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Research Paper

A Rapid microwave assisted synthesis of novel 1,4-dihydropyridines derivatives under aqueous medium

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Abstract: An environment friendly synthesis of 1,4-dihydropyridine derivatives was developed by one pot multi component reaction of pyrazole aldehyde, EAA/MAA, 3-amino crotononitrile and Fe⁺³ montmorillonite clay K-10/ HY-zeolite under microwave irradiation in aqueous medium. The structures of all synthesized compounds were well characterized by Mass, FT-IR, ¹H NMR and elemental analysis.

Introduction

In recent years, an increasing interest has been persistent on the synthesis of 1,4-dihydropyridine compounds due to their remarkable biological activity.^[1] 1,4-Dihydropyridine substance frame works forming an vital class of Ca⁺² channel blockers such as Nifedipin and Amlodipine which are clinically significant Anti hypertensive drugs.^[2] 1,4-Dihydropyridines were first synthesized by Hantzsch^[3] using a ketoester, aldehydes and ammonia under reflux in methanol or ethanol which takes longer time with low yields.^[5-6] Over the few years a great variety of 1,4-dihydropyridines have been synthesized that have different substitutions on C₃ and C₅ positions of DHP ring^[4]

various procedures, likes microwaves^[7] ionic liquids^[8] high temperature at reflux^[9] TMSCl-NaI^[10] InCl₂^[11] I₂^[12] Baker's yeast^[13] catalysts^[14] and metal triflates.^[15] Even though a large number of modified methods have been reported^[16] under improved conditions, most of the reported methods suffer from some drawbacks like unsatisfactory yields, high temperature, harsh reaction conditions, long reaction time and extensive workup procedure.^[17] Thus, the development of a method for the preparation of 1,4-dihydropyridine derivatives is an active area of research and there is a scope for further improvement towards milder reaction conditions and higher product yields. The 1,4-dihydropyridines having dicyano groups at the 3 & 5 positions, various symmetric and asymmetric DHPs have been reported in the literature.^[18] Earlier, we have reported 1,4-

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dihydropyridine derivatives by conventional methods using benzoyl acetone, aldehyde and ammonium acetate in methanol which exhibits potent MDR reversal activity in tumour cell lines.^[19] In addition, the structures of DHPs containing dicyano at 3 & 5 position were established by x-ray study.^[20] Moreover, pyrazole framework containing compounds are well known for its antimicrobial^[21] anti-inflammatory^[21] analgesic^[21] anti HIV, anticancer and hypoglycaemic activities.^[22] Numerous, pyrazoles are utilize as insecticides and pesticides due to their herbicidal and fungicidal activity.^[23] Recently, pyrazoles containing aryl substituted emerged as p38 Kinase inhibitors, antiparasitic activities.^[24]

Materials and Methods

All Melting points of the synthesized compounds were recorded by open capillary method and are uncorrected. Formation of the compounds was routinely checked by TLC on silica gel-G plates of 0.5 mm thickness and spots were located by iodine and UV. All the reaction was carried out in **Q-pro-M** microwave synthesizer. The IR spectra were recorded on a **Shimadzu FT-IR-8400** instrument using KBr pellet method. Mass spectra were recorded on Shimadzu **GC-MS-QP-2010** model using Direct Injection Probe technique. ¹H NMR was determined in CDCl₃/DMSO solution on a **Bruker Ac 400 MHz** spectrometer. Elemental analysis of the all the synthesized compounds were carried out on Elemental **Vario EL III Carlo Erba 1108** model and the results are in agreements with the structures assigned.

Experimental

All the pyrazole aldehyde derivatives were prepared by reported method.^[25] A mixture of pyrazole aldehyde (0.01mol), 3-amino

crotonitrile (0.01mol) and Methyl acetoacetate or Ethyl acetoacetate (0.01mol) and HY-zeolite/ Fe⁺³ K-10 montmorillonite clay in 10 ml water was subjected to **Q-pro microwave** synthesizer for appropriate time in a flat bottom stoppered flask. The progress and the completion of reaction were checked by silica gel-G F₂₅₄ thin layer chromatography using ethyl acetate: hexane (3:2) as a mobile phase. The solid product was obtained after cooling and then filtered and washed first with glacial acetic acid and then with hexane.

Result and Discussion

Initially, we have developed a proficient and environment friendly methodology for the synthesis of DHPs. We observed in our studies that by the reaction of aldehyde, 3-amino crotonitrile, EAA/MAA in water under reflux without catalysts takes almost 48 hrs with poor yields. To improve the yield and reaction time, we have taken two catalyst HY-zeolite/ Fe⁺³ K-10 montmorillonite clay and performed the reaction with various pyrazole aldehydes, EAA/MAA, 3-amino crotonitrile in water under microwave irradiation. It was observed that the reaction time was shorter with high yield in Fe⁺³ K-10 montmorillonite clay as compairs to HY-zeolite. (**Table.1**)

Conclusion

In conclusion, we have exhibit green protocol for the synthesis and cyclization reaction of pyrazole aldehydes, EAA/MAA, 3-amino crotonitrile in water. This method is rapid, high yielding, environment friendly and water is easily available green solvent.

Spectral Data

Methyl 5-cyano-1,4-dihydro-2,6-dimethyl-4-(1,3-diphenyl-1*H*-pyrazol-4-yl)pyridine-3-carboxylate (5a): MP: 182-184 °C; IR (cm⁻¹): 3489, 3367, 3198, 2974, 2897, 2332, 2260, 1707, 1660, 1587, 1519, 1435, 1356, 1282, 744, 688. MS: m/z = 426.17; ¹H NMR (DMSO-d₆) δ ppm: 2.14(s, 6H), 2.58(s, 3H), 4.91(s, 1H), 6.91-6.99(d, 2H), 7.20-7.22(t, 2H), 7.29-7.31(t, 1H), 7.45-7.49(t, 2H), 7.60-7.62(d, 1H), 7.71-7.73(d, 2H), 7.95(s, 1H), 8.74(s, 1H). MS: m/z: 410.17; Anal. Calcd. for C₂₅H₂₂N₄O₂: C, 73.15; H, 5.40; N, 13.65; O, 7.80; Found: C, 73.06; H, 5.36; N, 13.61; O, 7.79(%).

Methyl 5-cyano-1,4-dihydro-2,6-dimethyl-4-(1-phenyl-3-*p*-tolyl-1*H*-pyrazol-4-yl)pyridine-3-carboxylate (5b): MP: 198-200 °C; IR (cm⁻¹): 3469, 3307, 3191, 2984, 2857, 2312, 2250, 1727, 1650, 1577, 1509, 1455, 1366, 1289, 749, 698. MS: m/z = 424.49; ¹H NMR (DMSO-d₆) δ ppm: 2.16(s, 6H), 2.50(s, 3H), 3.15(s, 3H), 4.81(s, 1H), 7.28-7.32(t, 2H), 7.33-7.38(t, 1H), 7.47-7.51(t, 2H), 7.64-7.66(d, 2H, *J*=8.0 Hz), 7.73-7.75(d, 2H, *J*=8.0 Hz), 7.94(s, 1H), 8.77(s, 1H). Anal. Calcd. for C₂₆H₂₄N₄O₂: C, 73.56; H, 5.70; N, 13.20; O, 7.54 Found: C, 73.49; H, 5.60; N, 13.19; O, 7.48(%).

Methyl 4-(3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-5-cyano-1,4-dihydro-2,6-dimethylpyridine-3-carboxylate (5c): MP: 178-180 °C; IR (cm⁻¹): 3459, 3347, 3190, 2984, 2898, 2342, 2262, 1707, 1662, 1587, 1509, 1455, 1346, 1292, 1241, 1108, 745-689. MS: m/z = 444(M⁺), 446(M²⁺); ¹H NMR (DMSO-d₆) δ ppm: 2.19(s, 6H), 2.59(s, 3H), 4.92(s, 1H), 6.93-6.95(d, 2H, *J*=8.0 Hz), 7.21-7.24(t, 2H), 7.28-7.34(t, 1H), 7.49-7.52(t, 2H), 7.79-7.81(d, 2H, *J*=8.0 Hz), 7.98(s, 1H), 8.84(s, 1H). Anal. Calcd. for C₂₅H₂₁ClN₄O₂: C, 67.49; H, 4.76; N,

12.59; O, 7.19 Found: C, 76.29; H, 5.04; N, 18.50(%).

Methyl 5-cyano-1,4-dihydro-2,6-dimethyl-4-(3-(4-nitrophenyl)-1-phenyl-1*H*-pyrazol-4-yl)pyridine-3-carboxylate (5d): MP: 202-204 °C; IR (cm⁻¹): 3459, 3347, 3188, 2954, 2857, 2342, 2240, 1717, 1669, 1581, 1545, 1518, 1445, 1366, 1272, 749, 689. MS: m/z = 455.47; ¹H NMR (DMSO-d₆) δ ppm: 2.21(s, 6H), 2.68(s, 3H), 4.89(s, 1H), 6.98-7.00(d, 2H, *J*=8.0 Hz), 7.21-7.25(t, 2H), 7.31-7.36(t, 1H), 7.49-7.53(t, 2H), 7.74-7.76(d, 2H, *J*=8.0 Hz), 7.85(s, 1H), 8.78(s, 1H). Anal. Calcd. for C₂₅H₂₁N₅O₄: C, 65.93; H, 4.65; N, 15.38; O, 14.05 Found: C, 65.84; H, 4.55; N, 15.30; O, 14.01(%).

Methyl 5-cyano-1,4-dihydro-4-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-2,6-dimethylpyridine-3-carboxylate (5e): MP: 208-210 °C; IR (cm⁻¹): 3611, 3581, 3489, 3367, 3198, 2974, 2897, 2332, 2260, 1707, 1660, 1587, 1519, 1435, 1356, 1282, 1250, 1117, 744, 688. MS: m/z = 426.17; ¹H NMR (DMSO-d₆) δ ppm: 2.24(s, 6H), 3.48(s, 3H), 4.81(s, 1H), 5.45(s, 1H), 6.90-6.93(d, 1H), 7.22-7.26(t, 2H), 7.39-7.41(t, 1H), 7.49-7.54(t, 2H), 7.62-7.65(d, 1H), 7.77-7.80(d, 2H), 7.85(s, 1H), 8.84(s, 1H). Anal. Calcd. for C₂₅H₂₂N₄O₃: C, 70.41; H, 5.20; N, 13.14; O, 11.25 Found: C, 70.33; H, 5.19; N, 13.13; O, 11.13(%).

Methyl 5-cyano-1,4-dihydro-4-(3-(2-methoxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-2,6-dimethylpyridine-3-carboxylate (5f): MP: 192-194 °C; IR (cm⁻¹): 3574, 3473, 3429, 3402, 3203, 3097, 2999, 2347, 2196, 1780, 1658, 1508, 1464, 1375, 1323, 1247, 1134, 1022, 758, 709. MS: m/z = 440.49; ¹H NMR (DMSO-d₆) δ ppm: 1.83(s, 6H), 3.34 (s, 3H), 3.72 (s, 3H), 4.32 (s, 1H), 6.98-7.08 (m, 2H), 7.21-7.24(d, 1H), 7.27-7.32(t, 1H), 7.37-7.42(t, 1H), 7.47-7.52(t,

2H), 7.86-7.88(d, 2H, $J=8.0$ Hz), 8.52(s, 1H), 9.11(s, 1H). Anal. Calcd. for $C_{26}H_{24}N_4O_3$: C, 70.89; H, 5.49; N, 12.72; O, 10.90 Found: C, 70.71; H, 5.47; N, 12.65; O, 10.90(%).

Methyl 5-cyano-1,4-dihydro-2,6-dimethyl-4-(3-(3-nitrophenyl)-1-phenyl-1*H*-pyrazol-4-yl)pyridine-3-carboxylate (5g): MP: 188-190 °C; IR (cm^{-1}): 3479, 3368, 3192, 2934, 2893, 2331, 2261, 1717, 1661, 1577, 1530, 1518, 1445, 1354, 1283, 1241, 1101, 745, 689. MS: $m/z = 455.16$; 1H NMR (DMSO- d_6) δ ppm: 2.14(s, 6H), 2.48(s, 3H), 4.81(s, 1H), 6.94-6.98(d, 2H), 7.22-7.25(t, 2H), 7.32-7.36(t, 1H), 7.49-7.55(t, 2H), 7.62-7.67(d, 1H), 7.85(s, 1H), 8.84(s, 1H). Anal. Calcd. for $C_{25}H_{21}N_5O_4$: C, 65.93; H, 4.65; N, 15.38; O, 14.05 Found: C, 65.84; H, 4.56; N, 15.31; O, 14.07(%).

Methyl 5-cyano-4-(3-(4-fluorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-1,4-dihydro-2,6-dimethylpyridine-3-carboxylate (5h): MP: 172-174 °C; IR (cm^{-1}): 3509, 3357, 3190, 2984, 2898, 2330, 2261, 1717, 1661, 1589, 1518, 1434, 1354, 1281, 1241, 1108, 745, 689. MS: $m/z = 428$ (M^+), 430 (M^{+2}); 1H NMR (DMSO- d_6) δ ppm: 2.34(s, 6H), 2.59(s, 3H), 4.81(s, 1H), 6.91-6.99(d, 2H, $J=8.0$ Hz), 7.22-7.26(t, 2H), 7.39-7.41(t, 1H), 7.55-7.59(t, 2H), 7.73-7.75(d, 2H, $J=8.0$ Hz), 7.85(s, 1H), 8.94(s, 1H). Anal. Calcd. for $C_{25}H_{21}FN_5O_2$: C, 70.08; H, 4.94; N, 13.08; O, 7.47 Found: C, 70.03; H, 4.91; N, 13.07; O, 7.41(%).

Ethyl 5-cyano-1,4-dihydro-2,6-dimethyl-4-(1,3-diphenyl-1*H*-pyrazol-4-yl)pyridine-3-carboxylate (5i): MP: 206-208 °C; IR (cm^{-1}): 3479, 3368, 3188, 2978, 2887, 2342, 2250, 1727, 1665, 1581, 1529, 1425, 1346, 1272, 1245, 1117, 689. MS: $m/z = 424.19$; 1H NMR (DMSO- d_6) δ ppm: 1.39(t, 3H), 2.34(s, 6H), 2.78(q, 2H), 4.98(s, 1H), 6.91-6.96(d, 2H), 7.22-7.26(t, 2H), 7.39-7.41(t,

1H), 7.47-7.50(t, 2H), 7.62-7.64(d, 1H), 7.70-7.73(t, 2H), 7.85(s, 1H), 8.84(s, 1H). Anal. Calcd. for $C_{26}H_{24}N_4O_2$: C, 73.56; H, 5.70; N, 13.20; O, 7.54 Found: C, 73.43; H, 5.61; N, 13.07; O, 7.49(%).

Ethyl 5-cyano-1,4-dihydro-2,6-dimethyl-4-(1-phenyl-3-*p*-tolyl-1*H*-pyrazol-4-yl)pyridine-3-carboxylate (5j): MP: 222-224 °C; IR (cm^{-1}): 3479, 3387, 3158, 2975, 2877, 2352, 2268, 1717, 1669, 1589, 1529, 1445, 1346, 1283, 1244, 1109, 748, 689. MS: $m/z = 438.52$; 1H NMR (DMSO- d_6) δ ppm: 1.48(t, 3H), 2.16(s, 6H), 2.45(s, 3H), 2.81(q, 2H), 4.92(s, 1H), 6.97-6.99(d, 2H, $J=8.0$ Hz), 7.25-7.29(t, 2H), 7.41-7.46(t, 1H), 7.51-7.56(t, 2H), 7.72-7.74(d, 2H, $J=8.0$ Hz), 7.98(s, 1H), 8.84(s, 1H). Anal. Calcd. for $C_{27}H_{26}N_4O_2$: C, 73.95; H, 5.98; N, 12.78; O, 7.30 Found: C, 73.83; H, 5.91; N, 12.77; O, 7.29(%).

Ethyl 4-(3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-5-cyano-1,4-dihydro-2,6-dimethylpyridine-3-carboxylate (5k): MP: 212-214 °C; IR (cm^{-1}): 3489, 3389, 3159, 2979, 2879, 2332, 2288, 1707, 1679, 1569, 1529, 1455, 1356, 1282, 1245, 1119, 749, 687. MS: $m/z = 458$ (M^+), 460 (M^{+2}); 1H NMR (DMSO- d_6) δ ppm: 1.49(t, 3H), 2.44(s, 6H), 2.88(q, 2H), 4.99(s, 1H), 6.97-6.99(d, 2H, $J=8.0$ Hz), 7.23-7.27(t, 2H), 7.31-7.35(t, 1H), 7.49-7.55(t, 2H), 7.75-7.77(d, 2H, $J=8.0$ Hz), 7.97(s, 1H), 8.84(s, 1H). Anal. Calcd. for $C_{26}H_{23}ClN_4O_2$: C, 68.04; H, 5.05; N, 12.21; O, 6.97 Found: C, 68.03; H, 5.01; N, 12.17; O, 6.94(%).

Ethyl 5-cyano-1,4-dihydro-2,6-dimethyl-4-(3-(3-nitrophenyl)-1-phenyl-1*H*-pyrazol-4-yl)pyridine-3-carboxylate (5l): MP: 188-190 °C; IR (cm^{-1}): 3489, 3397, 3168, 2985, 2878, 2352, 2278, 1707, 1689, 1586, 1520, 1539, 1435, 1345, 1284, 1245, 1108, 749, 687. MS: $m/z = 469.18$; 1H NMR (DMSO- d_6) δ ppm: 1.39(t, 3H), 2.24(s, 6H),

2.78(q, 2H), 4.93(s, 1H), 7.22-7.27(t, 2H), 7.31-7.34(t, 1H), 7.47-7.51(t, 2H), 7.64-7.68(d, 1H), 7.74-7.79(d, 2H), 7.97(s, 1H), 8.84(s, 1H), 9.02(s, 1H). Anal. Calcd. for C₂₆H₂₃N₅O₄: C, 66.51; H, 4.94; N, 14.92; O, 13.63 Found: C, 66.43; H, 4.91; N, 14.87; O, 13.59(%).

Ethyl 5-cyano-1,4-dihydro-2,6-dimethyl-4-(3-(4-nitrophenyl)-1-phenyl-1*H*-pyrazol-4-yl)pyridine-3-carboxylate (5m): MP: 192-194 °C; IR (cm⁻¹): 3459, 3377, 3058, 2976, 2878, 2322, 2261, 1727, 1689, 1588, 1551, 1539, 1435, 1343, 1273, 1234, 1101, 738, 679. MS: m/z = 469.18; ¹H NMR (DMSO-d₆) δ ppm: 1.59(t, 3H), 2.24(s, 6H), 2.88(q, 2H), 4.71(s, 1H), 6.97-6.99(d, 2H, J=8.0 Hz), 7.30-7.35(t, 2H), 7.55-7.49(t, 2H), 7.70-7.72(d, 1H), 7.89-7.93(d, 2H, J=8.0 Hz), 7.85(s, 1H), 9.04(s, 1H). Anal. Calcd. for C₂₆H₂₃N₅O₄: C, 66.51; H, 4.94; N, 14.92; O, 13.63 Found: C, 66.43; H, 4.91; N, 14.87; O, 13.59(%).

Ethyl 5-cyano-1,4-dihydro-4-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-2,6-dimethylpyridine-3-carboxylate (5n): MP: 178-180 °C; IR (cm⁻¹): 3611, 3581, 3479, 3347, 3108, 2974, 2897, 2332, 2260, 1707, 1660, 1587, 1519, 1435, 1356, 1282, 1240, 1107, 744, 688. MS: m/z = 440.49; ¹H NMR (DMSO-d₆) δ ppm: 1.49(t, 3H), 2.34(s, 6H), 2.78(q, 2H), 4.71(s, 1H), 7.20-7.24(t, 2H), 7.25-7.30(t, 1H), 7.35-7.39(t, 2H), 7.61-7.64(d, 1H), 7.78-7.81(d, 2H), 7.99(s, 1H), 8.94(s, 1H), 9.04(s, 1H). Anal. Calcd. for C₂₆H₂₄N₄O₃: C, 70.89; H, 5.49; N, 12.72; O, 10.90 Found: C, 70.83; H, 5.51; N, 12.77; O, 10.89(%).

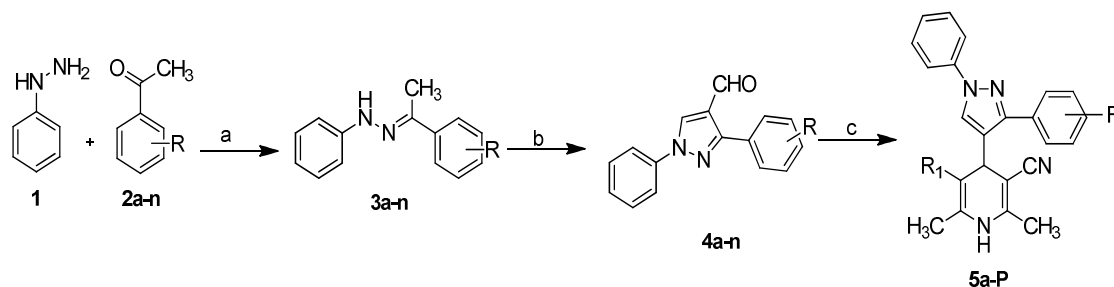
Ethyl 5-cyano-1,4-dihydro-4-(3-(2-methoxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-2,6-dimethylpyridine-3-carboxylate (5o): MP: 192-194 °C; IR (cm⁻¹): 3489,

3357, 3118, 2984, 2887, 2261, 2342, 1717, 1661, 1581, 1518, 1445, 1346, 1281, 1241, 1117, 744, 689. MS: m/z = 454.52; ¹H NMR (DMSO-d₆) δ ppm: 1.48(t, 3H), 2.04(s, 6H), 2.48(s, 3H), 2.68(q, 2H), 4.81(s, 1H), 7.30-7.36(t, 2H), 7.39-7.43(t, 1H), 7.55-7.59(t, 2H), 7.70-7.72(d, 1H), 7.79-7.83(d, 2H), 7.75(s, 1H), 8.94(s, 1H). Anal. Calcd. for C₂₇H₂₆N₄O₃: C, 71.35; H, 5.77; N, 12.33; O, 10.56 Found: C, 71.31; H, 5.61; N, 12.27; O, 10.49(%).

Ethyl 5-cyano-4-(3-(4-fluorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-1,4-dihydro-2,6-dimethylpyridine-3-carboxylate (5p): MP: 202-204 °C; IR (cm⁻¹): 3419, 3307, 3101, 2970, 2890, 2322, 2261, 1707, 1669, 1586, 1509, 1425, 1326, 1283, 1241, 1117, 745, 685. MS: m/z = 442 (M⁺), 444 (M⁺); ¹H NMR (DMSO-d₆) δ ppm: 1.45(t, 3H), 2.17(s, 6H), 2.78(q, 2H), 4.81(s, 1H), 6.97-6.99(d, 2H, J=8.0 Hz), 7.29-7.32(t, 2H), 7.55-7.59(t, 2H), 7.67-7.69(d, 1H), 7.71-7.73(d, 2H, J=8.0 Hz), 7.85(s, 1H), 8.84(s, 1H). Anal. Calcd. for C₂₆H₂₃FN₄O₂: C, 70.57; H, 5.24; N, 12.66; O, 7.23 Found: C, 70.53; H, 5.21; N, 12.77; O, 7.19(%).

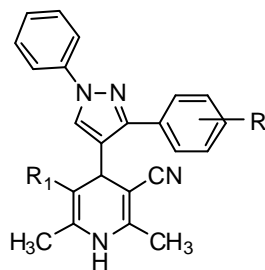
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Scheme 1. Synthesis of of alkyl 5-cyano-4-(1,3-diphenyl-1h-pyrazol-4-yl)-2,6-dimethyl-1,4-dihydropyridine-3-carboxylates. (a) Glacial CH_3COOH , EtOH, Stirring, 1 h (b) DMF- POCl_3 /70-80°C, reflux 5-6 h (c) 3-amino crotononitrile and EAA/MAA, Fe^{+3} K-10 montmorillonite clay/HY-zeolite, 10 ml water, MW(5-15 mins).

Table 1. Synthesis of 1,4-dihydropyridine derivatives in water under microwave condition(**5a-p**).



Code	Substitution		Time ^a (min)	Yield ^a %	Time ^b (min)	Yield ^b %
	R	R ₁				
5a	H	COOCH ₃	4	92	5	81
5b	4-CH ₃	COOCH ₃	6	87	7	80
5c	4-Cl	COOCH ₃	7	89	7	73
5d	4-NO ₂	COOCH ₃	9	91	9	82
5e	2-OH	COOCH ₃	7	89	7	80
5f	2-OCH ₃	COOCH ₃	8	87	9	77
5g	3-NO ₂	COOCH ₃	10	92	13	82
5h	4-F	COOCH ₃	6	89	8	79
5i	H	COOC ₂ H ₅	6	88	9	80
5j	4-CH ₃	COOC ₂ H ₅	6	86	8	76
5k	4-Cl	COOC ₂ H ₅	7	89	9	69
5l	3-NO ₂	COOC ₂ H ₅	12	89	17	79
5m	4-NO ₂	COOC ₂ H ₅	11	91	15	80
5n	2-OH	COOC ₂ H ₅	9	89	14	69
5o	2-OCH ₃	COOC ₂ H ₅	8	91	12	71
5P	4-F	COOC ₂ H ₅	8	89	14	69

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