

Tetraethylammonium 2-(*N*-hydroxycarbamoyl)benzoate: a powerful bifunctional metal-free catalyst for efficient and rapid cyanosilylation of carbonyl compounds under mild conditions†

Mohammad G. Dekamin,* Zahra Karimi and Mehdi Farahmand

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In contrast to tetrabutylammonium hydroxide, its tetraethylammonium counterpart reacts with *N*-hydroxyphthalimide to afford tetraethylammonium 2-(*N*-hydroxycarbamoyl)benzoate (TEAHCB) rather than tetraethylammonium phthalimide-*N*-oxyl (TEAPINO). TEAHCB contains at the same time benzoate and hydroxycarbamoyl functionalities in a proper geometry to activate reaction components as Lewis basic and Lewis acidic centers, respectively. TEAHCB was found to be able to efficiently catalyze very rapid cyanosilylation of a wide variety of carbonyl compounds at 0.15 mol% catalyst loading under solvent-free conditions at room temperature as a simple and readily available bifunctional organocatalyst.

Introduction

In recent years, organocatalytic (metal-free) protocols have received great attention from both practical and environmental standpoints. The rapid-growing interest in the development of organocatalytic protocols is due to their ability to perform organic reactions in wet solvents or under solvent-free conditions in an aerobic atmosphere and to avoid the possibility of heavy metals contamination of the products that may occur with the traditional metallic catalytic systems.¹ Hence, organocatalytic protocols seem to be especially attractive for the preparation of compounds that do not tolerate metal contamination, especially pharmaceuticals. Therefore, the use of organocatalysts is a valuable tool to address green chemistry principles.^{1,2} More recently, bifunctional organocatalysts have received considerable attention for different organic transformations such as Michael addition,³ Biginelli reaction,⁴ Strecker reaction⁵ or cyanosilylation of carbonyl compounds.⁶ Indeed, bifunctional and multifunctional catalysts present high potential for both catalysis and asymmetric synthesis.^{7,8} These catalysts contain both Lewis base and Lewis acid sites that activate nucleophilic and electrophilic substrates, respectively. The proper geometry of the catalytic centers is very important to incorporate reaction partners effectively in the catalytic cycle. As a result, such catalytic system assemblies promote reactions similar to the natural catalysis by enzymes. In addition, dual coordination by bifunctional organocatalysts

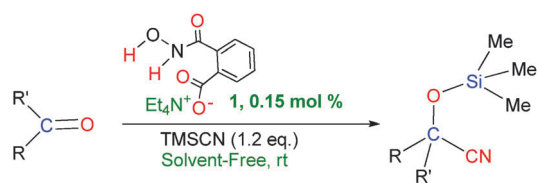
further accelerates the reaction by simultaneously enhancing the electrophilic character of one substrate and the nucleophilic character of the other.^{6b,8}

On the other hand, hydrocyanation and cyanosilylation of carbonyl compounds are among the most important strategies for C–C bond-forming reactions in organic synthesis. The adduct products provide versatile intermediates such as cyanohydrins and cyanohydrin trialkylsilyl ethers, respectively. In particular, cyanohydrin trimethylsilyl ethers are industrially valuable and important intermediates for the synthesis of α -hydroxy acids and esters, α -amino acids, acyloins, vicinal diols, β -amino alcohols and other biologically active compounds.^{6,9} For instance, cyanosilylation is the key step in the manufacture of (+)-biotin,^{10a} Ditropan or its analogues,^{10b} and insecticides such as cypermethrin and fluralinate.^{11a} Cyanohydrin trialkylsilyl ethers are generally prepared by the addition of trimethylsilyl cyanide (TMSCN), a safe and easily handled reagent compared to HCN, NaCN or KCN,^{6,9} to carbonyl compounds in the presence of Lewis acids,¹¹ Lewis bases^{10a,12} and double activating^{9b,13} or bifunctional^{10b,14} catalytic systems. Therefore, a large body of work has been devoted to the development of cyanohydrin trimethylsilyl ethers synthesis. However, many of these protocols often involve heavy or expensive transition metal catalysts, poor yield of the products or prolonged reaction times, inert atmosphere or anhydrous solvents, the use of hygroscopic catalysts and tedious work-up procedures.^{10–14}

Traditional Lewis acid catalytic systems promote cyanosilylation through direct complexation of the metal species to both the carbonyl group of aldehydes or ketones and the cyano group of TMSCN.^{9,11} On the other hand, Lewis basic catalysts including the majority of organocatalytic systems often react with the silicon atom of TMSCN to produce

Pharmaceutical and Biologically-Active Compounds Research Laboratory, Department of Chemistry, Iran University of Science and Technology, Tehran 16846-13114, Iran. E-mail: mdekamin@iust.ac.ir; Fax: +98-21-7322 7703

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R = Aryl, Heteroaryl, Alkenyl, Alkyl
R' = H, Alkyl, Aryl

Scheme 1 Cyanosilylation of carbonyl compounds using tetraethylammonium 2-(*N*-hydroxycarbamoyl)benzoate (TEAHCB, **1**).

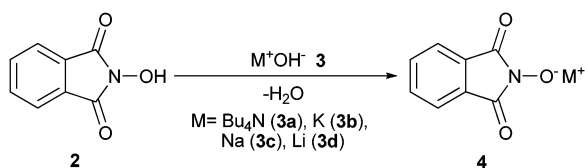
more reactive hypercoordinated silicon intermediates.^{12a,15–21} Hence, a few Lewis acid organocatalytic systems have been introduced for cyanosilylation of carbonyl compounds. Although catalysts such as *N*-iodosuccinimide²² or different alkyl triphenylphosphonium containing soft halide ions including iodide or bromide²³ have been introduced in recent years, the use of a hydrogen bond donor moiety is more feasible and practical in organocatalysis. Interestingly, hydrogen bonding has demonstrated significant effects on the catalytic activity of bifunctional organocatalysts.^{6,24–27} The use of different thio-urea derivatives,^{6,24} tetramethyl guanidine,²⁵ alkali-metal salts of α -aminoacids²⁶ and tetraethylammonium 2-(*N*-hydroxycarbamoyl)benzoate²⁷ has proved the influence of hydrogen bonding on the catalytic activity of bifunctional organocatalysts for cyanosilylation of carbonyl compounds.

In continuation of our interest to develop more efficient organocatalysts for cyanosilylation of carbonyl compounds,^{16c,18b–d,19a,27} we wish herein to report our recent findings on the improved and smooth addition of TMSCN to carbonyl compounds using tetraethylammonium 2-(*N*-hydroxycarbamoyl)benzoate (TEAHCB, **1**), as a new bifunctional organocatalyst, under solvent-free conditions (Scheme 1).

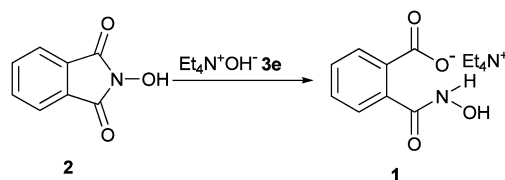
Results and discussion

In our preceding papers,^{18b,c,28} we have reported that the hydroxide ion in tetrabutylammonium hydroxide (TBAOH, **3a**) or alkali metal hydroxides **3b–d** reacts preferentially with the more acidic hydroxyl proton of *N*-hydroxyphthalimide (NHPI, **2**). This pattern of reactivity produces the corresponding salts of the phthalimide-*N*-oxyl (PINO) nucleophilic catalyst **4** which were successfully applied by our research group to facile cyanosilylation of carbonyl compounds,^{18b,c} protection of alcohols and phenols with hexamethyldisilazane,²⁹ and cyclotrimerization of isocyanates^{28,30} (Scheme 2).

Interestingly, in our previous research, we found that tetraethylammonium hydroxide (TEAOH, **3e**) reacts with the carbonyl groups of imide functionality of the phthalimide instead of the more acidic N–H proton to afford tetraethylammonium



Scheme 2 Different phthalimide-*N*-oxyl salts **4** produced by the reaction of NHPI (**2**) with TBAOH or alkali metal hydroxides **3a–d**.

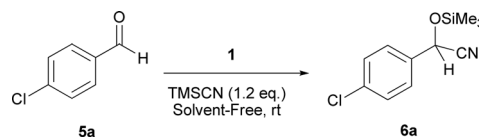


Scheme 3 Unusual reaction pathway of **2** and **3e** to produce TEAHCB (**1**).

2-(*N*-hydroxycarbamoyl)benzoate (TEACB) as a bifunctional organocatalyst.²⁷ In our hands, TEACB demonstrated higher catalytic activity in both cyanosilylation of carbonyl compounds and cyclotrimerization of isocyanates compared to the PINO nucleophile **4** in the typical catalytic systems.^{27,30} Hence, we decided to investigate the reactivity of TEAOH toward NHPI (**2**). It was found that although the imide moiety in the structure of **2** survived through the reaction with **3a–d**,^{18b,c} the situation is completely altered in the reaction with **3e** to afford TEAHCB (**1**) as a new bifunctional organocatalyst (Scheme 3).

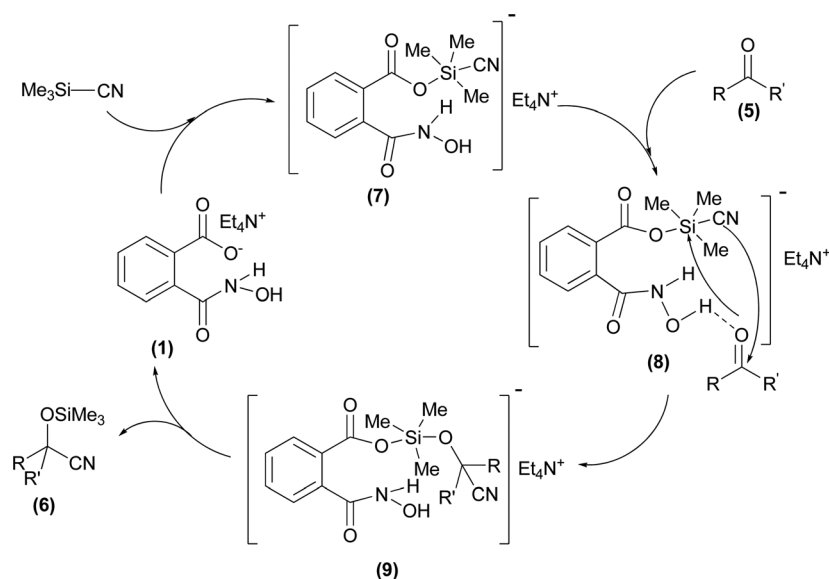
At first, a mixture of 4-chlorobenzaldehyde (**5a**) and TMSCN was treated with 0.3 mol% of TEAHCB (**1**) under solvent-free conditions at room temperature (Table 1). It was found that the cyanide addition occurred almost instantaneously to afford the desired trimethylsilylated cyanohydrin **6a** with 99% conversion in 5 min (entry 1). By employing lower catalyst loading, 0.15 mol%, the desired product was obtained in quantitative yield. Furthermore, the reaction was studied on a 10 mmol scale, and we were delighted to find that only a minute amount of **1** (0.08 mol%) was required to catalyze the cyanosilylation of **5a** at room temperature (entries 2 and 3). It is obvious that the best result in terms of turnover number (TON) and turnover frequency (TOF) could be achieved using 0.15 mol% catalyst loading of **1** (entry 2). On the other hand, no reaction was observed in the absence of **1** under similar reaction conditions (entry 4). Therefore, the lower catalyst loading required for this transformation compared to many organocatalytic systems having oxygen as their sole nucleophilic site¹⁸ and even TEACB²⁷ demonstrates the simultaneous role of benzoate functionality of catalyst **1** and hydrogen bonding

Table 1 Survey of optimal TEAHCB (**1**) catalyst loading for cyanosilylation of 4-chlorobenzaldehyde (**5a**)^a



Entry	Catalyst	Mol%	Time/ min	Conversion ^b (%)	TON ^c	TOF ^d / h ⁻¹
1	TEAHCB (1)	0.3	5	100	333	4000
2	TEAHCB (1)	0.15	8	100	667	5000
3	TEAHCB (1)	0.08	25	99	990	2376
4	—	—	120	0	—	—
5	TEACB ^e	0.5	15	98	196	784

^a TMSCN (3 mmol) was added to a mixture of 4-chlorobenzaldehyde (**5a**, 2.5 mmol) and TEAHCB (**1**) under solvent-free conditions at room temperature except for entry 3 where the reaction was performed on a 10 mmol scale. ^b Determined by GC analysis. ^c Turnover number. ^d Turnover frequency. ^e Tetraethylammonium 2-(*N*-hydroxycarbamoyl)benzoate as catalyst.²⁷



Scheme 4 Plausible mechanism for cyanosilylation of carbonyl compounds **5** catalyzed by TEAHCB (**1**).

formed by its *N*-hydroxycarbonyl moiety in a proper geometry in activating both TMSCN and carbonyl group for smooth cyanosilylation of diverse carbonyl compounds (Scheme 4, Table 2). It is expected that nucleophilic attack from the benzoate functionality of catalyst **1** on TMSCN produces pentavalent silicon intermediate **7** as the first reaction intermediate. The high reactivity of the pentavalent or hexavalent silicon intermediates to promote many organic transformations mediated by silicon reagents is well known.^{9c,12a,27,31} Therefore, the cyanide transfer from the pentavalent silicon atom to the activated carbonyl group by hydrogen bonding in complex **8** forms intermediate **9**. Subsequent decomposition of pentavalent intermediate **9** gives product **6** and regenerates catalyst **1**.

Encouraged by these results, other carbonyl compounds were subjected to cyanosilylation under optimal reaction conditions (TEAHCB 0.15 mol%, 1.2 equiv. of TMSCN, room temperature, solvent-free conditions). Table 2 shows that aromatic, heterocyclic and aliphatic aldehydes or ketones **5** have been effectively converted to the corresponding products **6**. The reactions proceed very cleanly at room temperature under mild conditions. After completion of the reaction (monitored by TLC), the catalyst could be easily separated from the reaction mixture by aqueous extraction. Therefore, a simple work-up affords the desired products without any chromatographic purification. In general, the reaction conditions are very mild and high to quantitative yields of the products could be obtained within very short reaction time.

No benzoin condensation or desilylation by-products were observed. Acid-sensitive aldehydes such as furfural (**5j**), thiophene-2-carbaldehyde (**5k**) and cinnamaldehyde (**5l**) produced the desired cyanohydrin trimethylsilyl ethers rather than products of polymerization or Michael addition in quantitative yields (Table 2, entries 10–12). This may indicate that the catalytic system selectively activates the carbonyl function and keeps the double bonds of these acid sensitive substrates intact.²⁷

As shown in Table 2, electronic effects and the nature of the substituents on the aromatic ring showed relatively strong effects on the required reaction time for the complete conversion of aldehydes. As a consequence of proposed bifunctional organocatalysis, substrates containing electron-withdrawing groups (entries 1 and 3–5) react much faster than ones bearing electron-donating groups (entries 7–11). This can be interpreted by considering that the cyanide transfer from the pentavalent silicon atom in complex **8** is the slowest step of the reaction mechanism (Scheme 4). However, 4-bromobenzaldehyde (**5b**) did not demonstrate any substantial substituent effect and its reaction required similar reaction time to benzaldehyde (**5f**). On the other hand, 4-methoxybenzaldehyde (**5h**) required shorter reaction time compared to 2-methoxybenzaldehyde (**5i**) due to proximity of the methoxy group to the carbonyl group in **5i** which impedes hydrogen bonding between the catalyst and the carbonyl moiety of the substrate. Furthermore, due to the steric bulk, ketones such as cyclohexanone (**5q**), acetophenone (**5r**), benzophenone (**5t**), and their derivatives required longer reaction times than aldehydes (entries 16–22).^{11d,f} The reaction of acyclic and cyclic aliphatic carbonyl compounds also afforded the corresponding products in very good yields in longer time compared to aromatic and heterocyclic carbonyl compounds (entries 13–17). Finally, this new catalytic system is far superior in terms of low catalyst loading and shorter reaction time as compared to other protocols for the addition of TMSCN to ketones (entries 16–22).^{11d,f,k,16,17,27}

The comparison of the present method with respect to the catalyst loading, required reaction time, and simplicity of performance with those reported in the literature reveals that a practical and very fast method for the cyanosilylation of carbonyl compounds has been established using TEAHCB as a new bifunctional organocatalyst with unique geometry. To illustrate the efficiency of the present method, Table 3 is shown to compare our results with some of organocatalytic protocols reported in the literature recently.

Table 2 Organocatalytic cyanosilylation of various carbonyl compounds **5** by TEAHCB (**1**) under optimized conditions^a

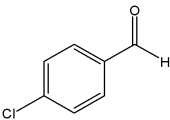
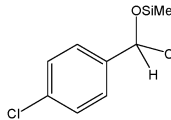
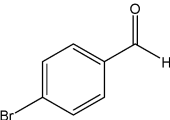
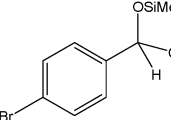
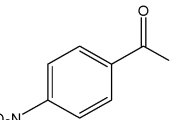
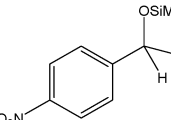
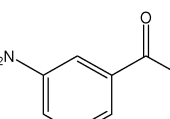
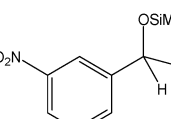
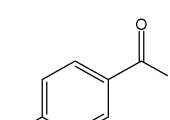
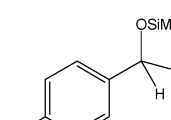
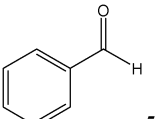
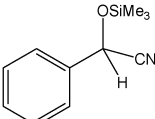
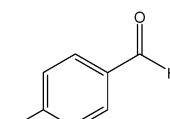
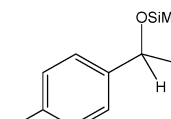
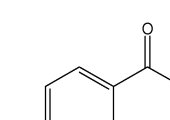
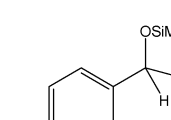
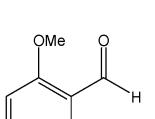
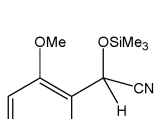
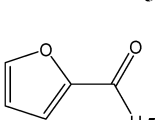
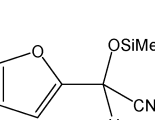
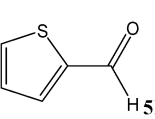
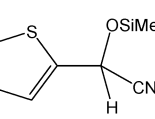
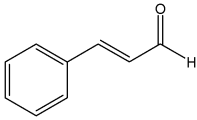
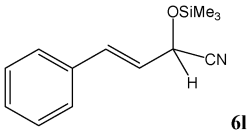
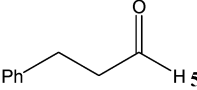
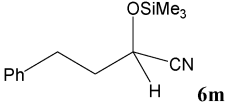
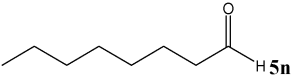
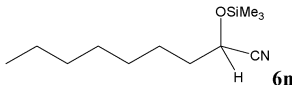
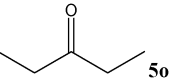
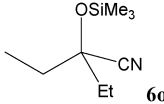
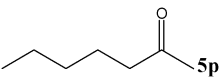
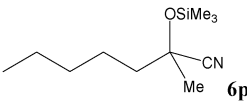
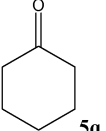
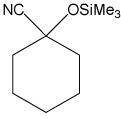
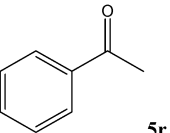
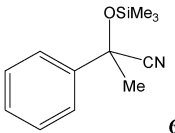
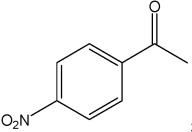
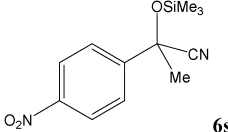
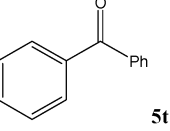
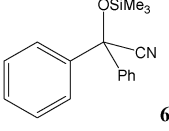
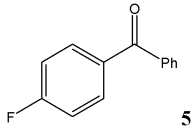
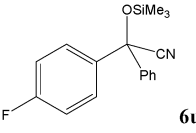
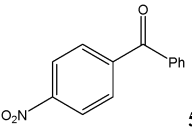
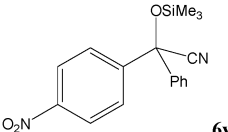
Entry	Carbonyl compound (5)	Time (min)	Product (6) ^b	Conversion (%) ^c	Ref.
1	 5a	8	 6a	100	11g
2	 5b	10	 6b	100	11h
3	 5c	2	 6c	100	11h
4	 5d	5	 6d	97	11n
5	 5e	3	 6e	99	16b
6	 5f	10	 6f	100	20a
7	 5g	15	 6g	97	11g
8	 5h	15	 6h	100	11g
9	 5i	20	 6i	99	11h
10	 5j	15	 6j	99	11g
11	 5k	15	 6k	100	11m

Table 2 (continued)

Entry	Carbonyl compound (5)	Time (min)	Product (6) ^b	Conversion (%) ^c	Ref.
12	 5l	15	 6l	99	11g
13	 5m	15	 6m	98	20a
14	 5n	15	 6n	100	11g
15	 5o	20	 6o	98	11m
16	 5p	20	 6p	95	12b
17	 5q	20	 6q	96	20a
18	 5r	25	 6r	90	20a
19	 5s	20	 6s	100	20a
20	 5t	30	 6t	70	20a
21	 5u	30	 6u	92	6d
22	 5v	30	 6v	95	19a

^a TMSCN (3 mmol) was added to a mixture of carbonyl compound **5** (2.5 mmol) and TEAHCB (**1**) (1.1 mg) under solvent-free conditions at room temperature. ^b All products are known and were well-characterized by IR and NMR spectral data as compared with those obtained from authentic samples or reported in the literature.^{6,11,12,16,19,20c} ^c Determined by GC analysis.

Table 3 Comparison of the results obtained by cyanosilylation of aldehydes and ketones with TMSCN in the presence of TEAHCB (1), with some of those catalyzed by NHCs (2), trisaminophosphines (3), imidazolium-carbodithioate zwitterions (4), and TEACB (5)

Entry	Substrate	Method [equivalent of TMSCN/ TOF (h ⁻¹)]				
		1 ^a	2 ^{20c,b}	3 ^{17a,b}	4 ^{19b,c}	5 ^{27a}
1	Benzaldehyde	1.2/4000	—	1.2/97.0	2/0.62	1.2/552.0
2	4-Chlorobenzaldehyde	1.2/5000	1.1/8.0	1.2/39.6	—	1.2/784.0
3	4-Methoxybenzaldehyde	1.2/2667	1.1/27.6	1.2/32.7	2/0.15	1.2/446.4
4	Cinnamaldehyde	1.2/2640	1.1/30.0	—	—	1.2/258.7
5	3-Phenylpropanal	1.2/2613	—	1.2/32.7	—	1.2/198.0
6	4-Nitroacetophenone	1.2/2000	—	—	—	1.2/99.0

^a Solvent-free conditions. ^b THF as solvent. ^c CH₂Cl₂ as solvent.

Conclusions

In summary, we have developed a highly efficient catalytic cyanosilylation reaction with broad substrate generality using TEAHCB as a new bifunctional organocatalyst in relatively short reaction time at room temperature. This can be the first example of use of TEAHCB as a simple and readily available bifunctional organocatalyst in organic synthesis. The important features of our method are: mild reaction conditions, very low catalyst loading, simple work-up, wide substrate scope, high to quantitative yield and simple preparation of the catalyst from inexpensive precursors.

Experimental section

Materials and instruments

FT IR spectra were recorded as KBr pellets on a Shimadzu FT IR-8400S spectrometer. ¹H NMR (500 MHz) and ¹³C NMR (125 MHz) spectra were obtained using a Bruker DRX-500 AVANCE spectrometer. All NMR spectra were determined in CDCl₃ or D₂O at ambient temperature. GC chromatograms were recorded on a Perkin-Elmer 8420 instrument. Microanalysis of catalyst **1** was carried out using a CHNS/O analyzer (Perkin-Elmer Series II, 2400). Melting points were determined using an Electrothermal 9100 apparatus and are uncorrected. All chemicals were purchased from Merck or Aldrich and used as received except for benzaldehyde, for which a fresh distilled sample was used. TEAHCB (**1**) was ground to a fine powder and then dried at 70 °C under reduced pressure for 1 h. All reactions were protected from air moisture using a CaCl₂ guard tube. Analytical TLC was carried out using Merck 0.2 mm silica gel 60 F-254 Al-plates. All compounds were well characterized by GC analysis, IR and NMR spectral data as compared with those obtained from authentic samples or reported in the literature.^{6,11,12,16,19,20}

Preparation of tetraethylammonium 2-(*N*-hydroxycarbamoyl)benzoate (TEAHCB, **1**)

To a 25 mL round bottom flask equipped with a magnetic stirrer and a condenser were added 4.23 mmol of *N*-hydroxyphthalimide **2** (MW = 163.13 g mol⁻¹, 0.69 g) and 4.23 mmol of tetraethylammonium hydroxide **3e** (FW = 147.26 g mol⁻¹, 20% w/w in water, *d* = 1.04 g mL⁻¹, 5.0 mL). The mixture was stirred at room temperature for 5 min and then refluxed for 1 h. After cooling to room temperature, the reaction mixture was evaporated to dryness under reduced pressure to give a deep red viscous liquid and then dissolved in absolute EtOH (5 mL). EtOAc was added dropwise

until a turbid solution was obtained and the mixture was heated until the disappearance of turbidity. After cooling, the white crystals of TEAHCB were filtered on a Büchner funnel; yield: 87%; mp = 140–142 °C; ¹H NMR (500 MHz, D₂O): δ = 1.15–1.19 (t, *J* = 7.3 Hz, 12H), 3.14–3.18 (q, *J* = 7.3 Hz, 8H), 7.36–7.38 (d, *J* = 7.4 Hz, 1H), 7.41–7.44 (t, *J* = 7.2 Hz, 1H), 7.46–7.50 (t, *J* = 7.50 Hz, 1H), 7.57–7.58 (d, *J* = 7.4 Hz, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ = 6.9, 52.3, 128.1, 128.7, 129.9, 131.2, 131.8, 138.3, 170.4, 175.6 ppm; Anal. calcd. for C₁₆H₂₆N₂O₄: C, 61.91; H, 8.44; N, 9.03%; found: C, 62.02; H, 8.46; N, 9.01%.

General procedure for cyanosilylation of carbonyl compounds

TMSCN (3.0 mmol, 0.38 mL) was added to a mixture of 2.5 mmol of a carbonyl compound and TEAHCB (1.1 mg). The obtained mixture was stirred at room temperature for 2–30 min. The reaction was monitored by TLC. After completion, the reaction mixture was quenched with water (2.5 mL) and the organic materials were extracted with EtOAc (2 × 2.5 mL). The obtained organic phase was washed with brine followed by water (2.5 mL) and dried over MgSO₄. The solvent was evaporated on a rotary evaporator to afford the desired products which in many cases were essentially pure cyanohydrin TMS ethers. Further purification of the products was performed by silica gel column chromatography (EtOAc–Hexane, 1 : 10). The isolated yields were in good agreement with those obtained by GC Analysis.

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Notes and references

- (a) C. Zhong and X. D. Shi, *Eur. J. Org. Chem.*, 2010, 2999; (b) J. Seayad and B. List, *Org. Biomol. Chem.*, 2005, **3**, 719; (c) D. W. C. MacMillan, *Nature*, 2008, **455**, 304; (d) T. Mitsudome, K. Nose, T. Mizugaki, K. Jitsukawa and K. Kaneda, *Tetrahedron Lett.*, 2008, **49**, 5464.
- (a) P. I. Dalko and L. Moisan, *Angew. Chem., Int. Ed.*, 2004, **43**, 5138; (b) K. Yamaguchi, T. Imago, Y. Ogasawara, J. Kasai, M. Kotani and N. Mizuno, *Adv. Synth. Catal.*, 2006, **348**, 1516.
- (a) C. L. Wu, W. J. Li, J. J. Yang, X. M. Liang and J. X. Ye, *Org. Biomol. Chem.*, 2010, **8**, 3244; (b) C. G. Oliva, A. M. S. Silva, D. Resende, F. A. A. Paz and J. A. S. Cavaleiro, *Eur. J. Org. Chem.*, 2010, 3449; (c) O. Andrey, A. Alexakis, A. Tomassini and G. Bernardinelli, *Adv. Synth. Catal.*, 2004, **346**, 1147; (d) D. Enders and A. Seki, *Synlett*, 2002, 26; (e) B. List, P. Pojarliev and

- H. Martin, *Org. Lett.*, 2001, **3**, 2423; (f) P. Bernal, R. Fernandez and J. M. Lassaletta, *Chem.–Eur. J.*, 2010, **16**, 7714.
- 4 (a) Y. Wang, H. Yang, J. Yu, Z. Miao and R. Chen, *Adv. Synth. Catal.*, 2009, **351**, 3057; (b) D. Ding and C. G. Zhao, *Eur. J. Org. Chem.*, 2010, 3802.
- 5 (a) X. Huang, J. L. Huang, Y. H. Wen and X. M. Feng, *Adv. Synth. Catal.*, 2006, **348**, 2579; (b) P. Vachal and E. N. Jacobsen, *Org. Lett.*, 2000, **2**, 867; (c) P. Vachal and E. N. Jacobsen, *J. Am. Chem. Soc.*, 2002, **124**, 10012.
- 6 (a) S. J. Zuend and E. N. Jacobsen, *J. Am. Chem. Soc.*, 2007, **129**, 15872; (b) Y. Shen, X. Feng, Y. Li, G. Zhang and Y. Jiang, *Eur. J. Org. Chem.*, 2004, 129; (c) X. Liu, B. Oin, X. Zhou, B. He and X. Feng, *J. Am. Chem. Soc.*, 2005, **127**, 12224.
- 7 (a) M. Shibasaki, H. Sasai and T. Arai, *Angew. Chem., Int. Ed.*, 1997, **36**, 1236; (b) G. J. Rowlands, *Tetrahedron*, 2001, **57**, 1865; (c) M. Shibasaki and N. Yoshikawa, *Chem. Rev.*, 2002, **102**, 2187.
- 8 (a) P. I. Dalko and L. Moisan, *Angew. Chem., Int. Ed.*, 2004, **43**, 5138; (b) M. S. Taylor and E. N. Jacobsen, *Angew. Chem., Int. Ed.*, 2006, **45**, 1520; (c) D. Cahard and J. A. Ma, *Angew. Chem., Int. Ed.*, 2004, **43**, 4566; (d) A. Hamza, G. b. Schubert, T. Soós and I. Pápai, *J. Am. Chem. Soc.*, 2006, **128**, 13151.
- 9 (a) R. J. H. Gregory, *Chem. Rev.*, 1999, **99**, 3649; (b) N. H. Khan, R. I. Kureshy, S. H. R. Abdi, S. Agrawal and R. V. Jasra, *Coord. Chem. Rev.*, 2008, **252**, 593; (c) J. Gawronski, N. Wascinska and J. Gajewy, *Chem. Rev.*, 2008, **108**, 5227; (d) M. Sakulsombat, P. Vongvilai and O. Ramstrom, *Org. Biomol. Chem.*, 2011, **9**, 1112; (e) M. G. Dekamin and Z. Mokhtari, *Tetrahedron*, 2012, **68**, 922; (f) D. A. Evans, L. K. Truesdale and G. L. Carroll, *J. Chem. Soc., Chem. Commun.*, 1973, 55; (g) K. Higuchi, M. Onaka and Y. Izumi, *J. Chem. Soc., Chem. Commun.*, 1991, 1035.
- 10 (a) M. Seki, M. Hatsuda, Y. Mori and S. Yamada, *Tetrahedron Lett.*, 2002, **43**, 3269; (b) S. Masumoto, M. Suzuki, M. Kanaia and M. Shibasaki, *Tetrahedron Lett.*, 2002, **43**, 8647.
- 11 (a) H. Firouzabadi, N. Iranpoor and A. A. Jafari, *J. Organomet. Chem.*, 2005, **690**, 1556; (b) K. Iwanami, J.-C. Choi, B. Lu, T. Sakakura and H. Yasuda, *Chem. Commun.*, 2008, 1002; (c) J. Wang, Y. Masui, K. Watanabe and M. Onaka, *Adv. Synth. Catal.*, 2009, **351**, 553; (d) M. L. Kantam, S. Laha, J. Yadav, B. M. Choudary and B. Sreedhar, *Adv. Synth. Catal.*, 2006, **348**, 867; (e) H. Yang, L. Zhang, P. Wang, Q. Yang and C. Li, *Green Chem.*, 2009, **11**, 257–264; (f) S. Kataoka, A. Endo, A. Harada, Y. Inagi and T. Ohmori, *Appl. Catal.*, A, 2008, **342**, 107; (g) C. Baleizão, B. Gigante, H. Garcia and A. Corma, *Tetrahedron*, 2004, **60**, 10461; (h) S. T. Kadam and S. S. Kim, *Appl. Organomet. Chem.*, 2009, **23**, 119; (i) A. Heydari and L. Ma'Mani, *Appl. Organomet. Chem.*, 2008, **22**, 12; (j) L. Mei, S. W. Wong, H. K. Liang and W. S. Xuan, *Appl. Organomet. Chem.*, 2008, **22**, 181; (k) A. Majhi, S. S. Kim and H. S. Kim, *Appl. Organomet. Chem.*, 2008, **22**, 407; (l) W. K. Cho, S. M. Kang, A. K. Medda, J. K. Lee, I. S. Choi and H. S. Lee, *Synthesis*, 2007, 507; (m) S. K. De and R. A. Gibbs, *J. Mol. Catal. A: Chem.*, 2005, **232**, 123; (n) T. Schareina, A. Zapf, A. Cotte, M. Gotta and M. Bellera, *Adv. Synth. Catal.*, 2011, **353**, 777; (o) N. Azizi and M. R. Saidi, *J. Organomet. Chem.*, 2003, **688**, 283; (p) B. Karimi and L. Ma'Mani, *Org. Lett.*, 2004, **6**, 4813.
- 12 (a) G. K. S. Prakash, H. Vaghoo, C. Panja, V. Surampudi, R. Kultyshev, T. Mathew and G. A. Olah, *Proc. Natl. Acad. Sci. U. S. A.*, 2007, **104**, 3026; (b) P. Phuengphai, S. Youngme, P. Gamez and J. Reedijk, *Dalton Trans.*, 2010, **39**, 7936; (c) S. S. Kim, J. Rajagopal and D. H. Song, *J. Organomet. Chem.*, 2004, **689**, 1734; (d) B. He, Y. Li, X. Feng and G. Zhang, *Synlett*, 2004, 1776.
- 13 (a) D. H. Ryu and E. J. Corey, *J. Am. Chem. Soc.*, 2005, **127**, 5384; (b) B. M. Trost and S. Martinez-Sanchez, *Synlett*, 2005, 627; (c) Z. Zeng, G. Zhao, P. Gao, H. Tang, B. Chen, Z. Zhou and C. Tang, *Catal. Commun.*, 2007, **8**, 1443; (d) A. Alaeddine, T. Roisnel, C. M. Thomas and J. Carpentiera, *Adv. Synth. Catal.*, 2008, **350**, 731.
- 14 (a) Y. Q. Wen, W. M. Ren and X. B. Lu, *Org. Biomol. Chem.*, 2011, **9**, 6323; (b) Y. Hamashima, D. Sawada, H. Nogami, M. Kanai and M. Shibasaki, *Tetrahedron*, 2001, **57**, 805; (c) Y. Hamashima, M. Kanai and M. Shibasaki, *Tetrahedron Lett.*, 2001, **42**, 691; (d) G. Rajagopal, S. S. Kim and S. C. George, *Appl. Organomet. Chem.*, 2007, **21**, 798; (e) Y. Xiong, X. Huang, S. Gou, J. Huang, Y. Wen and X. Feng, *Adv. Synth. Catal.*, 2006, **348**, 538.
- 15 (a) For a recent review on Lewis base catalysis, see: S. E. Denmark and G. L. Beutner, *Angew. Chem., Int. Ed.*, 2008, **47**, 1560; (b) For a review on selective catalysis using hard–soft acid and base (HSAB) principles, see: S. Woodward, *Tetrahedron*, 2002, **58**, 1017.
- 16 (a) S. E. Denmark and W. Chung, *J. Org. Chem.*, 2006, **71**, 4002; (b) I. V. P. Raj, G. Suryavanshi and A. Sudalai, *Tetrahedron Lett.*, 2007, **48**, 7211; (c) M. G. Dekamin and Z. Karimi, *J. Organomet. Chem.*, 2009, **694**, 1789; (d) M. L. Kantam, P. Sreekanth and P. L. Santhi, *Green Chem.*, 2000, **2**, 47.
- 17 (a) B. M. Fetterly and J. G. Verkade, *Tetrahedron Lett.*, 2005, **46**, 8061; (b) S. Matsukawa, I. Sekine and A. Iitsuka, *Molecules*, 2009, **14**, 3353.
- 18 (a) H. Zhou, F. X. Chen, B. Qin and X. Feng, *Synlett*, 2004, 1077; (b) M. G. Dekamin, J. Mokhtari and M. R. Naimi-Jamal, *Catal. Commun.*, 2009, **10**, 582; (c) M. G. Dekamin, S. Javanshir, M. R. Naimi-Jamal, R. Hekmatshoar and J. Mokhtari, *J. Mol. Catal. A: Chem.*, 2008, **283**, 29; (d) M. G. Dekamin, M. Farahmand, S. Javanshir and M. R. Naimi-Jamal, *Catal. Commun.*, 2008, **9**, 1352.
- 19 (a) M. G. Dekamin, R. Alizadeh and M. R. Naimi-Jamal, *Appl. Organomet. Chem.*, 2010, **24**, 229; (b) A. Blanrue and R. Wilhelm, *Synlett*, 2004, 2621.
- 20 (a) M. J. Fuchter, *Chem.–Eur. J.*, 2010, **16**, 12286; (b) J. J. Song, F. Gallou, J. T. Reeves, Z. Tan, N. K. Yee and C. H. Senanyake, *J. Org. Chem.*, 2006, **71**, 1273; (c) Y. Suzuki, M. D. Abu Bakar, K. Muramatsu and M. Sato, *Tetrahedron*, 2006, **62**, 4227; (d) Y. Fukuda, Y. Maeda, S. Ishii, K. Kondo and T. Aoyama, *Synthesis*, 2006, 589.
- 21 X. Wang and S. K. Tian, *Synlett*, 2007, 1416.
- 22 S. T. Kadam and S. S. Kim, *Catal. Commun.*, 2008, **9**, 1342.
- 23 (a) X. Wang and S. K. Tian, *Tetrahedron Lett.*, 2007, **48**, 6010; (b) Y. Teng and P. H. Toy, *Synlett*, 2011, 551.
- 24 (a) S. J. Zuend and E. N. Jacobsen, *J. Am. Chem. Soc.*, 2007, **129**, 15872; (b) S. Hun, H. Chen, J. W. Wiench, M. Pruski and V. S. Lin, *Angew. Chem., Int. Ed.*, 2005, **44**, 1826.
- 25 (a) L. Wang, X. Huang, J. Jiang, X. Liu and X. Feng, *Tetrahedron Lett.*, 2006, **47**, 1581; (b) S. Matsukawa and S. Fujikawa, *Tetrahedron Lett.*, 2012, **53**, 1075.
- 26 X. Liu, B. Oin, X. Zhou, B. He and X. Feng, *J. Am. Chem. Soc.*, 2005, **127**, 12224.
- 27 M. G. Dekamin, S. Sagheb-Asl and M. R. Naimi-Jamal, *Tetrahedron Lett.*, 2009, **50**, 4063.
- 28 M. G. Dekamin, F. M. Moghaddam, H. Saeidian and S. Mallakpour, *Monatsh. Chem.*, 2006, **137**, 1591.
- 29 M. G. Dekamin, N. Yazdaniinia, J. Mokhtari and M. R. Naimi-Jamal, *J. Iran. Chem. Soc.*, 2011, **8**, 537.
- 30 M. G. Dekamin, K. Varmira, M. Farahmand, S. Sagheb-Asl and Z. Karimi, *Catal. Commun.*, 2010, **12**, 226.
- 31 (a) G. K. S. Prakash, C. Panja, H. Vaghoo, V. Surampudi, R. Kultyshev, M. Mandal, G. Rasul, T. Mathew and G. A. Olah, *J. Org. Chem.*, 2006, **71**, 6806; (b) Y. Orito and M. Nakajima, *Synthesis*, 2006, 1391.