Available online at www.ilcpa.pl

International Letters of Chemistry, Physics and Astronomy

2 (2015) 73-81 ISSN 2299-3843

Simple and Efficient Three Component One-pot Synthesis of Pyrazolo[1,5,*a*]pyrimidines

Anil R. Morabia, Yogesh T. Naliapara*

Department of Chemistry, Singhania University, Jhunjhunu - 333515, Rajsthan, India

*E-mail address: naliaparachem@gmail.com

ABSTRACT

A series of novel 5-(2-bromophenyl)-N-cyclohexyl-2-(methylthio)-6-nitro-7-phenyl-4,7-dihydropyrazolo[1,5-*a*]pyrimidine-3-carboxamides were synthesized by a one-pot reaction of 5-amino-N-cyclohexyl-3-(methylthio)-1H-pyrazole-4-carboxamide, 1-(2-bromophenyl)-2-nitroethanone and aryl aldehydes in the presence of boric acid in water at refluxing temperature. Structures of compounds were demonstrated by Fourier transform infrared, ^{1}H NMR, ^{13}C NMR and elemental analysis. The advantages of this method are mild reaction condition, good yields, and operational simplicity.

Keyword**:** Pyrazolopyrimidine; 5-amino-N-cyclohexyl-3-(methylthio)-1H-pyrazole-4-carboxamide; 1-(2-bromophenyl)-2-nitroethanone; mild reaction condition

1. INTRODUCTION

Pyrazolo[1,5-*a*]pyrimidines are important pharmaceutical targets.[1] They and related fused heterocycles are of interest as potential bioactive molecules. Pyrazole and pyrimidine derivatives have attracted the attention of organic chemists because of their biological and chemotherapeutic importance. They are known to exhibit a wide range of biological activities and act as cSRC kinase inhibitors involved with ischemic brain pathology,[2] cyclin dependent kinase 1 (CDK1) inhibitors,[3] HIV reverse transcriptase inhibitors,[4] CCR1 antagonists,[5] protein kinase inhibitors,[6] antibacterial,[7] and herbicides and fungicides.[8] In last decade various synthetic methods have been reported for the synthesis of pyrazole[1,5-*a*]pyrimidine which involves 5-aminopyrazole and 1,3-bis-electrophilic compounds, such as β-dicarbonyl, alkoxymethylene- β -dicarbonyl, and β -enaminone compounds[9,10] and several starting from fused aminopyrazole,[11] but few from non-fused aminopyrazoles.[12]

As part of our interest in novel biologically active nitrogen-containing heterocyclic scaffolds and continuing our studies on the application of cyclocondensation procedures, we are here describing the reaction between 5-amino-N-cyclohexyl-3-(methylthio)-1H-pyrazole-4-carboxamide **Int-3**, 1-(2-bromophenyl)-2-nitroethanone **Int-b** and various substituted aldehyde **3a-z** in order to obtain the fused pyrazolo[1,5-a]pirimidines (Figure-3) **AM-3a-z**.

2. EXPERIMENTAL

Thin-layer chromatography was accomplished on 0.2 mm precoated plates of silica gel G60 F254 (Merck). Visualization was made with UV light (254 and 365 nm) or with an iodine vapor. IR spectra were recorded on a FTIR-8400 spectrophotometer using DRS prob. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra were recorded on a Bruker AVANCE II spectrometer in $CDCl_3$ and DMSO. Chemical shifts are expressed in δ ppm downfield from TMS as an internal standard. Mass spectra were determined using direct inlet probe on a GCMS-QP 2010 mass spectrometer (Shimadzu). Solvents were evaporated with a BUCHI rotary evaporator. Melting points were measured in open capillaries and are uncorrected.

❖ Synthesis of 1-(2-bromophenyl)-2-nitroethanol (Int-a).

A mixture of 2-bromobenzaldehyde (0.1 mol), nitromethane (0.1 mol) and sodium acetate (0.2 mol) was stirred at RT for 24 h. The reaction was monitored by TLC. After completion of reaction, the solvent was removed under reduced pressure. The residue was poured in water and extracted with ethylacetate. The organic layer was dried and evaporated to afford Int-a in form of viscous oil. This oil was forwarded to next step without further purification.

❖ Synthesis of 1-(2-bromophenyl)-2-nitroethanone (Int-b).

To the suspension of $K_2Cr_2O_7$(24.8 mmol) in 15ml water, **Int-a** was added drop wise at 0 °C. This mixture was allowed to stir for 30 min and then solution of sulphuric acid (10 ml con H_2SO_4 and 6 ml water) was drop wise added at same temperature. Here the exothermicity was controlled by keeping addition rate very slow. After completion of addition reaction mixture was stirred for 15 min at the same temp. Color of the reaction mixture turns dark green then it was poured over crushed ice. Separated solid was immediately filtered before temperature rise and was dissolved in saturated $NaHCO_3$ solution. Filtration was again carried out to separate non-dissolved matter. Filtrate was acidified with con HCl. Precipitated solid was filtered and wash with distilled water. Crystallization was carried out from methanol to afford pure **Int-b**.

❖ Synthesis of 2-cyano-*N*-cyclohexylacetamide (Int-1).

In a 250 mL round bottom flask equipped with magnetic stirrer and thermometer was placed ethyl 2-cyanoacetate (0.25 mol), cyclohexaylamine (0.25 mol) and toluene (100 mL). The reaction mixture was heated up to 110-115 °C for 8 h. The progress of reaction was monitored by thin layer chromatography. The reaction mixture was cooled to room temperature and the solid product was filtered, washed with toluene to afford 90% yield.

❖ Synthesis of 2-cyano-*N*-cyclohexyl-3,3-bis(methylthio)acrylamide (Int-2).

A 100 mL conical flask equipped with magnetic stirrer and septum was charged with a solution of 2-cyano-*N*-cyclohexylacetamide (**1**), (10 mmol) in DMF (10 mL). Dry K_2CO_3 (10 mmol) was added and the mixture was stirred at RT for 2 h. CS_2 (30 mmol) was added and the mixture was stirred for an additional 2 h at room temperature. Then, methyl iodide (20 mmol) was added at 0-5 °C and the mixture was stirred for 4 h at room temperature. The progress of the reaction was monitored by thin layer chromatography. After completion of the

reaction, it was poured into 50ml cold water. The precipitated crude product was purified by filtration followed by crystallization from EtOH.

❖ **Synthesis of 5-amino-*N*-cyclohexyl-3-(methylthio)-1*H*-pyrazole-4-carboxamide (Int-3).**

To the solution of 2-cyano-*N*-cyclohexyl-3,3-bis(methylthio)acrylamide (**2**) (0.1 mol) in isopropyl alcohol (100 mL), hydrazine hydrate (0.1 mol) was added. The reaction mixture was heated to reflux for 2 h. After completion of the reaction, it was poured into 50 mL cold water. The precipitated crude product was purified by filtration followed by crystallization from EtOH.

❖ **General synthesis of pyrazolopyrimidine (AM-3a-z).**

In 50 ml RBF **Int-b** (2.5 mmol), **Int-3** (2.5 mmol) and substituted aldehyde were suspended in 20 ml water under stirring on magnetic stirrer. H_3BO_3 (2.5 mmol) was added in to the reaction mixture and reaction mixture was refluxed for 10 to 12 h. The reaction was monitored by TLC. After the completion of reaction, water was decanted and solid residue was triturated with methanol to afford pure compound.

Figure 1. Reaction scheme for **Int-b**.

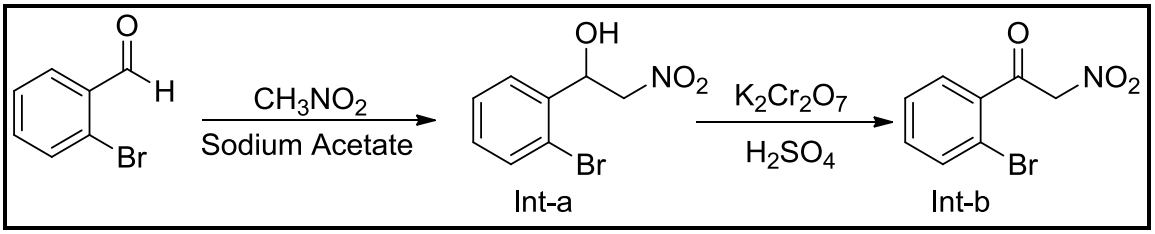


Figure 2. Reaction scheme for **Int-3**.

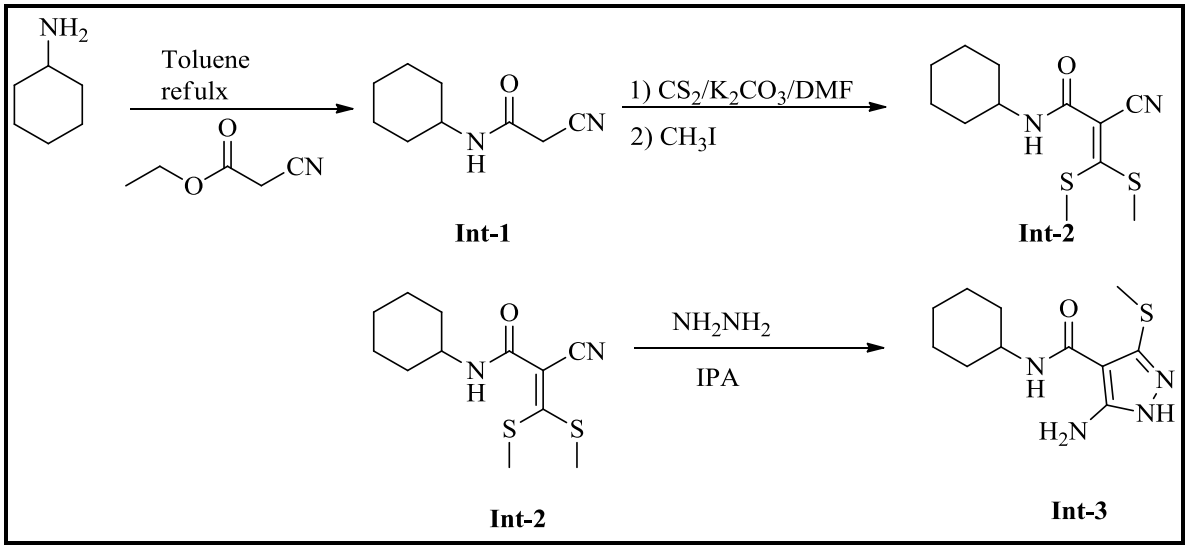
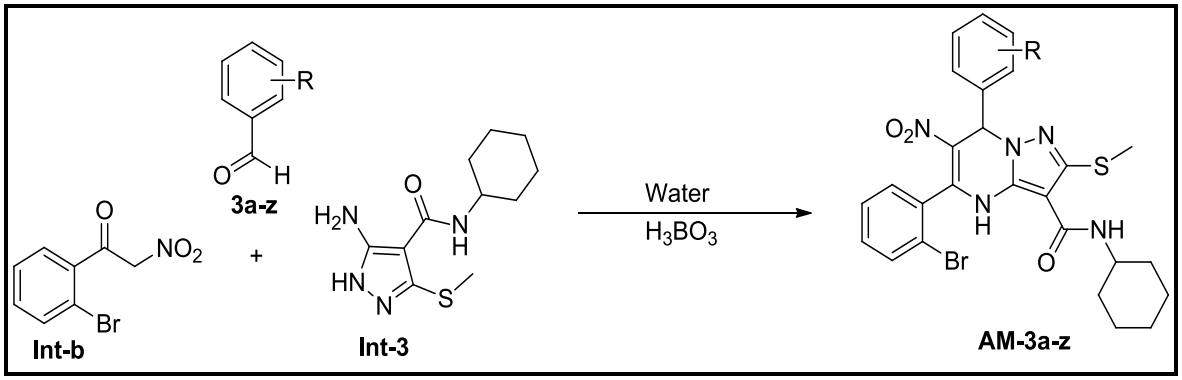


Figure 3. Reaction scheme for **AM-3a-z**.



1-(2-bromophenyl)-2-nitroethanone (Int-b):
IR (KBr): pale yellow solid; Melting range: 48-50 °C; R_f 0.24 (2:8 hexane-EtOAc); ^{1}H NMR: *δppm* 5.9(s, 2H, -CH_2-), 7.42-7.57(m, 3H, Ar-H), 7.77-7.79(m, 1H, Ar-H); MS (*m/z*): 199 (M^+).

5-(2-bromophenyl)-*N*-cyclohexyl-2-(methylthio)-6-nitro-7-phenyl-4,7-dihydropyrazolo[1,5-*a*]pyrimidine-3-carboxamide (AM-3a):
Yellow solid; Melting range: 196-198 °C; R_f 0.40 (4:6 hexane-EtOAc); IR (KBr): 3335, 2931, 2851, 1626, 1591, 1577, 1537, 1488, 1433, 1312, 1285, 1250, 1172, 1123, 1059, 974, 831, 753 cm^{-1}; ^{1}H NMR(400 MHz, DMSO): *δppm* 1.19-1.86(m, 2H, -CH_2-, cyclohexane), 2.39(s, 3H, -SCH_3), 3.8(m, 1H, -CH, cyclohexane), 6.71(s, 1H, -CH), 6.95(m, 1H, -NH), 7.18-7.48(m, 9H, Ar-H), 8.91(s, 1H, -NH); ^{13}C NMR (100 MHz, DMSO) *δppm*: 17.37, 24.49, 25.51, 33.88, 47.95, 60.69, 99.57, 123.72, 127.36, 127.84, 128.57, 128.90, 128.98, 130.16, 131.42, 132.30, 138.65, 139.44, 144.43, 162.32, 124.10, 132.72, 141.47; MS (*m/z*): 568 (M^+); Anal. Calcd for $C_{26}H_{26}BrN_5O_3S$: C, 54.93; H, 4.61; N, 12.32; Found: C, 56.52; H, 5.21; N, 11.34.

5-(2-bromophenyl)-7-(4-chlorophenyl)-*N*-cyclohexyl-2-(methylthio)-6-nitro-4,7-dihydropyrazolo[1,5-*a*]pyrimidine-3-carboxamide (AM-3b):
Yellow solid; Melting range: 208-210 °C; R_f 0.40 (4:6 hexane-EtOAc); IR (KBr): 3341, 2930, 2850, 1632, 1576, 1535, 1492, 1477, 1434, 1312, 1280, 1249, 1176, 1122, 1087, 1060, 975, 836, 774, 752 cm^{-1}; ^{1}H NMR(400 MHz, DMSO): *δppm* 1.18-1.85(m, 10H, cyclohexane) 2.41(s, 3H, -SCH_3), 3.7(m, 1H, cyclohexane), 6.68(s, 1H, -CH), 6.92-6.94(m, 1H, -NH), 7.24-7.44(m, 8H, Ar-H), 8.93(s, 1H, -NH); ^{13}C NMR (100 MHz, DMSO) *δppm*: 17.26, 25.49, 32.86, 48.00, 60.03, 99.70, 123.67, 127.70, 128.65, 128.90, 129.22, 130.21, 131.53, 132.09, 132.62, 134.91, 136.86, 137.17, 139.65, 141.83, 144.83, 162.23; MS (*m/z*): 603 (M^+); Anal. Calcd for $C_{26}H_{25}BrClN_5O_3S$: C, 51.79; H, 4.18; N, 11.62; Found: C, 53.47; H, 3.32; N, 14.48.

5-(2-bromophenyl)-*N*-cyclohexyl-7-(2,4-dichlorophenyl)-2-(methylthio)-6-nitro-4,7-dihydropyrazolo[1,5-*a*]pyrimidine-3-carboxamide (AM-3h):
Yellow solid; Melting range: 218-220 °C; R_f 0.38 (4:6 hexane-EtOAc); IR (KBr): 3333, 2929, 2850, 1626, 1578, 1535, 1489, 1438, 1397, 1315, 1288, 1253, 1226, 1175, 1104, 1057, 968, 860, 821 cm^{-1}; ^{1}H NMR(400 MHz, DMSO): *δppm* 1.19-1.85(m, 10H, cyclohexane), 2.40(s,

3H, -SCH_3), 3.88(m, 1H, -CH, cyclohexane), 6.68(s, 1H, -CH), 7.13-7.45(m, 9H, Ar-H, -NH, -CH), 9.01(s, 1H. -NH); ^{13}C NMR (100 MHz, DMSO) *δppm*:17.13, 25.50, 32.85, 48.02, 58.91, 99.29, 122.56, 127.42, 127.65, 128.56, 129.95, 130.04, 130.44, 131.55, 132.14, 132.60, 133.61, 134.51, 135.30, 139.53, 142.28, 144.86, 162.24; MS (*m/z*): 637 (M^+); Anal. Calcd for $C_{26}H_{24}BrCl_2N_5O_3S$: C, 48.99; H, 3.80; N, 10.99; Found: C, 51.27; H, 4.59; N, 9.34.

5-(2-bromophenyl)-*N*-cyclohexyl-7-(2-hydroxyphenyl)-2-(methylthio)-6-nitro-4,7-dihydropyrazolo[1,5-*a*]pyrimidine-3-carboxamide (AM-3k):
Yellow solid; Melting range: 218-220 °C; R_f 0.30 (4:6 hexane-EtOAc); IR (KBr): 3369, 3289, 3185, 2941, 2851, 1629, 1580, 1553, 1489, 1432, 1369, 1319, 1284, 1250, 1223, 1173, 1123, 1059, 1033, 975, 874, 819, 754 cm^{-1}; ^{1}H NMR(400 MHz, DMSO): *δppm* 1.16-1.81(m, 10H, cyclohexane), 2.50(s, 3H, -SCH_3), 3.75(m, 1H, -CH, cyclohexane), 6.80-7.46(m, 10H, Ar-H, -CH, -NH), 8.75(s, 1H, -OH), 8.96(s, 1H. -NH); ^{13}C NMR (100 MHz, DMSO) *δppm*: 13.59, 24.50, 25.47, 32.80, 48.09, 55.33, 99.35, 118.79, 120.92, 121.86, 124.58, 127.10, 127.43, 128.69, 130.16, 130.72, 131.43, 132.00, 132.38, 139.40, 142.73, 144.65, 154.89, 161.96 ; MS (*m/z*): 584 (M^+); Anal. Calcd for $C_{26}H_{26}BrN_5O_4S$: C, 53.43; H, 4.48; N, 11.98; Found: C, 53.97; H, 5.04; N, 11.31.

5-(2-bromophenyl)-*N*-cyclohexyl-7-(4-hydroxy-3-methoxyphenyl)-2-(methylthio)-6-nitro-4,7-dihydropyrazolo[1,5-*a*]pyrimidine-3-carboxamide (AM-3u): y
Yellow solid; Melting range: 138-140 °C; R_f 0.36 (4:6 hexane-EtOAc); IR (KBr): 3363, 2932, 2849, 1624, 1573, 1519, 1486, 1433, 1313, 1282, 1247, 1177, 1126, 1033, 977, 777, 757 cm^{-1}; ^{1}H NMR(400 MHz, DMSO): *δppm* 1.18-1.34(m, 10H, cyclohexane), 2.43(s, 3H, -SCH_3), 3.77(s, 3H, -OCH_3), 3.81(m, 1H, -CH, cyclohexane), 5.79(s, 1H, -OH), 6.65(s, 1H, -CH), 6.76-7.44(m, 8H, Ar-H, -NH), 8.89(s, 1H. -NH); ^{13}C NMR (100 MHz, DMSO); *δppm*: 17.46, 24.52, 25.49, 32.88, 47.95, 56.03, 60.55, 99.67, 110.32, 114.55, 119.56, 123.78, 127.37, 128.60, 129.94, 130.23, 131.40, 132.02, 132.40, 139.22, 141.20, 144.34, 146.18, 146.55, 162.36; MS (*m/z*): 614 (M^+); Anal. Calcd for $C_{27}H_{28}BrN_5O_5S$: C, 52.77; H, 4.59; N, 11.40; Found: C, 53.21; H, 3.98; N, 12.20.

5-(2-bromophenyl)-*N*-cyclohexyl-7-(3-cyclopropoxy-4-(difluoromethoxy)phenyl)-2-(methylthio)-6-nitro-4,7-dihydropyrazolo[1,5-*a*]pyrimidine-3-carboxamide (AM-3w):
Yellow solid; Melting range: 158-160 °C; R_f 0.38 (4:6 hexane-EtOAc); IR (KBr): 3335, 2929, 2853, 1623, 1578, 1574, 1494, 1433, 1313, 1280, 1219, 1173, 1125, 1052, 1007, 822, 769 cm^{-1}; ^{1}H NMR(400 MHz, DMSO): *δppm* 0.27(m, 2H, cyclopropane), 0.56(m, 2H, cyclopropane), 1.18-1.86(m, 10H, cyclohexane), 2.42(s, 3H, -SCH_3), 3.77-3.79(d, 1H, -CHF_2), 3.81(m, 1H, -CH, cyclohexane), 3.86(s, 1H, -CH), 6.334-7.43(m, 10H, Ar-H, -NH), 8.92(s, 1H. -NH); ^{13}C NMR (100 MHz, DMSO) *δppm*: 3.29, 10.07, 17.30, 25.48, 32.87, 47.99, 60.27, 73.95, 99.63, 113.50, 113.77, 116.08, 118.74, 122.65, 123.20, 127.40, 128.57, 129.98, 131.52, 132.00, 132.23, 136.65, 139.64, 141.65, 144.62, 150.57, 162.25; MS (*m/z*): 690 (M^+); Anal. Calcd for $C_{30}H_{30}BrF_2N_5O_5S$: : C, 52.18; H, 4.38; N, 10.14; Found: C, 52.77; H, 4.68; N, 10.79.

5-(2-bromophenyl)-*N*-cyclohexyl-7-(4-methoxyphenyl)-2-(methylthio)-6-nitro-4,7-dihydropyrazolo[1,5-*a*]pyrimidine-3-carboxamide (AM-3x):
Yellow solid; Melting range: 224-226 °C; R_f 0.40 (4:6 hexane-EtOAc); IR (KBr): 3342, 2930, 2850, 1628, 1576, 1541, 1481, 1477, 1430, 1312, 1276, 1246, 1174, 1121, 1030, 973, 840, 759 cm^{-1}; ^{1}H NMR(400 MHz, DMSO): *δppm* 1.17-1.78(m, 10H, cyclohexane), 2.38(s, 3H, -SCH_3), 3.68(m, 1H, -CH, cyclohexane), 3.73(s, 3H, -OCH_3), 6.63(s, 1H, -CH), 6.92-6.94(d,

2H, Ar-H, J = 8.4Hz), 7.37-7.39(d, 2H, Ar-H, J = 8.4Hz), 7.46-7.62(m, 4H, Ar-H), 10.85(s, 1H. -NH); MS (*m/z*): 598 (M^+); Anal. Calcd for $C_{27}H_{28}BrN_5O_4S$: C, 54.18; H, 4.72; N, 11.70; Found: C, 55.04; H, 5.11; N, 12.58.

Table 1. Physical data of compound AM-3a-z.

Entry	R	Time h	Yield %	Melting Range °C
AM-3a	-H	12	89	196-198
AM-3b	-4-Cl	12	78	208-210
AM -3c	-4-Br	12	86	238-240
AM -3d	-4(N,N-dimethylamino)	15	73	242-244
AM -3e	-4-Me	13	69	220-222
AM -3f	-4-F	12	85	228-230
AM -3g	-2-Cl	12	87	212-214
AM -3h	-2,4-di Cl	12	74	218-220
AM -3i	-3,4-di OMe	14	91	204-206
AM -3j	-3-OMe	14	86	218-220
AM-3k	-2-OH	16	82	218-220
AM -3l	-3-OH	16	79	216-218
AM -3m	-2,5-di OMe	15	82	176-178
AM -3n	-3-Cl	13	76	230-232
AM -3o	-3-Br	12	83	226-228
AM -3p	-4-OH	16	81	238-240
AM -3q	-2-NO_2	18	89	200-202
AM -3r	-3-NO_2	16	76	188-190
AM -3s	Cinnamaldehyde	10	79	146-148
AM -3t	Naphthaldehyde	11	74	178-180
AM -3u	-3-OMe-4-OH	14	63	138-140
AM -3v	-4-CN	12	88	222-224
AM -3w	-3-CHF_2	15	80	158-160
AM -3x	-4-OMe	15	87	224-226
AM -3y	-3-Me	13	93	196-198
AM -3z	-3-OH-4-OMe	16	77	142-144

Table 2. Optimization of yield with different solvent and catalyst for AM-3a.

Solvent	Catalyst	Yield %
Water	H_3BO_3	89
	Con HCl	73
	Acetic acid	61
Methanol	H_3BO_3	88
	Con HCl	70
	Acetic acid	65
DMF	H_3BO_3	84
	Con HCl	71
	Acetic acid	52
THF	H_3BO_3	77
	Con HCl	65
	Acetic acid	43
IPA	H_3BO_3	78
	Con HCl	68
	Acetic acid	32

3. RESULT AND DISCUSSION

Various methodologies have been described for the synthesis of pyrazolo[1,5-a]pyrimidines. During the course of our ongoing interest on synthesis of various heterocyclic compounds using 1-(2-bromophenyl)-2-nitroethanone, we observed that 1-(2-bromophenyl)-2-nitroethanone are versatile intermediate for the synthesis of pyrazolopyrimidines.

Here compound **AM-3a** was synthesized by different reaction condition like changing solvents and catalyst. It is found from TLC and mass analysis that in organic solvent product is formed but beside this the formed intermediates remains unreacted and it is not converted to final product even after very long time of reaction. Water is found best media for this conversion because in water all intermediates are converted in to final product. Three reagents con. HCl, acetic acid and Boric acid were used to obtain final compounds. In acetic acid product formation is very less but using con. HCl or Boric acid gives good yield. Here optimization is given with solvents, catalyst and yield in **Table 2**.

4. CONCLUSION

In summary, we have described the water mediated synthesis of nitro substituted triazolopyrimidine derivatives in moderate to good yield. The reaction of various substituted aldehydes with 1-(2-bromophenyl)-2-nitroethanone and 5-amino-*N*-cyclohexyl-3-

(methylthio)-1*H*-pyrazole-4-carboxamide afforded the triazolo pyrimidine derivatives in the presence boric acid and water as a solvent. We have confirmed the structure on the basis of spectroscopic technique.

References

[1] Moritani Y.; Shirai K.; Oi M., Pyrazolo[1,5-a]pyrimidine compounds as cannabinoid receptor antagonists. PCT Int. Appl. WO patent 2007046548.

[2] Mukaiyama H.; Nishimura T.; Kobayashi S.; Komatsu Y., *Bioorg. Med. Chem.* 16 (2008) 909-921.

[3] Huang S.; Lin R.; Yu Y.; Lu Y.; Connolly P.; Chiu G.; Li S.; Emanuel S.; Middleton S., *Bioorg. Med. Chem. Lett*. 17 (2007) 1243-1245.

[4] Saggar S.; Sisko J.; Tucker T.; Tynebor R.; Su D.; Anthony N.; Acoustic alert communication system with enhanced signal to noise. U. S. Patent Appl. 2007021442.

[5] Zhang P.; Pennell M.; Wright J.; Chen W.; Leleti M.; Li Y.; Li L.; Xu Y.; Azaindazole compounds and method of use. PCT Int. Appl. WO Patent 2007002293.

[6] (a) Chiu G.; Li, S.; Connolly P.; Middleton S.; Emanuel S.; Huang S.; Lin R.; Lu Y., 3-benzoimidazolyl-pyrazolopyrimidines useful in treatings kinase disorders disubstituted derivatives. PCT Int. Appl. WO patent 2006130673;

(b) Dwyer M., et al., *Bioorg. Med. Chem. Lett*. 17 (2007) 6216-6219.

[7] Ghorab M.M., Ismail Z.H., Abdel-Gawad S.M., Aziem A.A., *Heteroatom Chem*. 15 (2004) 57-62.

[8] Feurer A.; Luithle J.; Wirtz S.; Koenig G.; Stasch J.; Stahl E.; Schreiber R.; Wunder F.; Lang D., Novel 2,5-disubstituted pyrimidine derivatives. PCT Int. Appl. WO patent 2004009589.

[9] (a) Elnagdi M. H.; Elmoghayar M. R. H.; Elgemeie G. H., *Adv. Heterocycl. Chem.* 41 (1987) 319-376;

(b) Quiroga J.; Hormaza A.; Insuasty B.; Saitz C.; Canete A., *J. Heterocycl. Chem*. 35 (1998) 61-64;

(c) El-Taweel F.; Abu Elmaati T., *J. Chin. Chem. Soc*. 49 (2002) 1051-1055;

(d) Daniels R.; Kim K.; Lebois E.; Muchalski H.; Hughes M.; Lindsley C., *Tetrahedrone Lett*. 49 (2008) 305-310.

[10] (a) Simon C.; Constantieux T.; Rodriguez J., *Eur. J. Org. Chem*. 24 (2004) 4957-4980;

(b) Quiroga J.; Portilla J.; Aboni´a R.; Insuasty B.; Nogueras M.; Cobo J., *Tetrahedron Lett*. 48 (2007) 6352-6355;

(c) Quiroga J.; Mejı´a D.; Insuasty B.; Aboni´a R.; Nogueras M.; Sanchez A.; Cobo J., *J. Heterocycl. Chem*. 39 (2002) 51-54.

[11] (a) Reddy A.C.S.; Narsaiah B.; Venkataratnam R.V., *J. Fluorine Chem.* 86 (1997) 127-130;

(b) Krishnaiah, A.; Narsaiah, B. *J. Fluorine Chem.* 109 (2001) 183-187;

(c) Kanth S.R.; Reddy G.V.; Maitraie D.; Narsaiah B.; Rao P.S.; Kumar K.R.; Sridhar B., *J. Fluorine Chem*. 127 (2006) 1211-1221.

[12] Chebanov V.A.; Saraev V.E.; Desenko S.M.; Chernenko V.N.; Knyazeva I.V.; Groth U.; Glasnov T.N.; Kappe C. O., *J. Org. Chem*. 73 (2008) 5110-5118.

(Received 14 October 2014; accepted 31 October 2014)