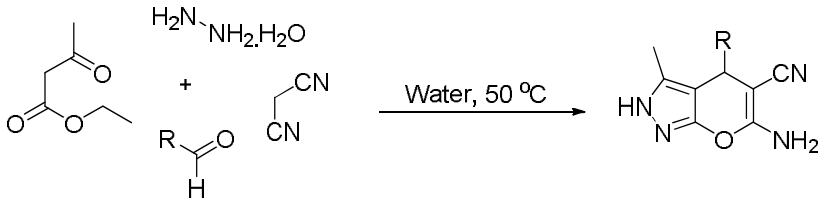
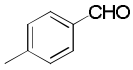
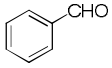
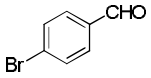
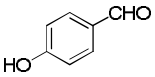
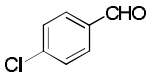
Supplementary data

A practical catalyst-free synthesis of 6-amino-4 alkyl/aryl-3-methyl-2,4-dihydropyrano[2,3-*c*]pyrazole-carbonitrile in aqueous medium

Manisha Bihani, Pranjal P Bora and Ghanashyam Bez*
Department of Chemistry, North Eastern Hill University, Shillong-793022, India

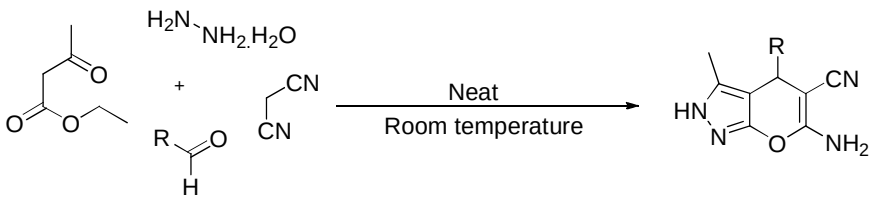
Table 1: Attempted synthesis of dihydropyrano[2,3-*c*]pyrazole employing reported method[a] by Shi et al.[1]

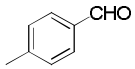
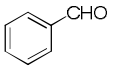
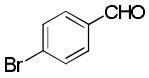
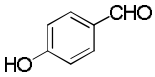
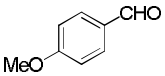


Entry	Aldehyde	Time(h)	% Yield (Reported[1])	% Yield[b] (Observed)
1		5	85	53
2		10	-	71
3		3	73	45
4		12	-	67
5		2	83	50
6		8	-	68
7		3	75	47
8		10	-	62
9		1	80	55
10		8	-	70

[a]Reaction of equimolar mixture of aryl aldehydes, hydrazine, ethyl acetoacetate and malononitrile in water at 50 °C under high stirring condition; [b]Isolated yield following the reported work-up procedure.

Table 2: Attempted synthesis of dihydropyrano[2,3-*c*]pyrazole employing reported method[a] by Reddy et al.[2]



Entry	Aldehyde	Time	% Yield (Reported[2])	% Yield[b] (Observed)
1		5 min	83	45
2		8 h	-	55[c]
3		6 min	53	34
4		8 h	-	42[c]
5		8 min	58	37
6		8 h	-	50[c]
7		10 min	48	32
8		8 h	-	47[c]
9		5 min	65	30
10		8 h	-	42[c]

[a]Reaction of equimolar mixture of aryl aldehydes, hydrazine, ethyl acetoacetate and malononitrile under vigorous stirring at room temperature; [b]Isolated Yield; [c]Reaction did not complete.

References

[1] Y. Zou, H. Wub, Y. Hua, H. Liu, X. Zhao, H. Ji, D. Shi, "A novel and environment-friendly method for preparing dihydropyrano[2,3-c]pyrazoles in water under ultrasound irradiation. " *Ultrasonics Sonochemistry*, vol. 18, no. 3, pp. 708-712, 2011.

[2] A. S. Nagarajan, B. S. R. Reddy, "Synthesis of substituted pyranopyrazoles under neat conditions via a multicomponent reaction " *Synlett*, no. 12, pp. 2002-2004, 2009.