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ARTICLE

Montnorillonite K-10 Supported Rapid Synthesis of 4-*N*-Pyrazolylpyrrolopyrimidines

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ABSTRACT

4-Hydrazinylpyrrolo[2,3-*d*]pyrimidines (**1**) have been reacted with different condensing reagents such as ethyl-2-methoxy acrylate and ethyl acetoacetate with and without the support of Montnorillonite K-10 to form respective 4-pyrazolylpyrrolopyrimidines (**3** and **5**) of synthetic and biological interests, where Montnorillonite K-10 supported synthesis of compounds **3** and **5** was found to be cleaner and faster.

KEYWORDS

4-Hydrazinylpyrrolopyrimidine, 4-*N*-Pyrazolylpyrrolopyrimidines, Ethyl acetoacetate, 2-Cyanoethylmethoxy acrylate, Montnorillonite K-10.

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INTRODUCTION

The present requirement of the chemist is to establish efficient synthesis pathways to resolve the environmental issues. Among Montnorillonite K-10 support has been widely used as efficient catalyst support to increase the potentiality of the reaction, providing simple, cleaner, faster and yield efficient reaction pathway. Further, montnorillonite K-10 can be recycled for further use without any activation [1,2]. Moreover, 4-hydrazinylpyrrolo-[2,3-*d*]pyrimidines (**1**) have been found versatile intermediate to undergo cyclization with reagent such as ethyl acetoacetate, triethyl orthofromate, formic acid, higher acids and nitrous acid to form variety of five membered heterocycles like pyrazole, isomeric triazole and tetrazole ring [3-8]. Synthesis of pyrazoles has been reported using hydrazines [9-19] and also by some other pathways [20,21]. In addition, Baricitinib and Ruxolitinib, involving pyrazolylpyrrolopyrimidine scaffold, found to be potent against rheumatoid arthritis and myelofibrosis [22-28].

Looking to the wide spectrum of biological and synthetic applications of pyrazolylpyrrolopyrimidines, we wished to synthesize novel derivatives of 4-pyrazolylpyrrolo[2,3-*d*]-pyrimidine [29-31]. Herewith the synthesis of 4-(*N*-pyrazolyl)-pyrazolo[2,3-*d*]pyrimidines have been reported from 4-hydrazinylpyrrolo[2,3-*d*]pyrimidines (**1**) by reacting it with 2-cyanoethylmethoxy acrylate (**2**) or ethyl acetoacetate (**4**) in boiling ethanol, in absence of Montnorillonite K-10 and in boiling isopropyl alcohol with Montnorillonite K-10 catalyzed reaction to form respective 4-*N*-pyrazolylpyrrolopyrimidines (**3** and **5**) of synthetic and biological interest.

EXPERIMENTAL

All the laboratory grade reagents were obtained commercially grade. The reactions were monitored by TLC, which was performed on Merck percolated plates (silica gel $60F_{254}$, 0.25 mm) and visualized by fluorescence quenching under UV light (254 nm). Melting points were determined by open capillary method and are uncorrected. The IR spectra were recorded on a Bruker 330-FT-IR spectrophotometer in the form of KBr pallets. ^{1}H NMR spectra were recorded (DMSO-d_6) on a Bruker (400 MHz). Chemical shift values are given in δ ppm. The mass spectra were recorded on LC-MS Agilent 1100 series.

General method for synthesis of ethyl 5-amino-1-(5,7-disubstituted 7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)-1*H*-pyrazole-4-carboxylates (3a-j) (Scheme-I)

Method I: A mixture of 4-hydrazinyl-5,7-disubstituted 7*H*-pyrrolo[2,3-*d*]pyrimidines (**1a-j**, 1 mmol) [3,5,7], (*Z*)-ethyl 2-cyano-3-methoxyacrylate (**2**, 1 mmol) and ethanol (5 mL) was refluxed for 4 h. The excess of solvent was removed under vacuum and the cold reaction mixture was poured on to the crushed ice. The white to off-white solid separated was filtered, washed with water and recrystallized from chloroform to give desired compounds **3a-j**.

Method II: A mixture of 4-hydrazinyl-5,7-disubstituted 7*H*-pyrrolo[2,3-*d*]pyrimidines (**1a-j**, 1 mmol), (*Z*)-ethyl 2-cyano-3-methoxyacrylate (**2**, 1 mmol), Montnorillonite K-10 (100 mg) and isopropyl alcohol (5 mL) was refluxed for 1 h, Montmorillonite K-10 was then removed by centrifugation, washed with 1-2 mL hot isopropyl alcohol and the decant was concentrated under vacuum to remove excess of solvent. The resultant reaction mass was treated with ice cold water. The white to off-white solid separated was filtered, washed with water and recrystallized from chloroform to give desired compounds **3a-j**.

Ethyl 5-amino-1-(5-(4-methoxyphenyl)-7-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)-1*H*-pyrazole-4-carboxylate (3a): m.p.: 155-156 ºC, Yield (method I: 74 %, method II: 85 %): IR (KBr, ν_{max}, cm^{-1}): 1712, 1521, ^{1}H NMR (DMSO-d_6): δ 1.1.33-1.37 (t, 3H, *J* = 7.2 Hz, CH_3), 3.87 (s, 3H, OCH_3), 4.28-4.33 (q, 2H, *J* = 7.2 Hz, CH_2), 5.69 (s, 2H, NH_2, D_2O exchangeable), 7.55-7.91 (m, 11H, Ar-H), 9.22 (s, H, Ar-H), MS: *m/z* 454 (M^+). Anal. (%) calcd. (found) for $C_{25}H_{22}N_6O_3$: C, 66.07 (66.02); H, 4.88 (4.85); N, 18.49 (18.55).

Ethyl 5-amino-1-(5-(4-chlorophenyl)-7-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)-1*H*-pyrazole-4-carboxylate (3b): m.p.: 160-161 ºC, Yield (method I: 81 %, method II: 90 %); IR (KBr, ν_{max}, cm^{-1}): 1698, 1504, ^{1}H NMR (DMSO-d_6): 1.34-1.38(t, 3H, *J* = 7.2 Hz, -CH_3), 4.31-4.36 (q, 2H, *J* = 7.2 Hz, CH_2), 5.71 (s, 2H, NH_2, D_2O exchangeable), 748-7.87 (m, 11H, Ar-H), 9.18 (s, H, Ar-H), MS: *m/z* 459 (M^+). Anal. (%) calcd. (found) for $C_{24}H_{19}N_6O_2Cl$: C, 62.81 (62.75); H, 4.17 (4.09); N, 18.31 (18.41).

Ethyl 5-amino-1-(5-phenyl-7-(4-methoxyphenyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)-1*H*-pyrazole-4-carboxylate (3c): m.p.: 164-165 °C, Yield (method I: 74 %, method II: 88 %); IR (KBr, ν_{max}, cm^{-1}): 1711, 1528, ^{1}H NMR (DMSO-d_6): δ 1.35-1.39(t, 3H, *J* = 6.8 Hz, CH_3), 3.88(s, 3H, OCH_3), 4.33-4.38 (q, 2H, *J* = 7.2 Hz, CH_2), 5.69(s, 2H, NH_2, D_2O exchangeable), 7.55-7.90 (m, 11H, Ar-H), 9.20 (s, H, Ar-H at C_3); MS: *m/z* 455 (M^+). Anal. (%) calcd. (found) for $C_{25}H_{22}N_6O_3$: C, 66.07 (66.02); H, 4.88 (4.86); N, 18.49 (18.53).

Ethyl 5-amino-1-(5,7-*bis*(4-methoxyphenyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)-1*H*-pyrazole-4-carboxylate (3d): m.p.: 170-171 ºC, Yield (method I: 78 %, method II: 89 %); IR (KBr, ν_{max}, cm^{-1}): 1693, 1511, ^{1}H NMR (DMSO-d_6): δ 1.31-1.34 (t, 3H, *J* = 7.2 Hz, CH_3), 3.86 (s, 6H, OCH_3), 4.30-4.35 (q, 2H, *J* = 6.8 Hz, CH_2), 5.65(s, 2H, NH_2, D_2O exchangeable), 7.62-7.90 (m, 10H, Ar-H), 9.19 (s, H, Ar-H at C3); MS: *m/z* 484 (M^+). Anal. (%) calcd. (found) for $C_{26}H_{24}N_6O_4$:C, 64.45 (64.42); H, 4.99 (4.97); N, 17.35 (17.39).

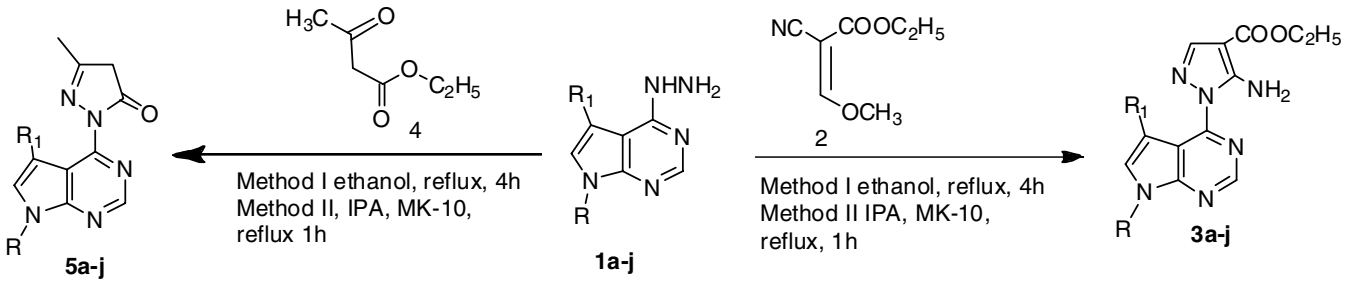
Ethyl 5-amino-1-(5-(4-chlorophenyl)-7-(4-fluorophenyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)-1*H*-pyrazole-4-carboxylate (3e): m.p.: 158-159 ºC, Yield (method I: 75 %, method II: 86 %); IR (KBr, ν_{max}, cm^{-1}): 1681, 1503, ^{1}H NMR (DMSO-d_6): δ 1.36-1.40 (t, 3H, *J* = 7.4 Hz, CH_3), 4.27-4.32 (q, 2H, *J* = 6.8 Hz, CH_2), 5.70(s, 2H, NH_2, D_2O exchangeable), 7.55-7.90 (m, 10H, Ar-H), 9.21 (s, H, Ar-H at C3); MS: *m/z* 477 (M^+). Anal. (%) calcd. (found) for $C_{24}H_{18}N_6O_2ClF$:C, 60.45 (60.41); H, 3.80 (3.74); N, 17.62 (17.69).

Ethyl 5-amino-1-(5,7-*bis*(4-chlorophenyl)-7*H*-pyrrolo-[2,3-*d*]pyrimidin-4-yl)-1*H*-pyrazole-4-carboxylate (3f): m.p.: 161-162 ºC, Yield (method I: 74 %, method II: 89 %); IR (KBr, ν_{max}, cm^{-1}): 1700, 1509, ^{1}H NMR (DMSO-d_6): δ 1.32-1.35 (t, 3H, *J* = 6.8 Hz, CH_3), 4.29-4.34 (q, 2H, *J* = 7.2 Hz, CH_2), 5.66(s, 2H, NH_2, D_2O exchangeable), 7.63-7.92 (m, 10H, Ar-H), 9.22 (s, H, Ar-H at C3); MS: *m/z* 493 (M^+). Anal. (%) calcd. for $C_{24}H_{18}N_6O_2Cl_2$: C, 58.43 (58.41); H, 3.68 (3.63); N, 17.03 (17.07).

Ethyl 5-amino-1-(5-phenyl-7-(4-bromophenyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)-1*H*-pyrazole-4-carboxylate (3g): m.p.: 166-167 ºC, Yield (method I: 76 %, method II: 87 %); IR (KBr, ν_{max}, cm^{-1}): 1701, 1524, ^{1}H NMR (DMSO-d_6): δ 1.33-1.37 (t, 3H, *J* = 7.2 Hz, CH_3), 4.28-4.33 (q, 2H, *J* = 6.4 Hz, CH_2), 5.67(s, 2H, NH_2, D_2O exchangeable), 7.51-7.88 (m, 11H, Ar-H), 9.24 (s, H, Ar-H at C3); MS: *m/z* 503 (M^+). Anal. (%) calcd. (found) for $C_{24}H_{19}N_6O_2Br$: C, 57.27 (57.21); H, 3.80 (3.74); N, 16.70 (16.79).

Ethyl 5-amino-1-(5-(4-chlorophenyl)-7-(4-bromophenyl)-7H-pyrrolo[2,3-*d*]pyrimidin-4-yl)-1*H*-pyrazole-4-carboxylate (3h): m.p.: 159-160 ºC, Yield (method I: 75 %, method II: 86 %); IR (KBr, ν_{max}, cm^{-1}): 1703, 1526, ^{1}H NMR (DMSO-d_6): δ 1.35-1.38 (t, 3H, *J* = 6.8 Hz, CH_3), 4.29-4.34 (q, 2H, *J* = 6.8 Hz, CH_2), 5.70(s, 2H, NH_2, D_2O exchangeable), 7.55-7.91 (m, 10H, Ar-H), 9.22 (s, H, Ar-H at C3); MS: *m/z* 538 (M). Anal. (%) calcd. (found) for $C_{24}H_{18}N_6O_2BrCl$: C, 53.60 (53.54); H, 3.37 (3.34); N, 15.63 (15.73).

Ethyl 5-amino-1-(5-(4-chlorophenyl)-7-(4-iodophenyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)-1*H*-pyrazole-4-carboxylate (3i): m.p.: 162-163 ºC, Yield (method I: 77 %, method II: 88 %); IR (KBr, ν_{max}, cm^{-1}): 1694, 1548, ^{1}H NMR (DMSO-d_6): δ 1.34-1.38(t, 3H, *J* = 6.8 Hz, CH_3), 4.28-4.34 (q, 2H, *J* = 7.2 Hz, CH_2), 5.68(s, 2H, NH_2, D_2O exchangeable), 7.55-7.91 (m, 10H, Ar-H), 9.23 (s, H, Ar-H at C3), MS: *m/z* 585 (M^+). Anal. (%) calcd. (found) for $C_{24}H_{18}N_6O_2Cl$:C, 49.29 (49.24); H, 3.10 (3.07); N, 14.37 (14.42).



5	R	R_1
5a	Ph	Ph
5b	Ph	4-OCH_3.Ph
5c	4-CH_3Ph	4-Cl.Ph
5d	4-OCH_3Ph	4-OCH_3Ph
5e	4-F.Ph	Ph
5f	4-F.Ph	4-Cl.Ph
5g	4-Cl.Ph	4-Cl.Ph
5h	4-Br.Ph	4-Cl.Ph
5i	4-I.Ph	4-OCH_3.Ph
5j	3-Cl,4-F.Ph	Ph

3	R	R_1
3a	Ph	4-OCH_3Ph
3b	Ph	4-Cl.Ph
3c	4-OCH_3Ph	Ph
3d	4-OCH_3Ph	4-OCH_3Ph
3e	4-F.Ph	4-Cl.Ph
3f	4-Cl.Ph	4-Cl.Ph
3g	4-Br.Ph	Ph
3h	4-Br.Ph	4-Cl.Ph
3i	4-I.Ph	4-Cl.Ph
3j	3-Cl,4-F.Ph	Ph

Scheme-I

Ethyl 5-amino-1-(5-phenyl-7-(3-flouro-4-chlorophenyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)-1*H*-pyrazole-4-carboxylate (3j): m.p.: 130-131 ºC, Yield (method I: 72 %, method II: 87 %); IR (KBr, ν_{max}, cm^{-1}): 1713, 1534, ^{1}H NMR (DMSO-d_6): δ 1.33-1.37(t, 3H, *J* = 7.2 Hz, CH_3), 4.28-4.33 (q, 2H, *J* = 6.8 Hz, CH_2), 5.72 (s, 2H, NH_2, D_2O exchangeable), 7.63-7.93 (m, 10H, Ar-H), 9.20 (s, H, Ar-H at C3), MS: *m/z* 477 (M^+). Anal. (%) calcd. (found) for $C_{24}H_{18}N_6O_2ClF$: C, 60.45 (60.42); H, 3.80 (3.76); N, 17.62 (17.69).

General method for synthesis of 1-(5,7-disubstituted 7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)-1*H*-pyrazol-5(4*H*)-one (5a-j) (Scheme-I)

Method I: A mixture of 4-hydrazinyl-5,7-disubstituted 7*H*-pyrrolo[2,3-*d*]pyrimidines (**1a-j**, 1 mmol), ethyl acetoacetate (**4**, 1 mmol) and ethanol (5 mL) was refluxed for 4 h. The cold reaction mixture was poured on to the crushed ice, white to off-white solid separated was filtered, washed with water and recrystallized from chloroform to give respective compound **5a-f**.

Method II: A mixture of 4-hydrazinyl-5,7-disubstituted 7*H*-pyrrolo[2,3-*d*]pyrimidines (**1a-j**, 1 mmol), ethyl acetoacetate (**4**, 1 mmol) Montnorillonite K-10 (100 mg) and isopropyl alcohol (5 mL) was refluxed for 1 h, then the clay was removed by centrifugation, washed with 1-2 mL hot isopropyl alcohol and the decant after filtration was concentrated under vacuum. The obtained mass was treated with crushed ice, white to off-white solid separated was filtered, washed with water and recrystallized from chloroform to give respective compound **5a-f**.

1-(5,7-Diphenyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)-3-methyl-1*H*-pyrazol-5(4*H*)-one (5a): m.p.: 218-220 ºC, Yield (method I: 74 %, method II: 86 %); IR (KBr, ν_{max}, cm^{-1}): 3360, 1718,1604,1500, ^{1}H NMR (DMSO-d_6): δ 0.90 (s, 3H, CH_3), 2.22 (s, 2H, CH_2), 7.55-7.92 (m, 12H, Ar-H); MS: *m/z* 367 (M^+). Anal. (%) calcd. (found) for $C_{25}H_{21}N_5O_4$: C, 71.92 (71.89); H, 4.66 (4.63); N, 19.06 (19.12).

1-(5-(4-Methoxyphenyl)-7-phenyl-7*H*-pyrrolo[2,3-*d*]-pyrimidin-4-yl)-3-methyl-1*H*-pyrazol-5(4*H*)-one (5b): m.p.: 188-189 ºC, Yield (method I: 79 %, method II: 89 %); IR (KBr, ν_{max}, cm^{-1}): 3392,1724, 1641,1540, ^{1}H NMR (DMSO-d_6): δ 0.91 (s, 3H, CH_3), 2.24 (s, 2H, CH_2), 3.87(s, 3H, OCH_3), 7.59-7.88 (m, 11H, Ar-H); MS: *m/z* 397 (M^+). Anal. (%) calcd. (found) for $C_{23}H_{19}N_5O_2$: C, 69.51 (69.48); H, 4.82 (4.79); N, 17.62 (17.68).

1-(5-(4-Chlorophenyl)-7-(*p*-tolyl)-7*H*-pyrrolo[2,3-*d*]-pyrimidin-4-yl)-3-methyl-1*H*-pyrazol-5(4*H*)-one (5c): m.p.: 192-194 ºC, Yield (method I: 75 %, method II, 86 %); IR (KBr, ν_{max}, cm^{-1}): 3384,1722, 1614,1500, ^{1}H NMR (DMSO-d_6): δ 0.93 (s, 3H, -CH_3), 2.20 (s, 2H, CH_2), 2.35 (s, 3H, CH_3), 7.52-7.89 (m, 10H, Ar-H); MS: *m/z* 416 (M^+). Anal. (%) calcd. (found) for $C_{23}H_{18}N_5OCl$: C, 66.43 (66.41); H, 4.36 (4.32); N, 16.84 (17.89).

1-(5,7-*bis*(4-Methoxyphenyl)-7*H*-pyrrolo[2,3-d]pyrimidin-4-yl)-3-methyl-1*H*-pyrazol-5(4*H*)-one (5d): m.p.: 179-180 ºC, Yield (method I: 80 %, method II: 90 %); IR (KBr, ν_{max}, cm^{-1}): 3354,1712, 1612,1510, ^{1}H NMR (DMSO-d_6): δ 0.92 (s, 3H, CH_3), 2.24 (s, 2H, CH_2), 3.88 (s, 6H, OCH_3), 7.57-7.90 (m, 10H, Ar-H); MS: *m/z* 427 (M^+). Anal. (%) calcd. (found) for $C_{24}H_{21}N_5O_3$: C, 67.44 (67.39); H, 4.95 (4.91); N, 16.38 (16.48).

1-(5-Phenyl-7-(4-fluorophenyl)-7*H*-pyrrolo[2,3-*d*]-pyrimidin-4-yl)-3-methyl-1*H*-pyrazol-5(4*H*)-one (5e): m.p.: 183-184 ºC, Yield (method I: 72 %, method II: 84 %); IR (KBr, ν_{max}, cm^{-1}): 3352, 1710, 1621,1518, ^{1}H NMR (DMSO-d_6): δ 0.90 (s, 3H, CH_3), 2.26 (s, 2H, CH_2), 7.55-7.94 (m, 11H, Ar-H); MS: *m/z* 385 (M^+). Anal. (%) calcd. (found) for $C_{22}H_{16}N_5OF$: C, 68.56 (68.52); H, 4.18 (4.15); N, 18.17 (18.23).

1-(5-(4-Chlorophenyl)-7-(4-fluorophenyl)-7*H*-pyrrolo-[2,3-*d*]pyrimidin-4-yl)-3-methyl-1*H*-pyrazol-5(4*H*)-one (5f): m.p.: 181-182 ºC, Yield (method I: 76 %, method II: 88 %); IR (KBr, ν_{max}, cm^{-1}): 3349,1731, 1609, 1521, ^{1}H NMR (DMSO-d_6): δ 0.93 (s, 3H, CH_3), 2.23 (s, 2H, CH_2), 7.49-7.86 (m, 10H, Ar-H); MS: *m/z* 420 (M^+). Anal. (%) calcd. (found) for $C_{22}H_{15}N_5OClF$: C, 62.94 (62.88); H, 3.60 (3.58), N, 16.68 (16.73).

1-(5,7-*bis*(4-Chlorophenyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)-3-methyl-1*H*-pyrazol-5(4*H*)-one (5g): m.p.: 189-190 ºC, Yield (method I: 72 %, method II: 84 %); IR (KBr, ν_{max}, cm^{-1}): 3373,1717, 1601, 1501, ^{1}H NMR (DMSO-d_6): δ 0.93 (s, 3H, CH_3), 2.23 (s, 2H, CH_2), 7.59-7.91 (m, 10H, Ar-H); MS: *m/z* 436 (M^+). Anal. (%) calcd. (found) for $C_{22}H_{15}N_5OCl_2$:C, 60.56 (60.54); H, 3.47 (3.43); N, 16.05 (16.09).

1-(5-(4-Chlorophenyl)-7-(4-bromophenyl)-7*H*-pyrrolo-[2,3-*d*]pyrimidin-4-yl)-3-methyl-1*H*-pyrazol-5(4*H*)-one (5h): m.p.: 191-192 ºC, Yield (method I: 78 %, method II: 89 %); IR (KBr, ν_{max}, cm^{-1}): 3399, 1720, 1609, 1509, ^{1}H NMR (DMSO-d_6): δ 0.92 (s, 3H, CH_3), 2.19 (s, 2H, CH_2), 7.63-7.93 (m, 10H, Ar-H); MS: *m/z* 481 (M^+). Anal. (%) calcd. (found) for $C_{22}H_{15}N_5OBrCl$:C, 54.96 (54.94); H, 3.14 (3.11); N, 14.57 (14.62).

1-(5-(4-Methoxyphenyl)-7-(4-iodophenyl)-7*H*-pyrrolo-[2,3-*d*]pyrimidin-4-yl)-3-methyl-1H-pyrazol-5(4*H*)-one (5i): m.p.: 167-168 ºC, Yield (method I: 72 %, method II: 83 %); IR (KBr, ν_{max}, cm^{-1}): 3378, 1710, 1656, 1520, ^{1}H NMR (DMSO-d_6): δ 0.91 (s, 3H, CH_3), 2.22 (s, 2H, CH_2), 3.87 (s, 3H, OCH_3) 7.59-7.92 (m, 10H, Ar-H); MS: *m/z* 523 (M^+). Anal. (%) calcd. (found) for $C_{23}H_{18}N_5O_2I$: C, 52.79 (52.76); H, 3.47 (3.44); N, 13.38 (13.43).

1-(5-Phenyl-7-(3-chloro-4-fluorophenyl)-7*H*-pyrrolo-[2,3-*d*]pyrimidin-4-yl)-3-methyl-1*H*-pyrazol-5(4*H*)-one (5j): m.p.: 133-134 ºC, Yield (method I: 71 %, method II: 83 %); IR (KBr, ν_{max}, cm^{-1}): 3368, 1712, 1600, 1510, ^{1}H NMR (DMSO-d_6): δ 0.91 (s, 3H, CH_3), 2.21 (s, 2H, CH_2), 7.55-7.90 (m, 10H, Ar-H); MS: *m/z* 420 (M^+). Anal. (%) calcd. (found) for $C_{22}H_{15}N_5OClF$: C, 62.94 (62.91); H, 8.44 (3.56); N, 14.68 (16.61).

RESULTS AND DISCUSSION

4-*N*-Pyrazolylpyrrolopyrimidines **3** and **5** were obtained in 72-80 % yield by conventional method I, while that of method II afforded increased by 10-15 %. Compounds **3** and **5** were obtained as white to off white coloured solid. The time required for method I was 4 h, that of method II was drastically reduced to 1 h. The catalyst was found efficient for three cycles without any activation. Structure elucidation of all the newly synthesized compounds was done on the basis of IR, NMR and mass spectroscopy In IR spectra of ester C=O of compound **3** appeared at 1732-1712 cm^{-1} while amino functionality gave signals at 3439-3295 cm^{-1}. In IR spectra of compound **5**, C=O of pyrazole ring observed at 1710-1693 cm^{-1}. ^{1}H NMR spectra of compound **3** gave triplet and quartet at δ 1.33 for 2H and at δ 4.28-4.39 for 3H due to ethyl protons of ester functionality. Amino protons appeared as broad singlet at δ 5.44-4.44 for 2H which were found to be D_2O exchangeable. ^{1}H NMR spectra of compound **5** gave peaks at δ 2.21-2.23 for ring methylene protons and δ 0.9-0.92 for methyl protons. Pyrazole proton at C3 was obtained at δ 9.2-9.23 in the case of compound **3**. Other aromatic protons of both the compounds obtained in the region δ 7.55-7.91. The obtained aminoester pyrazoles **3** and pyrazol-5-one **5** are the important building blocks for the construction of five and six membered nitrogen heterocycles as well as for Vilsmeier-Haack reaction, Knoevenagel condensation and Sciff's base formation [32-36]. In comparison, method II was found to be cleaner, faster and yield enhancing with reuse of catalyst.

Conclusion

In conclusion, a series of new ethyl 5-amino-1-(5,7-disubstituted 7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)-1*H*-pyrazole-4-carboxylates and 1-(5,7-disubstituted 7*H*-pyrrolo[2,3-d]pyrimidin-4-yl) 1*H*-pyrazol-5(4*H*)-ones of synthetic and biological importance from 4-hydrazinylpyrrolo[2,3-d]pyrimidines with and without Montnorillonite K-10 catalyst support were synthesized, where Montnorillonite K-10 catalyzed syntheses were found to be simple, rapid, cleaner and yield efficient.

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