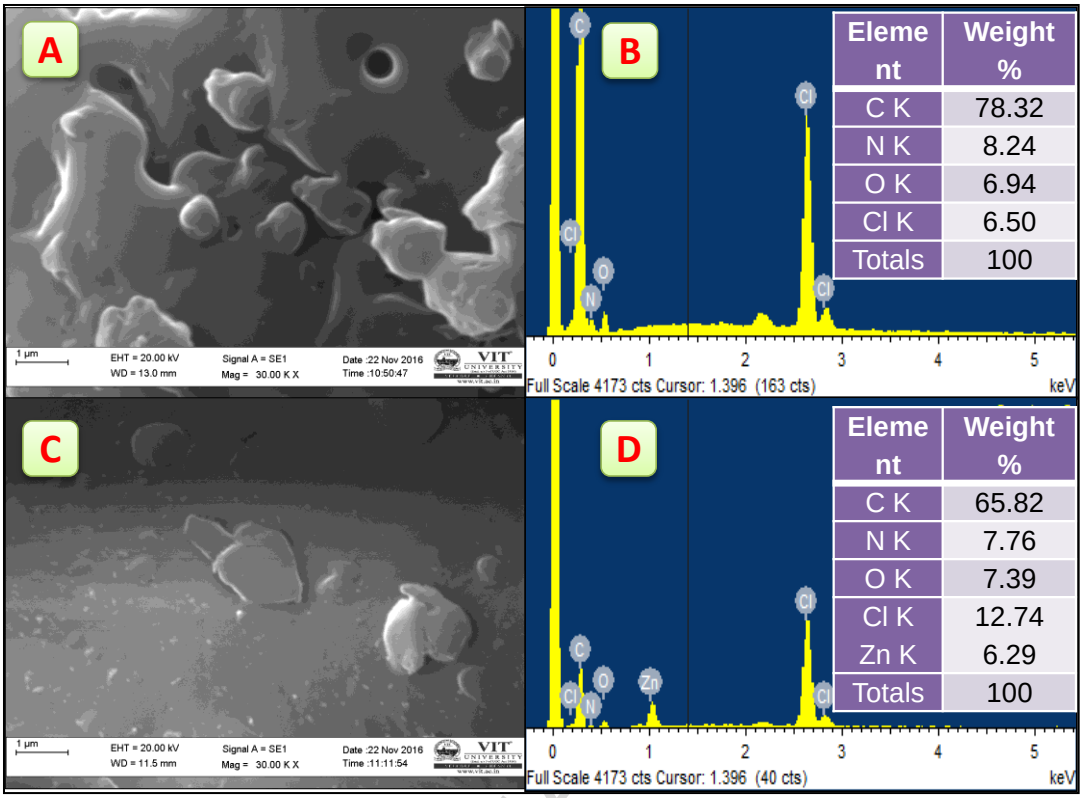


Fig. 2. SEM/EDX of PS-salen ligand (A/B) and PS-Zn-salen complex **(1f)** (C/D).

3.1.3. Thermal analysis

Thermal stability of the PS-Zn-salen complex **(1f)** was scrutinized using TGA under a nitrogen atmosphere with a heating rate of 10 $^{\circ}$C min^{-1} over a temperature range of 30-800 $^{\circ}$C (Fig. 3). There is slight weight loss (4.250%) below 120 $^{\circ}$C indicates the presence of a physically adsorbed solvent. The weight loss (36.48%) detected in the region 280-550 $^{\circ}$C due to a salen group of the complex begins to decompose. Above 550 $^{\circ}$C the complex exhibits final weight loss (13.86%) begins to crumble due to poly 1-(4-sec-butyl)benzyl)-1H-benzo[d]imidazole in the polymer supported Zn-salen complex. From TGA analysis it is observed that the weight loss is negligible up to 280 $^{\circ}$C and found to be thermally stable, therefore it is concluded that PS-Zn-salen **(1f)** catalyst is appropriate for high-temperature reaction.

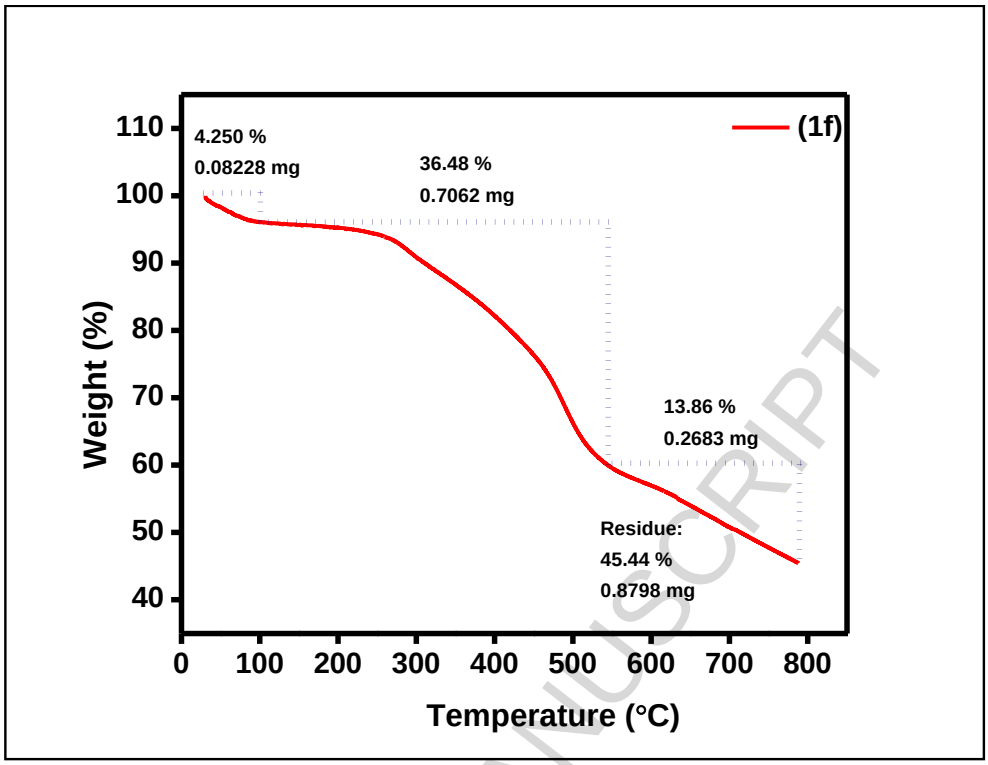


Fig. 3. Thermogravimetric Analysis (TGA) thermogram of PS-Zn-salen complex **(1f)**

*3.2. Catalytic activity of PS-Zn-salen complexes **(1f)**, **(1g)**, **(1h)**, **(1i)**, **(1j)**.*

The catalytic activity of synthesized polymer supported Zn-salen complexes was tested for one pot oxidative esterification reaction. Typically, the model reaction was performed by 3,4,5-trimethoxy benzaldehyde with methanol using H_2O_2 (30 %) as an oxidant in the presence of catalyst **1f** for 24h. The results of optimization experiments are summarized in Table 1. In the absence of a catalyst under similar conditions, 50% conversion was observed (Table 1, entry 1). Also, only 56% conversion was found when polymer supported salen ligand **1e** was used as a catalyst under similar reaction conditions (Table 1, entry 2).

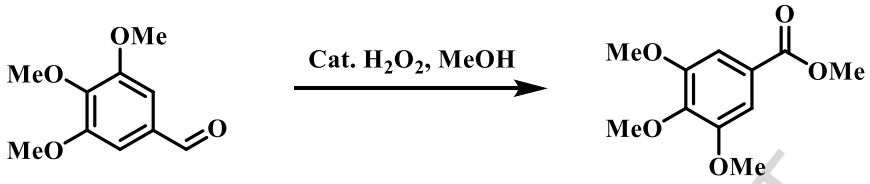
In order to optimize dose, varying the amount of catalyst, **1f** was demonstrated by model reaction at same reaction conditions (Table 1, entries 3-5). The reaction of 3,4,5-trimethoxy benzaldehyde with H_2O_2 (30 %) as an oxidant in the presence of 10 mg catalyst **1f** was found to be the optimum for this organic transformation (Table 1, entry 4). Further increase of the amount

of catalyst, there is no effect on the conversion of 3,4,5-trimethoxy benzaldehyde (Table 1, entries 5, 6).

Next, the effect of temperature on the esterification reaction was studied. We have performed the reactions by changing the temperature from room temperature to 80 °C (Table 1, entries 7-12). The reaction of 3,4,5-trimethoxy benzaldehyde in the presence of an optimum amount of catalyst was very slow at room temperature (Table 1, entry 7); while 70 °C was found to be the optimum temperature for this model reaction (Table 1, entry 11). Further increase of temperature to 80 °C, there is slight decrease in the yield of the ester under similar reaction conditions (Table 1, entry 12).

Moreover, to find the effect of time on the esterification was proved by changing the duration of the reactions (Table 1, entries 13-17). The reaction was found to be very slow in 8 h and afforded poor yield (Table 1, entry 13). While in longer reaction time 24 h was found to be the optimum time for 100% conversion of the desired product (Table 1, entry 17). Finally, with optimum reaction conditions (10 mg cat, 70 °C, and 24h), we tested the comparative catalytic activity of the other complexes **1g**, **1h**, **1i** and **1j** (Table 1, entries 18-21). The result was displayed admirable activity to get desired product 98 and 94% yield, using **1g** and **1h** respectively (Table 1, entries 18 and 19). Also, the complexes **1i** and **1j** also showed satisfactory catalytic activity with 80 and 81% yield. The comparative result revealed that **1f** is the best choice of catalyst.

Table 1. Optimization of the amount of catalyst, temperature and time in one pot oxidative esterification reaction.



Entry	Catalyst	Catalyst amount (mg)	Solvent	Temperature ($^{\circ}$C)	Time (hour)	Yield(%)[b]
1	**1f**	00	Methanol	70	24	50
2	**1e**[a]	10	Methanol	70	24	56
3	**1f**	5	Methanol	70	24	85
4	**1f**	10	Methanol	70	24	100
5	**1f**	15	Methanol	70	24	100
6	**1f**	20	Methanol	70	24	98
7	**1f**	10	Methanol	RT	24	58
8	**1f**	10	Methanol	40	24	62
9	**1f**	10	Methanol	50	24	67
10	**1f**	10	Methanol	60	24	87
11	**1f**	10	Methanol	70	24	100
12	**1f**	10	Methanol	80	24	98
13	**1f**	10	Methanol	70	8	84
14	**1f**	10	Methanol	70	12	90

15	**1f**	10	Methanol	70	16	94
16	**1f**	10	Methanol	70	20	96
17	**1f**	10	Methanol	70	24	100
18	**1g**	10	Methanol	70	24	98
19	**1h**	10	Methanol	70	24	94
20	**1i**	10	Methanol	70	24	80
21	**1j**	10	Methanol	70	24	81

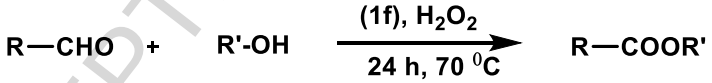
[a]1e = PS-salen ligand.
[b] Yield = GC-MS conversion.

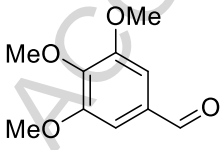
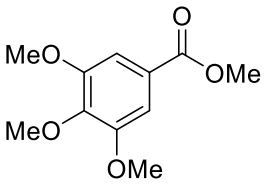
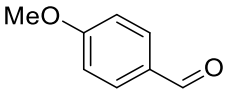
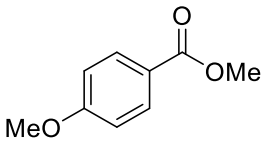
3.3. Effect of different aldehyde and alcohol substrates.

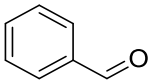
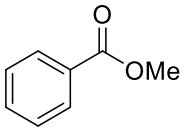
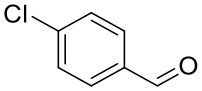
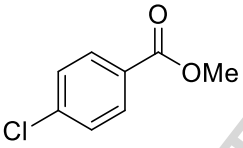
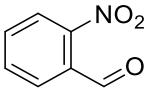
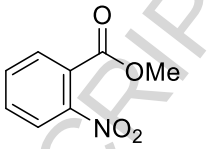
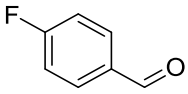
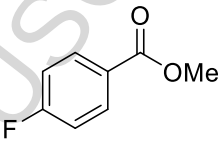
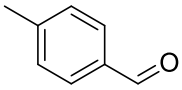
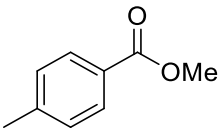
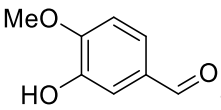
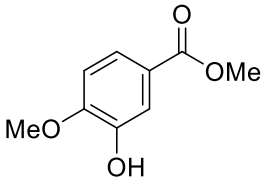
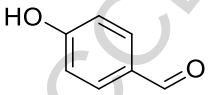
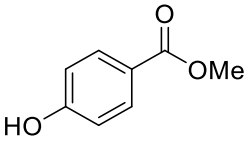
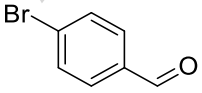
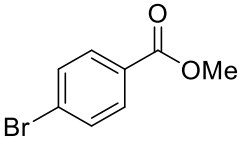
With the above-optimized conditions in hand, the possibility of the oxidative esterification of the catalyst **1f** was tested with varying aromatic aldehydes and alcohols respectively. The results were listed in Table 2. Overall, the reaction was benefited by electron donating as well as electron withdrawing groups attached to the aromatic ring. All the substrates were easily oxidized to give the desired product with good to excellent yields. The aromatic aldehyde without any substituent displayed excellent reactivity with both methanol and ethanol to get methyl benzoate or ethyl benzoate with 92 and 83% conversion respectively (Table 2, entries 3, 13). The aromatic aldehyde with electron donating substituents like OMe, Me groups reacted efficiently with both methanol and ethanol, under the optimized conditions to afford good to excellent yields (Table 2, entries 1-2, 7, 11-12 and 17). Aromatic aldehydes bearing electron withdrawing groups at a para position like Cl, Br were found to be more reactive with methanol as well as ethanol to get desired products with appreciable yields (Table 2, entries 4, 10 and 14, 20). In the case of 4-Fluorobenzaldehyde was somewhat reactive with methanol (Table

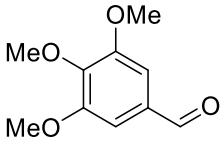
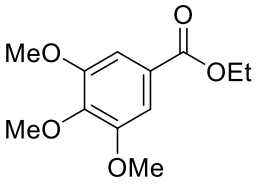
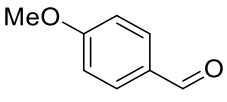
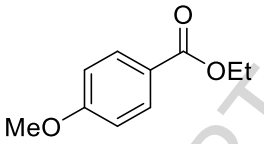
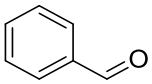
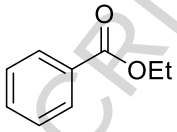
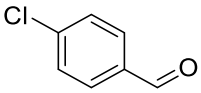
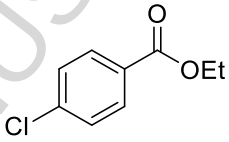
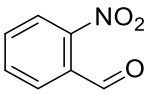
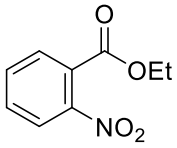
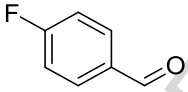
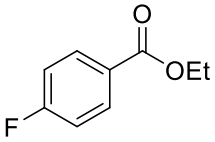
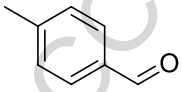
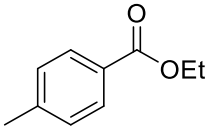
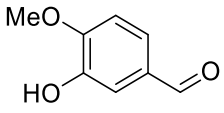
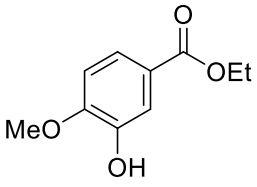
2, entry 6) but with ethanol showed commendable yield (Table 2, entry 16). In contrast, 4-hydroxybenzaldehyde with methanol exhibited satisfactory yield of 83% but less reactive with ethanol to offer 29% yield (Table 2, entries 9, 19). When aromatic aldehyde with good electron withdrawing group like 2-nitrobenzaldehyde undergo esterification with both methanol and ethanol, resulted in good yields of 75% and 66% respectively (Table 2, entries 5 and 15). In the case of 3-hydroxy-4-methoxybenzaldehyde reaction undergoes smoothly with methanol (Table 2, entry 8) as well as ethanol (Table 2, entry 8) to get preferred product 89 and 83%. Moreover, the reactivity of 3,4,5-trimethoxybenzaldehyde was tested with aliphatic allyl alcohol and aromatic benzyl alcohol. The result revealed that benzyl alcohol with aromatic aldehyde gave less yield 15% (Table 2, entry 22) compared to allyl alcohol 56% under optimized conditions (Table 2, entry 21). Therefore, it was found that oxidative esterification by PS-Zn-salen complex is better than or comparable with the literature reports (Table 3).

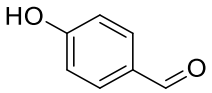
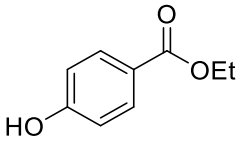
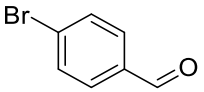
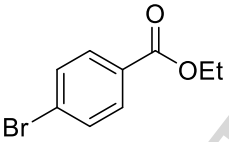
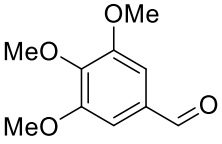
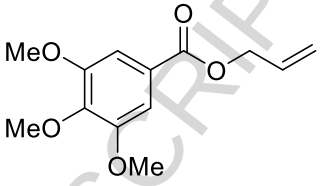
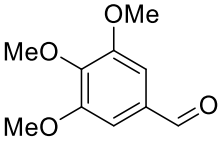
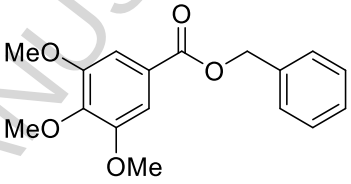
Table 2. Catalytic performance in one pot oxidative esterification reactions with various aromatic aldehydes with alcohols[a].



Entry	Aldehyde	Alcohol	Product	Yield (%)[a]
1		Methanol	 **2a**	100
2		Methanol	 **2b**	70

3		Methanol	 **2c**	92
4		Methanol	 **2d**	94
5		Methanol	 **2e**	75
6		Methanol	 **2f**	47
7		Methanol	 **2g**	91
8		Methanol	 **2h**	89
9		Methanol	 **2i**	67
10		Methanol	 **2j**	100

11		Ethanol	 **2k**	83
12		Ethanol	 **2l**	72
13		Ethanol	 **2m**	83
14		Ethanol	 **2n**	90
15		Ethanol	 **2o**	66
16		Ethanol	 **2p**	84
17		Ethanol	 **2q**	86
18		Ethanol	 **2r**	83

19		Ethanol	 **2s**	29
20		Ethanol	 **2t**	79
21		Allyl alcohol	 **2u**	56
22		Benzyl alcohol	 **2v**	15

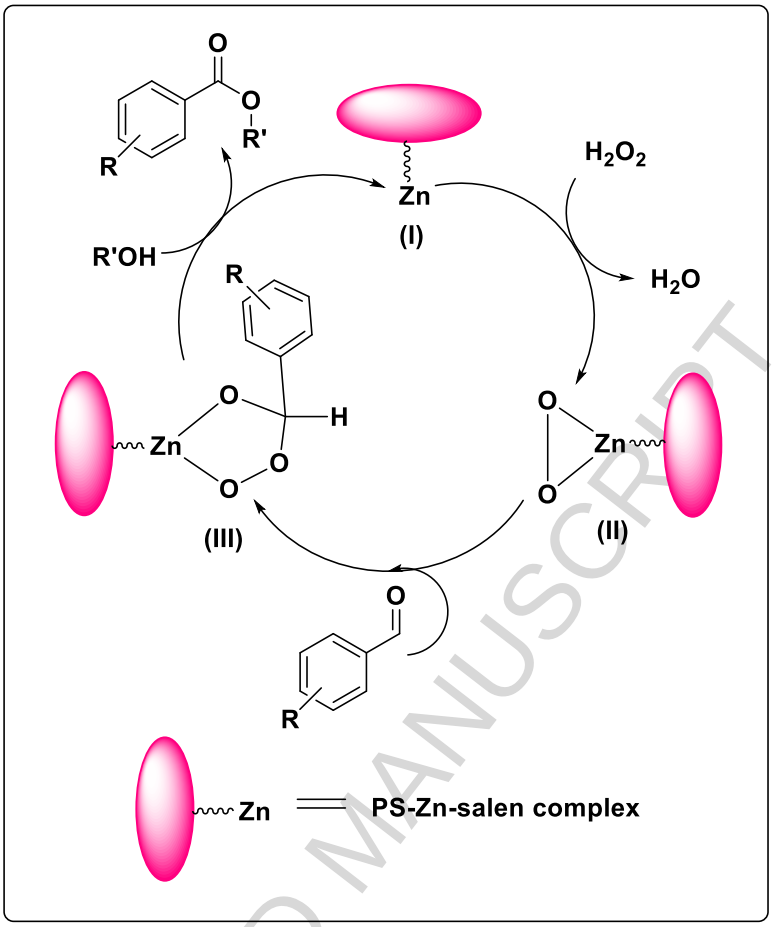
[a]Yield = GC-MS convention.

3.4. Control experiments and mechanistic investigation

Mechanically, it seems plausible that benzaldehyde is oxidized with PS-Zn-salen complex-H_2O_2 to the corresponding acid, which is esterified immediately with alcohol. However, opposing to this, it has been demonstrated in many cases that there is the formation of acetal as an intermediate [10]. To clarify, a set of the experiment were carried out (A) 3,4,5-trimethoxybenzaldehyde and H_2O_2 as an oxidant used without methanol and set (B) with methanol. Both sets of reaction were carried out at optimum reaction condition for 12h and the reaction mixture collected periodically and analyzed by GC-MS, results are given in supporting information (Fig. S16). In set (A) there is the detection of 3,4,5-trimethoxybenzoic acid (GC-MS Fig. S16A). But, in the set (B) we found the formation of methyl 3 4 5-trimethoxybenzoate along with 3,4,5-trimethoxybenzoic acid (GC-MS Fig. S16B). The study confirmed that the oxidative

esterification of benzaldehyde in an alcoholic medium does not proceed through an acetal intermediate as reported [10] but through insitu formation of benzoic acid [29].

Generally, the oxidation reactions with transition metal atoms, that H_2O_2 first binds to the metal center (I) and then transfers an oxygen atom to the substrate. Therefore, the activation of metal center results via the generation of the active species which may be bridging peroxo species (II). In the current case, it may be feasible that the beginning of the reaction PS-Zn-salen reacts with H_2O_2 to produce an active metal-peroxo intermediate which may be the active intermediate for the oxidative esterification of aldehydes to ester. This mechanism has been confirmed by Singh et al. for oxidative esterification of aldehydes using $CsPW_{11}Ni$ catalyst via metal-peroxo intermediate [29]. In the present case also similar mechanism can be expected (Scheme 3).



Scheme 3. Probable mechanism of oxidative esterification of aldehydes catalyzed by PS-Zn-salen complex **(1f)**.

Table 3. Comparison of PS-Zn-salen complex **(1f)** with other catalysts in one pot oxidative esterification of aldehydes to corresponding esters.

Entry	Catalyst	Catalyst dosage	Time (h)	Temp (°C)	Highest Yield (%)[b]	Ref.
1.	NHC-Fe	20 mol%	24	90	97[a]	[21]
2.	$BmimBF_4$	0.5 mL	24	25	90[a]	[24]
3.	Co_3O_4/rGO nanocomposite	5 mol%	6	60	93	[28]
4.	Imidazolium perrhenate	8 mol%	24	80	89	[39]
5.	Phosphotungstates anchor to MCM-41 and ZrO_2	100 mg	6	80	98	[44]

6.	PS-Zn-salen complex **(1f)**	10 mg	24	70	100	Present work

a = Isolated yield.
b = Yields determined by GC-MS.

3.4. Recycling and regeneration of the catalyst

In the present case, PS-Zn-salen complex behaves as a heterogeneous catalyst. After completion of the reaction, the resulting mixture was cool to room temperature, and the insoluble catalyst was separated by simple filtration. The separated catalyst was washed with ethanol, dried in hot air oven at 80 °C for 2h and used for the next run. The organic products were extracted with ethyl acetate and the conversion determines by GC-MS. The catalytic activity of the regenerated catalyst was estimated under the optimized conditions.

It was observed that PS-Zn-salen complex showed appreciable efficiency with 98% and 94% conversion of ester after 1st and 2nd cycle respectively (Fig. 4). However the conversion of ester has dropped to 74% up to 5th cycle compare to fresh catalyst. The average conversion for ester was found to be 87.4%. The stability of PS-Zn-salen complex was confirmed by using FT-IR and showed that the structure of the catalyst stayed intact during the esterification even after 5th recycle (Fig. 5).

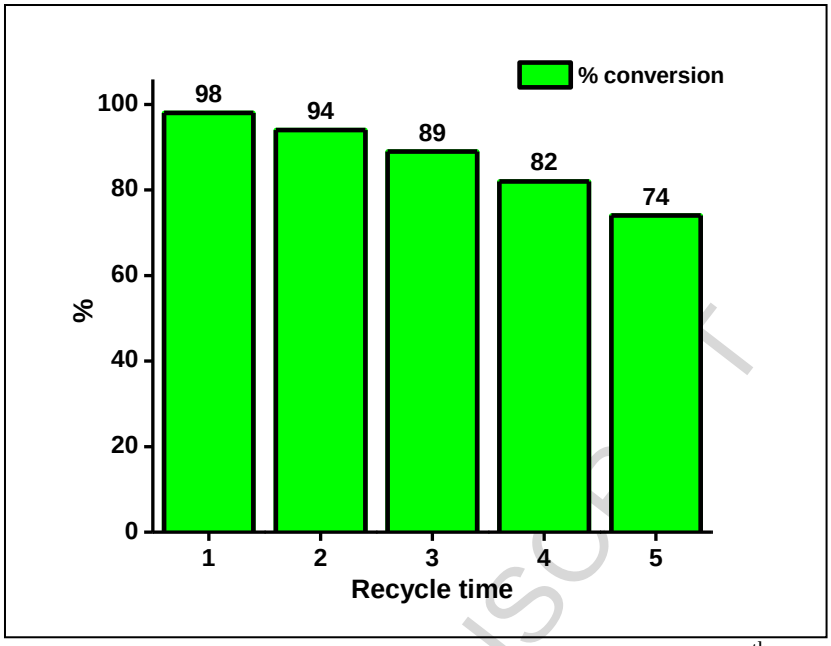


Fig. 4. Recyclability of PS-Zn-salen catalyst **(1f)** recovers up to 5th run.

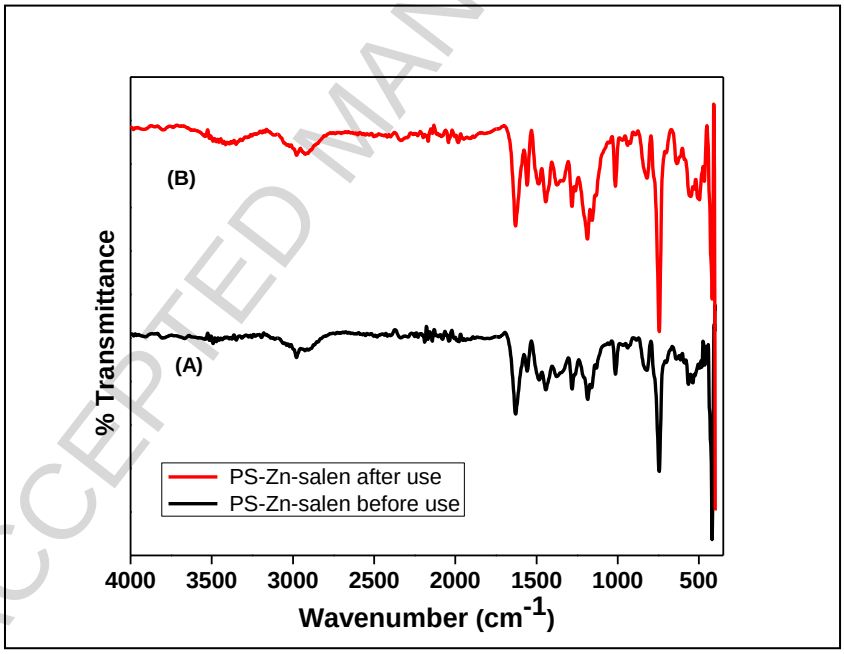


Fig. 5. FT-IR spectra of the PS-Zn-salen **(1f)** (A) before reaction (B) after the reaction.

3. Conclusion

In conclusion, we have successfully synthesized a new polymer supported Zn-salen complexes. The organic metal complex was clearly confirmed by FT-IR, EDX and SEM. The heterogeneous catalyst showed high thermal stability up to 280 °C and exhibited excellent catalytic activity in the one pot oxidative esterification reaction of aldehydes. The mechanism of oxidative esterification of aldehyde proceeded through acid formation which was confirmed GC-MS. The catalyst was reused up to 5^{th} successive run with the average conversion of ester 87.4%. The stability of the recycle catalyst was further confirmed by FT-IR analysis, which revealed that the PS-Zn-salen complex catalyzes esterification reaction without deterioration of the ordered structure. Also, the effect of counter anions of complex also studied which showed that there is no noticeable influence on the conversion of product. The high conversion of ester (up to 100%), with used of low catalyst amount, easy work up and environmentally benign protocol over the other reported procedure. Other studies of its applicability in synthetic renovations are currently on-going in our laboratory.

Acknowledgements

The authors express their deep gratitude to RGEMS for financial support and SIF DST-VIT-FIST for NMR, GC-MS, FT-IR and SEM/EDX VIT University, Vellore for providing essential facility to carry this article to this level. We are also thankful to the Dean, School of Advanced Sciences, special thanks to Mr. Murphy M and all the Scholars of our Research Laboratory, “Smart Materials Laboratory for Bio-sensing & Catalysis” VIT University Vellore, who have encouraged the authors during this period.

4. References

[1] S. Dey, S.K. Gadakh, A. Sudalai, Org. Biomol. Chem. 13 (2015) 10631-10640.

[2] A. Patel, S. Pathan, P. Prakashan, RSC Adv. 6 (2016) 51394-51402.

[3] J. Iqbal, R.R. Srivastava, J. Org. Chem.57 (1992) 2001-2007.

[4] M. Gomberg, C.C. Buchler, J. Am. Chem. Soc., 42 (1920) 2059-2072.

[5] F.Z. Su, J. Ni, H. Sun, Y. Cao, H.Y. He, K.N. Fan, Chem. Eur. J. 14 (2008) 7131-7135.

[6] B.A. Tschaen, J.R. Schmink, G.A. Molander, Org. Lett. 15 (2013) 500-503.

[7] M. Caporaso, G. Cravotto, S. Georgakopoulos, G. Heropoulos, K. Martina, S. Tagliapietra, Beilstein J. Org. Chem. 10 (2014) 1454–1461.

[8] A.F.P. Biajoli, F. Peringer, A.L. Monteiro, Catal. Commun. 2016 10.1016/j.catcom.2016.10.015.

[9] R. Gopinath, B. Barkakaty, B. Talukdar, B.K. Patel, J. Org. Chem. 68 (2003) 2944-2947.

[10] R. Gopinath, B.K. Patel, Org. Lett. 2 (2000) 577-579.

[11] W.J. Yoo, C.J. Li, J. Org. Chem. 71 (2006) 6266-6268.

[12] Y. Zhu, Y. Wei, RSC Adv. 3 (2013) 13668–13670.

[13] X.F. Wu, C. Darcel, Eur. J. Org. Chem. (2009) 1144-1147.

[14] N.A. Owston, A.J. Parker, J.M.J. Williams, Chem. Commun. (2008) 624–625.

[15] J. Zhang, G. Leitus, Y. Ben-David, D. Milstein, J. Am. Chem. Soc. 127 (2005) 10840-10841.

[16] J.B. Feng, J.L. Gong, Q. Li, X.F. Wu, Tetrahedron Lett. 55 (2014) 1657-1659.

[17] G.I. Nikishin, N.I. Kapustina, L.L. Sokova, O.V. Bityukov, A.O. Terentev, Tetrahedron Lett. 58 (2017) 352-354.

[18] J.J. Meng, M. Gao, Y.P. Wei, W.Q. Zhang, Chem. Asian J. 7 (2012) 872-875.

[19] M. Ji, X. Wang, Y.N. Lim, Y.W. Kang, H.Y. Jang, Eur. J. Org. Chem. (2013) 7881-7885.

[20] M.T. Berry, D. Castrejon, J.E. Hein, Org. Lett. 16 (2014) 3676-3679.

[21] J.N. Rosa, R.S. Reddy, N.R. Candeias, P.M.S.D. Cal, P.M.P. Gois, Org. Lett. 12 (2010) 2686-2689.

[22] F. Luo, C. Pan, J. Cheng, F. Chen, Tetrahedron 67 (2011) 5878-5882.

[23] D. Zhang, D. Pan, Catal. Commun. 20 (2012) 41-45.

[24] I. Chiarotto, M. Feroci, G. Sotgiu, A. Inesi, Tetrahedron 69 (2013) 8088-8095.

[25] S. Kegnaes, J. Mielby, U.V. Mentzel, T. Jensen, P. Fristrup, A. Riisage, Chem. Commun. 48 (2012) 2427-2429.

[26] K. Suzuki, T. Yamaguchi, K. Matsushita, C. Iitsuka, J. Miura, T. Akaogi, H. Ishida, ACS Catal. 3 (2013) 1845-1849.

[27] E. Rafiee, S. Eavani, J. Mol. Catal. A: Chem. 373 (2013) 30-37.

[28] V. Panwar, A. Al-Nafiey, A. Addad, B. Siebe, P. Roussel, R. Boukherroub, S.L. Jain, RSC Adv., 5 (2015) 88567-88573.

[29] S. Singh, A. Patel, P. Prakashan, Appl. Catal., A. 505 (2015) 131-140.

[30] B.R. Travis, M. Sivakumar, G.O. Hollist, B. Borhan, 5 (2003) 1031-1034.

[31] N.N. Karade, S.G. Shirodkar, B.M. Dhoot, P. B. Waghmare, J. Chem. Res. (2005) 274-276.

[32] N.N. Karade, V.H. Budhewar, A.N. Katkar, G.B. Tiwari, ARKIVOC (xi) (2006) 162-167.

[33] K. Ekoue-Kovi, Wolf, Chem. Eur. J. 14 (2008) 6302-6315.

[34] V.V. Zhdankin, ARKIVOC (i) (2009) 1-62.

[35] X.F. Wu, Tetrahedron Lett. 53 (2012) 3397-3399.

[36] K.R. Reddy, M. Venkateshwar, C.U. Maheswari, S. Prashanthi, Synth. Commun. 40 (2010) 186-195.

[37] T.M. Mineno, S. Yoshino, A. Ubukata, Green and Sustainable Chemistry 4 (2014) 20-23.

[38] K.K. Rajbongshi, M.J. Sarma, P. Phukan, Tetrahedron Lett. 55 (2014) 5358-5360.

[39] R. Xie, X. Wang, J. Wang, J. Ye, M. Zhou, S. Zang, J. Saudi Chem. Soc. (2016) http://dx.doi.org/10.1016/j.jscs.2015.12.007.

[40] C.S. Lin, B.C. Hong, G.H. Lee, RSC Adv. 6 (2016) 8243-8247.

[41] H. AlinezhadIran, K. Nemati, J. Org. Chem. 4 (2012) 911-915.

[42] R. V. Stevens, K. T. Chapman, C. A. Stubbs, W. W. Tam, K. F. Albizati, Tetrahedron Lett. 23 (1982) 4647-4650.

[43] B. Wang, W. Ran, W. Sun, K. Wang, Ind. Eng. Chem. Res. 51 (2012) 3932-3938.

[44] S. Singh, A. Patel, Catal. Lett. 144 (2014) 1557-1567.

[45] J. Xie, Q. Zhang, K.T. Chuang, Catal. Lett. 93 (2004) 181-184.

[46] J. Xie, Q. Zhang, K.T. Chuang, Appl. Catal., A 220 (2001) 215-221.

[47] K. Lavelle, J.B. McMonagle, Chem. Eng. Sci. 56 (2001) 5091-5102.

[48] J. Xie, Q. Zhang, K.T. Chuang, J. Catal. 191 (2000) 86-92.

[49] P.W. Yen, T.C. Chou, Appl. Catal., A 182 (1999) 217-223.

[50] A.G. Khiratkar, S.S. Kumar, P.R. Bhagat, RSC Adv. 6 (2016) 37757-37764.

[51] P.U. Naik, G.J. McManus, M.J. Zaworotko. R.D. Singer, Dalton Trans. (2008) 4834-4836.

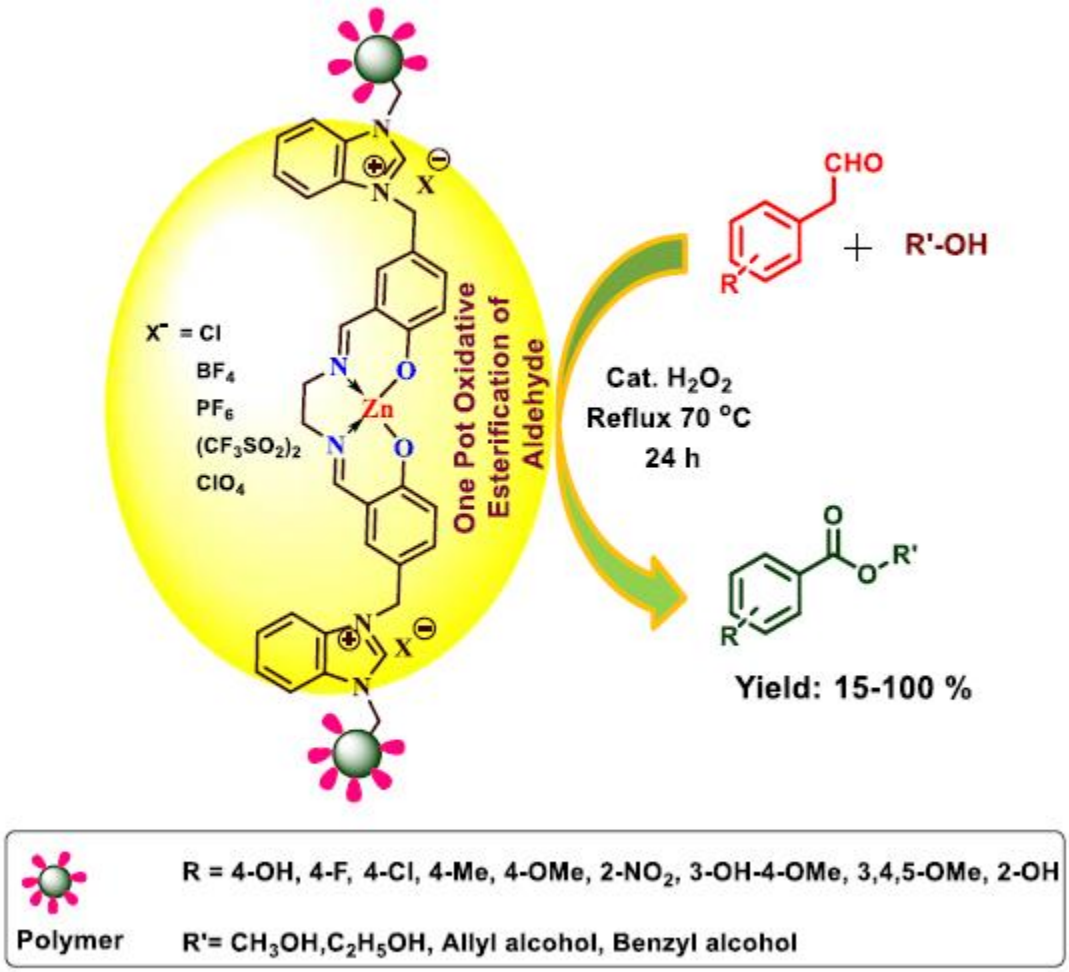
[52] P. Jeslin Kanaga Inba, B. Annaraj, S. Thalamuthu, M. A. Neelakantan, Bioinorg. Chem. Appl. (2013) 1-11.

[53] P.N. Muskawar, K. Thenzozhi, P.R. Bhagat, Appl. Catal., A. 493 (2015) 158-167.

[54] M. Ferguson, N. Giri, X. Huang, D. Apperley, S.L. James, Green Chem. 16 (2014) 1374-1382.

[55] D.N. Kumar, B.S. Garg, Spectrochim. Acta., A. 64 (2006) 141-147.

Graphical abstract



Highlights:

- Polymer supported Zinc-salen (PS-Zn-salen) complexes were synthesized
- Efficiency of catalysts for one pot oxidative esterification reactions has been confirmed
- PS-Zn-Salen catalyst afforded synthesis of methyl/ethyl benzoate with good to excellent yields using H_2O_2 as an oxidant
- Mechanistic path was confirmed by GC-MS showed benzoic acid as an intermediate
- Catalyst shown very good thermal stability and recyclability for 5^{th} run without substantial loss in activity