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Catalyst-free, efficient and one pot protocol for synthesis of nitriles from aldehydes using glycerol as green solvent

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ABSTRACT

We described herein the novel, efficient and one-pot catalyst free protocol for the synthesis of nitriles from aldehydes by using hydroxyl amine hydrochlorides in glycerol as a green solvent. This protocol was efficiently used for transformation of aromatic aldehydes bearing electron-withdrawing and electron-donating groups into a aryl nitriles in good to excellent yields. The methodology offers a very simple, efficient and environmentally benign procedure.

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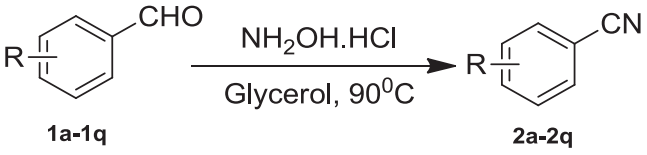
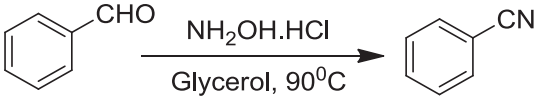
Nitriles are versatile synthetic precursors for the preparation of agricultural chemicals, polymers, pigments, dyes and pharmaceuticals.[1] In addition, they are used for preparation of amines, amidines, amides, aldehydes and carboxylic acid and nitrogen containing heterocyclic systems.[2] More-over, the cyano group itself is present in biologically active compound, such as Letrazole (used in the treatment of breast cancer), Periciazine (an antipsychotic drug), Citalopram (an antidepressant drug), HIV protease inhibitors, and 5-lipoxygenase inhibitors.[3] Numerous methods are reported in the literature for the synthesis of aryl nitriles using various reagents. Sandmeyer and Rosenmund-von Braun reactions are classic methods for the synthesis of aryl nitriles, but both methods require stoichiometric amounts of Copper(I)cyanide reagents and prefunctionlized starting materials.[4] The well developed transition-metal catalysed cyanation of aryl halides[5] and C—H cyanation reactions[6] also used for synthesis of aryl nitriles. Metal cyanide has been commonly used in direct cyanation reactions, such as KCN, NaCN, CuCN, AgCN, and TMSCN. The ammoxidation of toluene derivatives is an industrial scale method for nitrile synthesis.[7] The ammoxidation is applicable only to a limited number of substituted toluene derivatives and it is also requires high temperature and high pressure besides the use of excess ammonia restricts its application. Many methods have been reported that aldehydes can be directly converted into nitriles without isolation of aldoxime intermediates upon the one-pot treatment with hydroxylamine in the presence of various



Scheme 1. General scheme of reaction.

Table 1
Reaction conditions optimization.[a]



Entry	Temperature (°C)	Time (h)	Yield **2a**[b] (%)
1	Rt	24	–
2	60	12	43
3	90	7.0	90
4	90	24	–[c]
5	90	24	–[d]
6	120	7.0	90

[a] Reactions are performed using benzaldehyde 1a (1.0 mmol), hydroxylamine hydrochloride (1.0 mmol) in glycerol (5 mL).
[b] Yields are given for isolated product.
[c] Reaction performed without glycerol.
[d] Reaction performed in ethanol, methanol.

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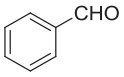
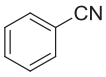
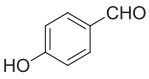
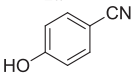
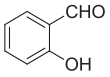
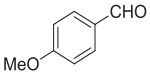
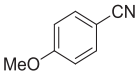
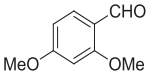
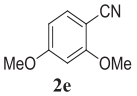
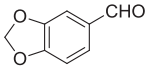
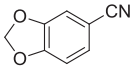
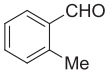
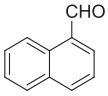
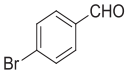
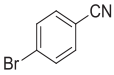
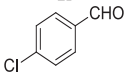
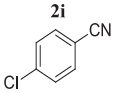
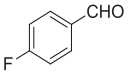
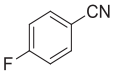
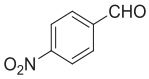
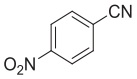
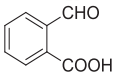
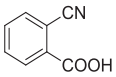
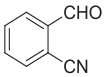
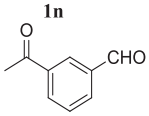
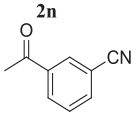
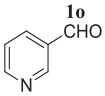
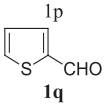
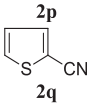
Table 2
Synthesis of organic nitriles 2a-2q using glycerol as solvent.[a]

Entry	Aldehyde (1)	Time (h)	Product (2)	Yield[b] (%)
1	 **1a**	7.0	 **2a**	90%
2	 **1b**	7.0	 **2b**	91%
3	 **1c**	7.0	 **2c**	90%
4	 **1d**	6.5	 **2d**	92%
5	 **1e**	6.5	 **2e**	93%
6	 **1f**	6.5	 **2f**	93%
7	 **1g**	7.0	 **2g**	89%
8	 **1h**	7.0	 **2h**	86%
9	 **1i**	8.5	 **2i**	85%
10	 **1j**	8.5	 **2j**	85%
11	 **1k**	9.0	 **2k**	83%
12	 **1l**	9.5	 **2l**	81%
13	 **1m**	9.5	 **2m**	80%
14	 **1n**	9.5	 **2n**	83%
15	 **1o**	8.0	 **2o**	83%
16	 1p	7.0	 **2p**	86%
17	 **1q**	7.0	 **2q**	86%

[a] Reactions are performed using aryl aldehydes **1a-1q** (1.0 mmol), hydroxylamine hydrochloride (1.0 mmol) in glycerol (5 mL).
[b] Yields are given for isolated product.

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