Simple and efficient esterification reaction catalyzed by Zinc chloride ($ZnCl_2$)

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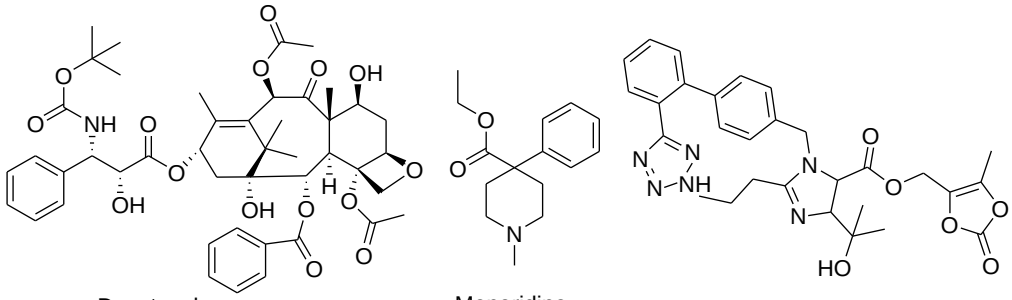
Abstract- A simple and efficient method is developed for the synthesis of phenyl benzoates (esters) by the condensation of various carboxylic acids with substituted phenols in the presence of anhydrous $ZnCl_2$ in $POCl_3$ .This Lewis acid catalyzed esterification reaction gives good to excellent yields of the corresponding phenolic esters.

Index Terms- Aromatic carboxylic acids, Phenols, Lewis acid, $POCl_3$ and Phenyl benzoates.

I. INTRODUCTION

The esterification reaction is one of the most fundamental organic transformations, and more environmentally benign alternative approaches to those currently used by the chemical industry are in strong demand.[1] The ester moiety is an important functional group that has found wide occurrences in polymers, pharmaceutical agents and biologically relevant natural products (**fig-1**), but are also used as protecting groups in synthesis.[2,3]

Fig-1: Representative biologically active molecules.

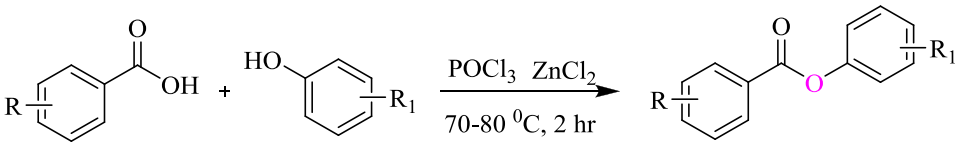


The carboxylic group can be converted to corresponding ester by reacting it with an alcohol in the presence of various homogeneous as well as heterogeneous catalysts. These subsumes conc. H_2SO_4, HCl, $SOCl_2$,[4] alkylchloroformate and Et_3N,[5] $C_6H_5OP(O)Cl_2$,[6] DCC and aminopyridine,[7] $SiO_2/NaHSO_4$,[8] amberlyst-15,[9] USY-zeolites,[10] MoO_3/ZrO_2,[11] $MgSO_4/H_2SO_4$,[12] salycilic resin/$FeCl_3$,[13] SiO_2,[14] celite/CsF,[15] dowex 50WX2,[16] β-zeolite,[17] Kaolinite clay,[18] H_3PO_4/TiO_2-ZrO_2,[19] etc. Besides the practical utility of heterogeneous catalysts, solubility of HPA in polar solvents and rapid catalyst deactivation of SiO_2, zeolites limit their use. Similarly though some catalysts have higher reactivity, the high operation temperature always gives a mixture of products. Generally, the use of stoichiometric amounts of multiple reagents limit the application of modern coupling reagents for esterification reaction.[20-31] All these and some more limitations encountered with many of the synthetic protocols triggered our interest to develop a new method. As part of our research program in developing synthetic methods,[32] herein we report, the synthesis of esters using zinc chloride as a catalyst. The catalyst zinc chloride is known in the literature for various organic transformations.[33]

II. RESULTS AND DISCUSSION

A mixture of the benzoic acid (1mmol), substituted phenols (1mmol), zinc chloride ($ZnCl_2$) (1 mmol) in phosphorousoxychloride ($POCl_3$, 2 vol.) was taken in to round bottom flask. Then mixture was stirred at 70-80 °C the reaction was completed within 1-2 hour to afford the corresponding product substituted benzoates (**3a**) in good yields as shown in (Scheme-1)

Scheme 1: Esterification of carboxylic acid and alcohols in presence of $ZnCl_2$, $POCl_3$.



R = F, Cl, NH_2, NO_2 R_1 = F, Cl, Br, CN, OCH_3, NH_2, NO_2

Scheme 1: Esterification of carboxylic acid and alcohols in presence of $ZnCl_2$, $POCl_3$

We have examined the effect of temperature on reaction rate and the amount of catalyst used in the reaction and the results were summarized in the table-1. There was no product formation in $POCl_3$ at room temperature, and at reflux condition partially product formation was observed even after 24 hours. The product was observed in presence of catalyst at room temperature after 24 hours. It was found that the ideal reaction conditions were 1.0eq of $ZnCl_2$ in $POCl_3$ at 75-80 °C.

Table 1: Optimization of reaction conditions for the synthesis of phenyl benzoates using zinc chloride:

S. No	Solvent	$ZnCl_2$ (eq)	Temperature (^{0}C)	Time (h)	Yield (%)
1	$POCl_3$	0	25-30	24	No conversion
2	$POCl_3$	0	75-80	24	20
3	$POCl_3$	0.5	25-30	24	33
4	$POCl_3$	0.5	75-80	5.0	70
5	$POCl_3$	1.0	75-80	1.0	88

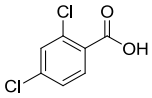
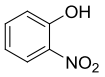
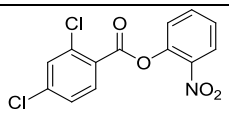
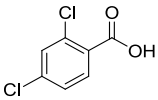
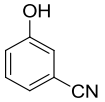
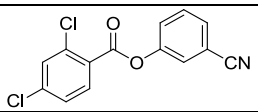
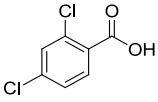
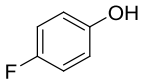
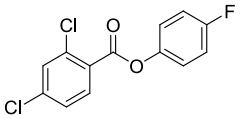
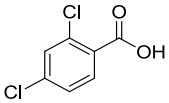
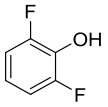
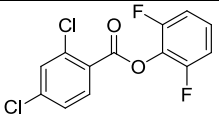
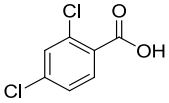
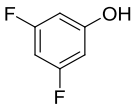
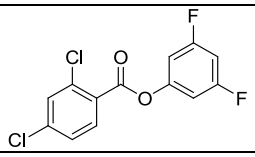
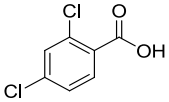
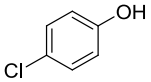
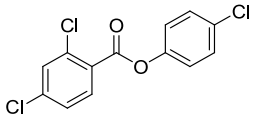
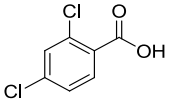
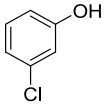
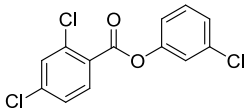
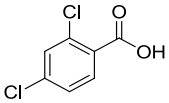
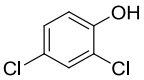
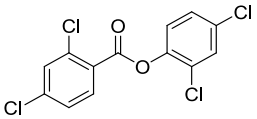
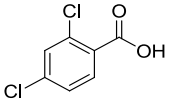
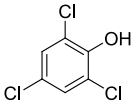
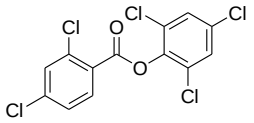
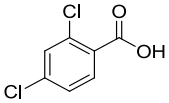
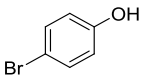
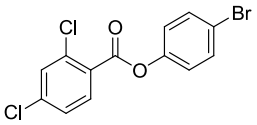
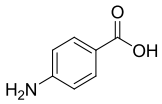
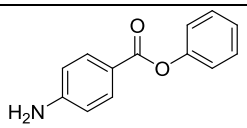
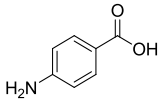
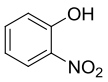
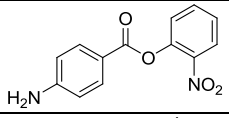
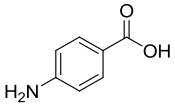
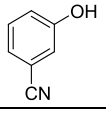
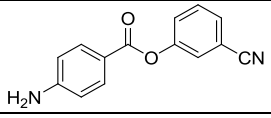
Encouraged by the results obtained with carboxylic acid and phenols at established reaction conditions, we have applied this methodology to various substrates. The results are summarized in table 2. Interestingly, the esterification with substituted phenols worked well at reflux temperature. This methodology is successfully applied to carboxylic acids; the carboxylic acids having different substitution on ring system (electron withdrawing and donating groups) were used for the condensation reaction without any difficulty. In general, all the reactions were carried out in $POCl_3$ at reflux, in the presence of $ZnCl_2$ as a catalyst using (10 mol %), the reaction was completed within 1 to 2 hours and the yields obtained varied from 75-90%. All the products were confirmed by their proton nuclear magnetic resonance (1H-NMR), infrared (IR) and Electron Impact ionization Mass Spectrometry (EIMS) data.

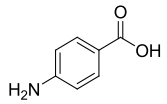
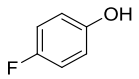
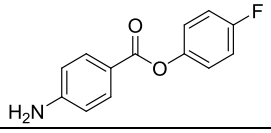
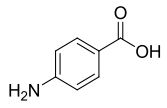
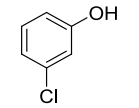
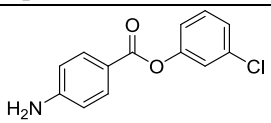
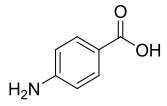
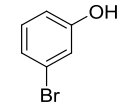
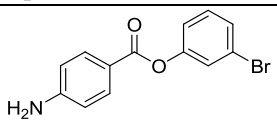
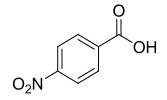
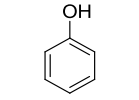
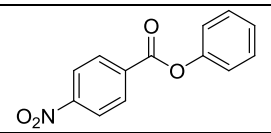
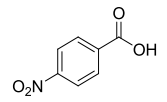
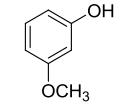
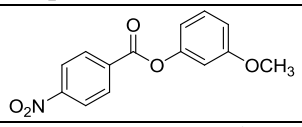
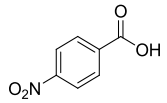
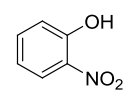
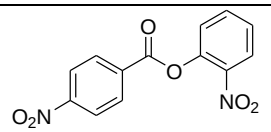
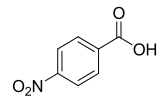
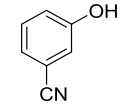
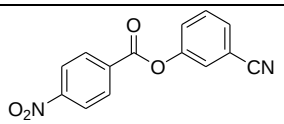
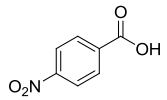
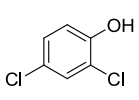
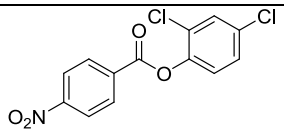
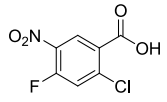
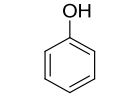
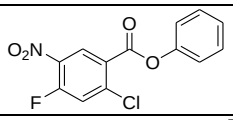
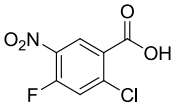
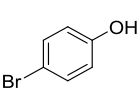
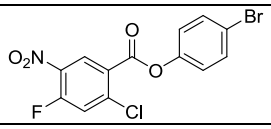
III. EXPERMENTAL SECTIONS

General Methods: Melting points were recorded on Buchi R-535 apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer FT-IR spectrophotometer using KBr discs. The reactions were monitored by TLC plates Merck Silica Gel 60, F254 and visualization with UV light (254 and 365nm) 1H NMR spectra were recorded on Bruker-400 spectrometer in $CDCl_3$ using TMS as internal reference. Mass spectra were recorded at ionization energy 70 eV on API Q Star pulsar spectrometer using elctrospray ionization.

General procedure: A mixture of the appropriate aromatic carboxylic acids (1mmol), substituted phenols (1mmol), zinc chloride ($ZnCl_2$) (1.0mmol) and phosphorousoxychloride ($POCl_3$, 2 vol.) was taken in to round bottom flask. Warm to 75-80 °C Then mixture was stirred for 2h at same temperature. The progress of reaction was monitored by TLC. Reaction mixture cooled to room temperature and added ice cold water lot-I (10 vol.) and stir for 30-60 min at 25-30 °C. The separated solid by filtration and washed with water lot-II (10 vol.) and dried the obtained material under vacuum, furnish the corresponding phenyl benzoates in good yields. (75-88%). All the products were characterized by their 1H NMR, IR and mass spectral data.

Table-2: Direct esterification of carboxylic acids with phenols catalyzed by $ZnCl_2/POCl_3$.

S. No	Acids	Phenols	Product	Time (h)	Yield (%)
a				2	75
b				1	90
c				1.5	80
d				2	72
e				2	77
f				1.5	82
g				2	70
h				1	91
i				1.5	78
j				1	90
k				1.5	78
l				1.5	81
m				2.0	68

n				1.5	80
o				2.0	93
p				2.5	65
q				1.5	82
r				2	82
s				1	90
t				1.5	86
u				1	89
v				1.5	89
w				1.0	88

2-Nitrophenyl 2, 4-dichlorobenzoate (3a): IR (KBr): υ 3102, 2867, 1748, 1584, 1518, 1471, 1353, 1208, 1085, 1021, 733 cm.-1; 1H NMR (400 MHz, DMSO-d6): δ 8.24 (dd, J1 = 1.6 Hz, J2 = 6.4 Hz,1H), 8.20 (d, J = 8.4 Hz, 1H), 7.93-7.89 (m, 2H), 7.72-7.67 (m, 2H), 7.65-7.61 (m, 1H).;EI-MS, m/z (%): 310 (M-2, 80), 138 (100).

3-Cyanophenyl 2, 4-dichlorobenzoate (3b): IR (KBr): υ 3101, 2231, 1741, 1582, 1482, 1276, 1237, 1152, 1093, 1042, 785 cm.-1; 1H NMR (400 MHz, DMSO-d6): δ 8.18 (d, J = 8.4 Hz, 1H), 7.94 (s, 1H), 7.89 (d, J = 1.6 Hz, 1H) 7.85 -7.82 (m, 1H), 7.74-7.72 (m, 1H), 7.72-7.7 1 (m, 1H), 7.68 (dd, J1 = 2.0 Hz, J2 = 8.0 Hz, 1H).; EI-MS, m/z (%): 290 (M-1, 100), 212 (25), 136 (40), 113 (70).

4-Fluorophenyl 2,4-dichlorobenzoate (3c): IR (KBr): υ 3101, 3081, 1741, 1582, 1507, 1417, 1373, 1234, 1182, 1091, 1035, 872 cm.-1; 1H NMR (400 MHz, CDCl3): δ 8.00 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 2.0 Hz, 1H), 7.38 (dd, J1 = 1.6 Hz, J2 = 8.4 Hz, 1H) 7.26 -7.18 (m, 2H), 7.13-7.09 (m,1H).; EI-MS, m/z (%): 283 (M-2, 20), 221 (25), 191 (70), 189 (100), 133 (30), 125 (35), 113 (25).

2, 6-Difluorophenyl 2,4-dichlorobenzoate (3d): IR (KBr): υ 3377, 3278, 3105, 1762, 1663, 1619, 1583, 1481, 1292, 1266, 1231, 1156, 1082, 1028, 876 cm.-1; 1H NMR (400 MHz, CDCl3): δ 8.1 (d, J = 8.4 Hz, 1H), 7.57 (d, J = 2.4 Hz, 1H), 7.40 (dd, J1 = 2.0 Hz, J2 = 8.8 Hz, 1H), 7.25 -7.19 (m, 1H), 7.03 (t, J = 7.6 Hz, 2H).; EI-MS, m/z (%): 302 (M-1, 70), 300 (100).

3,5-Difluorophenyl 2,4-dichlorobenzoate (3e): IR (KBr): υ 3091, 1745, 1608, 1465, 1378, 1281, 1242, 1140, 1121, 1044, 991, 839 cm.-1; 1H NMR (400 MHz, CDCl3): δ 7.98 (d, J = 8.4 Hz, 1H), 7.55 (s, 1H), 7.38 (d, J = 8.4 Hz, 1H) 6.85-6.83 (m, 2H), 6.78-6.74 (m, 1H).; EI-MS, m/z (%): 301 (M-2, 100), 257 (10), 129 (25).

4-Chlorophenyl 2, 4-dichlorobenzoate (3f): Solid. Mp.124-125, IR (KBr): υ 3098, 1741, 1682, 1580, 1489, 1373, 1241, 1206, 1086, 1036, 874 cm.-1; 1H NMR (400 MHz, DMSO-d6): δ 8.11 (d, J = 2.1 Hz, 1H), 7.87 (d, J = 2.0 Hz, 1H), 7.66 (dd, J1 = 1.6 Hz, J2 = 8.4 Hz, 1H) 7.56 -7.54 (m, 2H), 7.39-7.37 (m, 2H).; EI-MS m/z (%): 301 (M+18, 30), 255 (40), 135 (100), 113 (65).

3-Chlorophenyl 2, 4-dichlorobenzoate (3g): Solid. Mp. 99-100, IR (KBr): υ 3073, 2925 1741, 1585, 1468, 1259, 1238, 1197, 1092, 1034, 881, 774 cm.-1; 1H NMR (400 MHz, DMSO-d6): δ 8.14 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 1.6 Hz, 1H), 7.77 (dd, J1 = 1.6 Hz, J2 = 8.4 Hz, 1H), 7.54-7.50 (m, 2H), 7.42 (d, J = 7.6 Hz, 1H), 7.73 (dd, J1 = 1.2 Hz, J2 = 7.6 Hz, 1H).; EI-MS, m/z (%): 299 (M-2, 100), 191 (50), 189 (85), 147 (30), 145 (35).

2,4-Dichlorophenyl 2, 4-dichlorobenzoate (3h): IR (KBr): υ 3069, 2895 1739, 1523, 1468, 1262, 1230, 1201, 1108 ; 1H NMR (400 MHz, CDCl3): δ 8.11-8.09 (m, 1H), 7.56 (s, 1H), 7.50 (d, 2H), 7.72-7.67 (m, J = 1.2 Hz, 2H), 7.65-7.61 (m, 1H), 7.40-7.38 (m, 1H), 7.33-7.30 (m, 1H), 7.25-7.21 (m, 1H).; EI-MS, m/z (%): 338 (M+2, 45), 155 (100).

2, 4, 6-Trichlorophenyl 2, 4-dichlorobenzoate (3i): IR (KBr): υ 3110, 2242, 1749, 1589, 1488, 1269, 1242, 1154, 1093; 1H NMR (400 MHz, CDCl3): δ 8.14 (d, J = 8.4 Hz, 1H), 7.58 (s, 1H), 7.43-7.39 (m, 3H).; EI-MS. m/z (%): 369 (M-1, 10), 265 (30) , 195 (40), 135 (45), 113 (100); m/z (%): 371.41 (M+1, 61), 184 (100).

4-Bromophenyl 2, 4-dichlorobenzoate (3j): IR (KBr): υ 3095, 3075, 1742, 1580, 1484, 1373, 1260, 1241, 1201, 1162, 1090, 1065, 873 cm.-1; 1H NMR (400 MHz, CDCl3): δ 8.01 (d, J = 8.8 Hz, 1H), 7.56 -7.54 (m, 3H), 7.39 (dd, J1 = 2.0 Hz, J2 = 8.4 Hz, 1H) 7.54 -7.11 (m, 2H).; EI-MS, m/z (%): 345 (M-1, 30), 343 (65), 325 (45), 311 (50), 279 (95), 265 (100), 241 (47), 171 (35).

Phenyl 4-aminobenzoate (3k): 169-171 IR (KBr): υ 3412, 3336, 3229, 3029, 1704, 1639, 1596, 1491, 1279, 1191, 1167, 1071, 742 cm.-1; 1H NMR (400 MHz, CDCl3): δ 8.01 (dd, J1 = 2.0 Hz, J2 = 6.8 Hz, 2H),7.42-7.38 (m, 2H), 7.25-7.21 (m, 1H), 7.70-7.17 (m, 2H), 6.70 (dd, J1 = 1.6 Hz, J2 = 6.8 Hz, 2H), 4.18 (brs, 2H (NH2).; EI-MS, m/z (%): 214 (M+1, 28), 161 (20), 148 (24), 145 (55), 131 (30), 106 (100).

2-Nitrophenyl 4-aminobenzoate (3l): IR (KBr): υ 3112, 2198, 1730, 1542, 1491, 1268, 1237, 1184, 1081; 1H NMR (400 MHz, CDCl3): δ 8.56 (d, J = 2.0 Hz, 1H), 8.26 (dd, J1 = 2.0 Hz, J2 = 8.8 Hz, 1H), 8.07 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.8 Hz, 2H), 6.70 (d, J = 9.6 Hz, 2H), 4.3 (brs, 2H (NH2).; EI-MS, m/z (%): 259 (M+1, 30), 257 (20), 256 (88), 145 (55), 131 (25), 106 (100).

3-Cyanophenyl 4-aminobenzoate (3m): IR (KBr): υ 2955, 2188, 1741, 1509, 1454, 1330, 1242, 1236, 1140, 1021; 1H NMR (400 MHz, DMSO-d6): δ 8.00-7.96 (m 2H), 7.52- 7.46 (m, 4H), 6.71-6.68 (m, 2H).; EI-MS, m/z (%): 237 (M-1, 20), 154 (25), 119 (20), 118 (100). m/z (%): 338 (M+2, 45), 155 (100).

4-Fluorophenyl 4-aminobenzoate (3n): IR (KBr): υ 3105, 2228, 1732, 1595, 1491, 1268, 1240, 1162, 1085; 1H NMR (400 MHz, DMSO-d6): δ 7.79 (d, J = 8.8 Hz, 2H), 7.25 (s, 2H), 7.23 (s, 1H), 6.64 (d, J = 8.8 Hz, 2H), 6.15 (br, 2H (NH2).; EI-MS, m/z (%): 232 (M+1, 30), 210 (26), 181 (50), 132 (46), 106 (100).

3-Chlorophenyl 4-aminobenzoate (3o): IR (KBr): υ 3415, 2942. 2890, 1668, 1318, 1597, 1358, 1306, 1215, 1110, 869 cm.-1; 1H NMR (400 MHz, CDCl3): δ 7.98 (d, J = 8.0 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.25-7.21 (m, 2H), 7.11-7.09 (m, 1H), 6.69 (d, J = 8.4 Hz, 2H), 4.16 (brs, 2H).; EI-MS, m/z (%): 248 (M+1, 30), 164 (28), 143 (75), 131 (100), 117 (25).

3-Bromophenyl 4-aminobenzoate (3p): IR (KBr): υ 3424, 2930. 2901, 1721, 1308, 1602, 1312, 1255, 1124 cm.-1; 1H NMR (400 MHz, DMSO-d6): δ 7.74 (d, J = 8.4 Hz, 2H), 7.44-7.42 (m, 2H), 7.35 (t, J = 8.4 Hz, 1H), 7.20 (dd, J1 = 8.8 Hz, J2= 8.4 Hz, 1H), 6.60 (d, J1 = 8.4 Hz, 2H), 6.14 (brs, 2H).; EI-MS, m/z (%): 294 (M+2, 100).

Phenyl 4-nitrobenzoate (3q): Solid. Mp. 173-174, IR (KBr): υ 3465, 3110, 3085, 1741, 1607, 1527, 1407, 1268, 1027, 1013, 756 cm.-1; 1H NMR (400 MHz, CDCl3): δ 8.35 (q, 4H), 7.46 (t, J = 8.0 Hz, 2H), 7.31 (t, J = 7.6 Hz, 1H), 7.25-7.22 (m, 1H).; EI-MS, m/z (%): 244 (M+1, 100).

3-Methoxyphenyl 4-nitrobenzoate (3r): Solid. Mp. 121-122, IR (KBr): υ 3478, 3105, 3077, 2849, 1749, 1607, 1520, 1488, 1347, 1251, 1136, 1069, 1038, 713 cm.-1; 1H NMR (400 MHz, CDCl3): δ 8.39-8.34 (m, 4H), 7.35 (t, J = 8.0 Hz, 1H), 6.87-6.84 (m, 2H), 6.83-6.78 (m, 1H), 3.83 (s, 3H).; EI-MS, m/z (%): 273 (M-1, 80), 255 (30), 225 (50), 172 (90), 116 (100).

2-Nitrophenyl 4-nitrobenzoate (3s): Solid. Mp. 143-144, IR (KBr): υ 3466, 3108, 3079, 2859, 1740, 1607, 1590, 1607, 1522, 1347, 1321, 1273, 1271, 1089, 1072, 712 cm.-1; 1H NMR (400 MHz, CDCl3): δ 8.38-8.31 (m, 4H), 8.20-8.18 (m, 1H), 7.75 (t, J = 8.0 Hz, 1H), 7.50 (t, J = 8.0 Hz, 1H), 7.42-7.40 (m, 1H).; EI-MS, m/z (%): 289 (M+1, 20), 166 (100), 138 (90), 122 (20).

3-Cyanophenyl 4-nitrobenzoate (3t): IR (KBr): υ 3111, 3086, 2360, 2231, 1739, 1582, 1482, 1320, 1235, 1078, 799 cm.-1; 1H NMR (400 MHz, CDCl3): δ 8.38 (s, 4H), 7.64-7.59 (m, 3H), 7.57-7.51 (m, 1H). ; EI-MS, m/z (%): 269.2 (M+1, 100),

2, 4-Dichlorophenyl 4-nitrobenzoate (3u): IR (KBr): υ 3108, 3050, 2296, 1745, 1598, 1452, 1305, 1202, 1028 cm.-1; 1H NMR (400 MHz, CDCl3): δ 8.41-8.36 (m, 4H), 7.53 (d, J = 2.4 Hz, 1H), 7.35 (dd, J1 = 2.0 Hz, J2= 8.0Hz, 1H), 7.26-7.24 (m, 1H).; EI-MS, m/z (%): 313.2 (M+1, 20), 166 (100), 122 (25).

Phenyl 2-chloro-4-fluoro-5-nitrobenzoate (3v): IR (KBr): υ 3113, 3066, 1746, 1646, 1578, 1527, 1345, 1269, 1180, 1020, 777 cm.-1; 1H NMR (400 MHz, CDCl3): δ 8.88 (d, J = 8.0 Hz, 1H), 7.53 (m, 3H), 7.48-7.43 (m, 2H), 7.32 (t, J = 7.2 Hz, 1H), 7.25-7.23 (m, 2H).; EI-MS, m/z (%): 296.5 (M+1, 100).

4-Bromophenyl 2-chloro-4-fluoro-5-nitrobenzoate (3w): IR (KBr): υ 3119, 2924, 1749, 1618, 1586, 1531, 1483, 1346, 1271, 1194, 1066, 975, 801 cm.-1; 1H NMR (400 MHz, CDCl3): δ 8.86 (d, J = 7.2 Hz, 4H), 7.59-7.52 (m, 3H), 7.15 -7.13 (m, 2H).; EI-MS, m/z (%): 375 (M+1, 35), 371 (20), 357 (30), 354 (100).

IV. CONCLUSION

In conclusion, zinc chloride was found to be an efficient catalyst for the synthesis of esters in very good to excellent yields. This methodology offers several advantages: mild reaction conditions, enhanced reaction rates, easy isolation of products and operational simplicity. The scope and generality of this protocol was illustrated with respect to various aromatic carboxylic acids with phenol compounds.

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VI. REFERENCESS

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