J. Indian Chem. Soc.,
Vol. 92, August 2015, pp. 1-9

Amino group immobilized on polyvinyl alcohol as a reusable catalyst for highly accelerated *N*-formylation of amines using formic acid under solvent-free condition

Soodabeh Rezazadeh and Batool Akhlaghinia*

Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad, Mashhad 9177948974, Iran

E-mail : akhlaghinia@um.ac.ir *Fax* : 98-511-8795457

Manuscript received online 08 November 2014, accepted 15 December 2014

Abstract : Amino group immobilized on polyvinyl alcohol catalyzed, rapid, chemoselective and practical *N*-formylation of amines using formic acid under solvent-free conditions. The catalyst was found to be compatible with different functional groups and the *N*-formylation proceeded smoothly with amines bearing electron withdrawing as well as electron donating substituents. The process is remarkably simple and environmentally benign. The catalyst can be easily recovered and reused at least four times without any decrease in its high catalytic activity.

Keywords : Solventless *N*-formylation, formic acid, amine, polyvinyl alcohol (PVA).

Introduction

Formyl group as an useful and versatile amino-protecting group in peptide synthesis[1]. In addition, formamides serve as useful intermediates in the synthesis of medicinally important heterocycles such as substituted aryl imidazoles[2], 1,2-dihydroquinolines[3], oxazolidinones[4], cancer chemotherapeutic compounds[5] and as reagents for Vilsmeir formylation[6], synthesis of formamidines[7] and isocyanides[8]. Due to Lewis basicity of formamides they could be applied as catalysts in allylation[9] and hydrosilylation of carbonyl compounds[10]. Furthermore, asymmetric allylation of aldehydes has been achieved with chiral formamides[11].

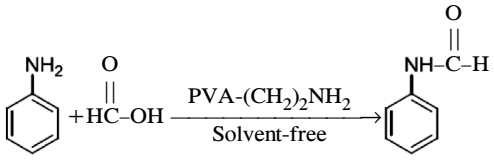
Numerous methods of formylation are reported in the literature. Acetic formic anhydride[12,13] chloral[14], activated formic acid using DCC[15], EDCI[16], activated formic acid esters[17–20], KF-Al_2O_3[21], ammonium formate[22], 2,2,2-trifluoroethyl formate[23], formic acid in combination with sodium formate[24], $ZnCl_2$[25], sulfated titania[26], Amberlite IR 120[27], indium metal[28], iodine[29], ZnO[30], have been used for this purpose. Polyethylene glycol medium[31], as well as solid supported reagents[32] such as silica supported perchloric acid[33], sulfonic acid supported hydroxyapatite encapsulated γ-Fe_2O_3[34], sulfated tungstate[35] have been also utilised. However, some of these methods are limited only to aromatic primary amines, some others use expensive toxic organic solvent, toxic, expensive reagents. Also, most of *N*-formylation methods involve rather complicated preparation of catalysts, long reaction time, high temperature and formation of side products. Therefore, development of low-cost, eco-friendly and recyclable catalytic method is of current interest[36,37]. Herein, we report a solventless method for the *N*-formylation of amines based on treatment with formic acid in the presence of PVA-NH_2.

Results and discussion

For initial optimization experiments, aniline was subjected to a set of reaction conditions. *N*-Formylation of aniline in the absence of any catalyst and solvent at room temperature was rather sluggish (Table 1, entries 1). At room temperature, the presence of PVA has no influence on the rate of *N*-formylation reaction, whereas PVA-NH_2[38] caused acceleration to some extent (Table 1, entry 2, 3). In order to study the effect of temperature, all reactions were carried out at 40 °C (Table 1, entries 4–6). It was observed PVA-NH_2 delivered improved results under this condition. Next the catalyst loading was optimised (Table 2, entries 9–11). *N*-Formylation reaction of aniline in the presence of 2.7 mol% of catalyst gave the best yield of the desired product. Notably, the presence of decreased the reaction rate (Table 1, entries 12–14).

The scope and limitations of the optimized reaction

Table 1. Optimization experiments for formylation of aniline



Entry	Molar ratio Aniline/HCO_2H	Catalyst	Cat (mol%)	Solvent	Temp. (°C)	Time (h/min)	Yield (%)
1	1/1	–	–	–	rt	5 h	90
2	1/1	PVA	5.4	–	rt	5 h	90
3	1/1	PVA-NH_2	5.4	–	rt	3.5 h	95
4	1/1	–	–	–	40	2.5 h	95
5	1/1	PVA	5.4	–	40	3 h	95
6	1/1	PVA-NH_2	5.4	–	40	15 min	95
7	1/2	PVA-NH_2	5.4	–	rt	1.5 h	95
8	1/2	PVA-NH_2	5.4	–	40	10 min	95
9	1/2	PVA-NH_2	2.7	–	40	10 min	95
10	1/1	PVA-NH_2	2.7	–	40	10 min	95
11	1/1	PVA-NH_2	1.3	–	40	30 min	95
12	1/1	PVA-NH_2	2.7	CH_2Cl_2	40	2 h	95
13	1/1	PVA-NH_2	2.7	CH_3CN	40	5 h	95
14	1/1	PVA-NH_2	2.7	MeOH	40	1 h/18 h	80/80

condition for *N*-formylation of various amines were evaluated. The results are presented in Table 2. *N*-Formylation of substituted anilines rapidly and efficiently irrespective of the substituents (Table 2, entries 1–12). Formylation of anilines containing electron-donating substituents such as CH_3, CH_2CH_3, OCH_3, were relatively fast than anilines with electron-withdrawing groups such as halogen and NO_2. *N*-Formylation of amines was chemoselective in bifunctional compounds containing OH/$CONH_2$ groups. (entries 13–14 and 20). This protocol was also successfully applied to primary and secondary aliphatic amines

Table 2. PVA-NH_2 catalyzed *N*-formylation of amines

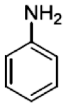
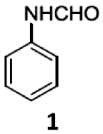
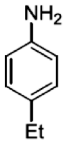
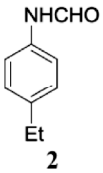
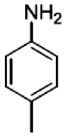
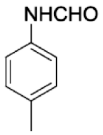
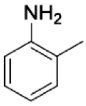
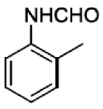
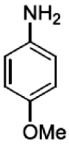
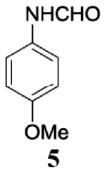
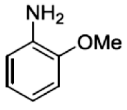
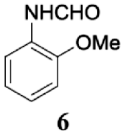
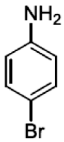
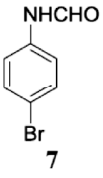
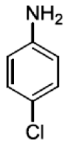
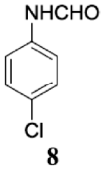
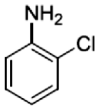
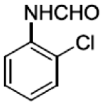
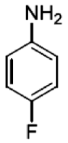
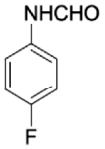
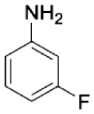
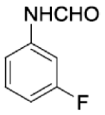
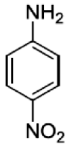
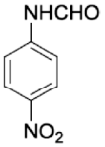
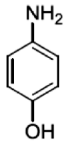
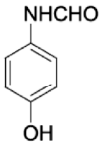
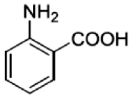
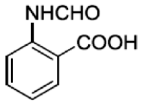
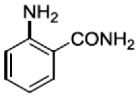
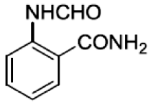
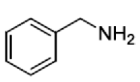
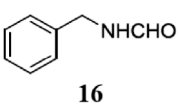
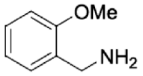
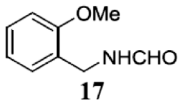
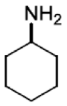
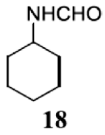
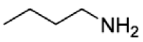
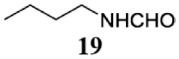
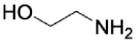
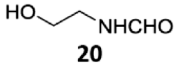
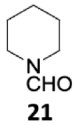
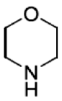
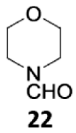
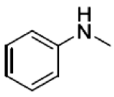
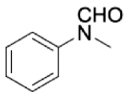
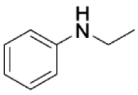
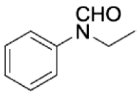
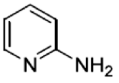
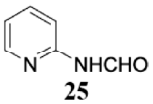
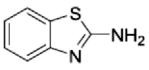
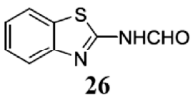
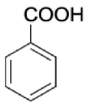
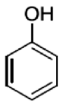
Entry	Substrate	Product	Time (min, h)	Isolated yield (%)
1		 **1**	10 min	95
2		 **2**	5 min	97
3		 **3**	5 min	98
4		 **4**	30 min	95
5		 **5**	5 min	95
6		 **6**	30 min	92
7		 **7**	90 min	98

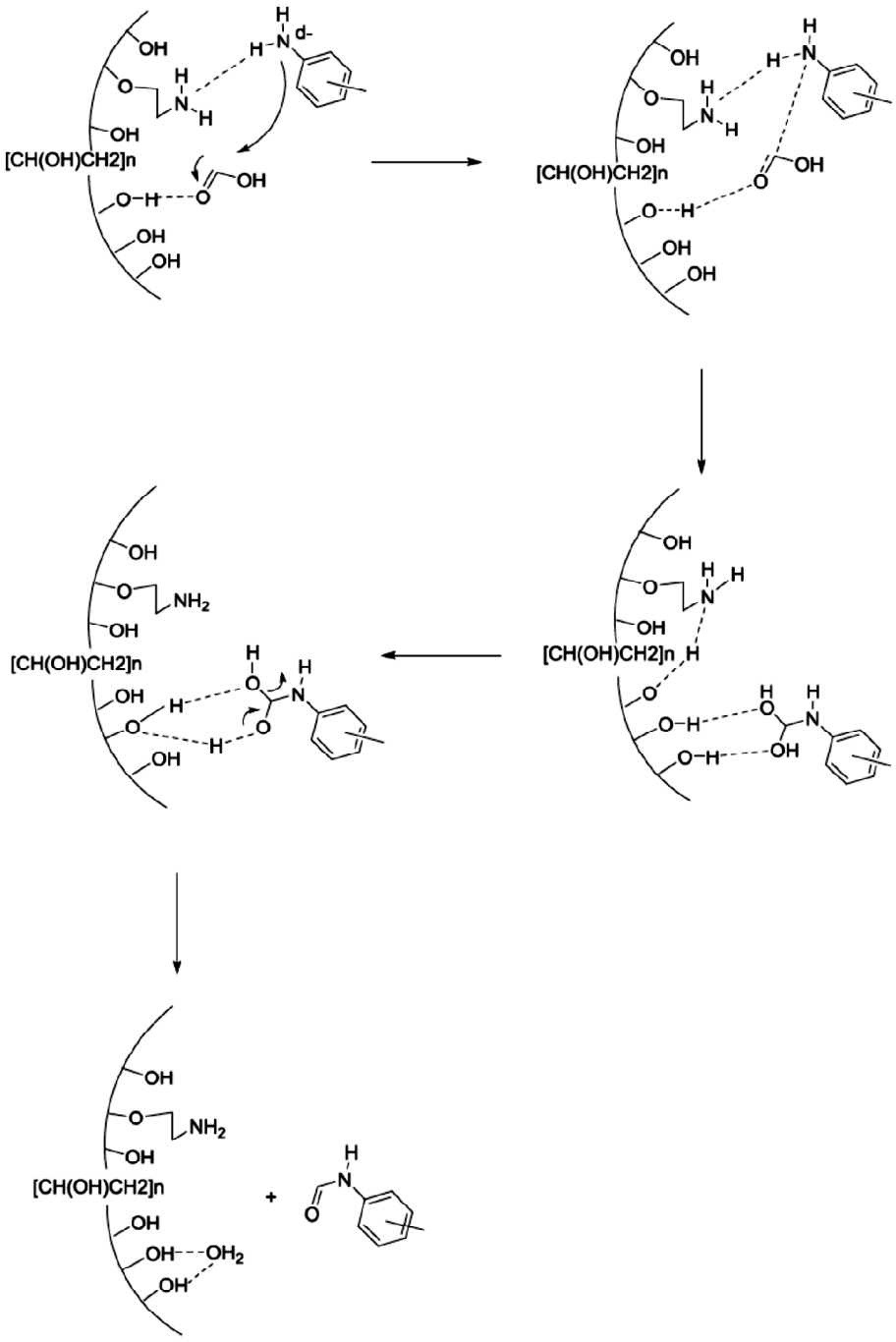
Table-2 (contd.)

8		 **8**	90 min	95
9		 **9**	120 min	95
10		 **10**	40 min	96
11		 **11**	30 min	95
12[a]		 **12**	120 min	95
13		 **13**	15 min	95
14[a]		 **14**	120/240 min	80/92
15[a]		 **15**	120/300 min	70/90
16		 **16**	5 min	98
17		 **17**	10 min	98
18		 **18**	Immediately	98
19		 **19**	Immediately	98
20		 **20**	10 min	95
21		 **21**	5 min	98
22		 **22**	10 min	95
23		 **23**	3 h	94
24		 **24**	3 h/4 h	80/96
25[a]		 **25**	20 min	97
26[a]		 **26**	30 min	98
27		No reaction	12 h	0
28		No reaction	12 h	0
29		No reaction	12 h	0

[a]Molar ratio of amine/formic acid : 1/3 was used.

(Table 2, entries 16–22). Secondary aromatic amines were good substrates for the reaction but because of steric effects, *N*-formylation was rather slow (Table 2, entries 23–24). The PVA-NH_2 catalyzed *N*-formylation strategy was studied for *N*-formylation of some selected heteroaromatic amines which provided the desired products in excellent yields (Table 2, entries 25–26). *O*-Formylation of carboxylic acid, alcohol and phenol derivatives under these reaction conditions was not successful (Table 2, entries 27–29).

A tentative mechanism of the reaction is dedicated in Scheme 1.



Scheme 1

Catalyst re-usability was assessed in the *N*-formylation of aniline. To this end, the reaction was stopped after 10 min (i.e. at 100% conversion) and the catalyst removed by filtration and washed with methanol several times. Table 3 shows the results obtained after four re-use cycles. As can be seen, no significant loss of activity of the catalyst was observed.

Conclusion

A basic catalyst consisting of PVA-supported ethanolamine proved highly efficient in the *N*-formylation of aromatic and aliphatic amines. The reagents used are inexpensive and neither inert atmosphere nor dry solvent are required for the success of the reaction. Moreover, the catalyst is stable, non-hygroscopic and resistant to air and heat. The reaction work-up and purification of the products is straightforward and provides the corresponding *N*-formylated amine in excellent yields. The catalyst was re-used at least four times with no appreciable loss of reactivity.

Experimental

The products were purified by column chromatography. The purity determinations of the products were accomplished by TLC on silica gel polygram STL G/UV 254 plates. The melting points of products were determined with an Electrothermal Type 9100 melting point apparatus. The FT-IR spectra were recorded on an Avatar 370 FT-IR Therma Nicolet spectrometer. The NMR spectra were provided on Brucker Avance 400 MHz instruments in $CDCl_3$. Elemental analyses were performed using a Costech 4010 CHNS Elemental Analyzer instrument. Mass spectra were recorded with a Varian-MAT spectrometer model CH7A at 70 eV; in *m/z* (rel. %). Thermogravimetric analysis (TGA) and differential thermogravimetric (DTG) were performed on a Shimadzu Thermogavimetric Analyzer (TG-50) under air atmosphere. All of the products were known compounds and characterized by the IR and comparison of their melting points with known compounds. The structure of selected products was further confirmed by ^1H NMR spectroscopy and mass spectrometry.

Preparation of PVA-NH_2[38] :

Ethanolamine (10 mL) was added directly to commercially available polyvinyl alcohol with average molecular weight of 72000 Da (0.5 g) at 80 °C. After 18 h magnetically stirring, methanol (40 mL) was added to the reaction mixture. The solid was filtered off, washed with methanol (5 × 50). The pale yellow precipitate was refluxed with methanol (100 mL) for 18 h. The hot mixture was filtrated and dried in a stove at 50 °C for 24 h.

Characterization of PVA-NH_2 :

FT-IR spectroscopy :

The catalyst structure was defined by FT-IR spectroscopy. Fig. 1 illustrates the FT-IR spectra of the PVA and PVA-NH_2. The peaks at 3549 and 3338 cm^{-1} due to N–H stretching of immobilized NH_2 on polyvinyl alcohol. In the low frequency region, the presence of the weak N–H bending vibration at 1668 cm^{-1} confirms the incorporation of amino groups. The peak of the C–N stretching vibration is normally observed in the range of 1250–1020 cm^{-1}.

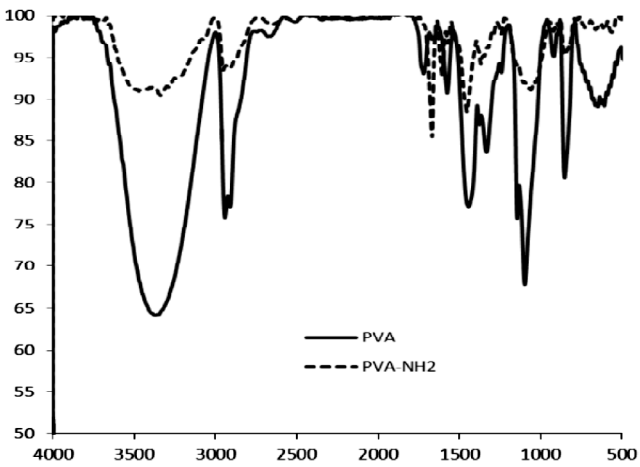


Fig 1. FT-IR spectra of PVA and PVA-NH_2.

Thermogravimetric analysis (TGA) :

Thermogravimetric studies of pure PVA and PVA-NH_2 at heating rate 10 °C /min was appeared in Fig. 2. It can be seen that both PVA and PVA-NH_2 exhibited a three-step degradation patterns. As PVA contain a small quantity of physically adsorbed water, the first stage of degradation represents the loss of physically adsorbed water, splitting or volatilization of small molecule and/or monomers (weight loss 4.6%, from 21–180 °C). On the other hand above 120 °C elimination of water could be resulted formation of C–C double bond, which consequently leads to formation of polyene. The second stage

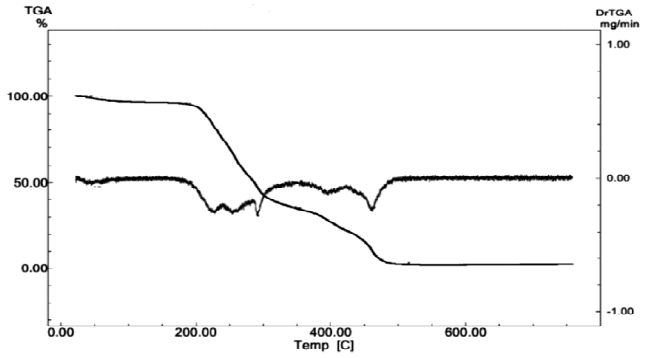


Fig 2. TGA /DTG thermograms of PVA.

(weight loss 54.5%, from 181–305 °C) corresponds to side chain decomposition. The higher value of weight loss in second stage was attributed to chemical degradation of some C–C bonds of polymer backbone. In the third stage (weight loss 36.3%, 306–474 °C) the complete decomposition of the main chain of polymer was occurred[39,40].

Typical procedure for N-formylation of aniline :

Aniline (0.093 g, 1 mmol) and PVA-NH_2 (0.100 g) were mixed thoroughly and treated with formic acid (0.046 g, 1 mmol) in an oil bath at 40 °C. The progress of reaction was monitored by TLC using *n*-hexane/ethyl acetate (1 : 1) as the solvent. After completion of the reaction the reaction mixture was allowed to cool, eluted with ethyl acetate, filtered and neutralized with saturated $NaHCO_3$ (5 ml). The organic layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure the crude product was recrystallized from Et_2O obtaining 0.114 g crystals (95% yield).

N-Phenylformamide (**1**) : Yield 95%; m.p. 47–48 °C (Lit. 46–48 °C)[41]; FT-IR (KBr) $\bar{\upsilon}$: 3267 (NH), 3133, 3058, 2982, 2874, 2778, 1691 (C=O), 1600, 1544, 1494, 1441, 1402, 1312, 1254, 1147, 1025, 902, 861, 753, 692, 654, 516 cm^{-1}; EIMS *m/z* (rel. int.) : 121 $[M]^+$ (100).

N-(4-Ethylphenyl)formamide (**2**) : Yield 97%; m.p. 43–44 °C (Lit. 42.5–44 °C)[42]; FT-IR (KBr) $\bar{\upsilon}$: 3195 (NH), 3115, 3043, 2964, 2920, 2865, 2761, 1685 (C=O), 1608, 1517, 1453, 1387, 1292, 1216, 1181, 1116, 1026, 963, 819, 762, 597, 541, 479 cm^{-1}; EIMS *m/z* (rel. int.) : 149 $[M]^+$ (100).

N-p-Tolylformamide (**3**) : Yield 98%; m.p. 49–51 °C (Lit. 49–52 °C)[43]; FT-IR (KBr) $\bar{\upsilon}$: 3191 (NH), 3105, 3033, 2918, 2869, 2774, 1695 (C=O), 1608, 1518, 1486, 1409, 1396, 1305, 1217, 1113, 1040, 937, 884, 814, 775, 707, 639, 597, 521, 473, 415 cm^{-1}; EIMS *m/z* (rel. int.) : 135 $[M]^+$ (80).

N-o-Tolylformamide (**4**) : Yield 95%; m.p. 58–59 °C (Lit. 58–59 °C)[44]; FT-IR (KBr) $\bar{\upsilon}$: 3250 (NH), 3207, 3046, 2876, 2782, 1686 (C=O), 1589, 1551, 1505, 1457, 1398, 1285, 1161, 1041, 886, 753, 642, 545, 450 cm^{-1}; EIMS *m/z* (rel. int.) : 135 $[M]^+$ (22).

N-(4-Methoxyphenyl)formamide (**5**) : Yield 95%; m.p. 60–62 °C (Lit. 62–64 °C)[45]; FT-IR (KBr) $\bar{\upsilon}$: 3245 (NH), 3191, 3128, 3049, 3000, 2968, 2937, 2893, 2837, 2779, 1677 (C=O), 1655, 1606, 1551, 1510, 1458, 1414, 1395, 1304, 1236, 1179, 1153, 1108, 1028, 874, 834, 807, 782, 694, 537, 516, 442, 413 cm^{-1}; EIMS *m/z* (rel. int.) : 151 $[M]^+$ (79), 152 $[M+1]^+$ (23).

N-(2-Methoxyphenyl)formamide (**6**) : Yield 92%; m.p. 79–80 °C (Lit. 80–81 °C)[46]; FT-IR (KBr) $\bar{\upsilon}$: 3253 (NH), 3190, 3129, 3044, 3006, 2961, 2917, 2877, 2833, 1694 (C=O), 1660, 1597, 1535, 1486, 1460, 1430, 1394, 1331, 1286, 1257, 1225, 1181, 1155, 1108, 1047, 1028, 922, 864, 813, 744, 724, 580, 506, 483, 449 cm^{-1}; EIMS *m/z* (rel. int.) : 151 $[M]^+$ (98).

N-(4-Bromophenyl)formamide (**7**) : Yield 98%; m.p. 115–117 °C (Lit. 115–119 °C)[41]; FT-IR (KBr) $\bar{\upsilon}$: 3284 (NH), 3257, 3184, 3113, 3050, 2871, 2771, 1669 (C=O), 1599, 1586, 1535, 1485, 1394, 1306, 1249, 1066, 1005, 878, 821, 772, 751, 514, 407 cm^{-1}; EIMS *m/z* (rel. int.) : 198 $[M-2]^+$ (100), 200 $[M]^+$ (100), 201 $[M+1]^+$ (12).

N-(4-Chlorophenyl)formamide (**8**) : Yield 95%; m.p. 98–100 °C (Lit. 99–100 °C)[43]; FT-IR (KBr) $\bar{\upsilon}$: 3295 (NH), 3260, 3192, 3120, 3059, 2998, 2893, 2790, 1686 (C=O), 1608, 1543, 1490, 1454, 1407, 1397, 1310, 1291, 1252, 1170, 1150, 1106, 1086, 1010, 932, 871, 836, 782, 767, 609, 517, 403 cm^{-1}; EIMS *m/z* (rel. int.) : 155 $[M]^+$ (31), 157 $[M+2]^+$ (7).

N-(2-Chlorophenyl)formamide (**9**) : Yield 95%; m.p. 77–78 °C (Lit. 76–80 °C)[47]; FT-IR (KBr) $\bar{\upsilon}$: 3251 (NH), 3115, 3042, 2990, 2901, 1670 (C=O), 1601, 1544, 1441, 1398, 1300, 1163, 1127, 1035, 939, 863, 739, 674, 537, 442 cm^{-1}; EIMS *m/z* (rel. int.) : 155 $[M]^+$ (86), 157 $[M+2]^+$ (15).

N-(4-Fluorophenyl)formamide (**10**) : Yield 96%; m.p. 63–65 °C (Lit. 63–65 °C)[48]; FT-IR (KBr) $\bar{\upsilon}$: 3179 (NH), 3077, 2983, 2941, 2867, 2778, 1649 (C=O), 1605, 1521, 1485, 1411, 1328, 1287, 1240, 1090, 1037, 830, 803, 755, 601, 520, 469 cm^{-1}; EIMS *m/z* (rel. int.) : 139 $[M]^+$ (25).

N-(3-Fluorophenyl)formamide (**11**) : Yield 95%; m.p. 63–64 °C (Lit. 63–64 °C)[5]; FT-IR (KBr) $\bar{\upsilon}$: 3279 (NH), 3223, 3166, 3091, 3051, 3007, 2884, 2831, 2786, 2708, 1693 (C=O), 1608, 1556, 1452, 1401, 1339, 1319, 1262, 1151, 1128, 1067, 996, 890, 817, 797, 693, 654, 504, 416 cm^{-1}; EIMS *m/z* (rel. int.) : 139 $[M]^+$ (35), 141 $[M+2]^+$ (71).

N-(4-Nitrophenyl)formamide (**12**) : Yield 95%; m.p. 194–196 °C (Lit. 194–196 °C)[44]; FT-IR (KBr) $\bar{\upsilon}$: 3263 (NH), 3215, 3086, 3047, 3018, 2888, 1688 (C=O), 1621, 1564, 1503, 1413, 1335, 1301, 1269, 1155, 1111, 853, 828, 752, 690, 538 cm^{-1}.

N-(4-Hydroxyphenyl)formamide (**13**) : Yield 95%; m.p. 134–137 °C (Lit. 135–137 °C)[41]; FT-IR (KBr) $\bar{\upsilon}$: 3321 (OH), 3190 (NH), 3101, 2888, 2802, 2671, 2614, 1673 (CO), 1566, 1513, 1400, 1317, 1253, 1167, 1106, 871, 828, 787, 709, 641, 529, 458, 431 cm^{-1}.

2-Formamidobenzoic acid (**14**) : Yield 92%; m.p. 168–169 °C (Lit. 167–169 °C)[33]; FT-IR (KBr) $\bar{\upsilon}$: 3436 (OH), 3209 (NH), 3068, 2923, 1686 (C=O carboxyl), 1611 (C=O formyl), 1590, 1507, 1442, 1388, 1291, 1157, 1043, 873, 848, 756, 702, 662, 642, 521, 485, 411 cm^{-1}; EIMS *m/z* (rel. int.) : 164 $[M-1]^+$ (24).

2-Formamidobenzamide (**15**) : Yield 90%; m.p. 118–120 °C (Lit. 119–122 °C)[49]; FT-IR (KBr) $\bar{\upsilon}$: 3378, 3207 (NH), 3096, 2892, 2802, 1704, 1629 (C=O), 1529, 1453, 1394, 1304, 1172, 1109, 1068, 866, 811, 750, 638, 538, 508 cm^{-1}.

N-Benzylformamide (**16**) : Yield 98%; m.p. 62–64 °C (Lit. 63–64 °C)[50]; FT-IR (KBr) $\bar{\upsilon}$: 3292 (NH), 3061, 3029, 1642 (C=O), 1568, 1495, 1451, 1384, 1338, 1300, 1141, 1073, 1037, 813, 738, 695, 628, 604, 574, 473, 463 cm^{-1}; EIMS *m/z* (rel. int.) : 135 $[M]^+$ (4).

N-[(2-Methoxyphenyl)methyl]formamide (**17**)[51] : Yield 98%; m.p. 86–90 °C; FT-IR (KBr) $\bar{\upsilon}$: 3200–2500 (NH), 2996, 2936, 2855, 2775, 2683, 1652 (C=O), 1576, 1500, 1461, 1371, 1333, 1252, 1169, 1111, 1034, 1012, 935, 773, 745, 693, 583, 433 cm^{-1}; EIMS *m/z* (rel. int.) : 167 $[M+2]^+$ (3), 165 $[M]^+$ (2.5).

N-Cyclohexylformamide (**18**) : Yield 98%; m.p. 30–31 °C (Lit. 30–31 °C)[52]; FT-IR (KBr) $\bar{\upsilon}$: 3390 (NH), 2931, 2852, 1616 (C=O), 1576, 1548, 1478, 1382, 1328, 1279, 1256, 1235, 1054, 1038, 889, 815, 714, 643, 616, 466, 408 cm^{-1}; EIMS *m/z* (rel. int.) : 127 $[M]^+$ (5).

N-Butylformamide (**19**) : Liquid[53]; yield 98%; FT-IR (neat) $\bar{\upsilon}$: 3412 (NH), 2955, 2921, 2851, 1640 (C=O), 1458, 1376, 1217, 1118, 1088, 771 cm^{-1}; EIMS *m/z* (rel. int.) : 100 $[M-1]^+$ (2).

N-(2-Hydroxyethyl)formamide (**20**) : Liquid[54]; yield 95%; FT-IR (neat) $\bar{\upsilon}$: 3551–2500, 1617 (C=O), 1378, 1345, 1071, 1017, 767, 473 cm^{-1}.

Piperidine-1-carbaldehyde (**21**) : Liquid[55]; yield 98%; FT-IR (neat) $\bar{\upsilon}$: 2925, 2863, 1661 (C=O), 1443, 1399, 1364, 1272, 1232, 1112, 1069, 1006, 931, 856, 768, 667, 595 cm^{-1}.

Morpholine-4-carbaldehyde (**22**) : Liquid[56]; yield 95%; FT-IR (neat) $\bar{\upsilon}$: 2974, 2925, 2863, 1658 (C=O), 1443, 1399, 1364, 1272, 1232, 1112, 1069, 1006, 931, 856, 768, 667, 595 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ : 7.98 (1H, s, CHO), 3.62 (2H, t, *J* 4.8 Hz, CH_2O), 3.58 (2H, t, *J* 4.8 Hz, CH_2O), 3.49 (2H, t, *J* 4.8 Hz, CH_2N), 3.33 (2H, t, *J* 4.8 Hz, CH_2N); ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 160.8 (C=O), 67.1 (C-O), 66.3 (C-O), 45.7 (C-N), 40.5 (C-N) .

N-Methyl-N-phenylformamide (**23**) : Liquid[57]; yield 94%; FT-IR (neat) $\bar{\upsilon}$: 3060, 2974, 2879, 2802, 1681 (C=O), 1596, 1497, 1413, 1350, 1313, 1270, 1116, 1029, 975, 820, 763, 697, 674, 536 cm^{-1}; EIMS *m/z* (rel. int.) : 135 $[M]^+$ (100).

N-Ethyl-N-phenylformamide (**24**) : Liquid[57]; yield 96%; FT-IR (neat) $\bar{\upsilon}$: 3064, 2976, 2935, 2874, 1679 (C=O), 1595, 1496, 1451, 1361, 1293, 1255, 1128, 1089, 1032, 815, 765, 698, 673, 549 cm^{-1}.

N-(Pyridin-2-yl)formamide (**25**) : Yield 97%; m.p. 67–69 °C (Lit. 69–70 °C)[58]; FT-IR (KBr) $\bar{\upsilon}$: 3363 (NH), 2786, 2700, 1689 (C=O), 1585, 1488, 1433, 1381, 1329, 1252, 1166, 1127, 978, 776, 683, 620, 553, 518, 441 cm^{-1}.

N-(Benzo[d]thiazol-2-yl)formamide (**26**) : Yield 98%; m.p. 252–255 °C (Lit. 254–256 °C)[59]; FT-IR (KBr) $\bar{\upsilon}$:

3411, 3292 (NH), 3119, 3083, 2827, 1628 (C=O), 1522, 1492, 1358, 1325, 1274, 1200, 1029, 882, 759, 694, 647, 515 cm^{-1}.

Acknowledgement

The authors gratefully acknowledge the partial support of this study by Ferdowsi University of Mashhad Research Council (Grant no. p/3/25246).

References

1. J. Martinez and J. Laur, *Synthesis* 1982, **1982**, 979.
2. B. C. Chen, M. S. Bednarz, R. Zhao, J. E. Sundeen, P. Chen, Z. Shen, A. P. Skoumbourdis and J. C. Barrish, *Tetrahedron Lett.,* 2000, **41**, 5453.
3. K. Kobayashi, S. Nagato, M. Kawakita, O. Morikawa and H. Konishi, *Chem. Lett.,* 1995, **24**, 575.
4. B. B. Lohray, S. Baskaran, B. S. Rao, B. Y. Reddy and I. N. Rao, *Tetrahedron Lett.,* 1999, **40**, 4855.
5. G. Petit, M. Kalnins, T. Liu, E. Thomas and K. Parent, *J. Org. Chem.*, 1961, **26**, 2563.
6. I. M. Downie, M. J. Earle, H. Heaney and K. F. Shuhaibar, *Tetrahedron*, 1993, **49**, 4015.
7. Y. Han and L. Cai, *Tetrahedron Lett.*, 1997, **38**, 5423.
8. F. Effenberger and J. Eichhorn, *Tetrahedron : Asymmetry*, 1997, **8**, 469.
9. S. Kobayashi and K. Nishio, *J. Org. Chem.*, 1994, **59**, 6620.
10. S. Kobayashi, M. Yasuda and I. Hachiya, *Chem. Lett.*, 1996, **25**, 407.
11. K. Iseki, S. Mizuno, Y. Kuroki and Y. Kobayashi, *Tetrahedron*, 1999, **55**, 977.
12. H. C. Sheehan and D. D. H. Yang, *J. Am. Chem. Soc.*, 1958, **80**, 1154.
13. P. Strazzoline, A. G. Giumanini and S. Cauci, *Tetrahedron*, 1990, **46**, 1081.
14. F. F. Blicke and C.-J. Lu, *J. Am. Chem. Soc.*, 1952, **74**, 3933.
15. J. Waki and J. Meienhofer, *J. Org. Chem.*, 1977, **42**, 2019.
16. F. M. F. Chen and N. L. Benoiton, *Synthesis*, 1979, **1979**, 709.
17. H. L. Yale, *J. Org. Chem.*, 1971, **36**, 3238.
18. L. Kisfaludy and O. Laszlo, *Synthesis*, 1987, **1987**, 510.
19. M. Nerveux, C. Bruneaum and P. H. Dixneuf, *J. Chem. Soc., Perkin Trans. 1*, 1991, 1197.
20. W. Duezek, J. Deutsch, S. Vieth and H.-J. Niclas, *Synthesis*, 1996, **1996**, 37.
21. M. Mihara, Y. Ishino, S. Minakata and M. Komatsu, *Synthesis*, 2003, **2003**, 2317.
22. P. G. Reddy, G. D. K. Kumar and S. Baskaram, *Tetrahedron*, 2000, **41**, 9149.
23. D. R. Hill, C.-N. Hsiao, R. Kurukulasuriya and S. J. Wittenberger, *Org. Lett.*, 2002, **4**, 111.
24. G. Brahmachari and S. Laskar, *Tetrahedron Lett.*, 2010, **51**, 2319.
25. A. Chandra Shekhar, A. Ravi Kumar, G. Sathaiah, V. Luke Paul, M. Sridhar and P. Shanthan Rao, *Tetrahedron Lett.*, 2009, **50**, 7099.
26. B. Krishnakumar and M. Swaminathan, *J. Mol. Catal. A : Chem.*, 2011, **334**, 98.
27. M. R. Mvthukur Bhojegowd, A. Nizam and M. A. Pasha, *Chin. J. Catal.*, 2010, **31**, 518.
28. J. G. Kim and D. O. Jang, *Synlett*, 2010, **2010**, 1231.
29. J. G. Kim and D. O. Jang, *Synlett*, 2010, **2010**, 2093.
30. M. Hosseni-Sarvari and H. Sharghi, *J. Org. Chem.*, 2006, **71**, 6652.
31. B. Das, K. Meddeboina, P. Balasubramanayam, V. D. Boyapati and K. D. Nandan, *Tetrahedron Lett.*, 2008, **49**, 2225.
32. L. D. Luca, G. Giacomelli, A. Porcheddu and M. Salaris, *Synlett*, 2004, **2004**, 2570.
33. M. I. Ansari, M. K. Hussain, N. Yadav, P. K. Gupta and K. Hajela, *Tetrahedron Lett.*, 2012, **53**, 2063.
34. L. Ma'mani, M. Sheykhan, A. Heydari, M. Faraji and Y. Yamini, *Appl. Catal. (A)*, 2010, **377**, 64.
35. S. P. Pathare, R. V. Sawant and K. G. Akamanchi, *Tetrahedron Lett.*, 2012, **53**, 3259.
36. P. T. Anastas and T. C. Williamson, in : "Green Chemistry, Frontiers in Benign Chemical Syntheses and Processes", Oxford University Press, California, 1998.
37. Q. Zhang, S. Zhang and Y. Deng, *Green Chem.*, 2011, **13**, 2619.
38. M. Mora, C. Jiménez-Sanchidrián, F. J. Urbano and J. R. Ruiz, *Catal. Lett.*, 2010, **134**, 131.
39. N. Othman, N. A. Azahari and H. Ismail, *Malaysia. Polymer J.*, 2011, **6**, 147.
40. O. W. Guirguis and M. T. H. Moselhey, *Nat. Sci.*, 2012, **4**, 57.
41. M. Hong and G. Xiao, *J. Fluorine Chem.*, 2013, **146**, 11.
42. K. B. Wiberg, T. M. Shryne and R. R. Kintner, *J. Am. Chem. Soc.*, 1957, **79**, 3160.
43. K. Bahrami, M. M. Khodaei, M. Sheikh Arabi and H. Targhan, *Tetrahedron Lett.*, 2013, **54**, 5064.
44. L. Ming and W. Zhao-Gang, *RSC Advances*, 2014, **4**, 1234.
45. E. J. Barreiro, C. A. M. Fraga, R. B. Lacerda, A. L. P. Miranda, N. C. Romeiro, L. L. da.Silva and C. K. F. de Lima, *Bioorg. Med. Chem.*, 2009, **17**, 74.

46. H. J. Rosenkranz, B. Winkler-Lardelli, H.-J. Hansen and H. Schmid, *Helv. Chim. Acta*, 1974, **57**, 887.
47. D. Habibi, M. Nasrollahzadeh, H. Sahebekhtiari and A. Taghipour, *Lett. Org. Chem.*, 2013, **10**, 209.
48. C. Adam, S. L. Cockroft, I. K. K. B. Mati and Muchowska, *J. Am. Chem. Soc.*, 2013, **135**, 9976.
49. D. T. Zentmyer and E. C. Wagner, *J. Org. Chem.*, 1949, **14**, 967.
50. R. M. Lanigan, T. D. Sheppard and P. Starkov, *J. Org. Chem.*, 2013, **78**, 4512.
51. M. Toshiaki and H. Rumi, *Bull. Chem. Soc. Jpn.*, 2010, **83**, 52.
52. R. G. Cooks and P. Sykes, *J. Chem. Soc. (C)*, 1968, 2864.
53. K. C. J. Paul, N. J. M. Roeland and D. Wiendelt, *J. Am. Chem. Soc.*, 1988, **110**, 6818.
54. H. Dai, P. R. Chang, F. Peng, J. Yu and X. Ma, *J. Polym. Res.*, 2009, **16**, 529.
55. K. Masato, N. Ryoji, T. Masaki and T. Hidemasa, *Bull. Chem. Soc. Jpn.,* 1996, **69**, 1695.
56. R. Malakooti, S. Sobhani, N. Razavi, S. Shafiei and R. Mokhtari, *Collect. Czech. Chem. Commun.*, 2011, **76**, 1979.
57. J. Ning, S. Tao, W. Guolin, X. Zejun, Z. Chun, Z. Liangren and J. Ning, *Org. Lett.*, 2012, **14**, 2362.
58. W. L. F. Armarego, *J. Chem. Soc.*, 1965, 2778.
59. S. Claude, R. Tabacchi, L. Duc, R. Fuchs and K.-J. Boosen, *Helv. Chim. Acta*, 1980, **63**, 682.