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Synthesis of pyrazolopyridine and pyrazoloquinoline derivatives by one-pot, three-component reactions of arylglyoxals, 3-methyl-1-aryl-1*H*-pyrazol-5-amines and cyclic 1,3-dicarbonyl compounds in the presence of tetrapropylammonium bromide

https://doi.org/10.1515/gps-2019-0022
Received September 06, 2018; accepted March 19, 2019.

Abstract: Pyrazolopyridine and pyrazoloquinoline derivatives were obtained by a one-pot, three-component reaction of arylglyoxals, 3-methyl-1-aryl-1*H*-pyrazol-5-amines and cyclic 1,3-dicarbonyl compounds in the presence of tetrapropylammonium bromide at 80°C in water through *Knoevenagel* and *Micheal* reactions, followed by intramolecular condensation, unexpected dearoylation and oxidation. Mild reaction conditions, high yields, simplicity of work up procedure, starting materials availability and clean product formation are some of the main advantages of this synthetic strategy.

Keywords: arylglyoxals; cyclic 1,3-dicarbonyl compounds; 3-methyl-1-aryl-1*H*-pyrazol-5-amines; pyrazolopyridines; pyrazoloquinolines; tetrapropylammonium bromide

1 Introduction

It has been reported that, more than 90% of compounds analysed by pharmaceutical companies are nitrogen-containing heterocycles [1], and the nitrogen-containing heterocycles exhibit excellent biological and pharmaceutical activities.

The synthesis of pyrazolo[3,4-*b*]pyridine derivatives by microwave-assisted one-pot reaction between 5-aminopyrazole derivatives, paraformaldehyde and β-diketones catalyzed by $InCl_3$ in aqueous media was recently reported [2].

The presence of pyrazoloquinoline moieties in numerous natural products makes them an important class of heterocyclic compounds with several biological and pharmacological activities, such as anti-mycobacterial [3], anti-microbial [4], anti-viral [5]. Pyrazolopyridines have also received more attention because of their wide range of biological and pharmacological properties, such as anti-pyretic [6] and anxiolytic [7], antimalarial [8], and this has made such derivatives increasingly important.

The reaction of several starting materials in one pot may allow the formation of the corresponding product in high yields and minimize the use of hazardous organic solvents during separation and work-up steps which leads to a green procedure [9].

Tetrapropylammonium bromide (TPAB) is a readily available and an inexpensive catalyst with many catalytical applications in organic reactions [10,11].

Several studies have been conducted on the synthesis of a new series of heterocyclic compounds using one-pot, multicomponent reactions in our laboratory [12-20]. In continuation of our previous studies, we were interested to investigate the possibility of the synthesis of a new series of pyrazolopyridine and pyrazoloquinoline derivatives by the one-pot, three-component reaction of arylglyoxals, 3-methyl-1-aryl-1*H*-pyrazol-5-amines and cyclic 1,3-dicarbonyl compounds in the presence of TPAB as a catalytic. However, surprisingly, it was found that unexpected dearoylation occurred during the reaction to provide the corresponding pyrazolopyridines and pyrazoloquinolines as the final products in high yields.

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2 Experimental

All chemicals were purchased from Merck and Acros companies and used without any purification. The completion of reactions were controlled by thin layer chromatography (TLC) silica gel on aluminium plates. Melting points were measured with a Philip Harris C4954718 apparatus and are uncorrected. Infrared spectra were recorded with thermo Nicolet Nexus 670 FT-IR using KBr pellets. The ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance AQS 300 MHz spectrometer using $CDCl_3$ as solvent, relative to tetramethylsilane (TMS) as the internal standard. Mass spectra were measured on a Varian Matt 311 spectrometer and high resolution spectra were obtained by Kratos MS 25RF spectrometer.

General procedure for the synthesis of products 5a-i

A mixture of arylglyoxals **1a-i** (1 mmol), 3-methyl-1-aryl-1*H*-pyrazol-5-amines **2a-c** (1 mmol) and cyclic 1,3-dicarbonyl compounds **3a-e** (1 mmol) in the presence of TPAB (20 mol%) in water/acetone (1:2, 10 mL) was stirred at 80°C for an appropriate time (monitored by TLC, CH_2Cl_2: hexane: MeOH/15:15:1). Half of the solvent was evaporated and the precipitate was filtered and washed with H_2O/EtOH (1:2) to give the desired products **5a-i** in 90-98% yield.

Recovering of TPAB

After filtration of products **5a-i** and washing the precipitate with water, the filtrate was extracted with $CHCl_3$ and the aqueous phase was separated. Evaporation of water gave TPAB, which may be recrystallized from Et_2O as white crystals.

3-Methyl-1-phenyl-6,7-dihydrocyclopenta[*b*]pyrazolo[4,3-*e*]pyridin-5(1*H*)-one (5a)

White powder; yield 96% (253 mg); mp: 213-216°C (lit. [2], 215-217°C); IR (KBr, cm^{-1}): 2945, 2877, 1681, 1593, 1502, 1480, 1416, 1381, 1326, 1264, 1222, 1182, 1015, 912, 880, 837, 758, 688, 609; ^{1}H NMR ($CDCl_3$) δ (ppm) 8.36 (s, 1H, Ar), 7.79 (d, *J* = 8.4 Hz, 2H, Ar), 7.58 (t, *J* = 8.1 Hz, 2H, Ar), 7.40 (t, *J* = 7.5 Hz, 1H, Ar), 3.46-3.44 (m, 2H, CH_2), 2.88-2.83 (m, 2H, CH_2), 2.32 (s, 3H, CH_3); ^{13}C-NMR ($CDCl_3$) δ (ppm): 192.7, 174.2, 153.7, 144.5, 140.5, 134.3, 131.6, 129.4, 122.6, 121.1, 113.7, 36.1, 29.3, 13.9; MS (EI): *m/z* (%): 263 [M]$^+$ (35), 234 (10), 141 (37), 140 (12), 139 (100), 111 (46), 77 (21).

3-Methyl-1-phenyl-1,6,7,8-tetrahydro-5*H*-pyrazolo[3,4-*b*]quinolin-5-one (5b)

White needles; yield 90% (249 mg); mp: 126-128°C (lit. [2], 128-130°C, and lit. [21], 123-124); IR (KBr, cm^{-1}): 3030, 2955, 1662, 1617, 1527, 1459, 1363, 1189, 1119, 1066, 1004, 847, 754, 694; ^{1}H-NMR ($CDCl_3$) δ (ppm): 8.77 (s, 1H, Ar), 8.30 (d, *J* = 7.8 Hz, 2H, Ar), 7.53 (t, *J* = 7.8 Hz, 2H, Ar), 7.32 (t, *J* = 7.2 Hz, 1H, Ar), 3.29 (t, *J* = 6.3 Hz, 2H, CH_2), 2.78 (t, *J* = 6.3 Hz, 2H, CH_2), 2.68 (s, 3H, CH_3), 2.25 (quin, *J* = 6.3 Hz, 2H, CH_2); ^{13}C-NMR ($CDCl_3$) δ (ppm): 197.5, 163.9, 145.1, 130.5, 129.1, 126.0, 123.1, 120.9, 116.8, 116.4, 104.8, 38.9, 33.8, 22.0, 12.5; MS (EI): *m/z* (%): 277 [M]$^+$ (13), 271 (11), 239 (15), 205 (13), 165 (15), 135 (92), 77 (46), 43 (100).

3,8,8-Trimethyl-1-phenyl-1,6,7,8-tetrahydro-5*H*-pyrazolo[3,4-*b*]quinolin-5-one (5c)

White powder; yield 92% (281 mg); mp: 167-169°C; IR (KBr, cm^{-1}): 3347, 3067, 2959, 2936, 2869, 1683, 1593, 1504, 1481, 1417, 1380, 1269, 1235, 1121, 1090, 1012, 979, 821, 779, 750, 685, 624; ^{1}H NMR ($CDCl_3$) δ (ppm) 8.74 (s, 1H, Ar), 8.27 (d, *J* = 8.1 Hz, 2H, Ar), 7.53 (t, *J* = 7.2 Hz, 2H, Ar), 7.34 (t, *J* = 7.2 Hz, 1H, Ar), 2.55 (s, 3H, CH_3), 2.27 (bs, 2H, CH_2), 1.58 (bs, 2H, CH_2), 1.16 (s, 6H, 2×CH_3); ^{13}C-NMR ($CDCl_3$) δ (ppm): 196.8, 163.4, 162.3, 151.4, 144.6, 144.2, 130.8, 130.2, 128.1, 122.0, 120.3, 52.2, 47.7, 32.9, 27.0, 18.8; MS (EI): *m/z* (%): 305 [M]$^+$ (5), 300 (6), 140 (32), 112 (28), 97 (14), 83 (100), 70 (19), 56 (44) and HRMS (ESI): calcd. for $C_{19}H_{19}N_3O$ [M]$^+$ 305.1528; found: 305.1542.

3,7,7-Trimethyl-1-phenyl-1,6,7,8-tetrahydro-5*H*-pyrazolo[3,4-*b*]quinolin-5-one (5d)

White needles; yield 97% (296 mg); mp: 163-165°C (lit. [2], 165-167°C, and lit. [22], 165-166°C); IR (KBr, cm^{-1}): 2951, 2932, 2359, 1678, 1569, 1593, 1494, 1416, 1376, 1281, 1243, 1116, 1023, 758, 679, 556; ^{1}H NMR ($CDCl_3$) δ (ppm) 8.74 (s, 1H, Ar), 8.30 (d, *J* = 9 Hz, 2H, Ar), 7.54 (d, *J* = 9 Hz, 2H, Ar), 7.32 (t, *J* = 9 Hz, 1H, Ar), 3.18 (s, 2H, CH_2), 2.67 (s, 3H, CH_3), 2.63 (s, 2H, CH_2), 1.15 (s, 6H, 2×CH_3); ^{13}C-NMR ($CDCl_3$) δ (ppm): 197.5, 162.6, 151.6, 145.1, 139.2, 129.9, 129.0, 125.9, 122.1, 120.9, 116.7, 52.4, 47.5, 32.9, 28.3, 12.5; MS (EI): *m/z*

(%): 306 $[M+1]^+$ (27), 305 $[M]^+$ (100), 290 (8), 277 (7), 249 (43), 220 (8), 180 (15), 129 (6), 77 (14).

1-(3-Chlorophenyl)-3,7,7-trimethyl-1,6,7,8-tetrahydro-5*H*-pyrazolo[3,4-*b*]quinolin-5-one (5e)

White solid; yield 98% (332 mg); mp: 148-150°C; IR (KBr, cm^{-1}): 3102, 2955, 2872, 1683, 1590, 1479, 1454, 1379, 1275, 1239, 1141, 1093, 899, 872, 778, 741, 679, 554; ^{1}H NMR ($CDCl_3$) δ (ppm) 8.75 (s, 1H, Ar), 8.46 (s, 1H, Ar), 8.32 (d, *J* = 7.5 Hz, 1H, Ar), 7.45 (t, *J* = 7.5 Hz, 1H, Ar), 7.26 (bd, overlapped by $CDCl_3$ impurity peak, 1H, Ar), 3.21 (s, 2H, CH_2), 2.67 (s, 3H, CH_3), 2.64 (s, 2H, CH_2), 1.17 (s, 6H, 2×CH_3); ^{13}C-NMR ($CDCl_3$) δ (ppm): 197.4, 162.9, 151.8, 145.6, 134.8, 131.1, 128.9, 126.7, 124.8, 124.7, 121.6, 116.9, 114.0, 52.4, 47.5, 33.0, 27.9, 13.3; MS (EI): *m/z* (%): 341 $[M+2]^+$ (39), 339 $[M]^+$ (100), 283 (45), 250 (15), 214 (13), 179 (13), 149 (13), 111 (23), 83 (47), 71 (45), 57 (42) and HRMS (ESI): calcd. for $C_{19}H_{18}ClN_3O$ $[M]^+$ 339.1138; found: 339.1110.

1-(4-Chlorophenyl)-3,7,7-trimethyl-1,6,7,8-tetrahydro-5*H*-pyrazolo[3,4-*b*]quinolin-5-one (5f)

White solid; yield 95% (322 mg); mp: 144-146°C (lit. [22], 148-149°C); IR (KBr, cm^{-1}): 3106, 2957, 2932, 2870, 1679, 1594, 1576, 1499, 1475, 1447, 1382, 1270, 1241, 1218, 1141, 1090, 1013, 829, 691, 557, 503; ^{1}H NMR ($CDCl_3$) δ (ppm) 8.75 (s, 1H, Ar), 8.33 (d, *J* = 8.7 Hz, 2H, Ar), 7.48 (d, *J* = 8.7 Hz, 2H, Ar), 3.19 (s, 2H, CH_2), 2.67 (s, 3H, CH_3), 2.64 (s, 2H, CH_2), 1.27 (s, 6H, 2×CH_3); ^{13}C-NMR ($CDCl_3$) δ (ppm): 197.4, 163.6, 162.9, 151.8, 134.8, 131.1, 128.9, 126.7, 122.4, 121.6, 116.9, 52.3, 47.4, 33.0, 27.2, 13.3; MS (EI): *m/z* (%): 341 $[M+2]^+$ (34), 339 $[M]^+$ (98), 283 (38), 278 (100), 217 (19), 179 (14), 139 (31), 112 (30), 105 (88), 77 (41), 57 (24).

3-Methyl-1-phenylindeno[1,2-*b*]pyrazolo[4,3-*e*]pyridin-5(1*H*)-one (5g)

Yellow solid; yield 91% (283 mg); mp: 245-247°C (lit. [2], 246-248°C); IR (KBr, cm^{-1}): 3088, 2959, 2867, 1690, 1580, 1556, 1471, 1314, 1232, 1165, 1058, 947, 846, 760, 678, 593; ^{1}H-NMR ($CDCl_3$) δ (ppm): 8.42 (s, 1H, Ar), 8.29 (d, *J* = 7.2 Hz, 1H, Ar), 8.01 (d, *J* = 8.1 Hz, 1H, Ar), 7.89 (d, *J* = 7.8 Hz, 2H, Ar), 7.66 (t, *J* = 6.9 Hz, 1H, Ar), 7.59 (t, *J* = 7.8 Hz, 1H, Ar), 7.49 (t, *J* = 7.5 Hz, 2H, Ar), 7.41 (t, *J* = 6.9 Hz, 1H, Ar), 2.29 (s, 3H, CH_3); ^{13}C-NMR ($CDCl_3$) δ (ppm): 192.3, 173.0, 169.3, 164.5, 153.2, 142.8, 141.3, 138.7, 136.9, 131.8, 130.6, 129.5, 125.8, 125.1, 120.1, 113.1, 108.3, 35.2; MS (EI): *m/z* (%): 312 $[M+1]^+$ (43), 311 $[M]^+$ (100), 296 (30), 270 (24), 241 (14), 214 (10), 139 (36), 111 (19), 77 (32), 51 (10).

1-(3-Chlorophenyl)-3-methylindeno[1,2-*b*]pyrazolo[4,3-*e*]pyridin-5(1*H*)-one (5h)

Yellow powder; yield 90% (311 mg); mp: 230-232°C; IR (KBr, cm^{-1}): 3098, 2969, 2879, 1711, 1670, 1589, 1560, 1482, 1435, 1316, 1243, 1188, 1089, 1007, 947, 846, 764, 726, 676, 593; ^{1}H-NMR ($CDCl_3$) δ (ppm): 8.44 (s, 1H, Ar), 8.29 (d, *J* = 8.4 Hz, 1H, Ar), 8.04 (d, *J* = 7.5 Hz, 1H, Ar), 7.87 (d, *J* = 7.5 Hz, 1H, Ar), 7.69 (t, *J* = 7.8 Hz, 1H, Ar), 7.67 (t, *J* = 6.9 Hz, 1H, Ar), 7.51 (t, *J* = 7.5 Hz, 1H, Ar), 7.48 (s, 1H, Ar), 7.36 (d, *J* = 7.8 Hz, 1H, Ar), 2.29 (s, 3H, CH_3); ^{13}C-NMR ($CDCl_3$) δ (ppm): 198.6, 181.2, 180.9, 169.0, 167.4, 166.2, 163.6, 162.9, 162.8, 151.8, 145.6, 140.3, 134.8, 134.7, 131.1, 128.9, 126.7, 121.6, 119.4, 11.9; MS (EI): *m/z* (%): 347 $[M+2]^+$ (2), 345 $[M]^+$ (4), 327 (22), 311 (100), 296 (20), 270 (15), 241 (10), 139 (30), 111 (15), 77 (17) and HRMS (ESI): calcd. for $C_{20}H_{12}ClN_3O$ $[M]^+$ 345.0669; found: 345.0699.

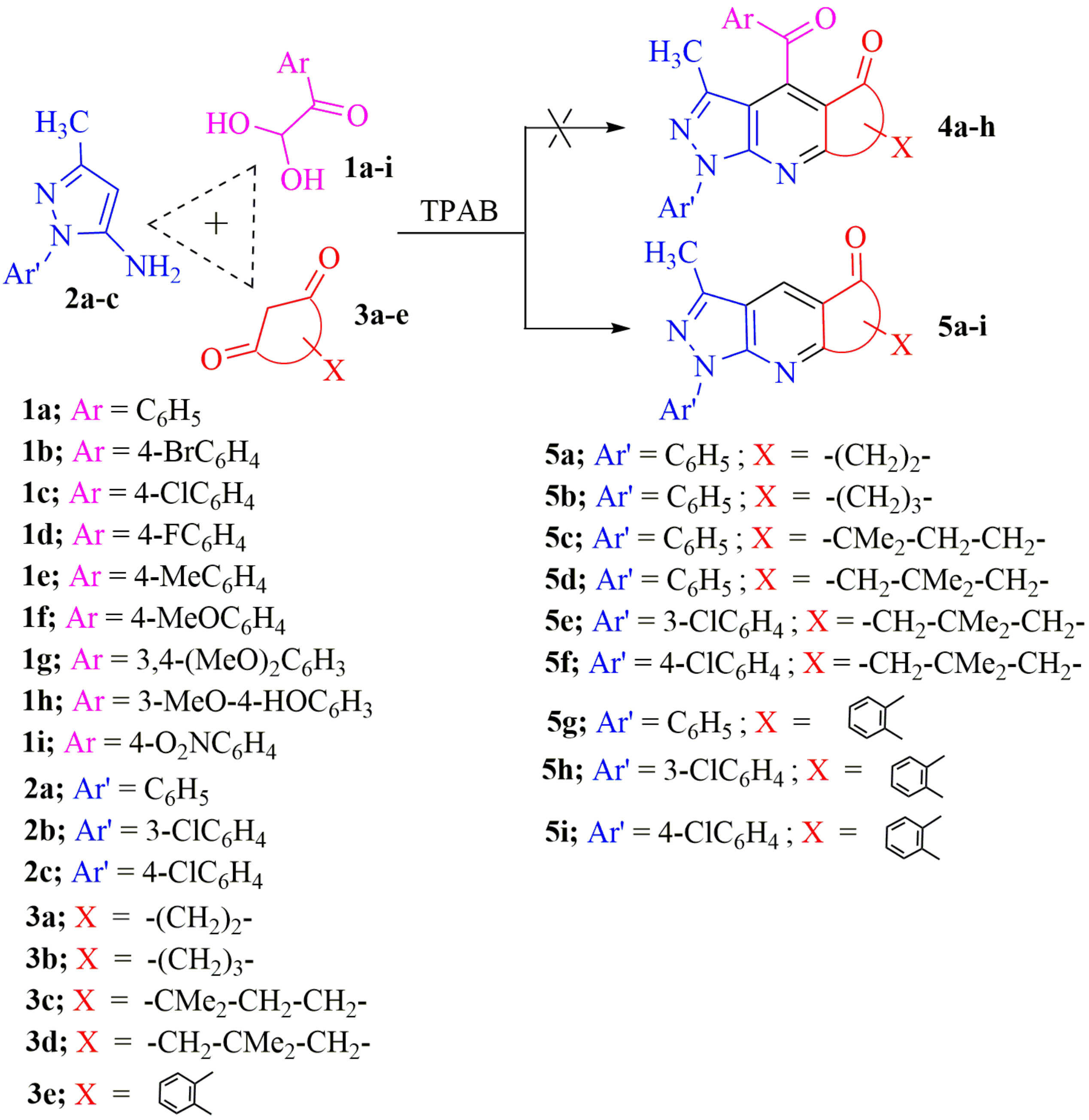
1-(4-Chlorophenyl)-3-methylindeno[1,2-*b*]pyrazolo[4,3-*e*]pyridin-5(1*H*)-one (5i)

Yellow solid; yield 94% (324 mg); mp: 221-223°C; IR (KBr, cm^{-1}): 3089, 2929, 1721, 1678, 1581, 1562, 1488, 1318, 1244, 1189, 1087, 945, 847, 765, 729, 596; ^{1}H-NMR ($CDCl_3$) δ (ppm): 8.84 (s, 1H, Ar), 8.14 (d, *J* = 8.1 Hz, 1H, Ar), 7.82 (t, *J* = 8.1 Hz, 1H, Ar), 7.64 (d, *J* = 8.1 Hz, 1H, Ar), 7.52 (t, *J* = 8.1 Hz, 1H, Ar), 7.36 (d, *J* = 7.8 Hz, 2H, Ar), 7.03 (d, *J* = 7.2 Hz, 2H, Ar), 2.50 (s, 3H, CH_3); ^{13}C-NMR ($CDCl_3$) δ (ppm): 202.1, 184.9, 182.1, 178.4, 177.0, 175.9, 175.0, 149.9, 144.9, 140.1, 128.4, 128.3, 128.1, 125.1, 122.7, 120.6, 113.2, 35.2; MS (EI): *m/z* (%): 347 $[M+2]^+$ (1), 345 $[M]^+$ (2), 311 (11), 298 (8), 269 (5), 139 (100), 111 (40), 84 (16) and HRMS (ESI): calcd. for $C_{20}H_{12}ClN_3O$ $[M]^+$ 345.0669; found: 345.0601.

3 Results and discussion

We earlier found that the reactions of arylglyoxals **1** with 3-methyl-1-phenyl-1*H*-pyrazol-5-amine (**2**) and cyclic 1,3-dicarbonyl compounds **3** carried out under catalyst-free conditions in H_2O/EtOH at 80°C afforded 4-aroyl-pyrazolo[3,4-*b*]pyridine derivatives **4a-h** by a one-pot, three-component reaction in excellent yields [23]. However, it was found that the same reaction in the presence of TPAB as a homogeneous catalyst in H_2O/acetone at 80°C gave pyrazolopyridines **5a**, **5g-i** and pyrazoloquinolines **5b-f** as final products in high yields due to unexpected dearoylation occurrence, with no sign of the formation of any 4-aroyl-pyrazolo[3,4-*b*]pyridine derivatives **4a-h** formation (Scheme 1).

The reaction of 4-bromophenylglyoxal monohydrate (**1b**), 3-methyl-1-phenyl-1*H*-pyrazol-5-amine (**2a**) and dimedone (**3d**) in 1:1:1 molar ratio using several catalysts, was chosen as a model reaction (Scheme 1). For optimization, the model reaction was carried out using various solvents, catalysts and reaction times as indicated in Table 1. Consequently, the highest yield (97%) was

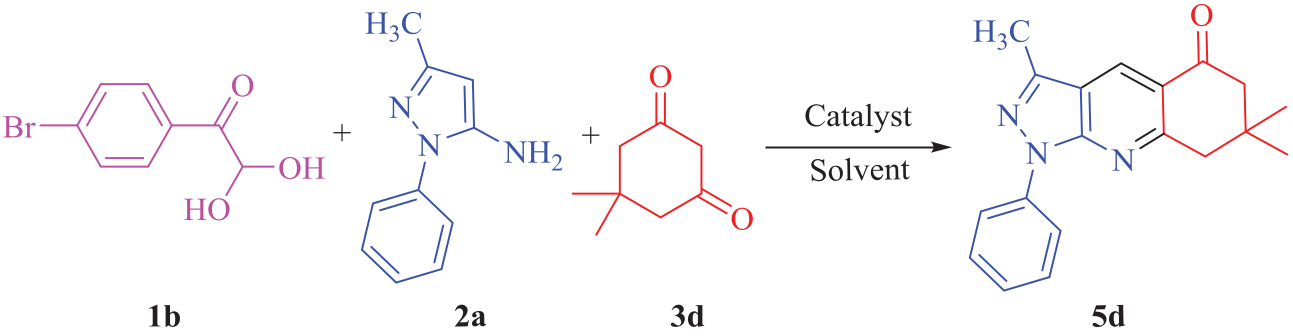


1a; Ar = C_6H_5
1b; Ar = $4\text{-}BrC_6H_4$
1c; Ar = $4\text{-}ClC_6H_4$
1d; Ar = $4\text{-}FC_6H_4$
1e; Ar = $4\text{-}MeC_6H_4$
1f; Ar = $4\text{-}MeOC_6H_4$
1g; Ar = $3,4\text{-}(MeO)_2C_6H_3$
1h; Ar = $3\text{-}MeO\text{-}4\text{-}HOC_6H_3$
1i; Ar = $4\text{-}O_2NC_6H_4$
2a; Ar' = C_6H_5
2b; Ar' = $3\text{-}ClC_6H_4$
2c; Ar' = $4\text{-}ClC_6H_4$
3a; X = $\text{-}(CH_2)_2\text{-}$
3b; X = $\text{-}(CH_2)_3\text{-}$
3c; X = $\text{-}CMe_2\text{-}CH_2\text{-}CH_2\text{-}$
3d; X = $\text{-}CH_2\text{-}CMe_2\text{-}CH_2\text{-}$
3e; X =

5a; Ar' = C_6H_5 ; X = $\text{-}(CH_2)_2\text{-}$
5b; Ar' = C_6H_5 ; X = $\text{-}(CH_2)_3\text{-}$
5c; Ar' = C_6H_5 ; X = $\text{-}CMe_2\text{-}CH_2\text{-}CH_2\text{-}$
5d; Ar' = C_6H_5 ; X = $\text{-}CH_2\text{-}CMe_2\text{-}CH_2\text{-}$
5e; Ar' = $3\text{-}ClC_6H_4$; X = $\text{-}CH_2\text{-}CMe_2\text{-}CH_2\text{-}$
5f; Ar' = $4\text{-}ClC_6H_4$; X = $\text{-}CH_2\text{-}CMe_2\text{-}CH_2\text{-}$
5g; Ar' = C_6H_5 ; X =
5h; Ar' = $3\text{-}ClC_6H_4$; X =
5i; Ar' = $4\text{-}ClC_6H_4$; X =

Scheme 1: Synthesis of pyrazolopyridines and pyrazoloquinolines **5a-i**.

Table 1: Model reaction for the synthesis of compound **5d**.



Entry	Solvent	Catalyst (20 mol%)	Temperature (°C)	Yield (%)[a]
1	H_2O	No catalyst	RT-Reflux	N.R.
2	H_2O	*p*-TSA	RT-Reflux	N.R.
3	H_2O	Alginate sodium	RT-Reflux	N.R.
4	H_2O	*L*-cysteine	RT-Reflux	N.R.
5	H_2O	*L*-proline	RT-Reflux	N.R.
6	H_2O	TPAB	RT-Reflux	Trace
7	EtOH	*p*-TSA	RT-Reflux	N.R.
8	EtOH	Alginate sodium	RT-Reflux	N.R.
9	EtOH	*L*-cysteine	RT-Reflux	N.R.
10	EtOH	*L*-proline	RT-Reflux	N.R.
11	EtOH	TPAB	RT-Reflux	Trace
12	Acetone	*p*-TSA	RT-Reflux	N.R.
13	Acetone	Alginate sodium	RT-Reflux	N.R.
14	Acetone	*L*-cysteine	RT-Reflux	N.R.
15	Acetone	*L*-proline	RT-Reflux	N.R.
16	Acetone	TPAB	RT-Reflux	Trace
17	H_2O/EtOH (1:2)	*p*-TSA	RT-Reflux	N.R.
18	H_2O/EtOH (1:2)	Alginate sodium	RT-Reflux	N.R.
19	H_2O/EtOH (1:2)	*L*-cysteine	RT-Reflux	N.R.
20	H_2O/EtOH (1:2)	*L*-proline	RT-Reflux	N.R.
21	H_2O/EtOH (1:2)	TPAB	RT-Reflux	12
22	H_2O/Acetone (1:2)	*p*-TSA	RT-Reflux	N.R.
23	H_2O/Acetone (1:2)	Alginate sodium	RT-Reflux	N.R.
24	H_2O/Acetone (1:2)	*L*-cysteine	RT-Reflux	Trace
25	H_2O/Acetone (1:2)	*L*-proline	RT-Reflux	N.R.
26	**H_2O/Acetone (1:2)**	**TPAB**	**80°C**	**97**[b]

[a] Isolated yield.

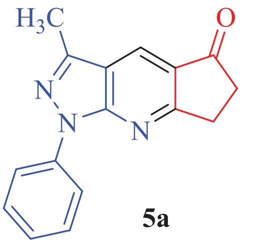
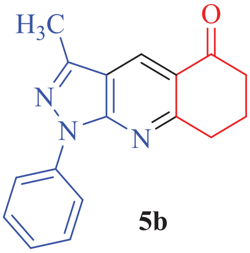
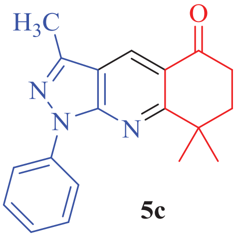
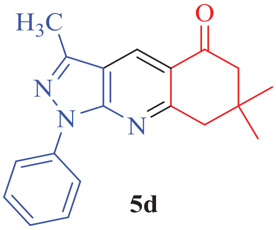
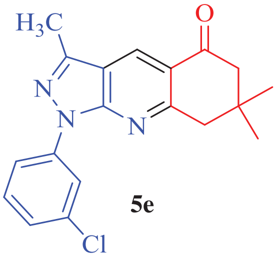
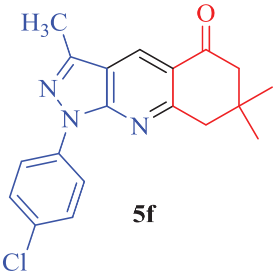
[b] The bold type (entry 26) refers to the best reaction conditions.

obtained, using TPAB as catalyst and H_2O/acetone (1:2) as solvent, at 80°C (entry 26). The arylglyoxals **1a-i** and the 3-methyl-1-aryl-1*H*-pyrazole-5-amines **2a-c** were prepared according to the literature methods [24] and [25] respectively.

After optimizing the reaction conditions, the scope of this reaction was examined with a series of electron rich and electron deficient arylglyoxals and various cyclic 1,3-dicarbonyl compounds [such as cyclopentane-1,3-dione (**3a**), cyclohexane-1,3-dione (**3b**), 4,4-dimethylcyclohexane-1,3-dione (**3c**), dimedone (**3d**) and indane-1,3-dione (**3e**)] to form a series of corresponding pyrazolopyridines and pyrazoloquinolines. The reaction times, melting points and yields of all products are summarized in Table 2. It should be mentioned that the reaction with 4-nitroarylglyoxal (**1i**) gave **4i** as a final product with no sign of corresponding dearoylation product **5d** formation.

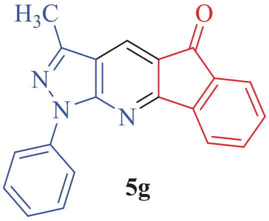
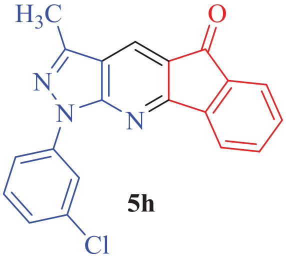
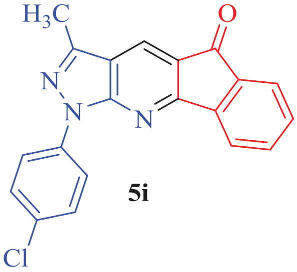
The proposed mechanism of this reaction involves the initial *Knoevenagel* condensation of arylglyoxals

Table 2: The reaction condition, melting points and yields of products **5a-i**.

Entry	Product	Reaction time (h)	M.p. (°C)	Yield (%)
1	 **5a**	3	213-216	96
2	 **5b**	4	126-128	90
3	 **5c**	4	167-169	92
4	 **5d**	3	163-165	97
5	 **5e**	3	148-150	98
6	 **5f**	3	144-146	95

(*Continued*)

Table 2: (Continued).

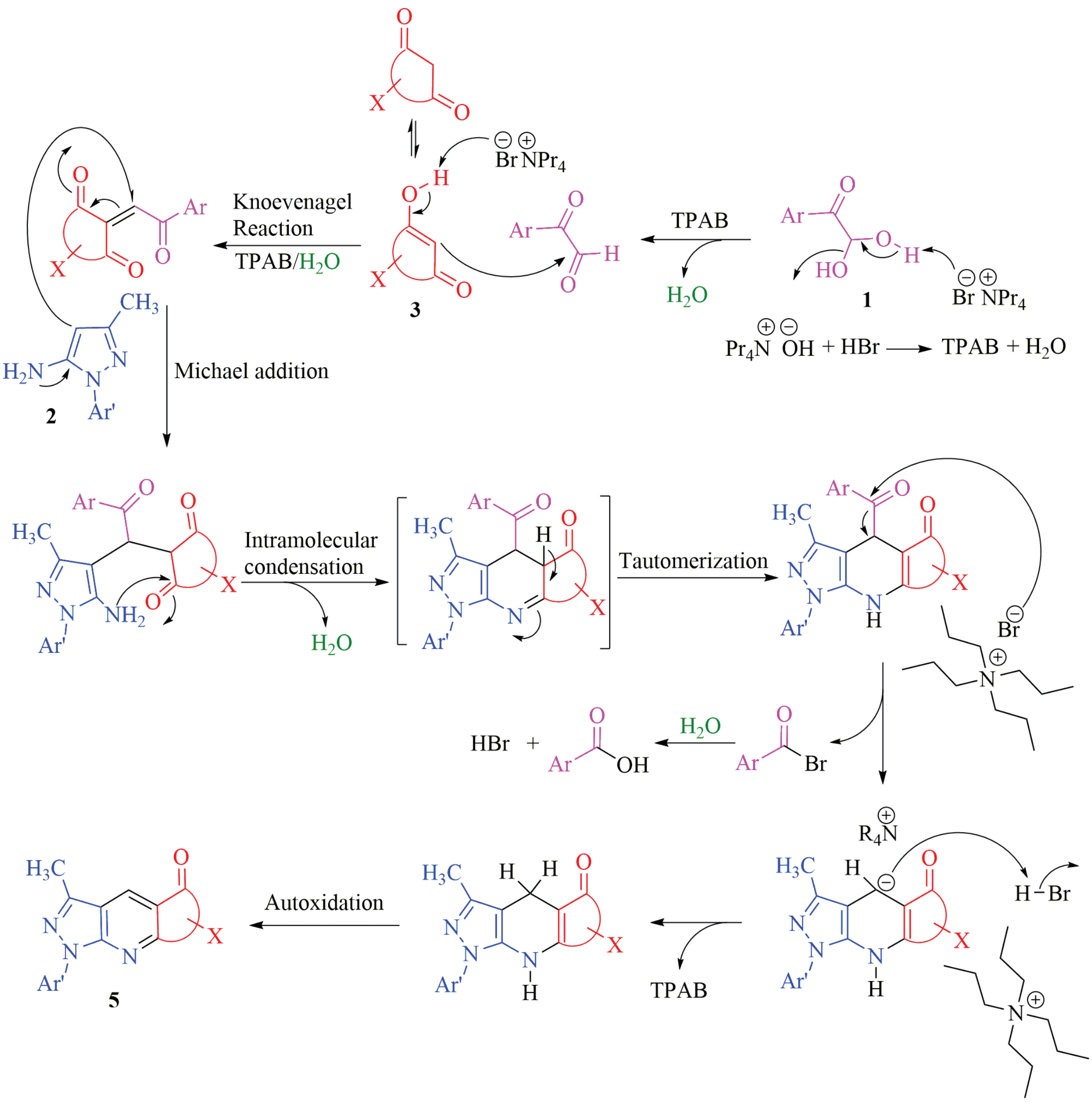
Entry	Product	Reaction time (h)	M.p. (°C)	Yield (%)
7	 **5g**	3	245-247	91
8	 **5h**	3	230-232	90
9	 **5i**	4	221-223	94

1 with cyclic 1,3-dicarbonyl compounds **3** to form the corresponding intermediate as shown in Scheme 2. Following the *Michael* addition of 3-methyl-1-aryl-1*H*-pyrazol-5-one **2** to this intermediate will form the desired pyrazolopyridine and pyazoloquinoline derivatives through intermolecular cyclization, dearoylation and autoxidation. There is no report on TPAB acting as dearoylating agent in the literature.

Isolation and identification of benzoic acid and 3,4-dimethoxybenzoeic acid from the literature in the case of **5a** and **5g** was accomplished to confirm the dearoylation step, as the melting points, TLC, FT-IR, ^{1}H and ^{13}C-NMR of both acids were identical with those of the authentic samples.

The structures of all products were characterized by their spectral data for new compounds or by comparison with those of authentic samples, in the case of known products.

As an important factor, the recyclability of catalyst (TPAB) was also investigated for synthesis of compound **5d**.



Scheme 2: A plausible mechanistic pathway for the formation of **5**.

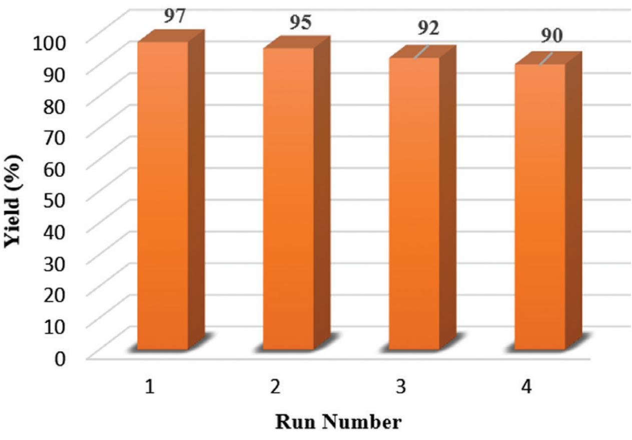


Figure 1: Reusability of TPAB for the synthesis of **5d**.

The catalyst was recovered and reused for four times to show no significant loss on catalytic performance of TPAB as shown in Figure 1.

4 Conclusions

Synthesis of a new series of pyrazolopyridines and pyrazoloquinolines was reported using a one-pot, three-component procedure in the presence of TPAB as a catalyst. The proposed procedure provides a new synthetic route for synthesis of pyrazolopyridine and pyrazoloquinoline derivatives, which may have pharmaceutical and biological applications. High yields, using green solvent, easily available starting materials, operational simplicity and the recoverable catalyst are some of the advantages of our procedure.

Acknowledgements: The authors gratefully acknowledge the financial support from Urmia University. We thank Professor R.H. Prager from Flinders University of Australia for proof-reading of this article.

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