Polyhedron 31 (2012) 332-338

Contents lists available at SciVerse ScienceDirect

Polyhedron



journal homepage: www.elsevier.com/locate/poly

Highly efficient and chemoselective trimethylsilylation of alcohols and phenols with hexamethyldisilazane (HMDS) catalyzed by reusable electron-deficient [Ti^{IV}(salophen)(OTf)₂]

Maryam Yadegari^a, Majid Moghadam^{b,*}, Shahram Tangestaninejad^b, Valiollah Mirkhani^b, Iraj Mohammadpoor-Baltork^b

^a Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran ^b Department of Chemistry, Catalysis Division, University of Isfahan, Isfahan 81746-7344, Iran

ARTICLE INFO

Article history: Received 11 June 2011 Accepted 17 September 2011 Available online 24 September 2011

Keywords: Titanium Schiff base HMDS Alcohol Phenol TMS-ether

ABSTRACT

In the present work, highly efficient trimethylsilylation of alcohols and phenols with hexamethyldisilazane (HMDS) catalyzed by high-valent $[Ti^{IV}(salophen)(OTf)_2]$ is reported. Under these conditions, primary, secondary and tertiary alcohols as well as phenols were silylated in short reaction times and high yields. It is noteworthy that this method can be used for chemoselective silylation of primary alcohols in the presence of secondary and tertiary alcohols and phenols. The catalyst was reused several times without loss of its catalytic activity.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

The protection of hydroxyl groups is an important reaction especially in the synthesis of fine chemicals and natural products. Several methods such as acetylation, tetrahydropyranylation, methoxymethylation and trimethylsilylation have been reported for protection of hydroxyl groups [1,2]. The common method for the silvlation of hydroxy functional groups is the use of hexamethyldisilazane (HMDS). One disadvantage of HMDS is its poor silylating power in the absence of a suitable catalyst which needs forceful conditions and long reaction times in many cases [3]. To solve this problem, a variety of catalysts including (CH₃)₃SiCl [4], ZrCl₄ [5], ZnCl₂ [6], K-10 montmorillonite [7], LiClO₄ [8], H₃PW₁₂O₄₀ [9], iodine [10], InBr₃ [11], zirconium sulfophenyl phosphonate [12], CuSO₄·5H₂O [13], sulfonic acid-functionalized nanoporous silica [14], MgBr₂·OEt₂ [15], LaCl₃ [16], poly(N-bromobenzene-1,3-disulfonamide) and *N*,*N*,*N*',*N*'-tetrabromobenzene-1,3-disulfonamide [17], Fe(TFA)₃ [18], Fe₃O₄ [19], (*n*-Bu₄N)Br [20], trichloroisocyanuric acid (TCCA) [21], HClO₄-SiO₂ [22], Pd [23], ZrO(OTf)₂ [24], LiClO₄-SiO₂ [25], PhMe₃N⁺Br₃⁻ [26], poly(4-vinylpyridinium tribromide) [27], 1,3-dichloro-5,5-dimethylhydantoin (DCH) and/or trichloromelamine (TCM) [28] sulfamic acid [29] and H₅IO₆/KI

[30] have been reported for trimethylsilylation of alcohols and phenols. Although these procedures provide an improvement, many of these catalysts or activators need long reaction times, drastic reaction conditions or tedious work up, or are moisture sensitive or expensive. Hence, introduction of new procedures to circumvent these problems is still in demand.

Schiff base complexes of Mn, Fe, Ru, Cr, Co and V have found many applications in organic chemistry [31]. These compounds have been used as catalyst in the oxidation of alkenes and alkanes, sulfides, amines and alcohols. Titanium Schiff bases have been used as catalyst for polymerization of ethylene and propene [32], regio- and stereoselective epoxidation of allylic alcohols [33], asymmetric ringopening of epoxides by dithiophosphorus acid [34], enantioselective catalytic ring-opening of epoxides with carboxylic acids [35], efficient kinetic resolution of terminal epoxides by means of catalytic hydrolysis [36], enantioselective trimethylsilylcyanation of aldehydes [37,38], oxidation of sulfides to sulfoxides with hydrogen peroxide [39], enantioselective ring-opening of *meso*-epoxides with ArSH [40], asymmetric alkynylation of aldehydes [41] and enantioselective Pinacol coupling of aryl aldehydes [42].

Electron-deficient complexes of Fe, Cr, Sn and V have been used as mild Lewis acids in organic transformations [43–60]. In this paper, we report the use of high-valent titanium(IV)salophen trifluoromethanesulfonate, $[Ti^{IV}(salophen)(OTf)_2]$, in the rapid and highly efficient silylation of alcohols and phenols with HMDS at room temperature (Scheme 1).



^{*} Corresponding author. Tel.: +98 311 7932712; fax: +98 311 6689732. *E-mail address*: moghadamm@sci.ui.ac.ir (M. Moghadam).

^{0277-5387/\$ -} see front matter @ 2011 Elsevier Ltd. All rights reserved. doi:10.1016/j.poly.2011.09.023



Scheme 1. Trimethylsilylation of alcohols and phenols with HMDS catalyzed by [Ti^{IV}(salophen)(OTf)₂].

 Table 1

 Optimization of catalyst amount in the silylation of benzyl alcohol with HMDS catalyzed by [Ti^{IV}(salophen)(OTf)₂] at room temperature.^a

Entry	Catalyst amount (%mol)	Solvent	Time (min)	Yield (%) ^b
1	1	CH ₃ CN	1	44
2	2	CH₃CN	1	56
3	3	CH₃CN	1	79
4	0	CH_2Cl_2	1	16
5	0.1	CH_2Cl_2	1	33
6	0.1	CH_2Cl_2	10	47
7	0.5	CH_2Cl_2	1	42
8	1	CH_2Cl_2	1	75
9	2	CH_2Cl_2	1	100
10	3	CH_2Cl_2	1	100
11	2	EtOAc	1	37
12	2	n-Hexane	1	15
13	2	CHCl ₃	1	30

 $^{\rm a}$ Reaction conditions: benzyl alcohol (1 mmol), HMDS (0.7 mmol), solvent (1 mL).

^b GC vield.

2. Experimental

vAll chemicals were purchased from Merck or Fluka chemical companies. FT-IR spectra were obtained with potassium bromide pellets in the range 400–4000 cm⁻¹ with a Nicolet Impact 400D spectrometer. Gas chromatography experiments (GC) were performed with a Shimadzu GC-16A instrument using a 2 m column packed with silicon DC-200 or Carbowax 20 m. In the GC experiments, *n*-decane was used as an internal standard. ¹H NMR spectra were recorded on a Bruker-Avance AQS 400 MHz spectrometer.

2.1. Preparation of [Ti^{IV}(salophen)Cl₂]

In a typical procedure, a solution of TiCl₄(THF)₂ (669 mg, 2.0 mmol) in dry THF (10 mL) was added slowly to a solution of H₂Salophen (633 mg, 2.0 mmol) in THF (10 mL), resulting in a red-brown solution. The reaction mixture was stirred under reflux at 70 °C for 1 h, and then cooled to room temperature, and the solvent was evaporated. The solid was slurried with Et₂O (20 mL), filtered through a fine-fritted funnel, washed with additional Et₂O, and dried under vacuum at 80 °C for 2 h [61].

2.2. Preparation of [Ti^{IV}(salophen)(OTf)₂]

To a solution of $[Ti^{IV}(salophen)Cl_2]$ (434 mg, 1 mmol) in CH₂Cl₂ (15 mL) was added an acetonitrile solution (15 mL) of AgOTf (513.9 mg, 2 mmol), producing a brown precipitate. The AgCl was filtered through a fine fritted funnel, and the filtrate was concentrated to dryness. The solid was extracted with CH₂Cl₂ and the resulting solid was isolated [61].

¹H NMR (400 MHz, CD₃OD) δ = 9.44 (s, 2H, H–C=N), 8.10 (dd, 2H, Ar, ¹*J* = 6.2, ²*J* = 3.2 Hz), 7.95 (d, 2H, Ar, *J* = 7.6 Hz), 7.72 (m, 2H, Ar), 7.64 (dd, 2H, Ar, ¹*J* = 6.4, ²*J* = 3.2 Hz), 7.18 (m, 2H, Ar), 6.96 (d, 2H, Ar, *J* = 8 Hz); ¹³C NMR (100 MHz, CD₃OD) δ = 116.53, 117.24 (CH), 117.58 (O–C–C), 121.24 (CF₃), 123.62, 130.41, 136.37, 138.10 (CH), 141.46 (N–C), 160.56 (O–C), 161.64 (N=CH). IR (KBr): *v*(CC=N) 1603, *v*(SC=O) 1168 and *v*(C–F) 1280.

2.3. General procedure for trimethylsilylation with HMDS catalyzed by $[Ti^{IV}(salophen)(OTf)_2]$

To a mixture of alcohol or phenol (1 mmol), HMDS (0.7 mmol per OH group) in CH_2Cl_2 (1 mL) was added $[Ti^{IV}(Salophene)(OTf)_2]$ (0.01 mmol) and stirred at room temperature for appropriate time



Scheme 2. The preparation route for catalyst.

Table 2 Trime thus indexion of clockeds with UMDC cotches

Trimethylsilylation of alcohols with HMDS	catalyzed by [Ti ^{IV} (salophen)(OTf) ₂]	at room temperature.ª
---	---	-----------------------

Entry	Hydroxy compound	TMS ether	Time (min)	Yield (%) ^b
1	CH ₂ OH	CH ₂ OSiMe ₃	1	100
	Me	Me		
2	UH	OSIMe ₃	1	90
2			1	100
3	MeO — CH ₂ OH	MeO CH ₂ OSiMe ₃	1° 1 ^d	100 96
			I ^c	95
4	CH ₂ OH	$\sim CH_2OSIMe_3$	4	95
	OMe	OMe	1	100
5	t-Bu CH ₂ OH	t-Bu — CH ₂ OSiMe ₃	1 ^c 1 ^d	99 97
	_		1 ^e	95
6	СІ——СН,ОН	Cl-CH ₂ OSiMe ₃	15	90
			15 ^c 15 ^d	90 89
			15 ^e	87
7	СH ₂ OH	CH ₂ OSiMe ₃	6	90
	O ₂ N	O ₂ N		
8	O.N CH.OH	O ₂ N CH ₂ OSiMe ₂	15	100
			15 ^c	98
			15 ^e	95 94
9	CH ₂ OH	CH ₂ OSiMe ₃	35	90
	NO ₂	NO ₂		
10	CI-CH2OH	Cl-CH ₂ OSiMe ₃	10	90
		Cl		
11	СH ₂ OH	CH ₂ OSiMe ₃	10	100
	Br	Br		
12	ОН	OSiMe,	1	100
12			1° 1 ^d	94
	`N´	N´	1 ^e	94
13	CH ₂ CH ₂ CH ₂ OH	CH ₂ CH ₂ CH ₂ OSiMe ₃	8	90
14	OH	OSiMe ₃	15	90
15	ОН	OSiMe ₃	15	95
16	ОН	OSiMe ₃	10	96
	OH	OSiMe ₃		
17			10	100
			-	

Entry	Hydroxy compound	TMS ether	Time (min)	Yield (%) ^b
18	ОН	OSiMe ₃	15	97
19	СН ₃	CH ₃	15	98
20	Me Me OH	Me Me OSiMe ₃	25	96
21	OH	OSiMe ₃	25	98

Table 2 (continued)

_

^a Reaction conditions: alcohol (1 mmol), HMDS (0.7 mmol), catalyst (1 mol%), CH₂Cl₂ (1 mL).

^b GC yield.

.

^{c-e} Data refers to second, third and fourth runs, respectively.

(Table 1). The progress of the reaction was monitored by GC or TLC. After the reaction was complete, the solvent was evaporated,

n-hexane (10 mL) was added and the catalyst was filtered off. The filtrates were washed with brine and dried over Na_2SO_4 and

Table 3 Trimethylsilylation of phenols with HMDS catalyzed by [Ti^{IV}(Salophen)(OTf)₂] at room temperature.^a

Entry	Phenol	TMS ether	Time (min)	Yield (%) ^b
1	ОН	OSiMe ₃	10	95
2	СІОН	ClOSiMe ₃	8	95
3	ОН	OSiMe ₃	8	95
	Cl	Cl		
4 ^c	но-Он	Me ₃ SiO-OSiMe ₃	20	97
5 ^c	ОН	OSiMe ₃	20	95
	OH	OSiMe ₃		
6 ^c	ОН	OSiMe ₃	20	95
	ÓH	Me ₂ SiO		
7 ^c	ОН	OSiMe ₃	1	100
	НО ОН	Me ₃ SiO OSiMe ₃		

	•)			
Entry	Phenol	TMS ether	Time (min)	Yield (%) ^b
8	O2N-OH	O ₂ N-OSiMe ₃	15	94
9	Н ₃ С-ОН	H ₃ C OSiMe ₃	15	90
10	Н ₃ С	OSiMe ₃ H ₃ C	4	95

Table 3 (continued)

^a Reaction conditions: phenol (1 mmol), HMDS (0.7 mmol), catalyst (1 mol%), CH₂Cl₂ (1 mL).

^b GC yield.

^c Reaction was performed with 0.7 mmol of HMDS per OH group.

concentrated under reduced pressure to afford the crude product. The identity of the products was verified by ¹H NMR and IR spectral data.

3. Results and discussion

3.1. Trimethylsilylation of alcohols and phenols with HMDS catalyzed by [Ti^{IV}(salophen)(OTf)₂]

The preparation route for the [Ti^{IV}(salophen)(OTf)₂] catalyst is shown in Scheme 2. First, the catalytic activity of [Ti^{IV}(salo-

phen)(OTf)₂], [Ti^{IV}(salophen)Cl₂] and [Ti^{IV}(salophen)(OPh)₂] was investigated in the silvlation of benzyl alcohol with HMDS. The results showed that the catalytic activity of these catalysts is in the following order: $[Ti^{IV}(salophen)(OTf)_2](100\%) > [Ti^{IV}(salophen)Cl_2]$ $(61\%) > [Ti^{IV}(salophen)(OPh)_2] (37\%)$. The results clearly show that introducing the OTf groups on the Ti(salophen) increases the electron-deficiency of the catalyst which in turn increases the catalytic activity of [Ti^{IV}(salophen)(OTf)₂] in the trimethylsilylation with HMDS. The reaction parameters such as catalyst amount and kind of solvent were also optimized in the reaction of benzyl alcohol with HMDS. When the same reaction was carried out using differ-

Table 4

Selective silylation of alcohols and phenols catalyzed by [Ti^{IV}(salophen)(OTf)₂] in CH₂Cl₂.^a



Reaction conditions for a binary mixture: 1 mmol of each alcohol or phenol, HMDS (0.7 mmol), catalyst (1 mol%), CH₂Cl₂ (1 mL). ^b GC yield.

Table 5

Comparison of the results obtained for the trimethylsilylation of benzyl alcohol catalyzed by [Ti^{IV}(salophen)(OTf)₂] with those obtained by the recently reported catalysts.

OH Catalyst OSiMe ₃								
Entry	Catalyst	HMDS (mmol)	Catalyst (mol%)	T (°C)	Time (min)	Yield (%)	TOF (h^{-1})	Ref.
1	[Ti ^{IV} (salophen)(OTf) ₂]	0.7	1	R.T.	1	100	6000	This work
2	ZrCl ₄	0.8	2	R.T.	1	95	2850	[5]
3	$H_{3}PW_{12}O_{40}$	0.8	1	55-60 °C	23	90	235	[9]
4	Iodine	0.8	1	R.T.	2	98	2940	[10]
5	CuSO ₄ ·5H ₂ O	0.7	1	R.T.	12	98	490	[13]
6	Sulfonic acid@nanoporous silica	0.6	3	R.T.	55	99	36	[14]
7	$MgBr_2 \cdot OEt_2$	0.6	5	R.T.	5	98	235	[15]
8	LaCl ₃	0.7	10	R.T.	3 h	91	3	[16]
9	N,N,N',N'-tetrabromobenzene-1,3-disulfonamide	1.4	4	R.T.	30	90	45	[17]
10	Fe(TFA) ₃	0.7	2.5	R.T.	5	92	442	[18]
11	Fe ₃ O ₄	1	10	R.T.	5	98	118	[19]
12	Trichloroisocyanuric acid (TCCA)	0.8	6	R.T.	4 h	90	3.8	[21]
13	HClO ₄ -SiO ₂	0.8	2.5	R.T.	2	98	1176	[22]
14	ZrO(OTf) ₂	2	0.5	R.T.	1	92	11 040	[24]

ent amounts of catalyst, the highest yield was obtained in the presence of 1 mol% of [Ti^{IV}(salophen)(OTf)₂]. A lower amount of catalyst did not improve the yield of the product even after longer reaction time. In order to choose the reaction media, the above mentioned reaction was performed in different solvents. Among CH_2Cl_2 , CH_3CN , EtOAc and *n*-hexane and chloroform, the highest yield was observed in CH_2Cl_2 . Since, the catalyst has a heterogeneous nature in CH_2Cl_2 , therefore, the catalyst reusability in this solvent is simpler, and therefore dichloromethane was used as solvent.

Under the optimized reaction conditions, a wide range of alcohols including primary (benzylic and linear ones), secondary and tertiary alcohols were successfully trimethylsilylated with HMDS in the presence of [Ti^{IV}(salophen)(OTf)₂]. In the case of benzylic alcohols, electron-withdrawing substituents require longer reaction times for completion, while benzylic alcohols bearing electron-donating substituents were completed in shorter reaction times (Table 2). The results in Table 2 also show that steric hindrance of *ortho* substituents did not affect the reaction time. The only exception is 2-nitrobenzyl alcohol. It seems that intramolecular hydrogen bonding between hydroxyl and nitro groups reduces the acidity of alcohol and therefore the silylation require longer reaction time.

In the case of linear, secondary and tertiary alcohols the reaction times were longer in comparison with benzylic alcohols.

The trimethylsilylation of phenols was also investigated and the corresponding TMS-ethers were produced in high yields (Table 3).

Due to the high catalytic activity of [Ti^{IV}(salophen)(OTf)₂] in the trimethylsilylation of both alcohols and phenols, therefore, we decided to investigate the chemoselectivity of the presented method. In this manner, a set of competitive reactions was conducted between primary or secondary and tertiary alcohols or phenols (Table 4). The results indicated that primary alcohols are more reactive in the presence of secondary or tertiary alcohols and also phenols. It is important to note that due to the lesser nucleophilicity of sterically hindered alcohols and phenols in comparison with primary benzylic alcohols, only primary benzylic alcohols were silylated with 0.7 mmol of HMDS (Table 4, entries 1, 2 and 4). However, in the presence of 1.1 mmol of HMDS, both phenol and benzyl alcohol were silylated completely.

In order to show the effectiveness of the presented method in the silylation reactions, we compared the obtained results in the trimethylsilylation of benzyl alcohol with HMDS catalyzed by $[Ti^{IV}(salophen)(OTf)_2]$ with some of those reported in the literature

(Table 5). Some of catalysts such as sulfonic acid@nanoporous silica [14], LaCl₃ [16] and TCCA [21] need long reaction times (1–4 h). H₃PW₁₂O₄₀ needs high temperature [9]. *N*,*N*,*N*',*N*'-tetrabromobenzene-1,3-disulfonamide [17] and ZrO(OTf)₂ [24] were carried out with high amounts of HMDS. ZrCl₄ is degraded in the presence of moisture [5]. SiMe₃Cl is carcinogen [4]. MgBr₂·OEt₂ [15], LaCl₃ [16], Fe₃O₄ [19] and TCCA [21] need high catalyst amount (5– 10%). Except ZrO(OTf)₂ [24], which needs 2 mmol HMDS, the [Ti^{IV}(salophen)(OTf)₂] is much efficient than the others and higher TOF was observed. On the other hand, simple preparation of the catalyst, short reaction times, using low catalyst amount and HMDS, high product yields and the reusability of the catalyst are noteworthy advantages of this catalytic system.

3.2. Catalyst reusability

Finally, the reusability of the catalyst was tested in the reaction of 4-chlorobenzyl alcohol as a model substrate. It was observed that the activity of catalyst did not decrease after four consecutive times (Table 2, entry 6). For a complete study, the reusability of catalyst was also investigated in the trimethylsilylation of different substrates such as 4-methoxybenzyl alcohol (Table 2, entry 3), 4*tert*-butylbenzyl alcohol (Table 2, entry 5), 3-pyridylmethanol (Table 2, entry 8) and 4-nitrobenzyl alcohol (Table 2, entry 12) with HMDS. As can be seen, the results are as same as for 4-chlorobenzyl alcohol.

Acknowledgement

The partial support of this work by University of Isfahan and the Islamic Azad University is gratefully acknowledged.

References

- T.W. Greene, P.G.M. Wuts, Protective Groups in Organic Synthesis, second ed., Wiley, New York, 1991.
- [2] P.J. Kocienski, in: R. Enders, R. Noyori, B.M. Trost (Eds.), Protective Groups, Thieme, Stuttgart, 1994.
- [3] C.A. Bruyenes, T.K. Jurriens, J. Org. Chem. 47 (1982) 3966.
- [4] P. Gautret, S. El-Ghammarti, A. Legrand, D. Coutrier, B. Rigo, Synth. Commun. 26 (1996) 707.
- [5] F. Shirini, E. Mollarazi, Catal. Commun. 8 (2007) 1393.
- [6] H. Firouzabadi, B. Karimi, Synth. Commun. 23 (1993) 1633.
- [7] Z.H. Zhang, T.S. Li, F. Yang, C.G. Fu, Synth. Commun. 28 (1998) 3105.
- [8] M.R. Saidi, N. Azizi, Organometallics 23 (2004) 1457.
- [9] H. Firouzabadi, N. Iranpoor, K. Amani, F. Nowrouzi, J. Chem. Soc., Perkin Trans. 1 (2002) 2601.

- [10] B. Karimi, B. Golshani, J. Org. Chem. 65 (2000) 7228.
- [11] J.S. Yadav, B.V.S. Reddy, A.K. Basak, G. Baishya, A. Venkat Narsaiah, Synthesis (2006) 3831.
- [12] M. Curini, F. Epifano, M.C. Marcotullio, O. Rosati, Synth. Commun. 29 (1999) 541.
- [13] B. Akhlaghinia, S. Tavakoli, Synthesis (2005) 1775.
- [14] D. Zareyeea, B. Karimi, Tetrahedron Lett. 48 (2007) 1277.
- [15] M.M. Mojtahedi, H. Abbasi, M.S. Abaee, J. Mol. Catal. A: Chem. 250 (2006) 6.
- [16] A.V. Narsaiah, J. Organomet. Chem. 692 (2007) 3614.
- [17] R. Ghorbani-Vaghei, M.A. Zolfigol, M. Chegeny, H. Veisi, Tetrahedron Lett. 47 (2006) 4505.
- [18] H. Firouzabadi, N. Iranpoor, A.A. Jafari, M.R. Jafari, J. Organomet. Chem. 693 (2008) 2711.
- [19] M.M. Mojtahedi, M.S. Abaee, M. Eghtedari, Appl. Organomet. Chem. 22 (2008) 529.
- [20] F. Shirini, M. Abedini, J. Iran. Chem. Soc. 5 (2008) S87.
- [21] A. Khazaei, M.A. Zolfigol, A. Rostami, A. Ghorbani Choghamarani, Catal. Commun. 8 (2007) 543.
- [22] H.R. Shaterian, F. Shahrekipoor, M. Ghashang, J. Mol. Catal. A: Chem. 272 (2007) 142.
- [23] E. Shirakawa, K. Hironaka, H. Otsuka, T. Hayashi, Chem. Commun. (2006) 3927.
 [24] M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork, S.
- Chahardahcheric, Z. Tavakoli, J. Organomet. Chem. 693 (2008) 2041.
- [25] N. Azizi, R. Yousefi, M.R. Saidi, J. Organomet. Chem. 691 (2006) 817.
- [26] A. Ghorbani-Choghamarani, N. Cheraghi-Fathabad, Chin. J. Catal. 31 (2010) 1103.
- [27] A. Ghorbani-Choghamarani, M.A. Zolfigol, M. Hajjami, Kh. Darvishi, L. Gholamnia, Collec. Czech. Chem. Commun. 75 (2010) 607.
- [28] A. Ghorbani-Choghamarani, K. Amani, M.A. Zolfigol, M. Hajjami, R. Ayazi-Nasrabadi, J. Chin. Chem. Soc. 56 (2009) 255.
- [29] A. Rostami, F. Ahmad-Jangi, M.R. Zarebin, J. Akradi, Synth. Commun. 40 (2010) 1500.
- [30] M.A. Zolfigol, A. Khazaei, E. Kolvari, N. Koukabi, H. Soltani, M. Behjunia, Helv. Chim. Acta 93 (2010) 587.
- [31] N.S. Venkataramanan, G. Kuppuraj, S. Rajagopal, Coord. Chem. Rev. 249 (2005) 1249.
- [32] M. Strianese, M. Lamberti, M. Mazzeo, C. Tedesco, C. Pellecchia, J. Mol. Catal. A: Chem. 258 (2006) 284.
- [33] A. Soriente, M. De Rosa, M. Lamberti, C. Tedesco, A. Scettri, C. Pellecchi, Mol. Catal. A: Chem. 235 (2005) 253.
- [34] Z. Zhou, Z. Li, W. Quanyong, B. Liu, K. Li, G. Zhao, Q. Zhou, C. Tang, J. Organomet. Chem. 691 (2006) 5790.
- [35] E.N. Jacobsen, F. Kakiuchi, R.G. Konsler, J.F. Larrow, M. Tokunaga, Tetrahedron Lett. 38 (1997) 773.

- [36] M. Tokunaga, J.F. Larrow, F. Kakiuchi, E.N. Jacobsen, Science 227 (1997) 936.
- [37] A. Gama, L.Z. Flores-López, G. Aguirre, M. Parra-Hake, R. Somanathan, T. Cole, Tetrahedron:Asymmetry 16 (2005) 1167.
- [38] S. Liang, X.R. Bu, J. Org. Chem. 67 (2002) 2702.
- [39] M. De Rosa, M. Lamberti, C. Pellecchia, A. Scettri, R. Villano, A. Soriente, Tetrahedron Lett. 47 (2006) 7233.
- [40] J. Sun, F. Yuan, M. Yang, Y. Pan, C. Zhu, Tetrahedron Lett. 50 (2009) 548.
- [41] X. Jia, L. Yin, X. Zhao, X.S. Li, Chin. Chem. Lett. 18 (2007) 275.
- [42] A. Chatterjee, T.H. Bennur, N.N. Joshi, J. Org. Chem. 68 (2003) 5668.
- [43] S. Tangestaninejad, M.H. Habibi, V. Mirkhani, M. Moghadam, Synth. Commun. 32 (2002) 1337.
 [44] M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork, R.
- Shaibani, J. Mol. Catal. A: Chem. 219 (2004) 73. [45] M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork, R.
- S.A. Taghavi, J. Mol. Catal. A: Chem. 274 (2007) 217.
- [46] K. Suda, M. Sashima, M. Izutsu, F. Hino, J. Chem. Soc., Chem. Commun. (1994) 949.
- [47] T. Takanami, R. Hirabe, M. Ueno, F. Hino, K. Suda, Chem. Lett. (1996) 1031.
- [48] T. Takanami, M. Hayashi, K. Iso, H. Nakamoto, K. Suda, Tetrahedron 62 (2006) 9467.
- [49] T. Takanami, M. Hayashi, K. Suda, Tetrahedron Lett. 46 (2005) 2893.
- [50] K. Suda, K. Baba, S. Nakajima, T. Takanami, Chem. Commun. (2002) 2570.
- [51] K. Suda, T. Kikkawa, S. Nakajima, T. Takanami, J. Am. Chem. Soc. 126 (2004) 9554.
- [52] S. Tangestaninejad, M.H. Habibi, V. Mirkhani, M. Moghadam, J. Chem. Res. (S) (2001) 365.
- [53] M. Moghadam, S. Tangestaninejad, V. Mirkhani, R. Shaibani, Tetrahedron 60 (2004) 6105.
- [54] S. Gharaati, M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork, F. Kosari, Inorg. Chim. Acta 363 (2010) 1995.
- [55] M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork, S. Gharaati, Appl. Organomet. Chem. 23 (2009) 446.
- [56] M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork, S.A. Taghavi, Catal. Commun. 8 (2007) 2087.
- [57] M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork, S. Gharaati, Polyhedron 29 (2010) 212.
- [58] M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork, S. Gharaati, Inorg. Chim. Acta 363 (2010) 1523.
- [59] S.A. Taghavi, M. Moghadam, I. Mohammadpoor-Baltork, S. Tangestaninejad, V. Mirkhani, A.R. Khosropour, V. Ahmadi, Polyhedron 30 (2011) 2244.
- [60] K. Suda, S. Nakajima, Y. Satoh, T. Takanami, Chem. Commun. (2009) 1255.
- [61] H. Chen, P.S. White, M.R. Gagne, Organometallics 17 (1998) 5358.