1-Ethyl-3-methylimidazolium acetate as a highly efficient organocatalyst for cyanosilylation of carbonyl compounds with trimethylsilyl cyanide

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1-Ethyl-3-methylimidazolium acetate is introduced as a robust organocatalyst for solvent-free cyanosilylation of carbonyl compounds with trimethylsilyl cyanide (TMSCN). The catalyst loading can be reduced to as low as 0.1–0.0001 mol % under mild reaction conditions, giving considerably high TOF values from 10,843 h$^{-1}$ to 10,602,410 h$^{-1}$ in the field of organocatalyzed transformations. The present protocol not only tolerates with extensive carbonyl compounds but also provides somewhat insight into the mechanism of ionic liquids (ILs)-catalyzed reactions.

Cyanohydrins$^{1-4}$ are one of the key synthetic intermediates since they can be elaborated into a number of valuable organic compounds, i.e. β-amino alcohols, α-hydroxy acids, α-amino acids, etc.$^{5,6}$ Hence, much effort and consideration have been devoted to the synthesis of cyanohydrins$^{1-4}$. Lapworth and Arthur were among the first to report on the synthesis of cyanohydrins by the addition of hydrogen cyanide (HCN) to carbonyl compounds$^{7}$. However, due to the toxicity and difficulties in handling of HCN, a number of alternative cyanating reagents with less harmful and easily manageable properties have been subsequently introduced$^{1-4}$. Among other cyanating reagents, TMSCN is one of the most accessed reagents for cyanohydrins synthesis, allowing them to be prepared as cyanohydrin trimethylsilyl ethers$^{1-4,7-14}$. In this respect, the development of efficient catalysts for the addition of TMSCN to carbonyl compounds has been the focal research point. As a consequence, various Lewis acids, Lewis bases, metal alkoxides, as well as inorganic salts have been successfully employed in promoting this transformation$^{3,12-24}$.

In the past decades, organocatalysis has received much attention and started to serve as the practical method in synthetic paradigm$^{25-29}$. The operational simplicity and readily availability of mostly inexpensive bench-stable catalysts compelled organocatalysis to develop into an important segment in common with metal- and bio-catalysis$^{25,30}$. Although organic species such as amines, phosphines, N-heterocyclic carbenes (NHCs) etc. have been employed as catalysts for the cyanosilylation of carbonyl compounds with TMSCN$^{19,22,25,26,31-35}$, most of them are encountered with some impediments, especially high catalyst loading and long reaction time. Therefore, some practical and highly efficient organocatalysts are still extremely desirable.

ILs have wide applications in chemistry such as powerful solvents, electrolytes, gas handling media, etc. due to their inherent assets, i.e. low vapor pressure, non-flammability, thermal stability, conductivity, and high gas solubility$^{36-41}$. Beyond the applications mentioned above, imidazolium-based ILs have also been demonstrated to be efficient organocatalysts for the degradation of cellulose$^{42,43}$. Loh and co-workers reported that [OMIM][PF$_6$] is an efficient and recyclable reaction media for the cyanosilylation of aldehydes$^{44}$. Later on, Lee and co-workers demonstrated that the catalytic activity of scandium triflate in [BMIM][SbF$_6$] was dramatically improved for the cyanosilylation of various aldehydes and ketones$^{45}$. In addition, polymer supported ILs have also been developed as catalysts for this transformation but with low catalytic efficiency$^{46-49}$. In continuation of our efforts to develop practically useful organocatalysts for the cyanosilylation$^{13,28}$, we envisaged that the ionic networks...
(organic cations and anions) in ILs may act as a stable and robust catalytic species for cyanosilylations\textsuperscript{41–48}. Herein, we present that 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc) is a highly efficient catalyst for such a transformation.

### Results and Discussion

We started our studies by examination of the catalytic activity of a set of imidazolium-based ILs, using the cyanosilylation of benzaldehyde with TMSCN as a model reaction (Table 1). In the presence of 0.01 mol % of catalyst loading, imidazolium-based ILs with various counter anions demonstrated different catalytic activities. Imidazolium-based ILs with counter anions such as OAc\textsuperscript{−}, SCN\textsuperscript{−} and (EtO\textsubscript{2})PO\textsubscript{2}\textsuperscript{−} were obviously efficient even with lower catalyst loading (0.005 mol %) in promoting this transformation, giving the product in excellent yield within 5 minutes (Table 1, entries 1–3). Imidazolium-based ILs with counter anions such as Cl\textsuperscript{−}, N(CN)\textsubscript{2}\textsuperscript{−}, ClO\textsubscript{4}\textsuperscript{−}, EtOSO\textsubscript{3}\textsuperscript{−}, BF\textsubscript{4}\textsuperscript{−} and Br\textsuperscript{−} generally gave the product in low to moderate yields (Table 1, entries 4–9). Among all the imidazolium-based ILs tested, [EMIM]OAc was the most efficient catalyst, which is in accordance with its basicity and accordingly underlines the possible anion-activation mechanistic mode. Furthermore, we performed several control experiments by switching imidazolium cation to other types of cations i.e., tetrabutylphosphonium, ammonium, sodium as well as potassium etc. (Table 1, entries 10–13), most of them were not efficient for this reaction with an exception of tetrabutylphosphonium cation (78% yield), suggesting that both cations and anions were essential for catalytic efficiencies. It is worth of noting that the catalytic activities of ILs and other salts having acetate anions seemed to agree with the interaction strength between cation and anion pairs\textsuperscript{49}. In the absence of catalyst, only trace amount of the desired product was detected (Table 1, entry 14). Among all the screened catalytic protocols, [EMIM]OAc ([\textit{1a}]) was found as an efficient catalyst for cyanosilylation of benzaldehyde with TMSCN. In view of the high efficacy and readily availability of \textit{1a}, we employed it as the corresponding catalyst for further cyanosilylation optimizations.

### Table 1. Survey of imidazolium-based ionic liquids as catalysts in the cyanosilylation of benzaldehyde with TMSCN.\textsuperscript{a} The reaction was carried out with benzaldehyde (1.0 mmol) and TMSCN (1.2 mmol) in the presence of 0.005 mol % of catalysts for 5 minutes under neat conditions.\textsuperscript{b} Yield was determined by \textsuperscript{1}H NMR.\textsuperscript{c} 0.01 mol % of catalyst was used.\textsuperscript{d} Without catalysts.

| Entry | Catalyst | Yield/% | TOF (h\textsuperscript{−1}) |
|-------|----------|---------|-----------------------------|
| 1     | [EMIM]OAc (\textit{1a}) | 94      | 226,506                     |
| 2     | [EMIM]SCN (\textit{1b}) | 91      | 219,277                     |
| 3     | [EMIM]([EtO]PO\textsubscript{2}) (\textit{1c}) | 90      | 216,867                     |
| 4     | [EMIM]Cl (\textit{1d}) | 50      | 120,482                     |
| 5\textsuperscript{e} | [EMIM]N(CN)\textsubscript{2} (\textit{1e}) | 71      | 85,542                      |
| 6\textsuperscript{e} | [EMIM]ClO\textsubscript{4} (\textit{1f}) | 35      | 42,168                      |
| 7\textsuperscript{e} | [EMIM]EtOSO\textsubscript{3} (\textit{1g}) | 22      | 26,306                      |
| 8\textsuperscript{e} | [EMIM]BF\textsubscript{4} (\textit{1h}) | 23      | 27,710                      |
| 9\textsuperscript{e} | [EMIM]Br (\textit{1i}) | 13      | 15,662                      |
| 10    | Tetrabutylphosphonium acetate (\textit{1j}) | 78      | 187,951                     |
| 11\textsuperscript{f} | Potassium acetate (\textit{1k}) | Trace   | —                           |
| 12\textsuperscript{f} | Sodium acetate (\textit{1l}) | Trace   | —                           |
| 13\textsuperscript{f} | Ammonium acetate (\textit{1m}) | Trace   | —                           |
| 14\textsuperscript{f} | — | Trace | —                           |

\textsuperscript{a}The reaction was carried out with benzaldehyde (1.0 mmol) and TMSCN (1.2 mmol) in the presence of 0.005 mol % of catalysts for 5 minutes under neat conditions.\textsuperscript{b} Yield was determined by \textsuperscript{1}H NMR.\textsuperscript{c} 0.01 mol % of catalyst was used.\textsuperscript{d} Without catalysts.
Under the optimized reaction conditions, various aldehydes were subjected to this protocol and the results were summarized in Table 3. The cyanosilylation of benzaldehyde with TMSCN produced 94% yield within 5 minutes in the presence of 0.001–0.1 mol % of 1a under neat conditions at room temperature. The yield is 40% with 0.01 mol % of 1a in 30 minutes. The yield is 88% with 0.005 mol % of 1a in 30 minutes. 0.0001 mol % of 1a, TON values for aliphatic aldehydes (entries 7–9) are 560,000, 880,000, and 750,000, respectively.

Under the optimized reaction conditions, various aldehydes were subjected to this protocol and the results were summarized in Table 3. The cyanosilylation of benzaldehyde with TMSCN produced 94% yield within 5 minutes in the presence of 0.005 mol % of 1a under neat reaction conditions (Table 3, entry 1). Benzaldehyde derivatives substituted with electron withdrawing groups (EWGs) reacted much faster than those having electron donating groups (EDGs). Even with as low as 0.001 mol % of 1a, benzaldehyde derivatives having electron withdrawing substituents such as $p$-chloro and $m$-fluoro afforded excellent yield (Table 3, entries 2–3). In contrast, benzaldehyde derivatives substituted with EDGs such as 3-methoxyl group, a satisfactory yield was obtained when the catalyst loading was increased to 0.1 mol % (Table 3, entry 4). Cinnamaldehyde required prolonged reaction time to get a satisfactory yield, and was essentially converted to 1,2-adducts, meanwhile leaving the olefin functional group unchanged (Table 3, entry 5)\(^{12,50}\). In line with the electron poor aromatic aldehydes, 0.001 mol % of 1a was also effective enough for aliphatic aldehydes (Table 3, entries 7–9). To our delight, the catalyst loading of 1a can further be reduced to 0.0001 mol % for aliphatic aldehydes with a remarkable TOF value 10,602,410 h\(^{-1}\) (Table 3, entry 8).

### Table 2. Optimization of [EMIM]OAc (1a) catalyzed cyanosilylations\(^a\). \(^{a}\)The reaction was carried out with benzaldehyde/acetophenone (1.0 mmol) and TMSCN (1.2 mmol) in the presence of 0.001–0.1 mol % of 1a for 5 minutes. \(^b\)Determined by \(^1\)H NMR (isolated yields are given in parenthesis). \(^c\)30 minutes of reaction time. \(^d\)TON values for acetophenone are 1590 and 940 for entries 9 and 10, respectively.

| Entry | R   | Catalyst (mol %) | Solvent | Yield/%\(^b\) | TOF (h\(^{-1}\)) |
|-------|-----|------------------|---------|---------------|-----------------|
| 1     | H   | 0.01             | toluene | 94            | 113,253         |
| 2     | H   | 0.01             | CH\(_2\)Cl\(_2\) | 83            | 100,000         |
| 3     | H   | 0.01             | THF     | 85            | 102,409         |
| 4     | H   | 0.01             | CHCl\(_3\) | 88            | 107,228         |
| 5     | H   | 0.01             | CH\(_3\)CN | 48            | 57,831          |
| 6     | H   | 0.01             | neat    | 100           | 113,253         |
| 7     | H   | 0.005            | neat    | 94            | 226,506         |
| 8\(^c\) | H   | 0.001           | neat    | 87            | 174,000         |
| 9\(^c,d\) | Me  | 0.05            | neat    | (75)          | 3,000           |
| 10\(^e\) | Me  | 0.1             | neat    | (94)          | 11,325          |

### Table 3. Substrates scope of [EMIM]OAc (1a) catalyzed cyanosilylation of aldehydes\(^a\). \(^a\)The reaction was carried out with various aldehydes (1.0 mmol) and TMSCN (1.2 mmol) in the presence of 0.001–0.1 mol % of 1a for 5 minutes under neat conditions at room temperature. \(^b\)Determined by \(^1\)H NMR. \(^c\)0.001 mol % of 1a. \(^d\)0.1 mol % of 1a. \(^e\)The yield is 40% with 0.01 mol % of 1a in 30 minutes. \(^f\)0.001 mol % of 1a. \(^g\)The yield is 88% with 0.005 mol % of 1a in 30 minutes. \(^h\)0.001 mol % of 1a, TON values for aliphatic aldehydes (entries 7–9) are 560,000, 880,000, and 750,000, respectively.

| Entry | R     | Yield/%\(^b\) | TOF (h\(^{-1}\)) |
|-------|-------|---------------|-----------------|
| 1     | Ph    | 94            | 226,506         |
| 2\(^c\) | $p$-Cl-Ph | 100           | 1,204,820       |
| 3\(^c\) | $m$-F-Ph   | 100           | 1,204,820       |
| 4\(^c,d\) | $m$-MeO-Ph | 100           | 12,048          |
| 5\(^d\) | Cinnamyl | 100           | 120,482         |
| 6     | 2-Furyl | 88            | 214,458         |
| 7\(^d\) | Cyclohexyl | 56            | 6,746,988       |
| 8\(^d\) | $t$-Pr    | 88            | 10,602,410      |
| 9\(^d\) | Octyl   | 75            | 9,036,144       |
With the optimized reaction conditions in hand, ketones were employed as substrates and the results were summarized in Table 4. In the presence of 0.1 mol % of \(1a\), both aromatic and aliphatic ketones provided excellent yield (Table 4, entries 1–8). The substituent on aromatic ketones did not show considerable influence on the reaction outcomes. Under the same reaction conditions, \(1a\) is also capable to convert the relatively unreactive benzophenone into its product with excellent yield (Table 4, entry 9)\(^32\).

The exact mechanism for \(1a\) catalyzed cyanosilylation is still unclear. Our original mechanistic proposal was based on a synergistic activation mode, i.e., imidazolium cation interacts with carbonyl compounds by facilitating the attack of acetate anion activated TMSCN and it was considered that the reaction may proceed through hypervalent silicate intermediate 10, (Fig. 1)\(^29,51–54\). The formation of hypervalent silicate intermediate between acetate anion and TMSCN was confirmed by \(^1\)H NMR spectra of TMSCN and a 1:1 mixture of TMSCN and \(1a\) in CDCl\(_3\) (for detail of \(^1\)H NMR spectra, see Supplementary page S13). On the other hand, a connection with recently discovered "carbene from imidazolium-based ILs" was also under consideration\(^55–61\), in which the \(\textit{in situ}\) generated NHC by deprotonation of carbon-2 at imidazolium cation with its acetate anion may act as an efficient catalyst for cyanosilylation of carbonyl compounds\(^3,26,31–35,59\). In order to gain insight into this mechanistic mode, we intentionally blocked the C-2 position of imidazolium cation with a methyl group by preparing 1-ethyl-2,3-dimethylimidazolium acetate [EMMIM]OAc and employed in the cyanosilylation of benzaldehyde\(^62\).

Under relatively identical reaction conditions, cyanosilylation of benzaldehyde using [EMMIM]OAc as a catalyst gave 88% yield, which was comparable to the 94% yield afforded by \(1a\). As a consequence, we postulated that the \(\textit{in situ}\) generated NHC may not play a significant role in the catalytic performance of \(1a\) and a synergistic activation mode is probably the main reaction pathway (Fig. 1).

| Entry | \(R^1\) | \(R^2\) | Yield/%\(^b\) | TOF (h\(^{-1}\)) |
|-------|--------|--------|---------------|-----------------|
| 1     | Ph     | Me     | 94            | 11,325          |
| 2     | \(p\)-Cl-Ph | Me     | 95            | 11,445          |
| 3     | \(o\)-F-Ph | Me     | 95            | 11,445          |
| 4     | \(p\)-Br-Ph | Me     | 95            | 11,445          |
| 5     | \(p\)-i-Pr-Ph | Me     | 90            | 10,843          |
| 6     | \(p\)-Me-Ph | Me     | 93            | 11,205          |
| 7     | \(n\)-Bu | Me     | 95            | 11,445          |
| 8     | Cyclohexanone | —     | 94            | 11,325          |
| 9     | Ph     | Ph     | 92            | 11,084          |

Table 4. Substrates scope of [EMIM]OAc (1a) catalyzed cyanosilylation of ketones. *The reaction was carried out with various ketones (1.0 mmol) and TMSCN (1.2 mmol) in the presence of 0.1 mol % of \(1a\) for 5 minutes under neat conditions at room temperature. **Isolated yields.

Figure 1. Proposed mechanism for the cyanosilylation of carbonyl compounds (benzaldehyde as a model substrate). *Synergistic mode of activation by acetate anion (OAc\(^-\)) and imidazolium cation of [EMIM]OAc (1a).
Conclusions

In conclusion, we have developed a highly efficient cyanosilylation reaction of carbonyl compounds using commercially and readily available [EMIM]OAc (1a) as an organocatalyst. In the presence of 0.001–0.1 mol % of [EMIM]OAc, various aldehydes and ketones were converted to their corresponding products in excellent yields. The catalyst is truly active giving quite high TOF values from 10,843 h⁻¹ to 10,602,410 h⁻¹, which is among the most efficient organocatalysts. Mechanistic investigations based on experimental results revealed that the reaction operates via a synergistic activation mode, namely, imidazolium cation interacts with carbonyl compounds by facilitating the attack of acetate anion activated TMSCN. From a practical point of view, this protocol offers a cost effective and facile way for the synthesis of cyanohydrins. Asymmetric cyanosilylation of carbonyl compounds using imidazolium-based chiral ILs is under investigation in our laboratory and will be reported in due course.

Methods

General procedure for cyanosilylation of carbonyl compounds (benzaldehyde as a typical example with TMSCN catalyzed by IL [EMIM]OAc (1a)).

**Caution.** TMSCN must be used in a well-ventilated hood due to its high toxicity.

The reaction was carried out by placing freshly distilled TMSCN (1.2 mmol), 1a (0.005 mol %), and a teflon-coated magnetic stir bar into a Pyrex-glass screw cap vial. The solvent-free reaction was initiated by addition of freshly distilled benzaldehyde (1.0 mmol) and was stirred vigorously at room temperature. The reaction was monitored by TLC. After 5 minutes, the yield of benzaldehyde to its corresponding silylated cyanohydrin was determined by 1H NMR as 94%. For all other carbonyl compounds the same procedure with the same amount of reagents were used, as described earlier in Tables 1–4. In case of aldehydes the yields were determined by 1H NMR, whereas the yields of ketones were isolated by flash column chromatography on silica gel (eluent: n–hexane/ethyl acetate 40:1). All silylated cyanohydrin products of respective carbonyl compounds with TMSCN were confirmed by comparison of their 1H NMR spectral data with those of authentic data.

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Supplementary information

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Author Contributions

B.U. performed the experiments and prepared the manuscript draft. J.C. was responsible for analytical data preparation. Z.Z. supervised all of the work and revised the manuscript. H.X., Q.Y., Z.B., and Q.R. helped in improving the manuscript.

Additional Information

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