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Tetrabutylammonium cyanide catalyzed diasteroselective cyanosilylation of chiral α-hydroxyketones

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Dedicated to Dr. Juan Carlos del Amo. In Memoriam

Abstract—Tetrabutylammonium cyanide has been used as non-metallic catalyst for the diastereoselective cyanosilylation of α-hydroxyketones derived from the chiral pool. This affords α-substituted-α,β-dihydroxynitriles with high levels of asymmetric induction.

1. Introduction

The addition of cyanide to carbonyl compounds to afford cyanohydrins is a useful procedure for the synthesis of a variety of compounds, including α-hydroxyacids, β-amino-alcohols and derivatives thereof, all of them important starting materials for the preparation of biologically active compounds.[1] Various cyanide sources have been reported for this purpose. In particular, the use of TMSCN in organic synthesis has proven valuable from safety standpoints.[2] However, this compound is only effective in the transfer of the CN group to the carbonyl compound of aldehydes or ketones under the action of activators.[3]

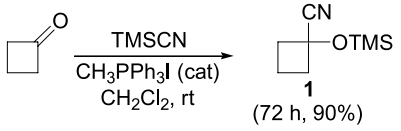
Despite the ubiquitous use of the cyanosilylation reaction for the functionalization of aldehydes, few methods have still been reported for the case of ketones and the use of non-metallic catalysts in this area is scarce.[4] In particular, the cyanation of α-hydroxyketones derived from the chiral pool is especially attractive, as this would render optically pure densely functionalized α,β-dihydroxinitriles, provided good levels of asymmetric induction could be attained. We describe herein our results on the use of ammonium salt catalysis for the diastereoselective cyanosilylation of optically pure α-hydroxyketones derived from lactic acid.

2. Results and discussion

Among others, in the search for new efficient non-metallic catalysts for cyanosilylation reactions with TMSCN, the use of phosphonium salts has been reported as a convenient catalytic method for the cyanosilylation of aldehydes.[5] Therefore, the utility of methyltriphenylphosphonium iodide as a catalyst for the cyanosilylation of ketones was tested first, using a variety of cyclic, acyclic and aromatic ketones under the reaction conditions previously reported for aldehydes (1 equiv TMSCN, 0.1 equiv CH_3PPh_3I, CH_2Cl_2, rt). However, only the higly reactive cyclobutanone was converted to the corresponding OTMS-cyanohydrin **1** (90% yield) after prolonged reaction time (Scheme 1).

Next, we turned our attention towards the closely related ammonium salts.[6] Treatment of acetophenone (Scheme 2), which was taken as model compound, with TMSCN (1 equiv) in the presence of Bu_4NCN (0.1 equiv) as catalyst readily afforded the corresponding OTMS-cyanohydrin **2** (95% yield, CH_2Cl_2, rt, 1 h).

In light of this result, a set of TBS-protected α-hydroxy-ketones **3** was tested in the cyanosilylation reaction with TMSCN catalyzed by Bu_4NCN (Scheme 3). The starting materials **3** were readily prepared from (*S*)-lactic acid and



Scheme 1.

Keywords: Tetrabutylammonium cyanide; α-Hydroxyketones; α,β-Dihydroxynitriles.
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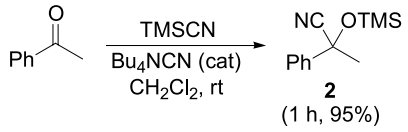
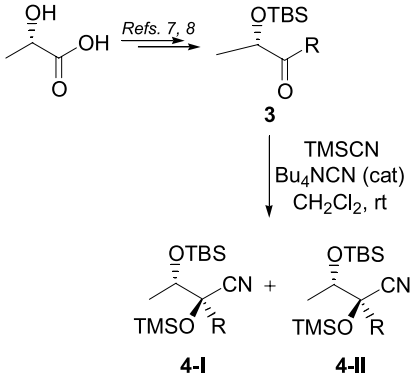


Scheme 2.



Scheme 3.

aryllithiums or Grignard reagents following literature procedures.[7,8]

Treatment of compounds **3** with TMSCN (1.0 equiv, CH_2Cl_2, rt, 1 h) in the presence of Bu_4NCN (0.1 equiv) afforded the corresponding α-substituted-α,β-dihydroxynitriles **4** in high yields in favor of diastereomers **4-I**. The results are gathered in Table 1.

Inspection of these data revealed that, although the cyanosilylation reaction of aliphatic ketones took place with low diastereoselectivity (entry 1), reactions with aromatic ketones (entries 2 and 3) and heteroaromatic ketones (entries 4 and 5) gave rise to compounds **4-I** with high yields and diastereoselective excesses superior to 80% in all cases. These results contrast with those previously reported using metal catalysts for the addition of TMSCN to α-hydroxyketones, where low levels of diastereoselectivity have been found.[4d]

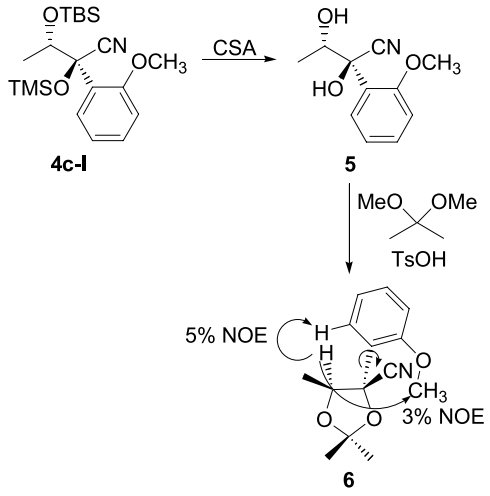
The stereochemical assignment of compounds **4** was carried out by using compound **4c-I** as model (Scheme 4). Deprotection of both silyl groups (CSA, MeOH, rt, 24 h) afforded diol **5**, which was cyclized to diolane **6** (2,2-dimethoxypropane, TsOH, toluene, rt, 16 h).

NOE measurements were carried out on the ^1H NMR

Table 1. Cyanosilylation of α-hydroxyketones **3**[a]

Entry	R	**3** (%[b])	**4** (%[b], **4-I**: **4-II**[c])
1	CH_3	**3a** (92)	**4a** (95, 75: 25)
2	Ph	**3b** (90)	**4b** (90, 90: 10)
3	*o*-CH_3O-Ph	**3c** (80)	**4c** (90, 100: 0)
4	2-Furyl	**3d** (75)	**4d** (90, 90: 10)
5	2-Thiazolyl	**3e** (90)	**4e** (95, 95: 05)

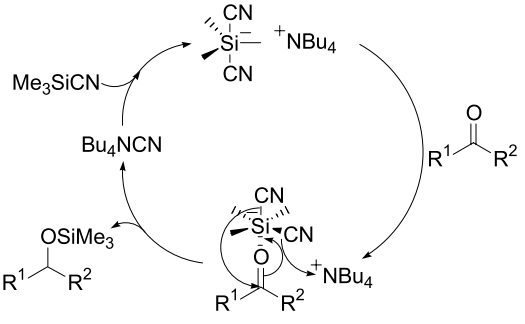
[a] Reactions carried out in CH_2Cl_2 at rt for 1 h, using 1 equiv of TMSCN and 0.1 equiv of Bu_4NCN.
[b] Pure, isolated yields.
[c] Determined by integration of the signals of the ^1H NMR spectra ($CDCl_3$, 250 MHz) of the crude reaction products.



Scheme 4.

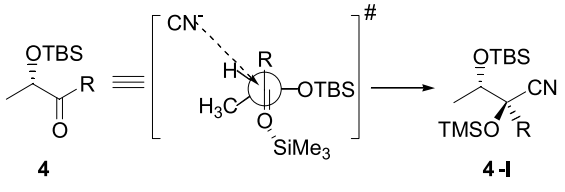
($CDCl_3$, 300 MHz) spectrum of compound **6**. Thus, saturation of the β-H signal (1H, $\delta=4.16$ ppm, q, $^3J=6.2$ Hz) gave rise to a 3% enhancement of the aryl-OCH_3 signal (3H, $\delta=3.92$ ppm, s) and a 5% enhancement of the *ortho*-H signal (1H, $\delta=7.63$ ppm, dd, $^3J=8.1$ Hz, $^4J=1.6$ Hz). This allowed a 1,2-*cis* relative configuration of the α-H and the aryl moiety in compound **6** to be established, and hence compound **4c-I** was assigned as (2*R*,3*S*)-3-(*t*butyldimethyl-silyloxy)-2-(2-methoxyphenyl)-2-trimethylsilyloxybutyro-nitrile.

The activation of TMSCN by Bu_4NCN can be interpreted (Scheme 5) by asumming the formation of a hypervalent silicon species by the interaction between both reagents, which can further coordinate the carbonyl group of the ketone and transfer one CN group, with regeneration of the catalyst at the same time.[9]



Scheme 5.

The stereochemical outcome of the cyanosilylation reaction (Scheme 6) can be understood under non-chelating conditions,[10] assuming therefore the reactive conformation



Scheme 6.

predicted by the Felkin–Ahn model. Thus, the attack of the CN group should take place *anti* to the oxygen substituent and from the diastereotopic face of the carbonyl group flanked by the smallest H group, following the Bürgi–Dunitz trajectory, to afford compounds **4** with a *syn* relative stereochemistry for both hydroxyl functionalities as major diastereomers.

3. Conclusion

In conclusion, the use of Bu_4NCN as a catalytic reagent for the diastereoselective cyanosilylation of α-hydroxyketones derived from the chiral pool with TMSCN has been reported in this paper. The method is simple, and reactions take place with high yields and diastereoselectivities in short reaction times, avoiding the use of metal catalysts.

4. Experimental

4.1. General

All reactions were carried out under an argon atmosphere. Column chromatography was performed on silica gel Merck 230–400 mesh. Optical rotations were determined using a Perkin–Elmer Instruments 241 polarimeter, concentrations are given in g/100 mL. NMR spectra were recorded on Bruker 200-AM (200 MHz) and on Bruker AM300 (300 MHz) instruments, using $CDCl_3$ as solvent. Compounds **3a**, **3b**, **3c**, and **3d** were synthesized using the method described by B. Stammen et al.[7] Compound **3e** was prepared using the method described by A. Dondoni et al.[8] Other chemicals were obtained from commercial sources and were used without further purification. Solvents were distilled and dried over molecular sieves.

4.2. Typical procedure for the cyanosilylation of α-(*tert*-butylsilyloxy)ketones 3

To a solution of the carbonyl compound (0.10 mmol) in dry CH_2Cl_2 (0.5 mL) was added, under argon and at room temperature, TMSCN (0.024 mL, 0.20 mmol) followed by a solution of Bu_4NCN (2.7 mg, 0.01 mmol) in dry CH_2Cl_2 (0.5 mL). The mixture was stirred at room temperature for 90 min. The solvent was eliminated by distillation under vacuum. The crude was diluted with Et_2O (10 mL) and washed with H_2O (2×10 mL). Drying of the organic phase with $MgSO_4$ was followed by evaporation of the solvent under vacuum. The products were purified by chromatography on silica gel (ethyl acetate/hexane).

4.2.1. 3-(*tert*-Butyldimethylsilyloxy)-2-methyl-2-trimethylsilyloxybutyronitrile, 4a. $[\alpha]_D^{20}=-4.6$ ($c=0.3$, $CHCl_3$) (diastereomeric mixture **4a-I**:**4a-II**=75:25). Data for **4a-I**, ^{1}H NMR: ($CDCl_3$, 300 MHz) δ 0.08 (s, 3H, CH_3–Si, TBS), 0.10 (s, 3H, CH_3–Si, TBS), 0.25 (s, 9H, 3×CH_3–Si, TMS), 0.91 (s, 9H, ^{t}Bu, TBS), 1.15 (d, 3H, $^3J=6.3$ Hz, CH_3–CH), 1.48 (s, 3H, CH_3–C–CN), 3.87 (q, 1H, $^3J=6.3$ Hz, CH–O) ppm; ^{13}C NMR: ($CDCl_3$, 50 MHz) δ −4.83 (CH_3–Si, TBS), −4.38 (CH_3–Si, TBS), 1.30 (3×CH_3–Si, TMS), 16.92 (*C*H_3–CH), 17.90 (Si–*C*–$(CH_3)_3$), 22.03 (*C*H_3–C–CN), 25.69 (3×CH_3, ^{t}Bu, TBS), 72.92 (CH–O), 74.21 (O–*C*–CN), 122.19 (CN) ppm. Data for **4a-II**: ^{1}H NMR: ($CDCl_3$, 300 MHz) δ 0.15 (s, 6H, 2×CH_3–Si, TBS), 0.25 (s, 9H, 3×CH_3–Si, TMS), 0.90 (s, 9H, ^{t}Bu, TBS), 1.30 (d, 3H, $^3J=6.1$ Hz, CH_3–CH), 1.57 (s, 3H, CH_3–C–CN), 3.64 (q, 1H, $^3J=6.1$ Hz, CH–O) ppm. Anal. calcd for $C_{14}H_{31}NO_2Si_2$: C, 55.76; H, 10.36; N, 4.64. Found: C, 55.89; H, 10.32; N, 4.58.

4.2.2. 3-(*tert*-Butyldimethylsilyloxy)-2-phenyl-2-trimethylsilyloxybutyronitrile, 4b. Data for **4b-I**, ^{1}H NMR: ($CDCl_3$, 300 MHz) δ 0.09 (s, 3H, CH_3–Si, TBS), 0.14 (s, 9H, 3×CH_3–Si, TMS), 0.16 (s, 3H, CH_3–Si, TBS), 0.93 (d, 3H, $^3J=6.2$ Hz, CH_3–CH), 0.94 (s, 9H, ^{t}Bu, TBS), 4.00 (q, 1H, $^3J=6.2$ Hz, CH–O), 7.00–7.80 (m, 5H, Ph) ppm; ^{13}C NMR: ($CDCl_3$, 50 MHz) δ −4.69 (CH_3–Si, TBS), −4.64 (CH_3–Si, TBS), 0.94 (3×CH_3–Si, TMS), 18.04 (Si–*C*–$(CH_3)_3$), 18.23 (*C*H_3–CH), 25.77 (3×CH_3, ^{t}Bu, TBS), 75.38 (CH–O), 80.05 (O–*C*–CN), 119.90 (CN), 126.50 (2×CH, Ph), 127.16 (CH, Ph), 128.09 (2×CH, Ph), 137.91 (C, Ph) ppm. Data for **4b-II**: ^{1}H NMR: ($CDCl_3$, 300 MHz) δ −0.48 (s, 3H, CH_3–Si, TBS), −0.09 (s, 3H, CH_3–Si, TBS), 0.12 (s, 9H, 3×CH_3–Si, TMS), 0.76 (s, 9H, ^{t}Bu, TBS), 1.39 (d, 3H, $^3J=6.0$ Hz, CH_3–CH), 3.85 (q, 1H, $^3J=6.0$ Hz, CH–O), 7.00–7.80 (m, 5H, Ph) ppm. Anal. calcd for $C_{19}H_{33}NO_2Si_2$: C, 62.75; H, 9.15; N, 3.85. Found: C, 62.83; H, 9.18; N, 3.64.

4.2.3. (2*R*,3*S*)-3-(*tert*-Butyldimethylsilyloxy)-2-(2-methoxyphenyl)-2-trimethylsilyloxy-butyronitrile, 4c. $[\alpha]_D^{20}=+22.0$ ($c=0.7$, $CHCl_3$), ^{1}H NMR: ($CDCl_3$, 300 MHz) δ 0.10 (s, 9H, 3×CH_3–Si, TMS), 0.13 (s, 6H, 2×CH_3–Si, TBS), 0.85 (s, 9H, ^{t}Bu, TBS), 1.16 (d, 3H, $^3J=6.2$ Hz, CH_3–CH), 3.89 (s, 3H, OCH_3), 4.52 (q, 1H, $^3J=6.2$ Hz, CH–O), 6.89 (d, 1H, $^3J=7.9$ Hz, CH_{Ar}–C–OCH_3), 6.97 (t, 1H, $^3J=7.5$ Hz, CH_{Ar}), 7.33 (td, 1H, $^3J=7.5$ Hz, $^4J=1.5$ Hz, CH_{Ar}), 7.54 (dd, 1H, $^3J=7.7$ Hz, $^4J=1.5$ Hz, CH_{Ar}) ppm; ^{13}C NMR: ($CDCl_3$, 50 MHz) δ −5.09 (CH_3–Si, TBS), −4.92 (CH_3–Si, TBS), 1.00 (3×CH_3–Si, TMS), 17.98 (Si–*C*–$(CH_3)_3$), 19.08 (*C*H_3–CH), 25.71 (3×CH_3, ^{t}Bu, TBS), 55.35 (OCH_3), 72.13 (CH–O), 78.96 (O–*C*–CN), 111.65 (*C*H_{Ar}–C–OCH_3), 119.55 (CN), 120.42 (CH_{Ar}), 126.57 (C_{Ar}), 129.06 (CH_{Ar}), 130.05 (CH_{Ar}), 156.30 (C_{Ar}–OCH_3) ppm. Anal. calcd for $C_{20}H_{35}NO_3Si_2$: C, 61.02; H, 8.96; N, 3.56. Found: C, 60.90; H, 8.74; N, 3.64.

4.2.4. 3-(*tert*-Butyldimethylsilyloxy)-2-(furan-2-yl)-2-trimethylsilyloxy-butyronitrile, 4d. $[\alpha]_D^{20}=+6.0$ ($c=0.4$, $CHCl_3$) (diastereomeric mixture **4d-I**:**4d-II**=90:10). Data for **4d-I**, ^{1}H NMR: ($CDCl_3$, 200 MHz) δ 0.05 (s, 6H, 2×CH_3–Si, TBS), 0.07 (s, 9H, 3×CH_3–Si, TMS), 0.91 (s, 9H, ^{t}Bu, TBS), 1.00 (d, 3H, $^3J=6.3$ Hz, CH_3–CH), 4.20 (q, 1H, $^3J=6.3$ Hz, CH–O), 6.38 (dd, 1H, $^3J=3.4$, 1.7 Hz, CH, Furyl), 6.58 (dd, 1H, $^3J=3.4$ Hz, $^4J=0.7$ Hz, CH, Furyl), 7.41 (dd, 1H, $^3J=1.7$ Hz, $^4J=0.7$ Hz, CH–O, Furyl) ppm; ^{13}C NMR: ($CDCl_3$, 50 MHz) δ −4.78 (CH_3–Si, TBS), −4.61 (CH_3–Si, TBS), 0.34 (3×CH_3–Si, TMS), 18.04 (Si–*C*–$(CH_3)_3$), 18.83 (*C*H_3–CH), 25.71 (3×CH_3, ^{t}Bu, TBS), 73.79 (CH–O), 77.18 (O–*C*–CN), 110.28 (CH, Furyl), 110.66 (CH, Furyl), 118.19 (CN), 142.53 (CH–O, Furyl), 149.85 (C–O, Furyl) ppm. Data for **4b-II**: ^{1}H NMR: ($CDCl_3$, 200 MHz) δ 0.04 (s, 6H, 2×CH_3–Si, TBS), 0.09 (s, 9H, 3×CH_3–Si, TMS), 0.90 (s, 9H, ^{t}Bu, TBS), 1.41 (d, 3H, $^3J=6.0$ Hz, CH_3–CH), 4.21 (q, 1H, $^3J=6.0$ Hz, CH–

O), 6.38 (dd, 1H, ^3J=3.4, 1.7 Hz, CH, Furyl), 6.62 (dd, 1H, ^3J=3.4 Hz, ^4J=0.7 Hz, CH, Furyl), 7.40 (dd, 1H, ^3J=1.7 Hz, ^4J=0.7 Hz, CH–O, Furyl) ppm. Anal. calcd for $C_{17}H_{31}NO_3Si_2$: C, 57.74; H, 8.84; N, 3.96. Found: C, 57.73; H, 8.79; N, 3.89.

4.2.5. 3-(*tert*-Butyldimethylsilyloxy)-2-(thiazol-2-yl)-2-trimethylsilyloxybutyronitrile, 4e. $[\alpha]_D^{20}=+33.6$ (c=1.2, $CHCl_3$) (diastereomeric mixture **4e-I**:**4e-II**=95:5).Data for **4e-I**, ^{1}H NMR: ($CDCl_3$, 300 MHz) δ −0.01 (s, 3H, CH_3–Si, TBS), 0.05 (s, 3H, CH_3–Si, TBS), 0.18 (s, 9H, 3×CH_3–Si, TMS), 0.88 (s, 9H, ^{t}Bu, TBS), 1.16 (d, 3H, ^3J=6.1 Hz, CH_3–CH), 4.17 (q, 1H, ^3J=6.1 Hz, CH–O), 7.39 (d, 1H, ^3J=3.2 Hz, CH–S, Thiazolyl), 7.82 (d, 1H, ^3J=3.2 Hz, CH–N, Thiazolyl) ppm; ^{13}C NMR: ($CDCl_3$, 75 MHz) δ −4.38 (2×CH_3–Si, TBS), 1.19 (3×CH_3–Si, TMS), 18.36 (Si–*C*–$(CH_3)_3$), 18.94 (*C*H_3–CH), 26.05 (3×CH_3, ^{t}Bu, TBS), 68.78 (CH–O), 77.85 (O–*C*–CN), 118.19 (CN), 121.04 (CH–S, Thiazolyl), 143.32 (CH–N, Thiazolyl), 168.91 (C, Thiazolyl) ppm. Data for **4e-II**: ^{1}H NMR: ($CDCl_3$, 300 MHz) δ −0.08 (s, 3H, CH_3–Si, TBS), 0.08 (s, 3H, CH_3–Si, TBS), 0.18 (s, 9H, 3×CH_3–Si, TMS), 0.83 (s, 9H, ^{t}Bu, TBS), 1.25 (d, 3H, ^3J=6.1 Hz, CH_3–CH), 4.32 (q, 1H, ^3J=6.1 Hz, CH–O), 7.39 (d, 1H, ^3J=3.2 Hz, CH–S, Thiazolyl), 7.82 (d, 1H, ^3J=3.2 Hz, CH–N, Thiazolyl) ppm. Anal. calcd for $C_{16}H_{30}N_2O_2SSi_2$: C, 51.85; H, 8.16; N, 7.56. Found: C, 51.59; H, 8.16; N, 7.58.

4.2.6. (2*R*,3*S*)-2,3-Dihydroxy-2-(2-methoxyphenyl)butyro-nitrile, 5. $[\alpha]_D^{20}=-5.3$ (c=2.3, $CHCl_3$), ^{1}H NMR: ($CDCl_3$, 200 MHz) δ 1.28 (d, 3H, ^3J=6.6 Hz, CH_3–CH), 2.72 (d, 1H, ^3J=4.4 Hz, *H*O–CH), 3.95 (s, 3H, OCH_3), 4.30 (m, 1H, CH–O), 4.63 (s, 1H, *H*O–C–CN), 7.00 (d, 1H, ^3J=8.3 Hz, CH_{Ar}–C–OCH_3), 7.08 (t, 1H, ^3J=7.9 Hz, CH_{Ar}), 7.39 (td, 1H, ^3J=7.9 Hz, ^4J=1.7 Hz, CH_{Ar}), 7.60 (dd, 1H, ^3J=7.7 Hz, ^4J=1.7 Hz, CH_{Ar}) ppm; ^{13}C NMR: ($CDCl_3$, 75 MHz) δ 18.11 (*C*H_3–CH), 56.28 (OCH_3), 71.80 (CH–O), 79.91 (O–*C*–CN), 112.35 (*C*H_{Ar}–C–OCH_3), 118.94 (CN), 121.90 (CH_{Ar}), 124.29 (C_{Ar}), 128.79 (CH_{Ar}), 131.28 (CH_{Ar}), 156.74 (C_{Ar}–OCH_3) ppm. Anal. calcd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32; N, 6.76. Found: C, 63.98; H, 6.39; N, 6.81.

4.2.7. (4*R*,5*S*)-4-Cyano-4-(2-methoxyphenyl)-2,2,5-trimethyl-1,3-dioxolane, 6. $[\alpha]_D^{20}=-2.1$ (c=1.4, $CHCl_3$), ^{1}H NMR: ($CDCl_3$, 300 MHz) δ 1.52 (s, 3H, CH_3, *C*−2), 1.66 (d, 3H, ^3J=6.2 Hz, CH_3–CH), 1.72 (s, 3H, CH_3, *C*-2), 3.92 (s, 3H, OCH_3), 4.16 (q, 1H, ^3J=6.2 Hz, CH–O), 6.98 (d, 1H, ^3J=8.2 Hz, CH_{Ar}–C–OCH_3), 7.15 (t, 1H, ^3J=7.8 Hz, CH_{Ar}), 7.38 (td, 1H, ^3J=7.8 Hz, ^4J=1.6 Hz, CH_{Ar}), 7.63 (dd, 1H, ^3J=8.1 Hz, ^4J=1.6 Hz, CH_{Ar}) ppm; ^{13}C NMR: ($CDCl_3$, 75 MHz) δ 16.81 (*C*H_3–CH), 26.53 (CH_3, *C*−2), 27.78 (CH_3, *C*-2), 55.87 (OCH_3), 80.73 (O–*C*–CN), 81.17 (CH–O), 111.18 (O–C–O), 112.24 (*C*H_{Ar}–C–OCH_3), 118.36 (CN), 121.44 (CH_{Ar}), 123.80 (C_{Ar}), 126.96 (CH_{Ar}), 131.09 (CH_{Ar}), 156.87 (C_{Ar}–OCH_3) ppm. Anal. calcd for $C_{14}H_{17}NO_3$: C, 68.00; H, 6.93; N, 5.66. Found: C, 67.84; H, 6.90; N, 5.68.

Acknowledgements

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References and notes

1. For recent reviews, see: (a) Gregory, R. J. H. *Chem. Rev.* **1999**, *99*, 3649. (b) North, M. *Tetrahedron: Asymmetry* **2003**, *14*, 147.
2. Groutas, W. C.; Felker, D. *Synthesis* **1980**, 861.
3. See Ref. 1 and: (a) Saravanan, P.; Anand, R. V.; Singh, V. K. *Tetrahedron Lett.* **1998**, *39*, 3823. (b) Somanathan, R.; Rivero, I. A.; Gama, A.; Ochoa, A.; Aguirre, G. *Synth. Commun.* **1998**, *28*, 2043. (c) Jenner, G. *Tetrahedron Lett.* **1999**, *40*, 491. (d) Ward, D. E.; Hrapechak, M.; Sales, M. *Org. Lett.* **2000**, *2*, 57. (e) Kantam, M. L.; Sreekanth, P.; Santhi, P. L. *Green Chem.* **2000**, *2*, 47. (f) Wang, Z. G.; Fetterly, B.; Verkade, J. G. *J. Organomet. Chem.* **2002**, *646*, 16. (g) Yadav, J. S.; Reddy, M. S.; Prasad, A. R. *Tetrahedron Lett.* **2002**, *43*, 9703. (h) Azizi, N.; Saidi, M. R. *J. Organomet. Chem.* **2003**, *688*, 283. (i) Lundgren, S.; Lutsenko, S.; Jonsson, C.; Moberg, C. *Org. Lett.* **2003**, *5*, 3663. (j) Baleizao, C.; Grigante, B.; Garna, H.; Corma, A. *J. Catal.* **2003**, *215*, 199. (k) Kim, J. H.; Kim, G. J. *Catal. Lett.* **2004**, *92*, 123.
4. See: (a) Golinski, M.; Brock, C. P.; Watt, D. S. *J. Org. Chem.* **1993**, *58*, 159. (b) Bandini, M.; Cozzi, P. B.; Melchiorre, P.; Umani-Ronchi, A. *Tetrahedron Lett.* **2001**, *42*, 3041. (c) Wilkinson, S. H.; Grover, P. T.; Vandenbossche, C. P.; Bakale, R. P.; Bhongle, N. N.; Wald, S. A.; Senanayake, C. H. *Org. Lett.* **2001**, *3*, 553. (d) Bandini, M.; Cozzi, P. G.; Garelli, A.; Melchiorre, P.; Umani-Ronchi, A. *Eur. J. Org. Chem.* **2002**, 3243. (e) Yadav, J. S.; Reddy, B. V. S.; Reddi, M. S.; Prasad, A. R. *Tetrahedron Lett.* **2002**, *43*, 9703. (f) Kim, S. S.; Kim, D. W.; Rajagopal, G. *Synthesis* **2004**, *213* and references cited therein.
5. Córdoba, R.; Plumet, J. *Tetrahedron Lett.* **2003**, *44*, 6157.
6. To the best of our knowledge, only an isolated report describing the use of Bu4NCN as catalytic agent for the cyanosilylation of 3-pentanone (84% yield) has been previously reported. See: Evans, D. A.; Truesdale, L. K. *Tetrahedron Lett.* **1973**, *14*, 4929.
7. Stammen, B.; Berlage, U.; Kindermann, R.; Kaiser, M.; Gunther, B.; Sheldrick, W. S.; Welzel, P.; Roth, W. R. *J. Org. Chem.* **1992**, *57*, 6566.
8. Dondoni, A.; Fantin, G.; Fogagnolo, H.; Pedrini, P. *Tetrahedron* **1989**, *45*, 5141.
9. Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371.
10. Reetz, M. *Angew. Chem., Int. Ed.* **1984**, *23*, 556.