Solvent-free Cyanosilylation of Carbonyl Compounds Catalyzed by NbCl₅

Soney C. George[a] and Sung Soo Kim*

*Department of Chemistry, Inha University, Incheon 402-751, Korea. *E-mail: sungsoo@inha.ac.kr*
Received March 16, 2007

A simple and convenient method for the addition of TMSCN to carbonyl compounds is described. NbCl₅ is found to possess a strong Lewis acid property to transform carbonyl compounds smoothly to the corresponding cyanosilylether in high yields (up to 99 %) in solvent- free conditions.

Key Words : Cyanohydrins, Aldehydes, Ketones, Solvent-free, NbCl₅

Introduction

Cyanosilylation of carbonyl compounds is one of the most efficient methods for the synthesis of silyated cyanohydrins. It is well known that cyanohydrins are important intermediates for the synthesis of α-hydroxy aldehydes, α-hydroxyacids, β-aminoalcohols, α-cyanoketones, etc.[1] Several reagents including Lewis acids, Lewis bases, metal alkoxides, bifunctional catalysts, iodine, inorganic salts have been found to effectively transfer the cyano group from TMSCN to carbonyl compounds.[2] But in many of the reported results presence of solvent and additives are essential for the cyanosilylation reactions.[3] In this connection we have developed several chiral[4] and achiral[5] catalysts for cyanosilylation of carbonyl compounds. There are various metal halides such as AlCl₃,[6a,6b] BiBr₃,[6c] BF₃,[6d] MgBr₂,[6d] SnCl₄,[6d] TiCl₄,[6d] InBr₃,[2a] InF₃,[6e] LnCl₃ (Ln = La, Ce, Sm),[6f] ZnI₂[6g] FeCl₃[6h] and LiCl,[6i] which are acting as Lewis acid catalysts for cyanosilylation of aldehydes. Recently, NbCl₅ has emerged as an efficient Lewis acid catalyst in promoting various organic transformations.[7] However no report has described so far the catalytic properties of NbCl₅ for cyanosilylation reactions. We wish to herein report a simple and efficient method for the synthesis of silylcyanoethers in presence of catalytic amount of NbCl₅ at rt in solvent- free conditions.

Results and Discussion

The catalytic activity of NbCl₅ has been tested for the reaction of benzaldehyde and TMSCN at rt. As shown in Table 1, NbCl₅ exhibits excellent catalytic activity under solvent- free conditions. 0.5 mol % of NbCl₅ gives silylether of 97% in 30 minutes (entry 2). With 1 mol % catalyst the yield was increased to 99% with duration of 15 minutes. The reaction time could be reduced from 15 min to 7 min by increasing the catalyst amount from 1 mol % to 3 mol%. In presence of CH₂Cl₂ as solvent, the reaction took 40 minutes to complete and yield was reduced to 94%. Consequently 1 mol% catalytic loading is considered optimal for present reactions. A series of carbonyl compounds react with TMSCN in the presence of NbCl₅ under solvent-free condi-

Table 1. Cyanosilylation of benzaldehyde under various conditions[a]
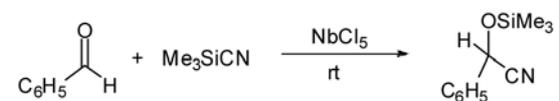
Entry	Catalyst (mol %)	Time (min)	Yield (%)[b]
1	0.1	50 h	65
2	0.5	30	97
3	1	15	99
4	3	7	99
5[c]	0.5	40	94

[a]NbCl₅ is added to a mixture of 1 mmole of the benzaldehyde and 1.2 equiv. TMSCN. [b]isolated yield. [c] in presence of CH₂Cl₂

tions at rt to give the cyanation products by utilizing the condition of entry 3 of Table 1.

Most of the aromatic and aliphatic aldehydes are converted into the corresponding cyanohydrin trimethylsilylether for relatively short reaction time in good to excellent isolated yields (entries 1-14) at rt. *p*-Tolualdehyde took less reaction time than *m*-tolualdehyde with 94% yield (entry 2, 3). The reaction of *p*-methoxy benzaldehyde completed in 40 min with 65% yield. On the other hand the reaction of *p*-*tert*-butyl benzaldehyde took 120 minutes to complete the reaction with yield of 85%. We have also noticed the influence *o*-, *p*- and *m*-chlorosubstituted benzaldehyde on cyanosilylation reaction (entry 6, 7, 8). *o*-Chloro benzaldehyde completed the reaction with 30 minutes with yield of 70% whereas the *p*- and *m*-chloro benzaldehydes completed the reaction within 10 minutes but the yield is reduced to 65% and 58% respectively. *m*-Phenoxybenzaldehyde took 15 minutes to obtain 83% yield [entry 9]. Acid sensitive 2-fulfuraldehyde [entry 10] gives the product with 65% yield at 40 min. This may indicate that the catalytic system selectively activate the carbonyl function and keep the furan ring intact. The reaction of naphthaldehyde with TMSCN was completed within 40 min with yield of 92% (entry 11). The silylcyanation of isobutryaldehyde was completed within 60 minutes with TMSCN with yield of 84%. Crotonaldehyde and cinnamaldehyde [entry 13 & 14] were predominately converted into 1, 2 adducts leaving the olefinic function intact. No conjugated addition product was observed. Unsubstituted benzaldehyde takes 15 min (entry 1) for the cyanosilylation which is the best result of present

1168   *Bull. Korean Chem. Soc.* **2007**, Vol. 28, No. 7

Soney C. George and Sung Soo Kim

Table 2. Cyanosilylation of various aldehydes and ketones with NbCl5[a]

Entry	Substrate	Time (min)	Yield (%)[b]
1		15	99
2		60	94
3		90	92
4		40	65
5		120	85
6		30	70
7		10	65
8		10	58
9		15	83
10		40	65
11		40	92
12	$(CH_3)_2$-CH-CHO	60	87
13		60	84
14		210	78
15		15	83
16		380	97
17		46h	90

[a]1 mmole of the benzaldehyde, 1 mol % of NbCl5, 1.2 equiv. TMSCN are stirred together. [b]isolated yield, (100% conversion according to ^{1}H NMR analysis)

reactions in terms of reaction time and yield.

We have also examined the catalytic activity of NbCl5 for several ketones (entries 15, 16 & 17). The 2-cyclohexen-1-one completed the reaction within 15 minutes but the yield is 83% (entry 15). 2-Octanone completed the reaction with 380
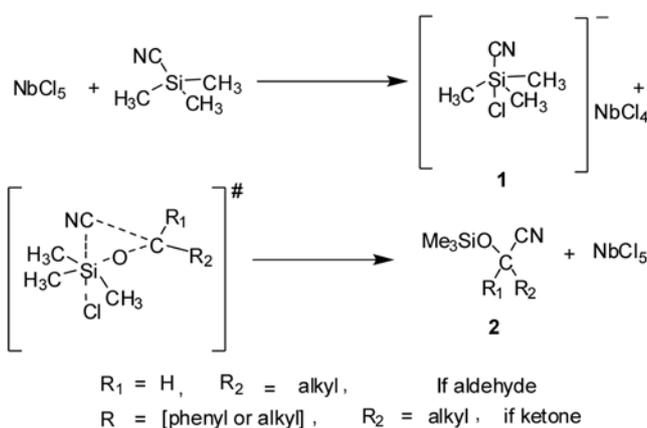
Scheme 1. Mechanism of cyanosilylation of carbonyl compounds catalyzed by NbCl5.

minutes with yield of 97%. The aromatic acetophenone took nearly 46 hours to complete the reaction with yield of 90%. The reactions with the aldehydes may be facile than with ketones due to the steric reason. The mechanism of cyano-silylation of carbonyl compounds catalyzed by NbCl5 is proposed as follows. NbCl5 can acts as a source of nucleo-philes Cl⁻. When NbCl5 acts a nucelophilic chloride ion, a pentavalent silicon compound is formed (**1**), which is the reactive species. The hypervalent silicon compound reacts with carbonyl compound so as to give rise to the cyano-silylether (**2**) (Scheme 1). There are various reports available regarding the formation of hypervalent silicate ions due to the presence of nucleophiles.[8] The ^{1}H NMR and ^{13}C NMR spectrum of both TMSCN and a mixture of TMSCN and NbCl5 are monitored. The CH_3 peak of TMSCN observed at δ 0.354 ppm was found to be shifted to 0.185 ppm in the ^{1}H NMR spectrum of mixture of TMSCN and NbCl5. The ^{13}C spectrum of TMSCN is also shifted from 1.98 ppm to δ 2.90 ppm. The shift of TMSCN peak in both ^{1}H NMR and ^{13}C NMR spectra may be due to the formation of pentavalent silicon compound as suggested in mechanism (Scheme 1).

In conclusion, we have developed a new, mild and efficient catalyst for cyanosilylation of various carbonyl compounds. The reported procedure clearly demonstrated that NbCl5 is an excellent catalyst for the preparation of racemic silylethers in relatively short reaction time with low catalyst loading under solvent-free conditions. The important features of our method are: mild reaction conditions, simple work up, solvent-free condition, inexpensive and readily available catalyst. The studies are in progress to confirm the mechanistic pathway as well as the reusability of the catalyst NbCl5.

Experimental Section

Silylcyanation of benzaldehyde; **2-phenyl-2-(trimethyl-silyloxy)acetonitrle** (Table 2, entry 1) A mixture of benzaldehyde (1mmole), dispersed NbCl5 (1 mol%) and TMSCN (1.2 equiv.) were stirred for 15 min at rt in a 10 mL round bottom flask. Then 0.5 mL of CH_2Cl_2 was added to the mixture and stirred for 10 min. The reaction mixture was

purified by silica gel flash chromatography by using EtOAc-hexane (1:9) mixture as eluent. The desired 2-phenyl-2-(trimethylsilyloxy)acetonitrile was obtained as colourless oil (yield 99%). The yield determined by ^{1}H NMR was 100%. ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 0.257 (s, 9H), 5.52 (s, 1H), 7.42-7.47 (m, 5H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ = −0.32, 63.59, 119.12, 126.29, 128.87, 129.27, 136.18. HRMS (EI): m/z calcd. for C$_{11}$H$_{15}$NOSi (M$^+$): 205.0923; found: 205.0912. The other substrates mentioned in Table 2 were also silylcyanted by using the same procedure.

2-(4-Methylphenyl)-2-trimethylsilyloxyacetonitrile (entry 2). ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 0.142 (s, 9H), 2.29 (s, 3H), 5.49 (s, 1H), 7.18 (d, 2H) 7.25 (d, 2H) ^{13}C NMR (CDCl$_3$, 100 MHz): δ = −0.28, 55.78, 63.87, 114.66, 119.47, 127.58, 128.78, 160.23. HRMS (EI): m/z calcd for C$_{12}$H$_{17}$NOSi (M$^+$): 219.1079; found: 219.1069.

2-(3-Methylphenyl)-2(trimethylsilyloxy)acetonitrile (entry 3). ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 0.232 (s, 1H), 2.38-2.42 (m, 3H) 7.26-7.28 (m, 4H) ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 0.123, 21.46, 63.72, 119.21, 123.41, 126.93, 128.74, 130.02, 136.07, 138.74.

2-(4-Methoxyphenyl)-2-(trimethylsilyloxy)acetonitrile (entry 4). ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 0.38 (s, 9H), 3.83 (s, 3H), 5.44 (s, 1H), 6.96 (d, 2H), 7.42 (d, 2H) ^{13}C NMR (CDCl$_3$, 100 MHz): δ = −0.26, 55.34, 63.34, 114.25, 119.32, 127.93, 128.46, 160.33. HRMS (EI): m/z calcd. for C$_{12}$H$_{17}$NO$_2$Si (M$^+$) : 235.1029; found : 235.1032.

2-(4-*tert*-Butylphenyl)-2-trimethylsilyloxy)acetonitrile entry 5). ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 0.23 (s, 9H), 1.32 (s, 9H), 5.38 (s, 1H), 7.09-7.21 (m, 5H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ = −0.39, 31.12, 34.52, 63.33, 119.28, 125.73, 126.04, 133.19, 152.47. HRMS (EI): m/z calcd. for C$_{15}$H$_{23}$NOSi (M$^+$) : 261.1549; found: 261.1552.

2-(2-Chlorophenyl-)-2-(timethylsilyloxy)acetonitrile (entry 6). ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 0.252 (s, 9H), 5.81 (s, 1H) 7.32-7.4 (m, 3H), 7.72 (d, 1H) ^{13}C NMR (CDCl$_3$, 100 MHz): δ = −0.206, 60.75, 127.46, 128.26, 129.64, 130.51.

2-(3-Chlorophenyl-)-2-(timethylsilyloxy)acetonitrile (entry 7). ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 0.25 (s, 9H), 5.42 (s, 1H) 7.35-7.37 (m, 3H), 7.47 (s, 1H) ^{13}C NMR (CDCl$_3$, 100 MHz): δ = −0.176, 62.93, 124.256, 126.39, 129.45, 130.14.

2-(4-Chlorophenyl-)-2-(timethylsilyloxy)acetonitrile (entry 8). ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 0.25 (s, 9H), 5.48 (s, 1H) 7.38-7.42 (m, 4H) ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 0.161, 63.01, 118.71, 127.05, 127.59, 129.09, 134.74.

HRMS (EI): m/z calcd. for C$_{11}$H$_{14}$ClNOSi (M+): 239.0533; found: 239.0539.

2-(3-Phenoxyphenyl)-2-(trimethylsilyloxy)acetonitrile (entry 9). ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 0.218 (s, 9H), 5.42 (s, 1H), 7.01-7.20 (m, 5H), 7.34-7.38 (m, 4H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ = −0.16, 63.28, 116.37, 118.85, 119.17, 119.30, 120.64, 123.75, 129.81, 130.22, 138.08, 156.39, 157.88.

2-Furanyl (trimethylsilyloxy)acetonitrile (entry 10). ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 0.21 (s, 9H), 5.58 (s, 1H), 6.41-6.43 (m, 1H), 6.57-6.6 (m, 1H), 7.4-7.52 (m, 1H). ^{13}C NMR (CDCl$_3$, 100 MHz): −0.42, 57.42, 109.71, 110.76,

117.12, 143.87, 148.23. HRMS (EI): m/z calcd. for C$_9$H$_{13}$NO$_2$Si (M$^+$): 195.0715; found: 195.0712.

2-(Naphthalene-1-yl)-2-(trimethylsilyloxy)acetonitrile (entry 11). ^{1}H NMR (200 MHz, CDCl$_3$): δ = 0.226 (s, 9H), 6.05 (s, 1H), 7.45-7.7 (m, 3H) 7.85-7.95 (m, 3H), 8.23 (d, 1H) ^{13}C NMR (CDCl$_3$, 100 MHz): δ = −0.285, 63.4, 118.45, 122.37, 125.62, 125.01, 126.3, 128.3, 131.01, 133.45, 136.12.

3-Methyl-2-trimethylsilyloxybutanenitrile (entry 12). ^{1}H NMR (200 MHz, CDCl$_3$): δ = 0.2 (s, 9H), 0.88-1.05 (m, 6H), 1.94-1.96 (m, 1H), 4.16 (d, 1H) ^{13}C NMR (CDCl$_3$, 100 MHz): δ = −0.335, 17.68, 33.921, 67.28, 119.94.

2-(Trimethylsilyloxy) pent-3-enenitrile) (entry 13). ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 0.24 (s, 9H), 1.74 (d, 3H), 4.90 (d, 1H), 5.51-5.62 (m, 1H), 5.93-6.04 (m, 1H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ = −0.40, 17.17, 61.92, 118.45, 126.06, 130.88. HRMS (EI): m/z calcd. for C$_8$H$_{15}$NOSi (M$^+$): 169.0922; found: 169.0917.

(E)-4-Phenyl-2-(trimethylsilyloxy)but-3-enenitrile (entry 14). ^{1}H NMR (CDCl$_3$, 200 MHz) δ = 0.32 (s, 9H), 5.18-5.19 (d, 1H), 6.18-6.23 (m, 1H), 6.78-6.81 (d, 1H) 7.28-7.42 (m, 5H) ^{13}C NMR (CDCl$_3$, 100 MHz): δ = −0.26, 64.2, 118.3, 127.5, 127.8, 128.3, 128.4, 128.6, 136.2. HRMS (EI): m/z calcd for C$_{13}$H$_{17}$NOSi (M$^+$): 231.1079; found: 231.1082.

1-(Trimethylsilyloxy)-2-cyclohexenecarbonitrile (entry 15). ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 0.24 (s, 9H), 1.74-1.86 (m, 2H), 1.91-1.98 (m, 2H), 2.04-2.18 (m, 2H) 5.72- 5.8 (m, 1H) 5.97-5.99 (d, 1H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 1.62, 18.45, 24.39, 37.00, 66.50, 121.80, 127.5, and 132.5 HRMS (EI): m/z calcd. for C$_{10}$H$_{17}$NOSi (M$^+$): 195.1079; found: 195.1072.

2-(Trimethylsilyloxy)-2-methyloctanenitrile (entry 16). ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 0.22 (s, 9H), 0.87-0.91 (t, 3H) 1.29-1.32 (m, 8H), 1.56 (s, 3H) 1.68-1.71 (m, 2H) ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 1.42, 14.12, 22.62, 24.32, 28.98, 29.05, 31.69, 43.44, 69.70, and 122.16. HRMS (EI): m/z calcd for C$_{12}$H$_{25}$NOSi (M+): 227.1705; found: 227.1710.

2-Trimethylsilyloxy-2-phenylpropanenitrile (entry 17). ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 0.16 (s, 9H), 1.84 (s, 3H), 7.36-7.55 (m, 5H) ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 0.89, 33.42, 71.46, 121.45, 124.46, 128.48, 141.87 HRMS (EI): m/z calcd. for C$_{12}$H$_{17}$NOSi (M$^+$): 219.1079; found: 219.1072.

Trimethyl silanecarbonitrile (TMSCN). ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 0.354.

^{13}C NMR (CDCl$_3$, 100 MHz): δ = 1.98, 126.97.

A mixture of Trimethyl silanecarbonitrile and NbCl₅. ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 0.185.

^{13}C NMR (CDCl$_3$, 100 MHz): δ = 2.90, 127.23.

References

1. (a) Gregory, R. J. H. *Chem. Rev.* **1999**, *99*, 3649. (b)Special symposium for the synthesis of nonracemic cyanohydrins, see: *Tetrahedron* **2004**, *60*, 10371. (c) Brunel, J. M.; Holmes, I. P.

Angew. Chem. Int. Ed. **2004**, *43*, 2752. (d) Kanai, M.; Kato, N.; Ichikawa, E.; Shibasaki, M. *Synlett* **2005**, 1491.

2. (a) Bandini, M.; Cozzi, P. G.; Garelli, A.; Melchiorre, P.; Umani-Ronchi, A. *Eur. J. Org. Chem.* **2002**, 3243. (b) Cordoba, R.; Plumet, J. *Tetrahedron Lett.* **2003**, *44*, 6157. (c) Chen, F.-X.; Liu, X.; Qin, B.; Zhou, H.; Feng, X.; Zhang, G. *Synthesis* **2004**, *14*, 2266. (d) Aspinall, H. C.; Bickley, J. F.; Greeves, N.; Kelly, R. V.; Smith, P. M. *Organometallics* **2005**, *24*, 3458. (e) Liu, Y.; Liu, X.; Xin, J.; Feng, X. *Synlett* **2006**, 1085.

3. (a) Hamashima, Y.; Sawada, D.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **1999**, *121*, 2641. (b) Hamashima, Y.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2000**, *122*, 7412. (c) Chen, F.; Feng, X.; Qin, B.; Zhang, G.; Jiang, Y. *Organic Lett.* **2003**, *5*, 949. (d) Ryu, D. H.; Corey, E. J. *J. Am. Chem. Soc.* **2005**, *127*, 5384. (e) Fuerst, D. E.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2005**, *127*, 8964. (f) Hatano, M.; Ikeno, T.; Miyamoto, T.; Ishihara, K. *J. Am. Chem. Soc.* **2005**, *127*, 10776. (g) Harada, T.; Kanda, K. *Organic lett.* **2006**, *8*, 3817.

4. (a) Kim, S. S.; Song, D. H. *Eur. J. Org. Chem.* **2005**, 1777. (b) Kim, S. S.; Lee, S. H. *Synth. Commun.* **2005**, *35*, 751. (c) Kim, S. S.; Lee, S. H.; Kwak, J. M. *Tetrahedron: Asymmetry* **2006**, *17*, 1165. (d) Kim, S. S. *Pure Appl. Chem.* **2006**, *78*, 977. (e) Kim, S. S.; Kwak, J. M. *Tetrahedron* **2006**, *62*, 49. (f) Kim, S. S.; Kwak, J. M.; Rajagopal, G. *Bull. Korean Chem. Soc.* **2006**, *27*, 1638.

5. (a) Kim, S. S.; Rajagopal, G.; Song, D. H. *J. Organomet. Chem.* **2004**, *689*, 1734. (b) Kim, S. S.; Kim, D. W.; Rajagopal, G. *Synthesis-Stuttgart* **2004**, 213. (c) Kim, S. S.; Rajagopal, G.; Kim, D. W.; Song, D. H. *Synth. Commun.* **2004**, *34*, 2973. (d) Rajagopal, G.; Kim, S. S.; Kwak, J. M. *Bull. Korean Chem. Soc.* **2006**, *27*, 1907. (e) Kim, S. S.; Rajagopal, G. *Synthesis-stuttgart* **2007**, *2*, 215. (f) Kim, S. S.; Rajagopal, G.; George, S. C. *Appl. Organomet. Chem.* **2007**, *21*, 198.

6. (a) Lidy, W.; Sundermeyer, W. *Chem. Ber.* **1973**, *106*, 587. (b) Evans, D. A.; Truesdale, L. K. *Tetrahedron Lett.* **1973**, 4929. (c) Komatsu, N.; Uda, M.; Suzuki, H.; Takahashi, T.; Domae, T.; Wada, M. *Tetrahedron Lett.* **1997**, *38*, 7215. (d) Reetz, M. T.; Drewes, M. W.; Harms, K.; Reif, W. *Tetrahedron Lett.* **1988**, *29*, 3295. (e) Loh, T.-P.; Xu, K.-C.; Ho, D. S. C.; Sim, K.-Y. *Synlett.* **1998**, 369. (f) Vougioukas, A. E.; Kagan, H. B. *Tetrahedron Lett.* **1987**, *28*, 5513. (g) Evans, D. A.; Truesdale, L. K.; Carroll, G. L. *J. Chem. Soc. Chem. Commu.* **1973**, 55. (h) Iwanami, K.; Aoyagi, M.; Oriyama, T. *Tetrahedron Lett.* **2005**, *46*, 7487. (i) Kurono, N.; Yamaguchi, M.; Suzuki, K.; Ohkuma, T. *J. Org. Chem.* **2005**, *70*, 6530.

7. (a) Howarth, J.; Gillespie, K. *Tetrahedron Lett.* **1996**, *37*, 6011. (b) Andrade, C. K. Z.; Oliveira, G. R. *Tetrahedron Lett.* **2002**, *43*, 1935. (c) Andrade, C. K. Z.; Azevedo, N. R. *Tetrahedron Lett.* **2001**, *42*, 6473. (d) Guo, Q.; Miyaji, T.; Hara, R.; Shen, B.; Takahashi, T. *Tetrahedron* **2002**, *58*, 7327. (e) Ortiz, A.; Quintero, L.; Hernandez, H.; Maldonado, S.; Mendoza, G.; Bernes, S. *Tetrahedron Lett.* **2003**, *44*, 1129. (f) Arai, S.; Sudo, Y.; Nishida, A. *Synlett* **2004**, *6*, 1104. (g) Yadav, J. S.; Subba Reddy, B. V.; Eeshwaraiah, B.; Reddy, P. N. *Tetrahedron* **2005**, *61*, 875. (h) Yadav, J. S.; Narsaiah, A. V.; Subba Reddy, B. V.; Basak, A. K.; Nagaiah, K. *J. Mol. Cat A: Chemi.* **2005**, *230*, 107.

8. (a) Liu, X.; Qin, B.; Zhou, X.; He, B.; Feng, X. *J. Am. Chem. Soc.* **2005**, *127*, 12224. (b) Kabayashi, S.; Nishio, K. *J. Org. Chem.* **1994**, *59*, 6620 (c) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371.