

Fe(Cp)₂PF₆: An efficient catalyst for cyanosilylation of carbonyl compounds under solvent free condition

Noor-ul H. Khan ^{*}, Santosh Agrawal, Rukhsana I. Kureshy,
Sayed H.R. Abdi, Surendra Singh, Raksh V. Jasra

*Discipline of Inorganic Materials and Catalysis, Central Salt and Marine Chemicals Research Institute (CSMCRI),
G.B. Marg, Bhavnagar 364 002, Gujarat, India*

Received 18 April 2007; received in revised form 12 June 2007; accepted 3 July 2007
Available online 15 July 2007

Abstract

An efficient method for the addition of trimethylsilyl cyanide (TMSCN) to various aldehydes and ketones has been described using Fe(Cp)₂PF₆ (2.5 mol%) as a catalyst under solvent free condition. Excellent yields of trimethylsilylether of cyanohydrin up to (94%) was achieved within 10 min.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Carbonyl compounds; Fe(Cp)₂PF₆; Solvent free synthesis; Cyanosilylation; Catalysis

1. Introduction

Cyanohydrins are versatile intermediates, which can easily be converted into wide variety of valuable classes of compounds, such as α -amino acids, α -hydroxy acids, β -amino alcohols, vicinal diols, α -hydroxy ketones [1] for their application in pharmaceuticals, agrochemicals and insecticides [2]. Cyanohydrins are typically prepared by the interaction of carbonyl compound with a cyanide source serving as nucleophile. Several useful cyanation reagents have been reported in the literature [3], among them, trimethylsilyl cyanide (TMSCN) seems to be one of the most effective and safe cyanation source for nucleophilic addition to carbonyl compounds. Generally, in the absence of a catalyst, no reaction occurs between TMSCN and carbonyl compounds. Frequently, Lewis acids such as Yb(CN)₃ [4], Yb(OTf)₃ [5], Cu(OTf)₂ [6], ZnI₂ [7], KCN:18-crown-6 [8], LiClO₄ [9], R₂SnCl₂ [10], Zr(KPO₄)₂ [11], MgBr₂ · Et₂O [12], CsF [13], VO(OTf)₂ [14], *N*-het-

erocyclic carbene [15], P(RNCH₂CH₂)N [16], InBr₃ [17], and FeCl₃ [18] both in stoichiometric and catalytic amounts have been used to catalyze the cyanation of carbonyl compounds. Besides, in situ generated catalyst containing various Lewis acid and *N,N*-dimethyl-*N*-oxide [19] have also been used for the generation of cyanohydrins. Nevertheless, these procedures often require drastic reaction conditions, with a tedious work up procedures under potentially hazardous solvents such as CH₂Cl₂, CH₃CN and THF. In continuation of our current interest in cyanation of aldehydes [20] and meeting the growing challenges for developing solvent-free [21] and environmentally benign synthetic protocol, we report here the addition of TMSCN to carbonyl compounds using Fe(Cp)₂PF₆ as a readily available catalyst to give cyanohydrintrimethylsilyl ethers in excellent yields under solvent-free conditions at room temperature.

2. Results and discussion

Addition of TMSCN to benzaldehyde used as a representative substrate was carried out with Fe(Cp)₂PF₆ (1–2.5 mol%) as a catalyst under solvent-free condition at

^{*} Corresponding author. Tel.: +91 0278 2567760; fax: +91 0278 2566970.

E-mail address: khan2593@yahoo.co.in (Noor-ul H. Khan).

room temperature and the results are summarized in Table 1. The best result in terms of yield (94%) for the formation of cyanohydrintrimethylsilylether was achieved with the catalyst loading of 2.5 mol% within 10 min (Table 1, entry 3).

Based on the above observations we extended this catalytic system ($\text{Fe}(\text{Cp})_2\text{PF}_6$; 2.5 mol%) for the cyanation of a variety of aromatic and aliphatic aldehydes under identical reaction conditions where good to excellent yield (65–94%) for the corresponding cyanohydrintrimethylsilylethers was achieved within 10 min (Table 2). The present catalytic protocol is quite general in nature (Yield; 72–94%) for the cyanation of 1-, 2-, and 3-substituted benzaldehydes (Table 2, entries 1–10) and works equally well (Yield; 75–92%) for the aliphatic terminal aldehydes (Table 2, entries 13–15). While aldehydes with heterocyclic ring system (Table 2, entries 16 and 17) gave moderate yields. Further, we have found that this catalytic system is reasonably effective for the bulkier aromatic aldehyde like naphthaldehyde (entry 11) conjugated and non-conjugated aldehydes viz., *E*-cinnamaldehyde and hydrocinnamaldehyde, respectively (entries 18 and 12, respectively). Furthermore, cyanation of 4-bromobenzaldehyde which is solid at room temperature gave corresponding cyanohydrintrimethylsilylether in high yield (90%) under our solvent free catalytic system in 10 min (entry 19). However, when the same reaction was conducted in CH_2Cl_2 as solvent the yield (61%) dropped considerably (entry, 20).

The present catalyst system was further tested for its efficacy for the cyanation of ketones. The results as given in the Table 3 clearly suggest that this system is excellent (94% yield of cyanohydrintrimethylsilylether) for the cyanation of a variety of ketones tested. Further, as compared to other solvent free protocols for the addition of TMS-CN to ketones (acetophenone, for example) our catalytic system is far superior in terms of low catalyst loading and shorter reaction time (Table 4). The cyanation of ketones is considered as problematic due to more steric hindrance around the carbonyl group of ketones than of aldehydes. It was surprising that our catalytic system showed nearly similar activity both for aldehydes and ketones (reaction completes in 10 min). To investigate the time profile of cat-

Table 2

Addition of TMS-CN to various aldehydes catalyzed by $\text{Fe}(\text{Cp})_2\text{PF}_6$ under solvent free condition^a

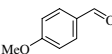
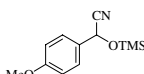

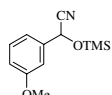

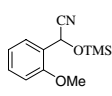
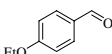
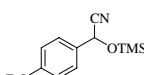

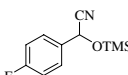

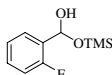

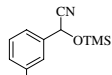
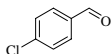
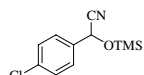
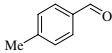
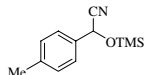

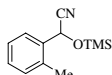
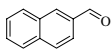
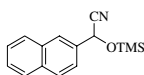
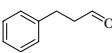
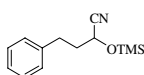
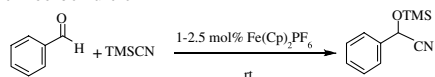
Entry	Substrate	Product	Time (min)	Yield ^b (%)
1			10	91
2			10	90
3			10	90
4			10	87
5			10	74
6			10	94
7			10	73
8			10	87
9			10	92
10			10	72
11			10	85
12			10	74

Table 1

The effect of catalyst loading on addition of TMS-CN to benzaldehyde under solvent-free condition^a



Entry	Mol (%)	Time (min)	Yield ^b (%)
1	1	10	79
2	2	10	88
3	2.5	10	94

^a The $\text{Fe}(\text{Cp})_2\text{PF}_6$ (1–2.5 mol%) was dissolved in aldehydes (1 mmol) and TMS-CN (1.3 mmol) was added in small fractions over period of 5 min.

^b Isolated yield.

Table 2 (continued)

Entry	Substrate	Product	Time (min)	Yield ^b (%)
13	CH ₃ (CH ₂) ₂ CHO		10	89
14	CH ₃ (CH ₂) ₄ CHO		10	92
15	CH ₃ (CH ₂) ₇ CHO		10	75
16			10	68
17			10	65
18			10	70
19			10 10	90 61 ^c

^a The Fe(Cp)₂PF₆ (2.5 mol%) was dissolved in aldehydes (1 mmol) and TMSCN (1.3 mmol) was added in small fractions over period of 5 min.

^b Isolated yield.

^c Using CH₂Cl₂ (0.2 ml) as a solvent.

alytic activity our catalyst, we monitored the cyanosilylation of acetophenone and benzaldehyde at an interval of 30 s. To our surprise acetophenone reacted more rapidly than benzaldehyde. To further understand the role of steric crowding (as reported in the literature [1e]), we further conducted the cyanosilylation reaction using benzophenone as a substrate. The results were still surprising; the rates were highest for benzophenone among the three substrates used here (Fig. 1). This behavior of catalyst which in turn is responsible for the activation of the substrate. As the availability of π -electrons in the case of benzophenone and acetophenone is more than benzaldehyde, stacking interaction would also be stronger for the former making it more active to react with TMSCN.

Based on the product distribution it is expected that the cyanation reaction would follow the reaction mechanism as depicted in Scheme 1. Ferrocenium ion is reported [23] to be Lewis acid; hence, it is expected to polarize the carbonyl group through weak interaction between oxygen of

Table 3

Addition of TMSCN to various ketones catalyzed by Fe(Cp)₂PF₆ under solvent free condition^a

Entry	Substrate	Product	Time (min)	Yield ^b (%)
1			10	93
2			10	89
3			10	90
4			10	91
5			10	94
6			10	92
7			10	93
8			10	80
9			10	91
10			10	93
11			10	90
12			1.5	100 ^c

^a The Fe(Cp)₂PF₆ (2.5 mol%) was dissolved in ketones (1 mmol) and TMSCN (1.3 mmol) was added in small fractions over period of 5 min.

^b Isolated yield.

^c GC conversion.

Table 4
The comparison of various catalysts towards addition of TMSCN to acetophenone

Entry	Catalyst	Mol (%)	Solvent	Time (min)	Yield ^a (%)
1	Fe(Cp) ₂ PF ₆	2.5	–	10	93
2	InBr ₃	1	CH ₂ Cl ₂	180	90 [17]
3	Cu(OTf) ₂	5	CH ₂ Cl ₂	1200	85 [6]
4	R ₂ SnCl ₂	10	–	2700	93 [10]
5	LiClO ₄	100	–	180	86 ^b [9b]
6	CsF	10	CH ₃ CN	60	95 [13b]
7	N-Methylmorpholine N-oxide	30	–	480	98 [22]
8	N-Oxide–Ti(O ⁱ Pr) ₄ [2/1]	10	CH ₂ Cl ₂	3720	82 [19b]
9	N-Heterocyclic carbene	0.5	DMF	60	80 [15a]
10	VO(OTf) ₂	1	CH ₃ CN	240	92 [14]
11	P(RNCH ₂ CH ₂) ₃ N	3	THF	60	90 [16]
12	(CH ₃ CH ₂) ₃ N	20	–	120	90 [21c]

^a Isolated yield.

^b GC conversion.

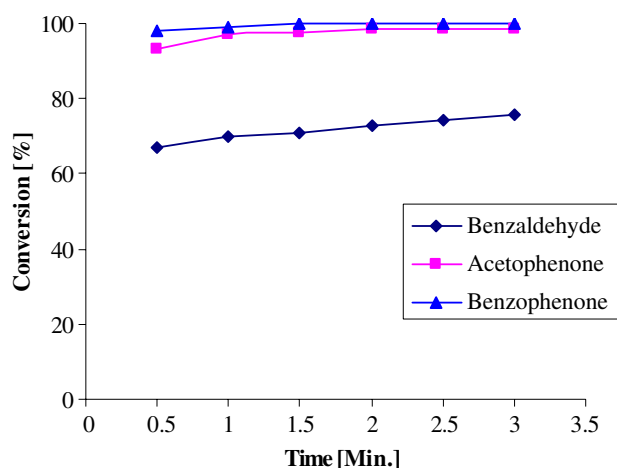
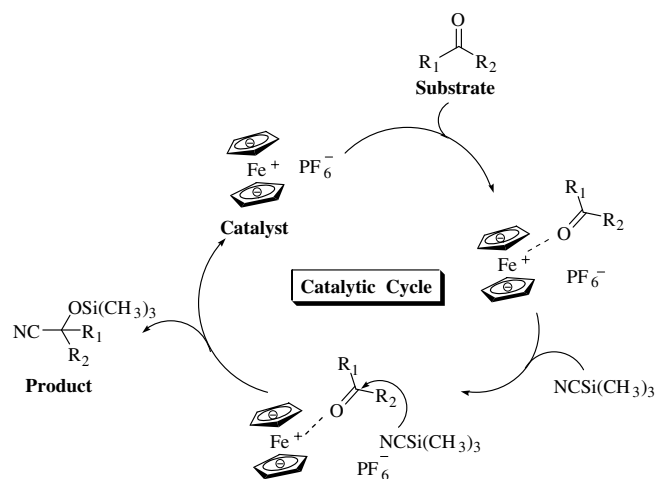


Fig. 1. Time dependent formation of cyanosilylether with Fe(Cp)₂PF₆.



Scheme 1. Proposed mechanism for cyanosilylation of carbonyl compound.

carbonyl group and Fe. The nucleophilic attack of cyanide ion on thus activated substrate would give the product and set free the catalyst for the next catalytic cycle.

3. Experimental

3.1. General

NMR spectra were obtained with a Bruker F113V spectrometer (200 MHz and 50 MHz for ¹H and ¹³C, respectively) and are referenced internally with TMS. Microanalysis of the products was carried out by a CHN analyzer (Perkin–Elmer Series II, 2400). The purification of the products was performed by silica gel (60–200 mesh) flash chromatography. The conversion was determined by capillary GC column SPB-5 (60 m) at 150 °C isotherm on a Shimadzu GC 2010. TMSCN, Acetophenone, 4-methyl acetophenone, 4-fluoro acetophenone, 2-chloro acetophenone, propiophenone (across organics), 2-methoxy acetophenone, 3-methoxy acetophenone, 2-fluoro acetophenone (Alfa Aesar), cyclohexanone (National Chemical India), 2-hydroxy acetophenone, 2-methyl benzaldehyde, 4-methyl benzaldehyde (Merck), Fe(Cp)₂PF₆, 2-bromo acetophenone, benzaldehyde, 4-methoxy benzaldehyde, 3-methoxy benzaldehyde, 2-methoxy benzaldehyde, 4-ethoxy benzaldehyde, 4-fluoro benzaldehyde, 2-fluoro benzaldehyde, 4-chloro benzaldehyde, 3-chloro benzaldehyde, naphthaldehyde, 2-thiophene-carboxaldehyde, 2-furan-carboxaldehyde, *E*-cinamaldehyde, hydrocinnamaldehyde, pentanal, hexanal, nonanal were purchased from Aldrich Chemicals and were used as received.

3.2. Typical experimental procedure for addition of TMSCN to aldehydes/ketones

To a mixture of catalyst Fe(Cp)₂PF₆ (2.5 mol%) and aldehydes/ketones (1 mmol) was added TMSCN (CAUTION: *Toxic!*, 1.3 mmol) in small fractions over a period of 5 min. The reaction was monitored on GC using a capillary column SPB-5 (60 m) at 150 °C isotherm and the product quantification was done by comparison of peak area with respect to dodacane used as an internal standard. The product was purified by flash column chromatography on silica gel (eluted with hexane/ethyl acetate = 95:5). The

purified products were characterized by ^1H and ^{13}C NMR and were in agreement with the reported values [13b,15,19b].

3.3. Characterization data of product

2-Hydroxy-2-phenylacetonitrile (derived from Table 1, entry 3). ^1H NMR (200 MHz, CDCl_3): δ = 4.14 (br s, 1H), 5.44 (s, 1H), 7.35–7.43 (m, 5H); ^{13}C NMR (50 MHz, CDCl_3): δ = 63.9, 119.8, 127.3, 129.7, 130.5, 134.2, 135.9 ppm. Elemental analysis. Anal. Calc. for $\text{C}_8\text{H}_7\text{NO}$: C, 72.16; H, 5.30; N, 10.52. Found: C, 72.08; H, 5.32; N, 10.48%.

2-Hydroxy-2-(4-ethoxyphenyl) acetonitrile (derived from Table 2, entry 4) ^1H NMR (200 MHz, CDCl_3): δ = 1.47 (t, J = 7.2, 3H), 3.67 (br s, 1H), 4.14 (q, J = 6.0, 2H), 5.54 (s, 1H), 6.94–7.42 (m, 4H); ^{13}C NMR (50 MHz, CDCl_3): δ = 15.4, 62.0, 65.1, 112.8, 115.1, 121.8, 131.9 ppm. Elemental analysis. Anal. Calc. for $\text{C}_{10}\text{H}_{11}\text{NO}_2$: C, 67.78; H, 6.26; N, 7.90. Found: C, 67.82; H, 6.24; N, 7.88%.

2-Hydroxy-2-(1'-naphthyl) acetonitrile (derived from Table 2, entry 11) ^1H NMR (200 MHz, CDCl_3): δ = 3.87 (br s, 1H), 6.03 (s, 1H), 7.37–8.06 (m, 7H); ^{13}C NMR (50 MHz, CDCl_3): δ = 62.7, 115.8, 119.5, 123.5, 125.7, 126.2, 127.1, 127.9, 129.6, 130.9, 131.4, 134.6 ppm. Elemental analysis. Anal. Calc. for $\text{C}_{12}\text{H}_9\text{NO}$: C, 78.67; H, 4.95; N, 7.65. Found: C, 78.62; H, 5.02; N, 7.68%.

2-Hydroxy-4-phenyl-butanenitrile (derived from Table 2, entry 12) ^1H NMR (200 MHz, CDCl_3): δ = 2.08–2.19 (m, 2H), 2.78 (t, J = 7.6, 2H), 3.44 (br s, 1H), 4.36 (t, J = 6.2, 1H), 7.17–7.33 (m, 5H); ^{13}C NMR (50 MHz, CDCl_3): δ = 31.3, 37.2, 60.9, 115.1, 127.2, 129.1, 129.3, 140.3 ppm. Elemental analysis. Anal. Calc. for $\text{C}_{10}\text{H}_{11}\text{NO}$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.55; H, 6.84; N, 9.71%.

2-Hydroxyheptanenitrile (derived from Table 2, entry 14). ^1H NMR (200 MHz, CDCl_3): δ = 0.87–1.90 (m, 11H), 2.80 (br s, 1H), 4.50 (m, 1H); ^{13}C NMR (50 MHz, CDCl_3): δ = 14.5, 23.1, 24.9, 31.7, 35.9, 62.1, 115.1 ppm. Elemental analysis. Anal. Calc. for $\text{C}_7\text{H}_{13}\text{NO}$: C, 66.10; H, 10.30; N, 11.0. Found: C, 66.12; H, 10.26; N 11.02%.

2-Hydroxy-2-(2'-thiophen) acetonitrile (derived from Table 2, entry 16). ^1H NMR (200 MHz, CDCl_3): δ = 3.68 (br s, 1H), 5.72 (s, 1H), 7.05–7.42 (m, 3H); ^{13}C NMR (50 MHz, CDCl_3): δ = 59.9, 115.1, 127.8, 128.0, 128.6 ppm. Elemental analysis. Anal. Calc. for $\text{C}_6\text{H}_5\text{NOS}$: C, 51.78; H, 3.62; N, 10.06. Found: C, 51.82; H, 6.60; N, 10.01%.

(E)-2-Hydroxy-4-phenyl-3-butenenitrile (derived from Table 2, entry 18). ^1H NMR (200 MHz, CDCl_3): δ = 3.45 (br s, 1H), 5.13 (d, J = 5.6, 1H), 6.19 (dd, J = 10.0, 5.8, 1H), 6.86 (d, J = 15.8, 1H), 7.32–7.39 (m, 5H); ^{13}C NMR (50 MHz, CDCl_3): δ = 62.5, 114.9, 123.1, 127.7, 129.5, 129.7, 129.8, 135.8 ppm. Elemental analysis. Anal. Calc. for $\text{C}_{10}\text{H}_9\text{NO}$: C, 75.45; H, 5.70; N, 8.80. Found: C, 75.42; H, 5.73; N, 8.78%.

2-Hydroxy-2-phenyl-propionitrile (derived from Table 3, entry 1). ^1H NMR (200 MHz, CDCl_3): δ = 1.84 (s, 3H), 4.02 (br s, 1H), 7.35–7.92 (m, 5H); ^{13}C NMR (50 MHz, CDCl_3): δ = 31.1, 71.2, 115.1, 125.1, 129.0, 129.2, 129.7, 133.9 ppm. Elemental analysis. Anal. Calc. for $\text{C}_9\text{H}_9\text{NO}$: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.48; H, 6.13; N, 9.55%.

2-(2-chloro-phenyl)-2-hydroxy-propionitrile (derived from Table 3, entry 9). ^1H NMR (200 MHz, CDCl_3): δ = 1.99 (s, 3H), 4.29 (br s, 1H), 7.29–7.71 (m, 4H); ^{13}C NMR (50 MHz, CDCl_3): δ = 28.5, 69.1, 114.8, 121.2, 127.2, 128.1, 130.9, 131.9, 137.4 ppm. Elemental analysis. Anal. Calc. for $\text{C}_9\text{H}_8\text{ClNO}$: C, 59.52; H, 4.42; N, 7.71. Found: C, 59.58; H, 4.40; N, 7.70%.

Acknowledgements

N. H. Khan is thankful to DST and CSIR Network project on Catalysis for financial assistance and also thankful to Dr. P. K. Ghosh, the Director, of the Institute for providing instrumentation facility.

References

- [1] (a) M. North, Synlett (1993) 807; (b) F. Effenberger, Angew. Chem. Int. Ed. Engl. 33 (1994) 1555; (c) M. North, in: A.R. Katritzky, O. Meth-Cohn, R.C. Wees, G. Pattenden (Eds.), Comprehensive Organic Functional Group 'Transformations', vol. 3, Pergamon Press, Oxford, 1995, Chapter 18; (d) R.J.H. Gregory, Chem. Rev. 99 (1999) 3649; (e) J.M. Brunel, I.P. Holmes, Angew. Chem. Int. Ed. 43 (2004) 2752; (f) M. North, Tetrahedron: Asymmetry 14 (2003) 147; (g) M. Schmidt, S. Herve, N. Klempier, H. Griengl, Tetrahedron 52 (1996) 7833; (h) A. Mori, H. Nitta, M. Kudo, S. Inous, Tetrahedron Lett. 32 (1991) 4333; (i) H. Griengl, H. Schwab, M. Fechter, TIBTECH 18 (2000) 252; (j) A. Schmid, J.S. Dordick, B. Hauer, A. Kiener, M. Wubbolts, B. Witholt, Nature (London) 409 (2001) 258; (k) H. Hirohara, M. ishizawa, Biosci. Biotechnol. Biochem. 62 (1998) 1.
- [2] T. Kusumoto, T. Hanamoto, T. Hiyama, S. Takehera, T. Shoji, M. Osawa, T. Kuriyama, K. Nakamura, T. Fujisawa, Chem. Lett. 19 (1990) 1615.
- [3] (a) A. Lapworth, J. Chem. Soc. 83 (1903) 995; (b) W.C. Groutas, D. Felker, Synthesis (1980) 861, and references cited therein; (c) A. Fujii, S. Sakaguchi, Y. Ishii, J. Org. Chem. 65 (2000) 6209; (d) Y. Kawasaki, A. Fujii, Y. Nakano, S. Sakaguchi, Y. Ishii, J. Org. Chem. 64 (1999) 4214.
- [4] S. Matsubara, T. Takai, K. Utimoto, Chem. Lett. (1991) 1447.
- [5] (a) Y. Yang, D. Wang, Synlett (1997) 861; (b) Y. Yang, D. Wang, Synlett (1997) 1379.
- [6] P. Saravanan, R.V. Anand, V.R. Singh, Tetrahedron Lett. 39 (1998) 3823.
- [7] P.G. Gassman, J.J. Talley, Tetrahedron Lett. 19 (1978) 3773.
- [8] W.J. Greenlee, D.G. Hangauer, Tetrahedron Lett. 24 (1983) 4559.
- [9] (a) G. Jenner, Tetrahedron Lett. 40 (1999) 491; (b) N. Azizi, M.R. Saidi, J. Organomet. Chem. 688 (2003) 283.
- [10] J.K. Whitesell, R. Apodaca, Tetrahedron Lett. 37 (1996) 2525.

- [11] M. Curini, F. Epifanio, M.C. Marcotullio, O. Rosati, M. Rossi, *Synlett* (1999) 315.
- [12] D.E. Ward, M.J. Hrapchak, M. Sales, *Org. Lett.* 2 (2000) 57.
- [13] (a) S.S. Kim, D.H.O. Song, *Lett. Org. Chem.* 1 (2004) 264;
(b) S.S. Kim, G. Rajagopal, D.H.O. Song, *J. Organomet. Chem.* 689 (2004) 1734.
- [14] K.De. Surya, A.G. Richard, *J. Mol. Catal. A: Chem.* 232 (2005) 123.
- [15] (a) J.J. Song, F. Gallou, J.T. Reeves, Z. Tan, N.K. Yee, C.H. Senanayake, *J. Org. Chem.* 71 (2006) 1273;
(b) Y. Suzuki, A. Bakar, M.D.K. Muramatsu, M. Sato, *Tetrahedron* 62 (2006) 4227.
- [16] B.M. Fetterly, J.G. Verkade, *Tetrahedron Lett.* 46 (2005) 8061.
- [17] M. Bandini, P.G. Cozzi, A. Garelli, P. Melchiorre, A.U. Ronchi, *Eur. J. Org. Chem.* (2002) 3243.
- [18] K. Iwanami, M. Aoyagi, T. Oriyama, *Tetrahedron Lett.* 46 (2005) 7487.
- [19] (a) F. Chen, X. Feng, B. Qin, G. Zhang, Y. Jiang, *Synlett* (2003) 558;
(b) Y. Shen, X. Feng, Y. Li, G. Zhang, Y. Jiang, *Tetrahedron* 59 (2003) 5667;
(c) F. Chen, X. Feng, Y. Li, G. Zhang, Y. Jiang, *Synlett* (2002) 793.
- [20] (a) N.H. Khan, S. Agrawal, R.I. Kureshy, S.H.R. Abdi, V.J. Mayani, R.V. Jasra, *Eur. J. Org. Chem.* (2006) 3175;
(b) N.H. Khan, S. Agrawal, R.I. Kureshy, S.H.R. Abdi, V.J. Mayani, R.V. Jasra, *Tetrahedron: Asymmetry* 17 (2006) 2659;
(c) N.H. Khan, S. Agrawal, R.I. Kureshy, S.H.R. Abdi, V.J. Mayani, R.V. Jasra, *J. Mol. Catal. A: Chem.* 264 (2007) 140.
- [21] (a) L. Wang, X. Huang, J. Jiang, X. Liu, X. Feng, *Tetrahedron Lett.* 47 (2006) 1581;
(b) S.S. Kim, G. Rajagopal, *Synthesis* 2 (2007) 215;
(c) A. Baeza, C. Nájera, M.G. Retamosa, J.M. Sansano, *Synthesis* 16 (2005) 2787.
- [22] S.S. Kim, D.W. Kim, G. Rajagopal, *Synthesis* 2 (2004) 213.
- [23] T.R. Kelly, S.K. Maity, P. Meghani, N.S. Chandrakumar, *Tetrahedron Lett.* 30 (1989) 1357.