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Zhi-Liang Shen [a] & Shun-Jun Ji [a]
[a] Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry and Chemical Engineering, Suzhou (Soochow) University, Suzhou, China
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Alkali Salt of L-Proline as an Efficient and Practical Catalyst for the Cyanosilylation of a Wide Variety of Carbonyl Compounds Under Solvent-Free Conditions

Zhi-Liang Shen and Shun-Jun Ji
Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry and Chemical Engineering, Suzhou (Soochow) University, Suzhou, China

Abstract: The alkali salt of L-proline was demonstrated to be an efficient and practical catalyst for the cyanosilylation of a wide variety of simple and functionalized carbonyl compounds under solvent-free conditions. The reactions proceeded smoothly at room temperature to afford the corresponding cyanohydrins in good to excellent yields.

Keywords: Cyanohydrin, cyanosilylation, L-proline salt, solvent-free condition, TMSCN

Cyanohydrins are highly versatile synthetic intermediates that can be conveniently transformed into various important building blocks, such as α-hydroxy carbonyl compounds, β-hydroxy amines, and α-amino acid derivatives.[1] In view of their importance, much attention has been focused on the development of practical methods for the synthesis of cyanohydrins. Among them, the cyanosilylation of carbonyl compounds using trimethylsilyl cyanide (TMSCN) is widely utilized for the synthesis of cyanohydrins. Various types of Lewis acids such as I_2,[2c] $Cu(OTf)_2$,[2d] $InBr_3$,[2e] $Yb(O_3SCF_3)_3$,[2p] and titanium complexes[2j,2k] were used to

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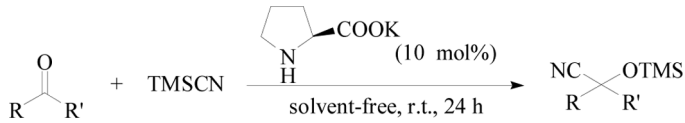
Address correspondence to Shun-Jun Ji, Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry and Chemical Engineering, Suzhou (Soochow) University, Suzhou 215123, China. E-mail: chemjsj@suda.edu.cn

promote this transformation. Some types of Lewis bases[2m,2z] or bifunctional catalysts[2a,2k,2w] were also demonstrated to be efficient catalysts for the mediation of the reaction.[2]

Recently, our group has described efficient and green methods for the synthesis of cyanohydrins using InF_3 in water[3] or simply employing immidazolium-based ionic liquid [omim]PF_6[4] as both reaction solvent and promoter. Although excellent yields were obtained for various aldehydes under the reaction conditions, ketones were proven to proceed sluggishly under the same reaction conditions. In addition, most of the reported methods for the cyanosilylation of carbonyl compounds are largely limited to aldehydes as well as more reactive aliphatic ketones.[2] Poor yields were obtained when the reactions were applied to aryl or sterically hindered ketones. Therefore, it is still desirable to develop a more general and practical method for the cyanosilylation of a wide variety of simple and functionalized carbonyl compounds.

In recent decades, because of the increasing concern about the harmful effects of organic solvents on the environment and humans, organic reactions that are operated without the participation of conventional organic solvents have aroused attention of organic chemists because the synthetic approach is efficient, economical, and environmentally friendly. Many organic reactions were reported to proceed efficiently under solvent-free conditions with mild reaction conditions, short reaction times, high yields, and sometimes enhanced selectivity.[5] Therefore, the application of a solvent-free synthetic approach to organic synthesis is an important and continued task worthy of chemists' attention. Herein, we report an efficient approach for the synthesis of cyanohydrins via the cyanosilylation of carbonyl compounds catalyzed by an alkali salt of L-proline under solvent-free conditions. This environmentally friendly method, without the use of volatile and toxic organic solvent, is applicable for various carbonyl compounds including aryl and sterically hindered carbonyl compounds.

Although there are many reports about the use of L-proline as catalyst in organic reactions, few reports in previous papers concern organic transformations promoted by an alkali salt of L-proline.[6] In our investigations, we found that a catalytic amount of potassium salt of L-proline (10 mol%) could catalyze the cyanosilylation of carbonyl compounds efficiently under solvent-free conditions (Scheme 1).



Scheme 1. Cyanosilylation of carbonyl compounds under solvent-free conditions.

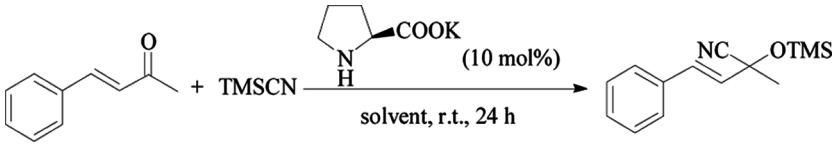
Initial study was focused on the reaction of 4-phenyl-3-buten-2-one with TMSCN in the presence of 10 mol% potassium salt of L-proline and different solvents. The results are summarized in Table 1.

As shown in Table 1, the cyanosilylation reaction proceeded more efficiently under solvent-free conditions than in organic solvents. The reaction proceeded smoothly at room temperature to afford the corresponding cyanohydrin in 83% yield under solvent-free conditions (Table 1, entry 1). However, poor yields (<10%) were obtained when water, methanol, and ionic liquid [hmim]PF_6 were used as reaction media (Table 1, entries 8–10).

With the success of the reaction, various aldehydes and ketones were tested under solvent-free conditions at room temperature. All the results are summarized in Table 2.

As shown in Table 2, the solvent-free approach works well for substituted and unsubstituted benzaldehyde (Table 2, entries 1–4) or acetophenone (Table 2, entries 8–13); good to excellent yields of the corresponding products were obtained. In addition, both the cyclic and open chain aliphatic carbonyl compounds (Table 2, entries 6, 7, and 20–22) were converted into the corresponding cyanohydrins in good yields. It should be noted that aromatic and aliphatic α,β-unsaturated carbonyl

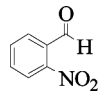
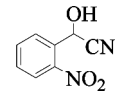
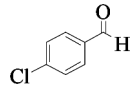
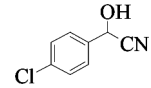
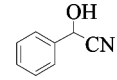
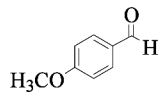
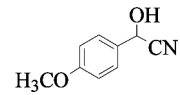
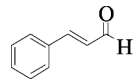
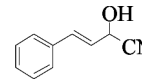
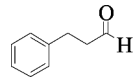
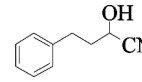
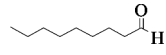
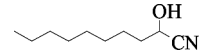
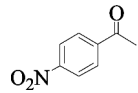
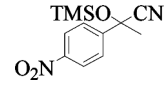
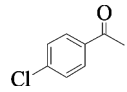
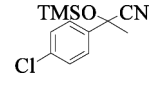
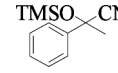
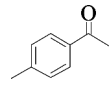
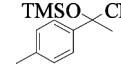
Table 1. Potassium salt of L-proline-catalyzed cyanosilylation of 4-phenyl-3-buten-2-one in different solvents



Entry	Solvent	Yield (%)[a]
1	—[b]	83
2	Et_2O	39
3	CH_3CN	80
4	THF	49
5	CH_2Cl_2	56
6	DMF	75
7	DMSO	54
8	H_2O	<10
9	MeOH	<10
10	[hmim]PF_6	<10

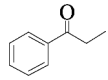
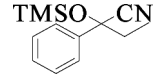
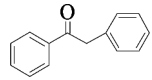
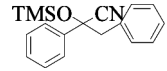
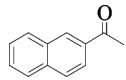
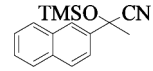
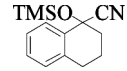
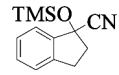
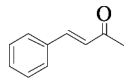
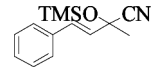
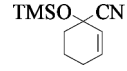
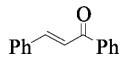
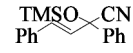
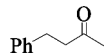
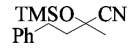
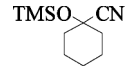
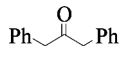
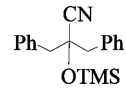
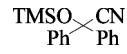
[a]Isolated yield.
[b]Solvent-free condition.

Table 2. Potassium salt of L-proline–catalyzed cyanosilylation of various carbonyl compounds under solvent-free conditions

Entry	Carbonyl compound	Product	Yield (%)[a]
1			83
2			91
3			84
4			87
5			82
6			90
7			73
8			90
9			89
10			83
11			64

(*Continued*)

Table 2. Continued

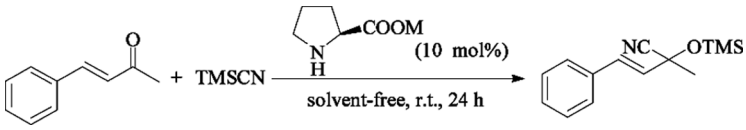
Entry	Carbonyl compound	Product	Yield (%)[a]
12			92
13			90
14			87
15			95
16			78
17			83
18			82
19			85
20			91
21			73
22			92
23			99

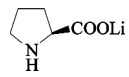
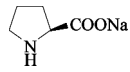
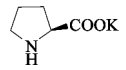
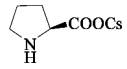
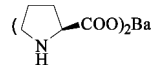
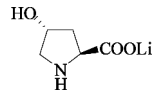
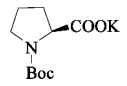
[a]Isolated yield.

compounds (Table 2, entries 5 and 17–19) underwent cyanation reaction efficiently to afford the desired products in good yields; no 1,4-adduct was observed under the reaction conditions. In the case of 1-indanone and 1-tetralone (Table 2, entries 15 and 16), they were also proven to be good substrates for cyanation reaction. Moreover, highly steric hindered substrate benzophenone could also react smoothly with TMSCN in the presence of the potassium salt of L-proline to afford the corresponding 1,2-adduct in excellent yield (99% yield, Table 2, entry 23).

In the following work, the catalytic activity of a series of alkali salts of L-proline and its derivatives have been investigated using 4-phenyl-3-buten-2-one as substrate. The results are outlined in Table 3. Under

Table 3. Different alkali salts of L-proline or its derivatives catalyzed cyanosilylation of 4-phenyl-3-buten-2-one under solvent-free conditions



Entry	Catalyst	Yield (%)[a]
1		91
2		75
3		83
4		82
5		82
6		90
7		58

[a]Isolated yield.

solvent-free conditions, the best yield (91%) was achieved utilizing lithium salt of L-proline as catalyst (Table 3, entry 1). However, the use of potassium salt of *t*-Boc protected L-proline (Table 3, entry 7) gave the product in only 58% yield. Therefore, it is suggested that both the secondary amine moiety and the metal carboxylate moiety of alkali salt of L-proline play important roles for good catalytic activity in the cyanation reaction. The reaction might proceed via the formation of a hypervalent silicate between nitrogen and TMSCN to facilitate the progress of the reaction.

In summary, we have developed an efficient and environmentally friendly protocol for cyanosilylation of variuos carbonyl compounds employing a catalytic amount of alkali salt of L-proline (10 mol%) under solvent-free conditions at ambient conditions. This method is quite general, and it works well with a wide variety of carbonyl compounds including aryl and sterically hindered ketones. The mild reaction conditions, high yields, good chemoselectivity, cheap catalyst, and environmentally benign reaction conditions make this method attractive for scale-up purposes.

EXPERIMENTAL

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance DPX 300 and Bruker AMX 400 spectrophotometer using tetramethyl silane (TMS) as an internal standard. High resolution mass spectrometry (HRMS) spectra were obtained using Finnigan MAT95XP GC/HRMS (Thermo Electron Corporation). Infrared (IR) spectra were recorded on a Bio-Rad FTS 165 Fourier transfrom infrared (FTIR) spectrometer.

The alkali salts of L-proline or its derivatives are prepared as follows: the same equivalents of alkali hydroxide and the corresponding amino acids were stirred in ethanol for several hours at room temperature; then the solvent was evaporated under reduced pressure, and the remaining solid was dried at 100 °C in an oven to give the corresponding alkali salt of L-proline.

General Procedure for the Cyanosilylation of Aldehyde

Aldehyde (1 mmol), followed by TMSCN (1 mmol), was added to a 10-mL round-bottomed flask charged with potassium salt of L-proline (0.1 mmol) at room temperature. After stirring for 12 h, another 1 mmol TMSCN was added subsequently and stirred for another 12 h. Then 2 mL THF and 2 mL 1 M aq. HCl were added to the flask, and it was stirred for a while. Following extraction with diethyl ether (10 mL × 3), drying over anhydrous $MgSO_4$, removing of the solvent, and passage through a column of silica gel gave the desired product, cyanohydrin.

General Procedure for the Cyanosilylation of Ketone

The reaction procedure was the same as cyanosilylation of aldehyde; only the workup procedure was different. After reaction, excess TMSCN was removed under reduced pressure, and then the residue was passed through a column of silica gel directly to give the silylated cyanohydrins.

Spectral and Analytical Data

2-Hydroxy-2-(2-nitrophenyl)acetonitrile (Table 2, Entry 1)[8c]

$R_f = 0.18$ (ethyl acetate/hexane = 1/4). FTIR (NaCl, neat): ν 3397, 2249 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 4.18$ (s, 1H), 6.21 (s, 1H), 7.64 (m, 1H), 7.80 (m, 1H), 7.99 (d, $J = 7.65$ Hz, 1H), 8.19 (d, $J = 8.43$ Hz, Hz, 1H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 146.9$, 134.8, 130.9, 130.8, 129.3, 125.8, 117.5, 60.4 ppm. HRMS (ESI, m/z): $[M - H]^+$. Calcd. for $C_8H_5N_2O_3$: 177.0300; found: 177.0306.

2-Hydroxy-2-(4-chlorophenyl)acetonitrile (Table 2, Entry 2)[8a]

$R_f = 0.09$ (ethyl acetate/hexane = 1/4). FTIR (NaCl, neat): ν 3422, 2251 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 4.72$ (s, 1H), 5.47 (s, 1H), 7.37 (d, $J = 1.62$ Hz, 4H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 135.6$, 133.5, 129.2, 127.9, 118.7, 62.5 ppm. HRMS (EI, m/z): $[M]^+$. Calcd. for C_8H_6ClNO: 167.0138; found: 167.0134.

2-Hydroxy-2-phenylacetonitrile (Table 2, Entry 3)[8a]

$R_f = 0.6$ (ethyl acetate/hexane = 1/2). FTIR (NaCl, neat): ν 3417, 2248 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.74$ (br, s, 1H), 5.50 (s, 1H), 7.41–7.52 (m, 5H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 63.4$, 118.8, 126.6, 129.1, 129.7, 135.2 ppm. HRMS (EI, m/z): $[M]^+$. Calcd. for C_8H_7NO: 133.0528; found: 133.0554.

2-Hydroxy-2-(4-methoxyphenyl)acetonitrile (Table 2, Entry 4)[8a]

$R_f = 0.16$ (ethyl acetate/hexane = 1/4). FTIR (NaCl, neat): ν 3418, 2240 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.80$ (s, 3H), 4.04 (s, 1H), 5.42 (s, 1H), 6.91 (d, $J = 8.82$ Hz, 2H), 7.40 (d, $J = 8.43$ Hz, 2H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 160.5$, 128.2, 127.5, 119.1, 114.4,

63.0, 55.4 ppm. HRMS (EI, m/z): $[M]^+$. Calcd. for $C_9H_9NO_2$: 163.0633; found: 163.0633.

2-Hydroxy-4-phenyl-3-butenenitrile (Table 2, Entry 5)[8a]

$R_f = 0.19$ (ethyl acetate/hexane = 1/4). FTIR (NaCl, neat): ν 3414, 2243 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 5.15$ (d, $J = 5.61$ Hz, 1H), 6.25 (d, $J = 6$ Hz, 1H), 6.90 (d, $J = 16.05$ Hz, 1H), 7.31–7.42 (m, 5H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 135.3$, 134.8, 129.1, 128.8, 127.1, 122.3, 118.3, 61.9 ppm. HRMS (EI, m/z): $[M]^+$. Calcd. for $C_{10}H_9NO$: 159.0684; found: 159.0688.

2-Hydroxy-4-phenylbutanenitrile (Table 2, Entry 6)[8a]

$R_f = 0.31$ (ethyl acetate/hexane = 1/4). FTIR (NaCl, neat): ν 3436, 2247 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 2.17$ (m, 2H), 2.85 (m, 2H), 4.16 (s, 1H), 4.42 (t, $J = 6.81$ Hz, 1H), 7.22–7.37 (m, 5H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 139.6$, 128.6, 128.3, 126.4, 120.0, 60.1, 36.4, 30.5 ppm. HRMS (EI, m/z): $[M]^+$. Calcd. for $C_{10}H_{11}NO$: 161.0841; found: 161.0843.

2-Hydroxy-*n*-decanenitrile (Table 2, Entry 7)[8d]

$R_f = 0.55$ (ethyl acetate/hexane = 1/4). FTIR (NaCl, neat): ν 3366, 2247 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.85$ (t, $J = 6.81$ Hz, 3H), 1.24–1.47 (m, 12H), 1.79 (q, $J = 6.84$ Hz, 2H), 4.17 (s, 1H), 4.42 (t, $J = 6.81$ Hz, 1H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 120.2$, 61.0, 34.9, 31.7, 29.2, 29.0, 28.8, 24.5, 22.5, 13.9 ppm. HRMS (EI, m/z): $[M\text{-}HCN]^+$. Calcd. for $C_9H_{18}O$: 142.1358; found: 142.1354.

2-Trimethylsilyloxy-2-(4-nitrophenyl)propanenitrile (Table 2, Entry 8)[2j,2r]

$R_f = 0.48$ (ethyl acetate/hexane = 1/6). FTIR (NaCl, neat): ν 2237 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.26$ (s, 9H), 1.90 (s, 3H), 7.76 (d, $J = 9.06$ Hz, 2H), 8.27 (d, $J = 8.7$ Hz, 2H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 0.9$, 33.3, 70.9, 120.6, 123.9, 125.7, 148.0, 148.9 ppm. HRMS (EI, m/z): $[M]^+$. Calcd. for $C_{12}H_{16}N_2O_3Si$: 264.0930; found: 264.0926.

2-Trimethylsilyloxy-2-(4-chlorophenyl)propanenitrile (Table 2, Entry 9)[2j,2r]

$R_f = 0.70$ (ethyl acetate/hexane = 1/6). FTIR (NaCl, neat): ν 2236 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.20$ (s, 9H), 1.84 (s, 3H), 7.38 (m, 2H), 7.48 (m, 2H), 8.13 (d, $J = 1.59$ Hz, 1H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 1.1$, 33.5, 71.1, 121.2, 126.1, 128.8, 134.6, 140.7 ppm. HRMS (EI, m/z): $[M]^+$. Calcd. for $C_{12}H_{16}ClNOSi$: 253.0690; found: 253.0689.

2-Trimethylsilyloxy-2-phenylpropanenitrile (Table 2, Entry 10)[2j,2r]

$R_f = 0.71$ (ethyl acetate/hexane = 1/6). FTIR (NaCl, neat): ν 2234 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.19$ (s, 9H), 1.87 (s, 3H), 7.35–7.57 (m, 5H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 1.0$, 33.6, 71.6, 121.6, 124.6, 128.6, 142.0 ppm. HRMS (EI, m/z): $[M\text{-}CH_3]^+$. Calcd. for $C_{11}H_{14}NOSi$: 204.0844; found: 204.0848.

2-Trimethylsilyloxy-2-(4-methylphenyl)propanenitrile (Table 2, Entry 11)[2j]

$R_f = 0.68$ (ethyl acetate/hexane = 1/6). FTIR (NaCl, neat): ν 2236 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.20$ (s, 9H), 1.86 (s, 3H), 2.38 (s, 3H), 7.22 (d, $J = 8.01$ Hz, 2H), 7.46 (d, $J = 8.43$ Hz, 2H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 1.0$, 21.0, 33.4, 71.5, 121.7, 124.5, 129.2, 138.4, 139.1 ppm. HRMS (EI, m/z): $[M]^+$. Calcd. for $C_{13}H_{19}NOSi$: 233.1236; found: 233.1235.

2-Trimethylsilyloxy-2-phenylbutenenitrile (Table 2, Entry 12)[2i]

$R_f = 0.67$ (ethyl acetate/hexane = 1/6). FTIR (NaCl, neat): ν 2235 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.16$ (s, 9H), 0.99 (t, $J = 7.43$ Hz, 3H), 2.01 (m, 2H), 7.34–7.42 (m, 3H), 7.52 (m, 2H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 0.9$, 8.6, 39.1, 76.2, 120.7, 125.1, 128.4, 128.5, 140.8 ppm. HRMS (EI, m/z): $[M]^+$, Calcd. for $C_{13}H_{19}NOSi$: 233.1236; found: 233.1236.

Benzyl-phenyl-trimethylsiloxy Acetonitrile (Table 2, Entry 13)[8e]

$R_f = 0.67$ (ethyl acetate/hexane = 1/6). FTIR (NaCl, neat): ν 2234 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.15$ (s, 9H), 3.27 (q, $J = 15.2$ Hz, 2H), 7.19–7.56 (m, 10H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = -0.4$, 51.0,

74.8, 119.2, 124.1, 126.2, 126.7, 127.3, 127.5, 129.8, 133.0, 139.6 ppm. HRMS (EI, m/z): $[M]^+$. Calcd. for $C_{18}H_{21}NOSi$: 295.1392; found: 295.1386.

2-Trimethylsilyloxy-2-(2-naphthyl)propanenitrile (Table 2, Entry 14)[2j]

$R_f = 0.58$ (ethyl acetate/hexane = 1/6). FTIR (NaCl, neat): ν 2234 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.29$ (s, 9H), 2.00 (s, 3H), 7.55–7.60 (m, 2H), 7.69 (dd, $J = 8.7$, 2.01 Hz, 1H), 7.88–7.96 (m, 3H), 8.13 (d, $J = 1.59$ Hz, 1H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 1.0$, 33.4, 71.7, 121.5, 122.3, 123.6, 126.6, 126.6, 127.6, 128.3, 128.7, 132.7, 133.1, 139.1 ppm. HRMS (EI, m/z): $[M]^+$. Calcd. for $C_{16}H_{19}NOSi$: 269.1236; found: 269.1236.

2-Trimethylsilyloxy-1,2,3,4-tetrahydronaphthalene-1-carbonitrile (Table 2, Entry 15)[2j,2r]

$R_f = 0.56$ (ethyl acetate/hexane = 1/6). FTIR (NaCl, neat): ν 2228 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.27$ (s, 9H), 1.94–2.41 (m, 4H), 2.85 (m, 2H), 7.14 (m, 1H), 7.29 (m, 2H), 7.71 (m, 1H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 1.2$, 18.6, 28.2, 37.6, 69.8, 122.0, 126.5, 127.9, 128.9, 129.2, 135.6, 136.0 ppm. HRMS (EI, m/z): $[M]^+$. Calcd. for $C_{14}H_{19}NOSi$: 245.1236; found: 245.1230.

1-Trimethylsilyloxy-1-indancarbonitrile (Table 2, Entry 16)[2j,2r]

$R_f = 0.56$ (ethyl acetate/hexane = 1/6). FTIR (NaCl, neat): ν 2227 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.21$ (s, 9H), 2.45 (m, 1H), 2.72 (m, 1H), 2.94–3.17 (m, 2H), 7.26–7.38 (m, 2H), 7.55 (dd,$J = 6.23$, 1.59 Hz, 1H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 1.1$, 29.3, 42.8, 76.4, 121.0, 124.0, 125.1, 127.3, 129.9, 142.1, 142.6 ppm. HRMS (EI, m/z): $[M]^+$. Calcd. for $C_{13}H_{17}NOSi$: 231.1079; found: 231.1078.

2-Trimethylsilyloxy-2-methyl-4-phenyl-3-butenenitrile (Table 2, Entry 17)[2j,r]

$R_f = 0.63$ (ethyl acetate/hexane = 1/6). FTIR (NaCl, neat): ν 2236 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.27$ (s, 9H), 1.77 (s, 3H), 6.16 (d, $J = 16.02$ Hz, 1H), 6.91 (d, $J = 16.02$ Hz, 1H), 7.29–7.45 (m, 5H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 1.4$, 30.9, 70.0, 120.7, 126.9, 128.6,

128.8, 129.6, 131.0, 135.2 ppm. HRMS (EI, m/z): $[M]^+$. Calcd. for $C_{14}H_{19}NOSi$: 245.1236; found: 245.1236.

2-Trimethylsilyloxy-2-cyclohexenecarbonitrile (Table 2, Entry 18)[2r]

$R_f = 0.71$ (ethyl acetate/hexane = 1/6). FTIR (NaCl, neat): ν 2230 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.23$ (s, 9H), 1.70–2.16 (m, 6H), 5.73 (d, $J = 10.02$ Hz, 1H), 5.95 (m, 1H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 1.5$, 18.3, 24.3, 36.9, 66.8, 121.8, 127.6, 132.5 ppm. HRMS (EI, m/z): $[M]^+$. Calcd. for $C_{10}H_{17}NOSi$: 195.1079; found: 195.1080.

2,4-Diphenyl-2-trimethylsiloxy-3-but-enenitrile (Table 2, Entry 19)[8b]

$R_f = 0.50$ (ethyl acetate/hexane = 1/6). FTIR (NaCl, neat): ν 2235 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.38$ (s, 9H), 6.32 (d, $J = 15.66$ Hz, 1H), 7.15 (d, $J = 15.66$ Hz, 1H), 7.36–7.53 (m, 8H), 7.70–7.73 (m, 2H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 1.2$, 75.0, 125.4, 126.9, 128.6, 128.6, 128.8, 129.6, 130.8, 135.0, 140.3 ppm. HRMS (EI, m/z): $[M]^+$. Calcd. for $C_{19}H_{21}NOSi$: 307.1392; found: 307.1390.

2-Trimethylsilyloxy-2-methyl-4-phenyl-3-butanenitrile (Table 2, Entry 20)[2j]

$R_f = 0.65$ (ethyl acetate/hexane = 1/6). FTIR (NaCl, neat): ν 2232 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.35$ (s, 9H), 1.68 (s, 3H), 2.09 (m, 2H), 2.90 (m, 2H), 7.24–7.38 (m, 5H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 1.2$, 28.9, 30.6, 45.1, 69.3, 121.7, 126.1, 128.2, 128.4, 140.6 ppm. HRMS (EI, m/z): $[M]^+$. Calcd. for $C_{14}H_{21}NOSi$: 247.1392; found: 247.1391.

1-Trimethylsilyloxy-1-cyclohexanecarbonitrile (Table 2, Entry 21)[2r]

$R_f = 0.75$ (ethyl acetate/hexane = 1/6). FTIR (NaCl, neat): ν 2233 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.22$ (s, 9H), 1.51–1.76 (m, 8H), 2.03 (t, $J = 7.64$ Hz, 2H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 1.4$, 22.6, 24.5, 39.3, 70.6, 121.9 ppm. HRMS (EI, m/z): $[M]^+$. Calcd. for $C_{10}H_{19}NOSi$: 197.1236; found: 197.1238.

Dibenzyl-trimethylsiloxy-acetonitrile (Table 2, entry 22)[8f]

$R_f = 0.60$ (ethyl acetate/hexane = 1/6). FTIR (NaCl, neat): ν 2232 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = -0.04$ (s, 9H), 3.10 (s, 4H), 7.40

(m, 10H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 0.3$, 47.8, 73.4, 120.2, 127.3, 128.1, 130.9, 134.4 ppm. HRMS (EI, m/z): $[M]^+$. Calcd. for $C_{19}H_{23}NOSi$: 309.1549; found: 309.1550.

Diphenyl-trimethylsiloxy-acetonitrile (Table 2, Entry 23)[8e]

$R_f = 0.55$ (ethyl acetate/hexane = 1/6). FTIR (NaCl, neat): ν 2234 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.18$ (s, 9H), 7.33–7.41 (m, 6H), 7.52–7.56 (m, 4H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 141.9$, 128.6, 128.5, 125.9, 120.7, 76.4, 0.9 ppm. HRMS (EI, m/z): $[M]^+$. Calcd. for $C_{17}H_{19}NOSi$: 281.1236; found: 281.1237.

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