

# Niobium(V) chloride-catalyzed synthesis of $\alpha$ -aminonitriles with simultaneous reaction of aldehydes, amines and trimethylsilyl cyanide

Anjoy Majhi, Sung Soo Kim\* and Ho Sub Kim

A simple and efficient one-pot method has been developed for the synthesis of  $\alpha$ -aminonitriles by concurrent reaction of aldehydes, amines and trimethylsilyl cyanide with a catalytic amount of  $\text{NbCl}_5$  (10 mol%) in  $\text{CH}_3\text{CN}$  at room temperature. Copyright © 2008 John Wiley & Sons, Ltd.

**Keywords:**  $\text{NbCl}_5$ ; catalysis; aldehydes; amines; trimethylsilyl cyanide;  $\alpha$ -aminonitriles

## Introduction

$\alpha$ -Aminonitriles are important intermediates for the preparation of many amino acids<sup>[1]</sup> and various nitrogen containing heterocycles such as imidazoles and thiadiazoles.<sup>[2]</sup>  $\alpha$ -Amino acids are also of great biological and economical importance due to their significance in chemistry and biology and as useful chiral building blocks.<sup>[3–7]</sup> Numerous methods describing the preparation of  $\alpha$ -aminonitriles have been reported in the literature.<sup>[8–21]</sup> However, most of these methods involve the use of strong acidic conditions, expensive reagents, extended reaction times, harsh conditions and tedious work-up, leading to the generation of a large amount of toxic waste. Recently,  $\text{NbCl}_5$  has emerged as an efficient Lewis acid catalyst in promoting various organic transformations.<sup>[22–27]</sup>  $\text{NbCl}_5$  has not been exploited for the synthesis of  $\alpha$ -aminonitriles.

In the light of our success in developing several catalytic systems for the synthesis of chiral<sup>[28–31]</sup> and racemic cyanosilyl ether,<sup>[32–35]</sup> we extend them to the Strecker-type reaction for the synthesis of  $\alpha$ -aminonitriles. Most recently, we have reported  $\text{NbCl}_5$  to be a catalyst for the synthesis of cyanohydrin trimethylsilyl ether.<sup>[36]</sup> We wish to herein report a simple and efficient method for the synthesis  $\alpha$ -aminonitriles in the presence of a catalytic amount of  $\text{NbCl}_5$  in  $\text{CH}_3\text{CN}$  at room temperature (r.t.).

## Experimental

In all cases the  $^1\text{H}$  NMR (200 MHz) spectra were recorded using a Varian Gemini 2000 spectrometer. Chemical shifts are reported in ppm in  $\text{CDCl}_3$  with tetramethylsilane as an internal standard.  $^{13}\text{C}$  NMR data were collected on a Varian Gemini 2000 spectrometer (100 MHz). GCMS data were recorded with a 1200L single quadrupole GC/MS system with 3800GC/Varian.

### General procedure for the synthesis of $\alpha$ -aminonitriles

A mixture of aldehyde (1 mmol), amine (1 mmol) and trimethylsilyl cyanide (1.2 mmol) in acetonitrile (1 ml) in the presence of  $\text{NbCl}_5$  (27.2 mg, 10 mol%) was stirred at room temperature. The completion of the reaction was monitored using thin-layer chromatography, then the reaction mixture was filtered and the

filtrate was concentrated. Water (10 ml) was added to the residue and the mixture was extracted with ether ( $3 \times 5$  ml). The extract was concentrated and the viscous mass was subject to silica gel flash column chromatography (silica gel, 4% EtOAc in hexane) to obtain pure  $\alpha$ -aminonitriles compound.

The spectral (IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR, GCMS and HRMS) data of some representative products are given below.

#### 2-(4-chlorophenyl)-2-(4-methylbenzylamino)acetonitrile (entry 8; Scheme 1)

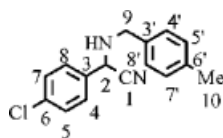
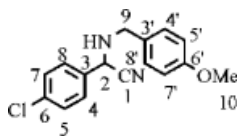
Yellow oil; IR (KBr): 3324, 3029, 2227, 1580, 1495, 1219, 1022, 919, 772, 696;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  (ppm) = 2.02 (brs, 1H, N-H), 2.40 (s, 3H, H-10), 3.97 (AB q,  $J$  = 13.2, 2H, H-9), 4.79 (s, 1H, H-2), 7.22–7.34 (m, 6H, Ar-H), 7.42 (d,  $J$  = 8.0 Hz, 2H, H-5, 6);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  (ppm) = 21.5 (C-10), 49.2 (C-2), 51.5 (C-9), 117.9 (CN, C-1), 127.2 (C-5, 7), 128.2 (C-5', 7') 128.6 (C-4', 8'), 129.6 (C-4, 8), 131.2 (C-3), 133.1 (C-6), 134.7 (C-6'), 136.3 (C-3'); GCMS:  $m/z$ : 270 [ $\text{M}^+$ ]; HRMS calcd for  $\text{C}_{16}\text{H}_{15}\text{ClN}_2$ : 270.0924. Found: 270.0916.

#### 2-(4-chlorophenyl)-2-(4-methoxybenzylamino)acetonitrile (entry 9; Scheme 2)

Light yellow oil; IR (KBr): 3322, 2932, 2228, 1611, 1491, 1248, 1219, 1093, 1033, 920, 772;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  (ppm) = 2.06 (brs, 1H, N-H), 3.82 (s, 3H, H-10), 3.91 (AB q,  $J$  = 13.2, 2H, H-9), 4.72 (s, 1H, H-2), 6.89–6.94 (m, 2H, H-5', 7'), 7.28–7.51 (m, 6H, Ar-H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  (ppm) = 50.5 (C-2), 52.5 (C-9), 55.1 (C-10), 113.8 (C-5', 7'), 118.2 (CN, C-1), 128.4 (C-5, 7), 128.9 (C-4, 8), 129.4 (C-4', 8'), 129.6 (C-3), 133.1 (C-3'), 134.7 (C-6), 158.9 (C-6'); GCMS:  $m/z$ : 286 [ $\text{M}^+$ ], 258, 120; HRMS calcd for  $\text{C}_{16}\text{H}_{15}\text{ClN}_2\text{O}$ : 286.0873. Found: 286.0880.

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**Scheme 1.** 2-(4-chlorophenyl)-2-(4-methylbenzylamino)acetonitrile.**Scheme 2.** 2-(4-chlorophenyl)-2-(4-methoxybenzylamino)acetonitrile.**2-(Benzylamino)-2-(3-fluorophenyl)acetonitrile**  
(entry 10; Scheme 3)

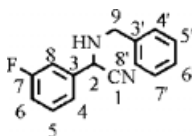
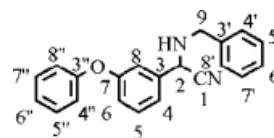
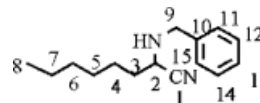
Colorless oil; IR (KBr): 3325, 3030, 2230, 1614, 1592, 1487, 1243, 1139, 1075, 964, 771, 699;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 4.02 (AB q,  $J$  = 13.0 Hz, 2H, H-9), 4.77 (s, 1H, H-2), 7.11 (d, 1H,  $J$  = 8.0 Hz, H-8), 7.30–7.46 (m, 8H, Ar-H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  (ppm) = 51.0 (C-2), 52.7 (C-9), 114.5 (C-6), 116.0 (C-8), 118.1 (CN, C-1), 122.7 (C-4), 127.6 (C-6'), 128.2 (C-4', 8'), 128.5 (C-5', 7'), 130.3 (C-5), 137.0 (C-3), 137.7 (C-3'), 164.0 (C-7); GCMS:  $m/z$ : 240 [ $\text{M}^+$ ], 213, 107, 105, 91; HRMS calcd for  $\text{C}_{15}\text{H}_{13}\text{FN}_2$ : 240.1063. Found: 240.1062.

**2-(Benzylamino)-2-(3-phenoxyphenyl)acetonitrile**  
(entry 12; Scheme 4)

Light yellow oil; IR (KBr): 3365, 3029, 2925, 2226, 1580, 1440, 1106, 1019, 825, 753, 692;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 2.3 (brs, 1H, NH), 4.03 (AB q, 2H,  $J$  = 13.4 Hz, H-9), 4.76 (s, 1H, HH-2), 7.05–7.13 (m, 2H, Ar-H), 7.22–7.47 (m, 12H, Ar-H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  (ppm) = 50.8 (C-2), 52.8 (C-9), 117.3 (C-8), 118.2 (CN, C-1), 118.7 (C-6), 118.9 (C-4'', 8''), 121.5 (C-4), 123.4 (C-6''), 127.3 (C-6'), 128.0 (C-4', 8'), 128.0 (C-5), 129.6 (C-5'', 7''), 129.9 (C-5', 7'), 136.4 (C-3), 137.7 (C-3'), 156.2 (C-7), 157.5 (C-3''); GCMS:  $m/z$  315 [ $\text{M} + \text{H}$ ], 314 [ $\text{M}^+$ ], 287; HRMS calcd for  $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}$ : 314.1419. Found: 314.1418.

**2-(benzylamino)octanenitrile** (entry 15; Scheme 5)

Brown oil; IR (KBr): 3321, 3030, 2928, 2857, 2220, 1453, 1219, 1132, 1028, 772, 698;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  (ppm) = 0.84 (t,  $J$  = 7.8 Hz, 3H, H-8), 1.21–1.44 (m, 8H, H-4, 5, 6, 7), 1.66 (q,  $J$  = 7.1 Hz, 2H, H-3), 2.04 (brs, 1H, N-H), 3.40 (t,  $J$  = 7.8 Hz, 1H, H-2), 3.77 (AB q,  $J$  = 7.2 Hz, 2H, H-9), 7.20–7.28 (m, 5H, Ar-H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  (ppm) = 13.9 (C-8), 22.3 (H-7), 25.4 (C-4), 28.5 (C-5), 31.4 (C-6), 33.4 (C-3), 49.6 (C-2), 51.5 (C-9), 120.2 (CN, C-1), 127.1 (C-13), 127.6 (C-11, 15), 128.2 (C-12, 14), 138.3 (C-10); GCMS:  $m/z$  230 [ $\text{M}^+$ ], 203.

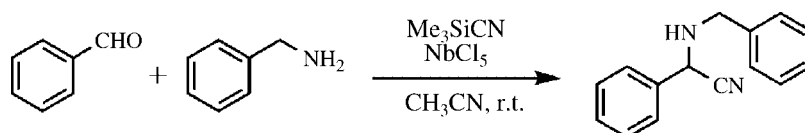
**Scheme 3.** 2-(Benzylamino)-2-(3-fluorophenyl)acetonitrile.**Scheme 4.** 2-(Benzylamino)-2-(3-phenoxyphenyl)acetonitrile.**Scheme 5.** 2-(benzylamino)octanenitrile.**N-benzylphenylglycine**

White solid; m.p. 221–222 °C; (lit.<sup>[40]</sup> 219–220 °C); HRMS calcd for  $\text{C}_{15}\text{H}_{15}\text{NO}_2$ : 241.1100. Found: 241.1087.

**Results and Discussion**

The catalytic activity of  $\text{NbCl}_5$  was tested for the reaction of benzaldehyde, benzyl amine and TMSN at r.t. As shown in Table 1, 5 mol%  $\text{NbCl}_5$  gives  $\alpha$ -aminonitriles with 70% yield in 1 h in  $\text{CH}_3\text{CN}$  (entry 3), while decreasing the catalyst loading up to 1 and 0.5 mol% it still gives lower yield, 68% (1 h) and 65% (1 h), of  $\alpha$ -aminonitriles, respectively (entries 1 and 2). With 10 mol% catalyst the yield was increased and afforded the corresponding 2-(benzylamino)-2-phenylacetonitrile in 96% yield within 25 min (entry 4); 15 mol%  $\text{NbCl}_5$  gave the corresponding product in 96% yield in 25 min (entry 5).  $\text{CH}_2\text{Cl}_2$  and THF took longer to complete the reaction and the yield was also reduced (entries 6 and 7). Only 50% conversion was observed without using any catalyst in  $\text{CH}_3\text{CN}$  at r.t. even after 1 h. Accordingly 10 mol%  $\text{NbCl}_5$  catalyst loading in  $\text{CH}_3\text{CN}$  as a solvent is considered optimal for the synthesis of  $\alpha$ -aminonitriles.

A variety of aldehydes including aromatic, aliphatic as well as  $\alpha,\beta$ -unsaturated ones and different amines were coupled in the presence of a catalytic amount of  $\text{NbCl}_5$  in  $\text{CH}_3\text{CN}$  at r.t. The reactions proceeded smoothly to afford the corresponding  $\alpha$ -aminonitriles in high yields in short reaction time (Table 2). The reactions are clean and highly selective, affording exclusively  $\alpha$ -aminonitriles. This method is equally effective with aldehydes bearing electron-donating and weakly electron-withdrawing substituents in the aromatic ring of aldehydes and amines as well. The reactions of *p*-methoxybenzaldehyde and *p*-tolualdehyde were completed in 25 min with 94 and 93% yields, respectively (entries 3 and 4). The reaction of *o*-chlorobenzaldehyde with benzylamine gave good results in 25 min with 93% yield (entry 5). The reaction of *p*-chlorobenzaldehyde both with aniline and benzylamine took place in 23 and 25 min with 94 and 96% yields, respectively (entries 6 and 7). The reaction of *p*-chlorobenzaldehyde with *p*-methylbenzylamine and *p*-methoxybenzylamine also proceeded nicely within 25 and 24 min with 95 and 92% yields, respectively (entries 8 and 9). *m*-Fluoro-benzaldehyde gave 95% yield in 23 min (entry 10). *m*-Phenoxybenzaldehyde took 30 and 24 min to complete the reaction with aniline and benzylamine to obtain 95 and 94% yields, respectively (entries 11 and 12). It should be noted that the reaction of 4-nitrobenzaldehyde and benzyl amine gave no reaction with formation of several unidentified products. It was observed that the reaction with cinnamaldehyde

**Table 1.** Three component synthesis of  $\alpha$ -aminonitriles under various conditions<sup>a</sup>

Entry	Catalyst (mol%)	Time	Yield (%) <sup>b</sup>
1	0.5	1 h	65
2	1	1 h	68
3	5	1 h	70
4	10	25 min	96
5	15	25 min	96
6	10	45 min	92 <sup>c</sup>
7	10	1 h	90 <sup>d</sup>

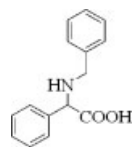
<sup>a</sup> NbCl<sub>5</sub> was added to a mixture of 1 mmol of benzaldehyde, 1 mmol of benzyl amine and 1.2 mmol of TMSCN. <sup>b</sup> Isolated yield. <sup>c</sup> In presence of CH<sub>2</sub>Cl<sub>2</sub>.<sup>d</sup> In the presence of THF.**Table 2.** NbCl<sub>5</sub> catalyzed three component synthesis of  $\alpha$ -aminonitriles<sup>a</sup>

Entry	Aldehyde	Amine	Product	Reaction time (min)	Yield (%) <sup>b</sup>
1	C <sub>6</sub> H <sub>5</sub> CHO	Ph-CH <sub>2</sub> -NH <sub>2</sub>		25 min	96
2	C <sub>6</sub> H <sub>5</sub> CHO	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>		4.5 h	87 <sup>[16]</sup>
				15 min <sup>c</sup>	94 <sup>[21]</sup>
				20 min	80 <sup>[37]</sup>
				20 min	95
				20 min	95
3	4-MeOC <sub>6</sub> H <sub>4</sub> CHO	Ph-CH <sub>2</sub> -NH <sub>2</sub>		3.5 h	90 <sup>[16]</sup>
				1 h	94 <sup>[11]</sup>
				10 h	84 <sup>[12]</sup>
				20 min	94 <sup>[37]</sup>
				25 min	94
4	4-MeC <sub>6</sub> H <sub>4</sub> CHO	Ph-CH <sub>2</sub> -NH <sub>2</sub>		20 min	81 <sup>[37]</sup>
				25 min	93
5	2-ClC <sub>6</sub> H <sub>4</sub> CHO	Ph-CH <sub>2</sub> -NH <sub>2</sub>		5.0 h	91 <sup>[16]</sup>
				25 min	93 <sup>[38]</sup>
6	4-ClC <sub>6</sub> H <sub>4</sub> CHO	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>		23 min	94
				1 h	90 <sup>[12]</sup>
7	4-ClC <sub>6</sub> H <sub>4</sub> CHO	Ph-CH <sub>2</sub> -NH <sub>2</sub>		20 min	91 <sup>[37]</sup>
				25 min	96
				25 min	96
8	4-ClC <sub>6</sub> H <sub>4</sub> CHO	4-MeC <sub>6</sub> H <sub>4</sub> -NH <sub>2</sub>		8 h	91 <sup>[12]</sup>
				25 min	95

**Table 2.** (Continued)

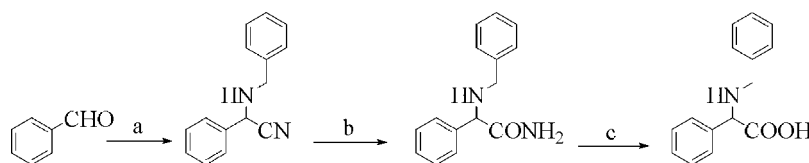
Entry	Aldehyde	Amine	Product	Reaction time (min)	Yield (%) <sup>b</sup>
9	4-ClC <sub>6</sub> H <sub>4</sub> CHO	4-MeOC <sub>6</sub> H <sub>4</sub> CHO		24 min	92
10	3-FC <sub>6</sub> H <sub>4</sub> CHO	Ph-CH <sub>2</sub> NH <sub>2</sub>		23 min	95
11	3-PhOC <sub>6</sub> H <sub>4</sub> CHO	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>		30 min	95
12	3-PhOC <sub>6</sub> H <sub>4</sub> CHO	Ph-CH <sub>2</sub> NH <sub>2</sub>		2.5 h 24 min	89 <sup>[16]</sup> 94
13	Ph-CH=CHO	Ph-CH <sub>2</sub> NH <sub>2</sub>		26 min	96
14	Ph-CH <sub>2</sub> CHO	Ph-CH <sub>2</sub> NH <sub>2</sub>		15 min <sup>c</sup> 20 min	90 <sup>[21]</sup> 68 <sup>[37]</sup>
15	Ph-CH <sub>2</sub> CHO	Ph-CH <sub>2</sub> NH <sub>2</sub>		30 min	91 <sup>[39]</sup>
16	Ph-CH <sub>2</sub> CHO	Ph-CH <sub>2</sub> NH <sub>2</sub>		37 min	93
17	Ph-CH <sub>2</sub> CHO	Ph-CH <sub>2</sub> NH <sub>2</sub>		35 min	90
18	Ph-CH <sub>2</sub> CHO	Ph-CH <sub>2</sub> NH <sub>2</sub>		5.5 h 20 min	89 <sup>[16]</sup> 82 <sup>[37]</sup>
19	Ph-CH <sub>2</sub> CHO	Ph-CH <sub>2</sub> NH <sub>2</sub>		35 min	89
20	Ph-CH <sub>2</sub> CHO	Ph-CH <sub>2</sub> NH <sub>2</sub>		1 h	84 <sup>[12]</sup>

<sup>a</sup> The structures of the products were settled from spectral (<sup>1</sup>H and <sup>13</sup>C NMR and MS) data. <sup>b</sup> Isolated yield after Silica gel flash column chromatography. <sup>c</sup> The reaction was carried out at 40 °C.

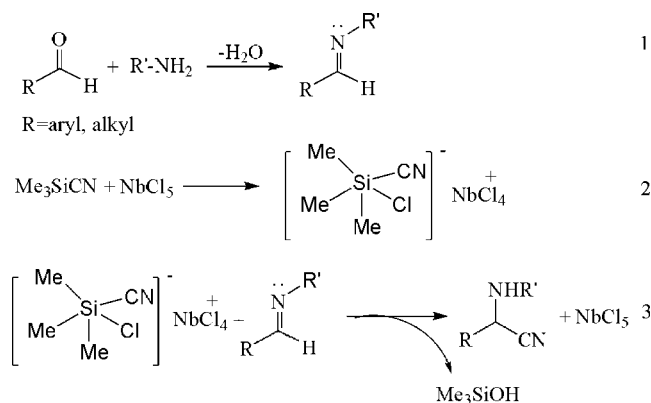
**Scheme 6.** N-benzylphenylglycine.

gave 96% yield of the corresponding aminocyano compound in 26 min (entry 13), whereas hydrocinnamaldehyde gave 91% yield in 30 min (entry 14). The reaction of heptaldehyde gives the corresponding product in 93% yield (entry 15). 2-Furaldehyde (entries 16 and 17) gave the corresponding aminonitrile compound in good yield. The acid-sensitive aldehydes such as 2-furaldehyde and cinnamaldehyde both gave the aminocyano compound in good yield. This may indicate that the catalytic system selectively activates the carbonyl function and keeps the furan ring and double bond of cinnamaldehyde intact. This method does not require any additives to promote the reaction. No cyanohydrin trimethylsilyl

ethers (an adduct between an aldehyde and trimethylsilylcyanide) were obtained under these reaction conditions because of the rapid formation of the imine intermediate by catalytic action of NbCl<sub>5</sub>. Some comparative results are also collected in Table 2. In contrast to our reaction time of 20–37 min, 5–10 h were required in the presence of 10 mol% BiCl<sub>3</sub>.<sup>[12]</sup> With montmorillonite KSF clay as a catalyst,<sup>[16]</sup> 3.0–5.5 h were taken for completion of the reaction in the presence of 1.0 g clay. One to eight hours of reaction time and 20 mol% I<sub>2</sub><sup>[17]</sup> were necessary for completion of the reaction. Recently a method utilizing 5 mol% Fe(Cp)<sub>2</sub>PF<sub>6</sub> was reported where 20 min were needed for the synthesis of  $\alpha$ -aminonitriles.<sup>[37]</sup> It is evident that 10 mol% NbCl<sub>5</sub> is a very efficient catalyst in terms of reaction time and yield for the synthesis of  $\alpha$ -aminonitriles. Diastereoselectivity of *o*-chlorobenzaldehyde and *o*-hydroxy-*p*-methoxybenzaldehyde was determined. It was observed that *o*-chlorobenzaldehyde gives 60:40 whereas *o*-hydroxy-*p*-methoxybenzaldehyde gives 81:19 diastereoselectivity. With a view to proving the efficacy of this methodology we undertook the synthesis of *N*-benzylphenylglycine from  $\alpha$ -aminonitriles (Scheme 7). The structure of *N*-benzylphenylglycine



**Scheme 7.** Reaction conditions: (a) the reaction conditions are exactly same as for the 'synthesis of  $\alpha$ -aminonitriles' in the Experimental section; (b, c) the literature procedure was followed.<sup>[38]</sup>



**Figure 1.** Plausible mechanism of the formation of  $\alpha$ -aminonitriles catalyzed by  $\text{NbCl}_5$ .

was settled from spectral ( $^1\text{H}$  NMR and HRMS) data and m.p. (Scheme 6). The spectral data ( $^1\text{H}$  NMR) and m.p. of the compound were compared with the literature values.<sup>[40]</sup>

A plausible mechanism for the reaction is as follows (Fig. 1). The initial step of the condensation of aldehyde and amine gives the formation of imine and water (1).  $\text{NbCl}_5$  can then act as a source of nucleophiles  $\text{Cl}^-$ .<sup>[36]</sup> Hypervalent silicon intermediate is formed from the addition of nucleophilic chloride ion (2). The *in situ*-generated imine could be polarized by the hypervalent silicon intermediate, which affords  $\alpha$ -aminonitriles (3).

## Conclusion

We have described very simple, convenient and practical method for the synthesis of  $\alpha$ -aminonitriles through three component coupling reaction of aldehydes, amines and trimethylsilyl cyanide. The procedure clearly demonstrates that  $\text{NbCl}_5$  is an excellent catalyst for the synthesis of  $\alpha$ -aminonitriles in short reaction time with low catalyst loading. Both aromatic and aliphatic aldehydes afford excellent yields of products whereas ketone yields no product at all under these reaction conditions. The important features of our method are: mild reaction conditions, simple work-up, inexpensive and readily available catalyst.

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