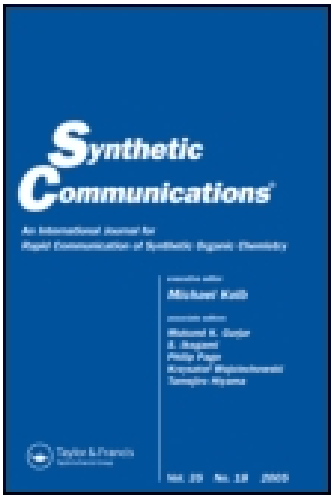

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Cyanosilylation of Aldehydes and Ketones Catalyzed by Nanocrystalline Magnesium Oxide

M. Lakshmi Kantam,[1] Koosam Mahendar,[1] Bojja Sreedhar,[1] K. Vijay Kumar,[1] and B. M. Choudary[2]
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Abstract: Cyanosilylation of various aldehydes and ketones with TMSCN proceeded smoothly under mild conditions to give the corresponding cyanohydrin trimethylsilyl ethers in the presence of nanocrystalline magnesium oxide. The cyanohydrin trimethylsilyl ethers of aldehydes produced cyanohydrins in good to high yields on treatment with 2 N HCl. ^{29}Si NMR spectral evidence proved that the reaction proceeds through the hypervalent silicate species by coordination to O^{2-}/O^{-} (Lewis basic site) of nanocrystalline magnesium oxide.

Keywords: Aldehydes, cyanohydrins, cyanohydrin trimethylsilyl ethers, cyanosilylation, ketones, nanocrystalline magnesium oxide, trimethylsilyl cyanide

INTRODUCTION

The cyanation reaction of carbonyl compounds is one of the most important methods to obtain polyfunctional molecules in organic synthesis.[1] Cyanohydrins or cyanohydrin trimethylsilyl ethers are highly versatile synthetic intermediates, which can be easily converted into α-hydroxy carbonyl derivatives, β-amino alcohols, and α-amino acids[2] for their application in pharmaceuticals and agrochemicals.[3]

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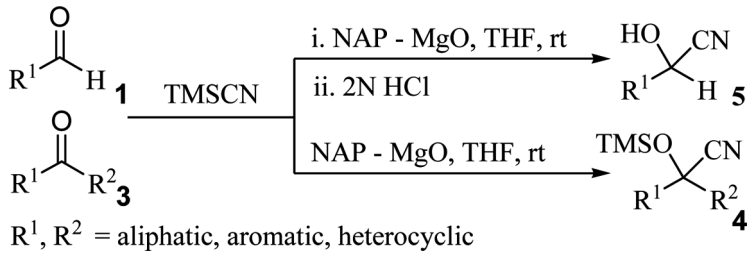
Generally, cyanohydrins are prepared by the interaction of carbonyl compounds with a cyanide source serving as nucleophile. Several useful cyanating reagents have been reported in the literature;[4] among them, trimethylsilyl cyanide (TMSCN) seems to be one of the most effective, safe, and easy to handle cyanating sources for the nucleophilic addition to carbonyl compounds. A variety of catalysts have been used to promote the cyanosilylation reactions, such as Lewis acids;[5] Lewis bases;[6] nonionic bases;[7] *N*-heterocyclic carbenes;[8] V-, Mn-, Al-, and Ti-salen complexes;[9] and organic/inorganic salts.[10] In recent years, many researchers have developed various catalysts[11] such as oxazaborolidinium ion, amino-thiourea, chiral Ti-TADDOLs that have been successfully applied in asymmetric cyanosilylation reactions. Shibasaki et al. designed Ti, Al-phosphine oxide bifunctional catalysts[12] using carbohydrate or binaphthol as scaffolds, and Feng et al. developed Ti, Al-*N*-oxide bifunctional catalysts[13] using various chiral ligands including proline, pyrrolidine and 1,2-diamino compounds for the asymmetric cyanosilylation reactions. However, there are some reports of cyanosilylation reaction using reusable solid acid, solid base catalysts and ionic liquids as heterogeneous catalysts.[14]

Nanocrystalline metal oxides find excellent applications as active adsorbents for gases, for destruction of hazardous chemicals,[15] and as catalysts for various organic transformations.[16] These high reactivities are due to high surface area combined with unusually reactive morphologies. In continuation of our work on nanomaterials, herein we report an effective cyanosilylation of aldehydes and ketones to give cyanohydrins by using nanocrystalline magnesium oxide (NAP-MgO) catalyst. The cyanohydrin trimethylsilyl ethers of aldehydes afforded cyanohydrins in good to high yields on treatment with 2 N HCl (Scheme 1).



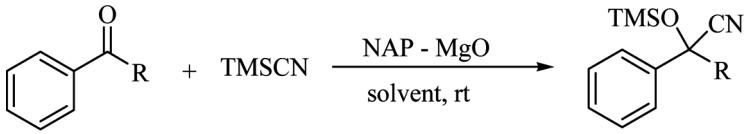
Scheme 1. NAP-MgO catalyzed cyanosilylation reaction between aldehydes or ketones and TMSCN. **3a** with TMSCN catalyzed by NAP-MgO. Reaction conditions: benzaldehyde **1a** or acetophenone **3a** (1 mmol), TMSCN (1.5 mmol for **1a**, 2 mmol for **3a**), NAP-MgO (0.1 g), and solvent (3 mL) at room temperature.

RESULTS AND DISCUSSION

To understand the relationship between structure and reactivity, various forms of magnesium oxide crystals CM-MgO (commercial MgO, SSA: $30\,m^2/g$), NA-MgO (NanoActive MgO, conventionally prepared MgO, SSA: $250\,m^2/g$), NAP-MgO (NanoActive plus MgO, aerogel-prepared MgO, SSA: $590\,m^2/g$)] were initially evaluated in the cyanosilylation reaction between acetophenone **3a** and TMSCNat room temperature. All these MgO crystals catalyze the cyanosilylation reaction in quantitative yields. However, NAP-MgO was more active than NA-MgO and CM-MgO in the cyanosilylation reaction (Table 1, entry 1).

Initially, we optimized the reaction with benzaldehyde **1a** and acetophenone **3a** as model substrates with TMSCN using NAP-MgO at room temperature (Table 1). Various solvents such as CH_2Cl_2, N,N-dimethylformamide (DMF), tetrahydrofuran (THF), $CHCl_3$, MeOH, and toluene were screened for the reaction between acetophenone **3a**

Table 1. Optimization of cyanosilylation reaction of benzaldehyde **1a** or acetophenone **3a** with TMSCN catalyzed by NAP-MgO



R = H **1a**
R = CH_3 **3a**

R = H **2a**
R = CH_3 **4a**

Entry	Substrate	Solvent	Time (h)	Yield (%)[a]
1	**3a**	THF	4,7[b], 12,[c] 8,[d] 5[e] 12[f]	92, 87,[b] 85,[c] 81,[d] 88,[e] 0[f]
	1a		2	93
2	**3a**	CH_2Cl_2	5	89
	1a		3	86
3	**3a**	DMF	6	86
	1a		3	81
4	**3a**	$CHCl_3$	8	78
5	**3a**	$PHCH_3$	10	71
6	**3a**	CH_3OH	12	N.R

[a]Isolated yield.
[b]NA-MgO.
[c]CM-MgO.
[d]Sil-NAP-MgO.
[e]Fourth cycle.
[f]Without catalyst.

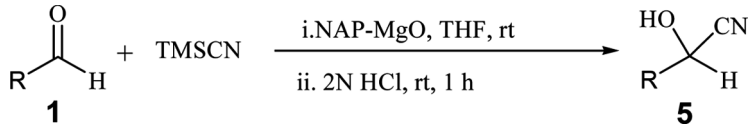
and TMSCN. A study on the solvent effect showed that THF provided the best yields of cyanohydrin trimethylsilyl ether **4a** (entry 1), whereas no product was observed with MeOH (entry 6). When the reaction between benzaldehyde **1a** and TMSCN was carried out in THF in the presence of NAP-MgO, the product cyanohydrin trimethylsilyl ether **2a** was obtained in higher yields than in CH_2Cl_2, DMF (Table 1, entries 1–3).

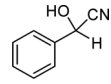
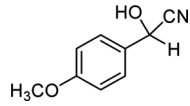
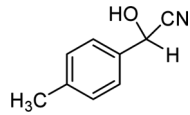
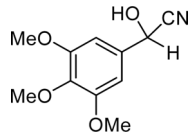
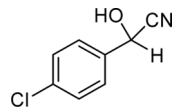
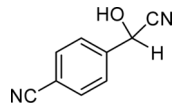
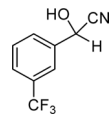
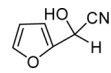
The cyanosilylated products obtained from aldehydes and TMSCN in the presence of NAP-MgO were further treated with 2 N HCl and afforded the corresponding cyanohydrins **5** as summarized in Table 2. As can be seen from Table 2, benzaldehyde, benzaldehydes bearing electron-withdrawing as well as electron-donating substituents, furfuraldehyde, and naphthaldehyde gave their corresponding cyanohydrins in good to high yields (entries 1–9), whereas 4-*N,N*-dimethyl benzaldehyde gave its cyanohydrin product in 72% of isolated yields (entry 14). Cinnamaldehyde produced the 1,2-addition product regioselectively, without formation of any 1,4-adduct (entry 10). The reaction of aliphatic aldehydes with TMSCN formed the corresponding cyanohydrins in good yields (entries 11–13).

As shown in Table 3, the reaction of aromatic, aliphatic, and heterocyclic ketones with TMSCN in the presence of NAP-MgO proceeded smoothly at room temperature to give the corresponding cyanohydrin trimethylsilyl ethers **4** in good to high yields. Highly conjugated naphthones gave their cyanosilylated products in yields comparable to other aromatic compounds (entries 7 and 8). Similar to aldehydes, α,β-unsaturated ketone (benzylideneacetone) reacted with TMSCN in the presence of NAP-MgO and afforded the 1,2-addition product regioselectively, rather than the 1,4-adduct (entry 9). It is noteworthy that ketones such as cyclohexanone, benzophenone, and α-tetralone took longer times for completion of the reaction under the optimized conditions (entries 10–12). This may be due to the steric hindrance of their reactive keto group.

As to the mechanism, there was no reaction between **1** or **3** and TMSCN without an NAP-MgO catalyst, which indicates that the catalyst is essential for the reaction (Table 1, entry 1). It was suggested that on the basis of proposed mechanism in our previous work,[16g] we assume that the cyanation of carbonyl compounds **1** or **3** with TMSCN proceeds through the formation of an active intermediate, hypervalent silicate **I** coordinated with the NAP-MgO in the present system as illustrated in Scheme 2.[6d,7b,16g,17] Trimethylsilyl cyanide is activated by O^{2-}/O^{-} (Lewis base) of NAP-MgO catalyst to form a hypervalent silicate **I** and coordinates with O^{2-}/O^{-} of the catalyst, polarizing the cyanide group to become more reactive. Meanwhile, carbonyl compound **1** or **3** is activated by Mg^{2+}/Mg^{+} (Lewis acid) of NAP-MgO. The highly reactive

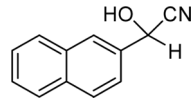
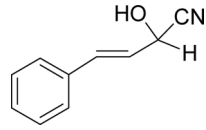
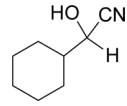
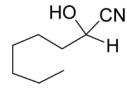
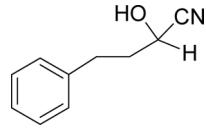
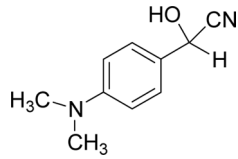
Table 2. Synthesis of various cyanohydrins by using NAP-MgO[a]



Entry	R	Product **5**	Time (h)	Yield (%)[b]
1	Ph		2	90
2	4-OCH_3-Ph		3	89
3	4-CH_3-Ph		3	81
4	3,4,5-OCH_3-Ph		4	82
5	4-Cl-Ph		3	82
6	4-CN-Ph		2	76
7	3-CF_3-Ph		4	84
8	Furfuryl		3	86

(*Continued*)

Table 2. Continued

Entry	R	Product **5**	Time (h)	Yield (%)[b]
9	2-Naphthyl		4	88
10	Cinnamyl		3	82
11	Cyclohexyl		5	79
12	CH_3-$(CH_2)_5^-$		4	84
13	Ph-$(CH_2)_2^-$		4	84
14	4-$N(CH_3)_2$−Ph		3	72

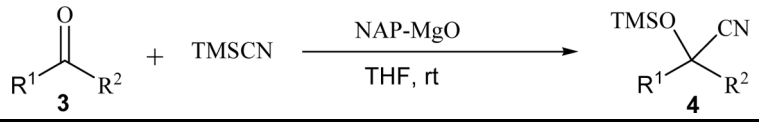
[a]Reaction conditions: (i) aldehyde **1** (1 mmol), TMSCN (1.5 mmol), NAP-MgO (0.1 g), and THF (3 mL) at room temperature; (ii) 2N HCl (2 mL) at room temperature.

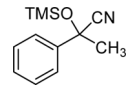
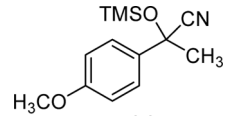
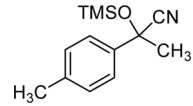
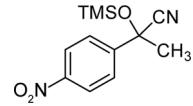
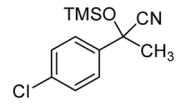
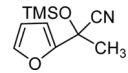
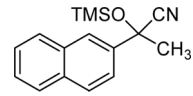
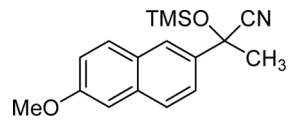
[b]Isolated yield.

cyanide ion attacks the carbonyl carbon and the trimethylsilyl group attacks the carbonyl oxygen, resulting in the formation of the silylated product **2** or **4**.

To confirm the hypothesis of hypervalent silicate intermediate **I**, ^{29}Si NMR (400-MHz) analyses were carried out at 25 °C in $CDCl_3$[17] using tetramethylsilane as an internal standard. All the experiments were performed in $CDCl_3$, as detailed in the experimental procedure. As illustrated in Table 4, entry 1, TMSCN affords a signal at $\delta = -11.45$ ppm

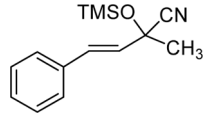
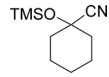
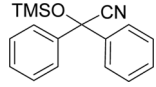
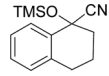
Table 3. Cyanosilylation reaction of various ketones with TMSCN catalyzed by NAP-MgO[a]



Entry	R^1, R^2	Product **4**	Time (h)	Yield (%)[b]
1	Ph, CH_3		4	92
2	4-OCH_3-Ph, CH_3		6	88
3	4-CH_3-Ph, CH_3		5	87
4	4-NO_2-Ph, CH_3		4	91
5	4-Cl-Ph, CH_3		4	85
6	Furfuryl, CH_3		6	81
7	2-Naphthyl, CH_3		4	90
8	(6-OMe)-2-Naphthyl, CH_3		5	89

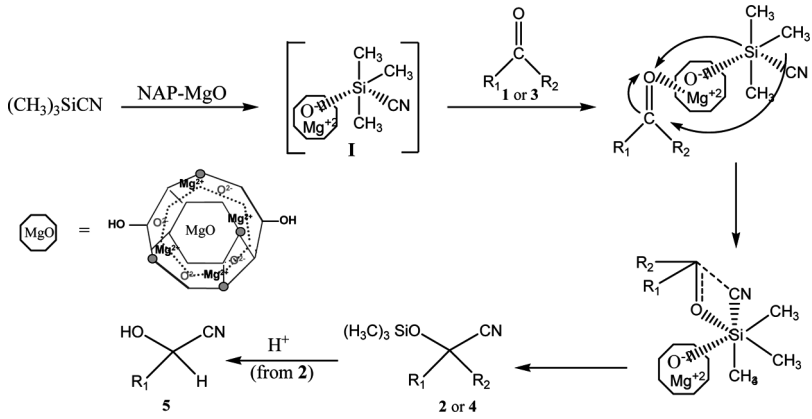
(*Continued*)

Table 3. Continued

Entry	R^1, R^2	Product **4**	Time (h)	Yield (%)[b]
9	Cinnamyl, CH_3		5	85
10	$-(CH_2)_5^-$		8	81
11	Ph, Ph		7	89
12	a-Tetralone		8	86

[a]Reaction conditions: acetophenone **3** (1 mmol), TMSCN (2 mmol), NAP-MgO (0.1 g), and THF (3 mL) at room temperature.
[b]Isolated yield.

(lit.[17]: $\delta = -11.5$). When TMSCN is added to the solution of NAP-MgO, another signal was found at $\delta = 7.07$ ppm (lit.[17]: $\delta = 7.1$ ppm) (Table 4, entry 2). The spectral changes strongly indicate



Scheme 2. Plausible mechanism for the cyanosilylation reaction using NAP-MgO.

Table 4. ^{29}Si NMR chemical shifts of several systems[a]

Entry	Components	δ (ppm)
1	TMSCN	−11.45
2	TMSCN + NAP-MgO	7.07, −11.45
3	TMSCN + Sil-NAP-MgO	7.05, −11.43
4	TMSCN + NAP-MgO + acetophenone	7.28, −11.52

[a]Reaction conditions: acetophenone **3a** (0.1 mmol), TMSCN (0.2 mmol), catalyst (0.01 g), and $CDCl_3$ (0.5 mL) at 25 °C.

that the environments around the silicon atoms of some TMSCN species are changed because of NAP-MgO. It is possible that these silicon atoms of TMSCN could form five- or six-coordinated hypervalent silicate species by coordination to O^{2-}/O^{-} (Lewis basic site) of NAP-MgO, but not the Brønsted basic site (Scheme 2).[18] This is proven, when TMSCN is added to the solution of Sil-NAP-MgO; an identical spectrum is observed with a signal at δ = 7.05 ppm as in NAP-MgO (Table 5, entry 3). When acetophenone is added to the solution of NAP-MgO and TMSCN, an almost identical spectrum is observed (Table 4, entry 4), which clearly suggests that the hypervalent silicate also exists. The little difference observed between its transition state and that of entry 2, according to the chemical shift, may be due to the coordination involvement of the carbonyl oxygen of ketone.

To understand the relationship between structure and reactivity of the catalyst in the cyanosilylation reaction, it is important to know the structure and nature of the reactive sites of NAP-MgO. NAP-MgO has a single-crystallite, three-dimensional polyhedral structure, which poses-ses high surface concentrations of edge/corner and various exposed crystal planes (such as 002, 001, 111), leading to inherently high surface reactivity per unit area. Thus, NAP-MgO indeed displayed the highest activity compared to that of NA-MgO and CM-MgO. Besides this, the NAP-MgO has Lewis acid sites Mg^{2+}, Lewis basic sites O^{2-} and O^{-}, lattice-bound and isolated Brønsted hydroxyls, and anionic and cationic vacancies.[18] Cyanosilylation reactions are known to be driven by base catalysts,[6] and accordingly, the surface –OH, O^{2-}, and O^{-} sites of these oxide crystals are expected to trigger these reactions. To examine the role of –OH, the Sil-NAP-MgO[18e] devoid of free –OH were tested in cyanosilylation reactions. It was found that the rate of the reaction was slow and required longer reaction time (Table 1, entry 1). Although both NAP-MgO and NA-MgO possess defined shapes and the same average concentrations of surface –OH groups, a possible rationale for the

display of higher reactivity to cyanohydrin trimethylsilyl ethers by the NAP-MgO is that the presence of more surface Lewis acid sites Mg^{2+} ions (21%) and –OH groups present on the edge and corner sites on the NAP-MgO, which are stretched in three-dimensional space, are more isolated and accessible for the reactants. Thus, NAP-MgO displays the highest activity compared to NA-MgO and CM-MgO. In the cyanosilylation reaction, O^{2-}/O^{-} (Lewis base) of NAP-MgO activates the trimethylsilyl cyanide, which forms a hypervalent silicate, and coordinates with O^{2-}/O^{-} of the NAP-MgO. The cyanosilylation reaction proceeds via dual activation of both substrates (electrophiles and nucleophiles) by NAP-MgO. Thus, the Lewis base moiety (O^{2-}/O^{-}) of the catalyst activates the TMSCN, and the Lewis acid moiety (Mg^{2+}/Mg^{+}) activates the aldehyde or ketone (Scheme 2).[12,13]

The NAP-MgO was reused for four cycles with consistent activity (Table 1, entry 1). After completion of the reaction, the catalyst was centrifuged and washed properly several times. The recovered catalyst was activated at 250°C for 1 h under a nitrogen atmosphere, before reuse.

In conclusion, nanocrystalline MgO is demonstrated to be an effective catalyst for the cyanation of aldehydes as well as ketones to afford the corresponding cyanohydrin trimethylsilyl ethers in good to high yields. Further, the cyanohydrin trimethylsilyl ethers obtained from aldehydes on treatment with 2 N HCl afforded cyanohydrins in good to high yields.

EXPERIMENTAL

General Remarks

Nanocrystalline MgO samples were obtained from Nanoscale Materials, Inc. (formerly Nantek, Inc.), Manhattan, Kansas, USA. All catalysts are calcined at 400 °C for 4 h before use. All chemicals were purchased from Aldrich Chemicals and S.D. Fine Chemicals, Pvt. Ltd., India, and used as received. All solvents were used laboratory reagent (LR) grade and used as received from S.D. Fine Chemicals Pvt. Ltd, India. ACME silica gel (100–200 mesh) was used for column chromatography, and thin-layer chromatography (TLC) was performed on Merck precoated silica gel 60-F_{254} plates. Melting points were measured in open capillary tubes and are uncorrected. The IR spectra of all compounds were recorded on a Nexus 670 Fourier transform infrared (FTIR) spectrometer (Necolet Corporation Ltd., USA) using KBr pellets or neat. The IR values are reported in reciprocal centimeters (cm^{-1}). The ^{1}H and ^{13}C NMR spectra were recorded on Varian-Gemini 200-MHz and Bruker-Avance 300-MHz spectrometers. The ^{29}Si NMR spectra were recorded on a Varian-Unity

400-MHz spectrometer. Chemical shifts (δ) are reported in parts per million (ppm), using TMS ($\delta = 0$) as an internal standard in $CDCl_3$. All the mass spectra were recorded on a GC-MS QP 2010 Plus (Shimadzu Corporation, Japan) and QSTAR XL high resolution mass spectrometer (Applied Biosystems, Foster City, USA).

Typical Procedure for the Synthesis of Cyanohydrins from Aldehydes

TMSCN (1.5 mmol) was added in one portion to a stirred solution of NAP-MgO (0.1 g) in THF (3 mL) at ambient temperature. After 5 min, aldehyde **1** (1 mmol) was added to the reaction mixture and stirred at room temperature. After completion of the reaction (as monitored by TLC), the reaction mixture was centrifuged to separate the catalyst. The catalyst was washed with THF (3×4 mL), and 2 mL of 2 N HCl was added to the combined THF solution and stirred for 1 h at room temperature. Ethyl acetate and water were added to this, and the product was extracted with ethyl acetate and washed with saturated sodium bicarbonate solution, followed by brine solution and water. The combined organic phase was removed under reduced pressure, and the crude product was purified by column chromatography on silica gel (60–120 mesh) using hexane/ethyl acetate in varying proportions as an eluent to afford the pure cyanohydrin product **5**. The spectroscopic data including IR, NMR, and mass spectra of the products were identical to those of authentic samples. The physical data and the spectroscopic data of selected cyanohydrins reported in Table 2 are given here.

Typical Procedure for the Synthesis of Cyanohydrin Trimethylsilyl Ethers from Ketones

TMSCN (2 mmol) was added to a stirred solution of NAP-MgO (0.1 g) in THF (3 mL) in one portion at ambient temperature. After 5 min, ketone **3** (1 mmol) was added to the reaction mixture and stirred at room temperature. After completion of the reaction (as monitored by TLC), the reaction mixture was centrifuged, and the catalyst was washed several times with ethyl acetate. The centrifugate was concentrated under reduced pressure to afford the crude product, which after flash chromatography on silica gel (60–120 mesh) using hexane/ethyl acetate (9:1) afforded the pure product **4**. The spectroscopic data including NMR and mass spectra of the products were identical to those of authentic samples. The physical data and the spectroscopic data of selected cyanohydrin trimethylsilyl ethers reported in Table 3 are given here.

DATA

2-Hydroxy-2-(3,4,5-trimethoxy Phenyl) Acetonitrile (Entry 4, Table 2)

Brown solid; mp 93–95 °C; IR (KBr): 2248, 3359 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 3.2 (d, $J = 7.4$ Hz, 1H), 3.8 (s. 3H), 3.86 (s, 6H), 5.39 (d, $J = 7.4$ Hz, 1H), 6.65 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 56.1, 60.8, 63.4, 103.5, 118.9, 131.2, 138.2, 153.3; EI-MS: $M^{+\cdot}$ (%): 223 (8), 196 (100), 181 (50), 165 (8).

2-Hydroxy-4-phenyl-3-butenenitrile (Entry 10, Table 2)

Pale yellow solid; mp 73–74 °C; IR (KBr): 3360, 2250, cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 2.74 (s, br, 1H), 5.12 (s, br, 1H), 6.24 (dd, $J = 5.3$, 15.9 Hz, 1H), 6.91 (d, $J = 15.9$ Hz, 1H), 7.29–7.42 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 61.8, 118.2, 122.2, 127.0, 128.8, 129.0, 134.7, 135.3; EI-MS: M^+ (%): 159 (38), 132 (27), 131 (75), 115 (39), 103 (60), 77 (78).

2-Cyclohexyl-2-hydroxy Acetonitrile (Entry 11, Table 2)

Colorless oil; IR (neat): 3440, 2246 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 1.07–1.38 (m, 5H), 1.7–1.91 (m, 6H), 3.38 (s, br, 1H), 4.24 (d, $J = 6.0$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 25.3, 25.8, 27.8, 28.1, 42.1, 66.1, 119.4; ESI-MS: m/z 157 $[M + NH_4]^+$.

2-Hydroxy-4-phenyl-butyronitrile (Entry 13, Table 2)

Colorless oil; IR (neat): 3477, 2245 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 2.06–2.2 (m, 2H), 2.81 (t, $J = 8.3$ Hz, 2H), 3.38 (s, br, 1H), 4.34 (q, 1H), 7.15–7.29 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 30.5, 36.4, 60.1, 120.0, 126.4, 128.4, 128.6, 139.5; EI-MS: M^+ (%): 161 (6), 134 (19), 105 (38), 91 (100), 77 (35).

(4-N,N-Dimethylamino-phenyl)-hydroxy-acetonitrile (Entry 14, Table 2)

Brown solid; mp 110–112 °C; IR (KBr): 3433, 2251 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 2.16 (d, $J = 6.4$ Hz, 1H), 2.98 (s, 6H), 5.38 (d, $J = 6.4$ Hz, 1H), 6.69 (d, $J = 8.9$ Hz, 2H), 7.35 (d, $J = 8.9$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 40.3, 63.7, 112.4, 119.1, 122.8, 128.1, 151.4; ESI-MS: m/z 177 $[M + H]^{+;}$ HRMS (ESI): Anal. calcd. for $C_{10}H_{13}N_2O$: 177.1027, found : 177.1034.

2-Trimethyl Silyloxy-2-(4′-methyl Phenyl)propanenitrile (Entry 3, Table 3)

Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.19 (s, 9H), 1.84 (s, 3H), 2.4 (s, 3H), 7.19 (d, $J = 8.3$ Hz, 2H), 7.42 (d, $J = 8.3$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 1.0, 21.0, 33.5, 71.5, 121.7, 124.5, 129.2, 138.5, 139.0; EI-MS: M^+ (%): 233 (82), 218 (100), 207 (13), 161 (18), 146 (35), 119 (35).

2-Trimethylsilyloxy-2-(furan-2-yl)-propanenitrile (Entry 6, Table 3)

Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.19 (s, 9H), 2.09 (s, 3H), 6.4 (dd, $J = 2.3$, 3.8 Hz, 1H), 6.6 (d, $J = 3.8$ Hz, 1H), 7.53 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): 0.5, 28.9, 65.9, 108.1, 110.7, 120.2, 143.1, 151.6; EI-MS: M^+ (%): 209 (12), 194 (100), 167 (32), 110 (32).

2-Trimethylsilyloxy-2-(6-methoxy-2-naphthyl)-propanenitrile (Entry 8, Table 3)

White solid; mp 79–81 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 0.16$ (s, 9H), 1.91 (s, 3H), 3.92 (s, 3H), 7.08 (d, $J = 2.3$ Hz, 1H), 7.15 (dd, $J = 2.3$, 9.1 Hz, 1H), 7.53 (dd, $J = 2.3$, 9.1 Hz, 1H), 7.73 (t, $J = 8.3$ Hz, 2H), 7.91 (s, 1H);^{13}C NMR ($CDCl_3$, 75 MHz): 1.1, 33.4, 55.3, 71.8, 105.6, 119.5, 121.7, 122.9, 123.6, 127.5, 128.2, 129.8, 134.4, 136.9, 158.4; EI-MS: M^+ (%): 299 (26), 284 (35), 200 (4), 185 (100).

2-Trimethylsilyloxy-2-methyl-4-phenyl-but-3-enenitrile (Entry 9, Table 3)

Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.24 (s, 9H), 1.73 (s, 3H), 6.02 (d, $J = 15.9$ Hz, 1H), 6.85 (d, $J = 15.9$ Hz, 1H), 7.24–7.39 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz):1.3, 30.8, 69.9, 120.6, 126.8, 128.5, 128.7, 129.5, 130.9, 135.0; EI-MS: M^+ (%): 245 (36), 230 (44), 146 (37), 131 (96), 115 (50), 103 (76).

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