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Note

p-Toluenesulfonic acid catalyzed rapid and efficient protocol for one-pot synthesis of α-amino nitriles

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A simple, rapid and efficient practical method for one-pot synthesis of α-amino nitriles has been achieved by a three-component condensation of carbonyl compounds, amines and trimethylsilyl cyanide in the presence of *p*-toluenesulfonic acid (*p*-TsOH) as a catalyst at ambient temperature. Operational simplicity, economic consideration, high yield, short reaction time and low toxicity are the key features associated with this protocol.

Keywords: *p*-TsOH, α-amino nitriles, one-pot three-component condensation, carbonyl compounds, amines, trimethylsilyl cyanide

α-Amino nitriles have tremendous significance in synthetic organic chemistry as they are the key intermediates in the synthesis of many α-amino acids[1], various nitrogen-containing heterocycles such as imidazoles and thiadiazoles[2], 4-amino-2,3-dihydroisothiazole-1,1-dioxides[3] and azaspironucleoside analogous of TSAO[4]. They are usually prepared by the nucleophilic addition of a cyanide anion to imines. The classical Strecker reaction for the synthesis of α-amino nitriles involves the treatment of carbonyl compounds with alkaline cyanides and salts of amines in aqueous medium[5]. The experimental procedure is tedious and thus, several modified methods have been reported using a variety of cyanide reagents such as α-trimethylsilyloxy nitrile, diethyl phosphorocyanidate and tri-*n*-butyltin cyanide[6], as well as catalysts such as $Sc(OTf)_3$ (Ref 7), $InCl_3$ (Ref 8), Pt-complex[9], Cd-salt[10], $BiCl_3$ (Ref 11), montmorillonite KSF clay[12], $Pr(OTf)_3$ (Ref 13), $NiCl_2$ (Ref 14), $RuCl_3$ (Ref 15), $CoCl_2$ (Ref 16), I_2 (Ref 17), (bromodimethyl)sulfonium bromide[18], $RhCl_3$ (Ref 19) and 2,4,6-trihydroxy-1,3,5-triazine (cyanuric acid)[20] under various reaction conditions. However, many of these methods involve the use of expensive reagents such as metal triflates, extended reaction times, harsh reaction conditions and also require tedious work-up procedure leading to the generation of a large amount of toxic waste with unsatisfactory yields of products. Furthermore, many of these catalysts are deactivated or decomposed by amines and water produced during imine formation. Thus, there is a need to develop a facile one-pot synthesis of α-amino nitriles using an inexpensive reagent.

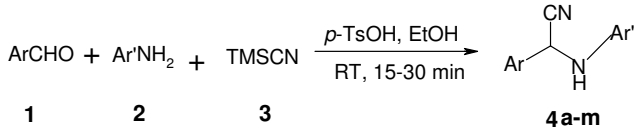
Over the past few years the use of *p*-toluenesulfonic acid (*p*-TsOH) as a catalyst has received considerable attention in different areas of organic synthesis[21]. Especially, it makes the reaction process convenient, cost effective and environmentally benign.

In continuation of the work to develop new organic transformations[22-30], herein is described the use of *p*-TsOH as an inexpensive catalyst for the synthesis of α-amino nitriles by a three-component condensation of carbonyl compounds, amines and trimethylsilyl cyanide (TMSCN). Although *p*-TsOH has been extensively used as a catalyst for a plethora of organic transformations[21], there are no reports on the use of *p*-TsOH as a catalyst for the synthesis of α-amino nitriles.

Results and Discussion

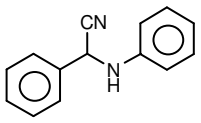
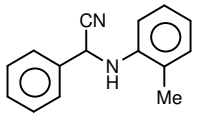
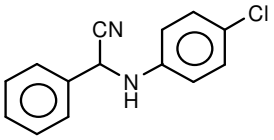
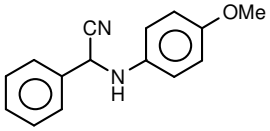
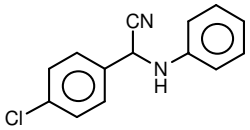
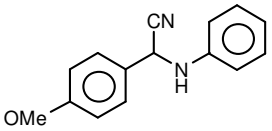
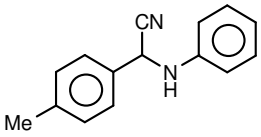
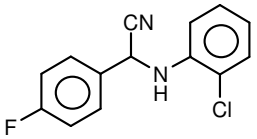
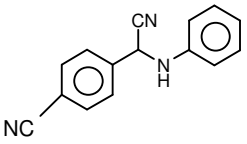
In view of the importance of α-amino nitriles in synthetic organic chemistry, herein is described a simple and efficient protocol for the three-component coupling reactions of aldehydes, amines and trimethylsilyl cyanide (TMSCN) to prepare α-amino nitriles using *p*-toluenesulfonic acid (*p*-TsOH) catalyst in ethanol under mild reaction conditions (**Scheme I**). Excellent yields of α-amino nitriles were obtained by carrying out the reactions in ethanol as solvent at RT in 15-30 min.

The treatment of benzaldehyde and aniline with TMSCN in the presence of a catalytic amount of *p*-TsOH in ethanol afforded the corresponding 2-(N-anilino)-2-phenylacetonitrile in 89% yield. To



Scheme I

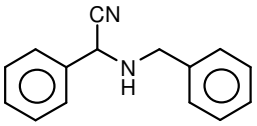
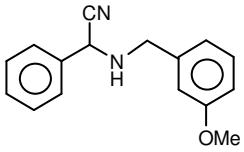
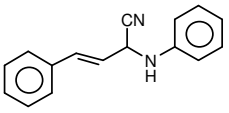
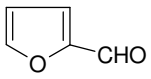
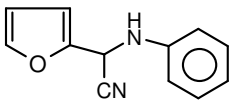
Table I — *p*-TsOH catalyzed one-pot synthesis of α-amino nitriles

Entry	Aldehyde (**1**)	Amine (**2**)	Product (**4a-m**)[a]	Reaction time (min)	Yield (%)[b]
a	C_6H_5CHO	$C_6H_5NH_2$		15	89
b	C_6H_5CHO	$2\text{-}MeC_6H_4NH_2$		15	91
c	C_6H_5CHO	$4\text{-}ClC_6H_4NH_2$		15	87
d	C_6H_5CHO	$4\text{-}OMeC_6H_4NH_2$		15	85
e	$4\text{-}ClC_6H_4CHO$	$C_6H_5NH_2$		25	83
f	$4\text{-}OMeC_6H_4CHO$	$C_6H_5NH_2$		20	87
g	$4\text{-}MeC_6H_4CHO$	$C_6H_5NH_2$		15	89
h	$4\text{-}FC_6H_4CHO$	$2\text{-}ClC_6H_4NH_2$		30	86
i	$4\text{-}CNC_6H_4CHO$	$C_6H_5NH_2$		30	85

—Contd

generalize this method, a variety of aldehydes were coupled with a range of anilines which resulted in the formation of the corresponding α-amino nitriles in good to excellent yields (**Table I**). A range of solvents (such as methanol, dichloromethane, dichloroethane, tetrahydrofuran, ethanol, and acetonitrile) were examined and ethanol emerged as the superior medium. Trimethylsilyl cyanide has been used as a safer and more effective cyanide anion source compared to various other cyanide reagents such as diethyl phosphorocyanidate, α-trimethylsilyloxy nitrile and tri-*n*-butyltin cyanide used in the Strecker process.

Table I — *p*-TsOH catalyzed one-pot synthesis of α-amino nitriles—*Contd*

Entry	Aldehyde (**1**)	Amine (**2**)	Product (**4a-m**)[a]	Reaction time (min)	Yield (%)[b]
j	C_6H_5CHO	$C_6H_5CH_2NH_2$		20	89
k	C_6H_5CHO	3-$OMeC_6H_4CH_2NH_2$		20	88
l	C_6H_5CH=CH-CHO	$C_6H_5NH_2$		20	87
m		$C_6H_5NH_2$		15	86

[a]All the reactions were carried out at RT
[b]Isolated yields after purification

These three-component coupling reactions proceed efficiently at ambient temperature with high selectivity. No undesired side-product (such as cyanohydrin trimethylsilyl ether, an adduct between the aldehyde and trimethylsilyl cyanide) could be detected because of the rapid formation of the imine intermediate.

The reactions are clean and highly selective affording exclusively α-amino nitriles in high yields in a short reaction time. This method is equally effective with aldehydes bearing electron-donating and electron-withdrawing substituents in the aromatic ring, and does not require any other additives to promote the reaction or any stringent reaction conditions to proceed. Furthermore, acid sensitive aldehydes such as furfuraldehyde and cinnamaldehyde worked well without any decomposition or polymerization under these reaction conditions.

The reaction conditions are mild enough to perform these reactions in the presence of either acid or base sensitive substrates. The scope and generality of this process is illustrated with respect to various amines and aldehydes including aromatic α,β-unsaturated and heterocyclic aldehydes and the results are presented in **Table I**. The progress of the reaction was monitored by thin-layer chromatography on silica gel. All yields refer to isolated products. The products are known molecules and were identified by comparing their spectral data and physical properties (**Table II**) with those of authentic samples.

2,4,6-Trichloro-1,3,5-triazine (TCT) is known to react with incipient moisture to form HCl along with 2,4,6-trihydroxy-1,3,5-triazine (cyanuric acid), which activates the imine system through hydrogen bonding and facilitate cyanation[20]. The conversion completely failed under anhydrous conditions. The catalytic activity of TCT is much less in solvents containing oxygen atom such as THF, EtOH, Et_2O, *etc*., than in $CHCl_3$, CH_2Cl_2, CH_3CN, *etc*., which do not contain oxygen atom. Such limitations are not found with *p*-TsOH catalyst.

In comparison with other catalysts such as $Sc(OTf)_3$, $InCl_3$, $BiCl_3$, KSF-clay, $Pr(OTf)_3$, $RuCl_3$, I_2, (bromodimethyl)sulfonium bromide, $RhCl_3$ and cyanuric acid employed for the aminocynation of benzaldehyde, *p*-TsOH shows more catalytic reactivity than the others in terms of the amount of catalyst required, reaction times, and yields of the product (**Table III**).

Experimental Section

All the reagents were commercially obtained and purified prior to use. Melting points were determined in an open capillary tube on a Cintex melting point

Table II — Product characterization data of *p*-TsOH catalyzed one-pot synthesis of α-amino nitriles

Entry	Product	Product characterization data
4a	2-(N-Anilino)-2-phenylacetonitrile	White crystalline solid, m.p. 73-74°C (Lit.73-74°C, Ref 13); IR (KBr): 3370, 3020, 2955, 2236, 1600, 1505, 1465, 1310, 1140, 995, 751 cm^{-1}; ^1H NMR($CDCl_3$): δ 4.0 (d, 1H, *J* = 8.1 Hz), 5.40 (d, 1H, *J* = 8.1 Hz), 6.74 (d, 2H, *J* = 8.0 Hz), 6.90 (t, 1H, *J* = 7.8 Hz), 7.25 (t, 2H, *J* = 7.8 Hz), 7.40-7.50 (m, 3H), 7.60-7.70 (m, 2H); MS: *m/z* 208 (M^+), 180, 116, 91, 77, 55.
4b	2-(N-2-Methylanilino)-2-phenylacetonitrile	Pale yellow solid, m.p. 73-74°C (Lit. 72-73°C, Ref 12); IR (KBr): 3365, 2935, 2855, 2238, 1605, 1515, 1460, 1275, 1035, 790 cm^{-1}; ^1H NMR($CDCl_3$): δ 2.20 (s, 3H), 3.38, (brd, 1H, NH, *J* = 8.1 Hz), 5.45 (d, 1H, *J* = 8.1 Hz), 6.80 (t, 2H, *J* = 7.9 Hz), 7.10 (d, 1H, *J* = 8.0 Hz), 7.20 (d, 1H, *J* = 7.9 Hz), 7.40-7.50 (m, 3H), 7.50 (d, 2H, *J* = 8.0 Hz); MS: *m/z* 222 (M^+), 194, 155, 141, 116, 106, 91, 73, 65, 45.
4c	2-(N-4-Chloroanilino)-2-phenylacetonitrile	Pale yellow solid, m.p. 107-110°C (Lit.108-110°C, Ref 18); IR (KBr): 3410, 2930, 2230, 1610, 1520, 1460, 1270, 1050, 790 cm^{-1}; ^1H NMR($CDCl_3$): δ 4.05 (d, 1H, *J* = 8.0 Hz), 5.30 (d, 1H, *J* = 8.0 Hz), 6.62 (d, 2H, *J* = 8.0 Hz), 7.15 (d, 2H, *J* = 8.0 Hz), 7.34-7.45 (m, 3H) 7.49-7.60 (m, 2H); MS: *m/z* 242 (M^+), 215, 178, 126.
4d	2-(N-4-Methoxyanilino)-2-phenylacetonitrile	Pale yellow solid, m.p. 95-96°C (Lit.94-96°C, Ref 18); IR (KBr): 3390, 2935, 2850, 2240, 1615, 1520, 1465, 1285, 1045, 790 cm^{-1}; ^1H NMR($CDCl_3$): δ 3.70 (s, 3H), 3.85 (d, 1H, *J* = 8.0 Hz), 5.30 (d, 1H, *J* = 8.0 Hz), 6.67 (d, 2H, *J* = 8.0 Hz), 6.79 (d, 2H, *J* = 8.0 Hz), 7.35-7.46 (m, 3H), 7.53-7.61 (m, 2H); MS: *m/z* 238 (M^+), 211, 210, 146.
4e	2-(N-Anilino)-2-(4-chloro-phenyl)acetonitrile	White solid, m.p. 110-112°C (Lit.109-112°C, Ref 12); IR (KBr): 3405, 2925, 2240, 1600, 1515, 1455, 1270, 1160, 1100, 791 cm^{-1}; ^1H NMR($CDCl_3$): δ 4.0 (d,1H,*J* = 8.1 Hz), 5.40 (d, 1H, *J* = 8.1 Hz), 6.74 (d, 2H, *J* = 8.0 Hz), 6.90 (t, 1H, *J* = 7.9 Hz), 7.16 (t, 2H, *J* = 7.9 Hz), 7.40 (d, 2H, *J* = 8.0 Hz), 7.60 (d, 2H, *J* = 8.0 Hz); MS: *m/z* 242 (M^+), 213, 149, 114, 91, 73, 59.
4f	2-(N-Anilino)-2-(4-methoxy-phenyl)acetontrile	White solid, m.p. 93-95°C (Lit.94-95°C, Ref 12); IR (KBr): 3382, 3050, 2932, 2245, 1600, 1500, 1454, 1300, 1118, 1040, 925, 765 cm^{-1}; ^1H NMR($CDCl_3$): δ 3.80 (s, 3H), 3.90 (d, 1H, *J* = 8.1 Hz), 5.30 (d, 1H, *J* = 8.1 Hz), 6.75 (d, 2H, *J* = 8.0 Hz), 6.80 (t, 1H, *J* = 7.9 Hz), 6.90 (d, 2H, *J* = 8.0 Hz), 7.25 (t, 2H, *J* = 7.9 Hz), 7.50 (d, 2H, *J* = 8.0 Hz); MS: *m/z* 238 (M^+), 211, 181, 167, 141, 104, 77, 51, 40.
4g	2-(N-Anilino)-2-(4-methyl-phenyl)acetonitrile	Yellow solid, m.p. 77-79°C (Lit.76-78°C, Ref 12); IR (KBr): 3305, 2925, 2850, 2225, 1690, 1575, 1460, 1215, 1140, 1015, 940, 765 cm^{-1}; ^1H NMR($CDCl_3$): δ 2.40 (s, 3H), 6.79 (d, 1H, *J* = 8.0 Hz), 6.90 (t, 1H, *J* = 7.8 Hz), 7.22-7.30 (m, 4H), 7.50 (d, 2H, *J* = 8.0 Hz); MS: *m/z* 222 (M^+), 194, 176, 131, 103, 91, 77, 41.
4h	2-(N-2-Chloroanilino)-2-(4-fluorophenyl)acetonitrile	White crystalline solid**,** m.p. 96-98°C (Lit.95-97°C, Ref 12); IR (KBr): 3410, 2930, 2230, 1610, 1520, 1460, 1270, 1050, 790 cm^{-1}; ^1H NMR($CDCl_3$): δ 4.66 (d, 1H, *J* = 8.1 Hz), 5.45 (d, 1H, *J* = 8.1 Hz), 6.90-6.95 (m, 2H), 7.15-7.35 (m, 4H), 7.59-7.65 (m, 2H); MS: *m/z* 260 (M^+), 234, 135, 100, 75.
4i	2-(N-Anilino)-2-(4-cyano-phenyl)acetonitrile	Pale yellow solid**,** m.p. 113-114°C (Lit.112-114°C, Ref 19); IR (KBr): 3415, 3065, 2250, 1610, 1505, 1440, 1300, 1260, 1150, 1050, 845, 760 cm^{-1}; ^1H NMR($CDCl_3$): δ 5.59 (s, 1H), 6.80-6.83 (d, 2H, *J* = 8.0 Hz), 6.95-7.03 (t, 1H, *J* = 8.0 Hz), 7.25-7.35 (m, 2H), 7.75 (m, 4H); MS: *m/z* 234 (M^+), 207, 146.
4j	2-(N-Benzylamino)-2-phenylacetonitrile	Colourless oil[12], IR (KBr): 3410, 2925, 2235, 1648, 1515, 1400, 1108, 1029, 920, 825, 751 cm^{-1}; ^1H NMR($CDCl_3$): δ 1.80 (brs, 1H, NH), 3.94 (AB q, 2H, *J* = 13.5 Hz), 4.70 (s,1H), 6.76 (d, 1H, *J* = 8.0 Hz), 7.15 (t, 1H, *J* = 7.8 Hz), 7.25-7.39 (m, 6H), 7.48-7.50 (m, 2H); MS: *m/z* 222 (M^+),195, 141, 131, 116, 106, 91, 77, 51.
4k	2-(N-3-Methoxybenzylamino)-2-phenylacetonitrile	Yellow liquid[12], IR (KBr): 3400, 2940, 2890, 2241, 1615, 1528, 1470, 1282, 1160, 1045, 790 cm^{-1}; ^1H NMR($CDCl_3$): δ 1.85 (brs, 1H, NH), 3.80 (s, 3H), 3.95 (AB q, 2H, *J* = 13.0 Hz), 4.70 (d, 1H, *J* = 13.0 Hz), 6.80-6.93 (m, 3H), 7.24 (t, 1H, *J* = 7.9 Hz), 7.30-7.55 (m, 5H); MS: *m/z* 252 (M^+), 225, 122, 91, 77.
4l	2-(N-Anilino)-2-cinnamylacetonitrile	Pale yellow solid, m.p. 118-120°C (Lit.117-119°C, Ref 12) IR (KBr): 3350, 2930, 2233, 1605, 1505, 1460, 1275, 1030, 975, 897, 746 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.80 (d, 1H, *J* = 8.1 Hz), 5.05 (m, 1H), 6.30 (dd, 1H, *J* = 6.9, 17.3 Hz), 6.78 (d, 1H, *J* = 8.0 Hz), 6.90 (t, 1H, *J* = 7.9 Hz), 7.08 (dd, 1H, *J* = 1.7, 17.3 Hz), 7.25-7.50 (m, 8H); MS: *m/z* 234 (M^+), 206, 128, 115, 77, 51.
4m	2-(N-Anilino)-2-furfurylacetonitrile	Dark brown solid, m.p. 69-71°C (Lit.68-70°C, Ref 12) IR (KBr): 3355, 2925, 2235, 1695, 1605, 1505, 1440, 1290, 1250, 1149, 1015, 880, 750 cm^{-1}; ^1H NMR ($CDCl_3$): δ 4.05 (d, 1H, *J* = 8.1 Hz), 5.40 (d, 1H, *J* = 8.1 Hz), 6.40 (m, 1H), 6.55 (m,1H), 6.80 (d, 2H, *J* = 8.0 Hz), 6.90 (t, 1H, *J* = 7.9 Hz), 7.25 (t, 2H, *J* = 7.9 Hz), 7.40 (m, 1H); MS: *m/z* 198 (M^+), 169, 155, 141, 115, 106, 92, 77, 51.

Table III — Comparison of the effect of catalysts in the synthesis of 2-(N-anilino)-2-phenylaceto nitrile[a]

Entry	Catalyst	Catalyst load (mole %)	Reaction time (min)	Yield (%)[b]
1	$Sc(OTf)_3$ (Ref 7)	10	1200	88
2	$InCl_3$ (Ref 8)	30	300	74
3	$BiCl_3$ (Ref 11)	10	600	84
4	KSF-clay (Ref 12)	more than 100	210	90
5	$Pr(OTf)_3$ (Ref 13)	10	600	89
6	$RuCl_3$ (Ref 15)	20	1200	74
7	I_2 (Ref 17)	10	60	90
8	(Bromodimethyl)-sulfonium bromide[18]	10	60	89
9	$RhCl_3$ (Ref 19)	35	60	86
10	Cyanuric acid[20]	10	35	86
11	*p*-TsOH (present study)	10	15	89

[a]All the reactions were carried out at RT
[b]Isolated yields after purification

apparatus and are uncorrected. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Varian Gemini-200 MHz spectrometer using TMS as an internal standard. Mass spectra were recorded on a VG micromass 7070H (70 eV) instrument. IR spectra were recorded on a Perkin-Elmer spectrum BX series FT-IR 5000 spectrometer using KBr optics. Column chromatography was carried out with silica gel 100-200 mesh and TLC with silica gel GF_{254}.

General procedure for the preparation of α-amino nitriles

To a mixture of an aldehyde (1 mmole), an amine (1 mmole) and trimethylsilyl cyanide (1.2 mmole) in ethanol (10 mL), *p*-toluenesulfonic acid (10 mole%) was added and the reaction mixture was stirred at RT. After completion of the reaction (monitored by TLC), the solvent was removed *in vacuo*, quenched with water (10 mL) and the crude product extracted with ethyl acetate (3 × 10 mL). The organic layer was washed with water (20 mL) and brine (20 mL) respectively, then dried using anhyd. $MgSO_4$, and concentrated *in vacuo*. The residue was subjected to column chromatography over silica gel (ethyl acetate:hexane, 1:9) as eluent to afford pure α-amino nitrile.

Conclusion

A very simple and efficient practical method for the synthesis of α-amino nitriles has been demonstrated through a one-pot three-component coupling of carbonyl compounds, amines, and trimethylsilyl cyanide using a catalytic amount of *p*-toluenesulfonic acid. The major advantage of this method is that it is truly a one-pot procedure that does not require a separate step to prepare an imine for subsequent use. The important features of this method include (i) operational simplicity, (ii) no need of any other additive to promote the reaction, (iii) short reaction times, (iv) the use of inexpensive and commercially available non-toxic catalyst, and (v) high yields of the desired products.

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