Tetrahedron Letters 53 (2012) 5773-5776

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

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



Solvent-free Heck and copper-free Sonogashira cross-coupling reactions catalyzed by a polystyrene-anchored Pd(II) phenyldithiocarbazate complex

Mohammad Bakherad*, Ali Keivanloo, Shahrzad Samangooei

School of Chemistry, Shahrood University of Technology, Shahrood, Iran

ARTICLE INFO

Article history: Received 15 May 2012 Revised 27 July 2012 Accepted 15 August 2012 Available online 24 August 2012

Keywords: Heck reaction Sonogashira reaction Aryl halides Polystyrene-anchored Pd(II) phenyldithiocarbazate complex

ABSTRACT

A new polystyrene-anchored Pd(II) phenyldithiocarbazate complex is synthesized and characterized. This Pd-complex behaves as an efficient heterogeneous catalyst in the Heck coupling and copper-free Sono-gashira coupling reactions under aerobic conditions. Furthermore, the catalyst shows good thermal stability and recyclability.

© 2012 Elsevier Ltd. All rights reserved.

Palladium-catalyzed cross-coupling reactions for the formation of carbon–carbon bonds have emerged as a powerful method in organic synthesis.¹ Among them, the Mizoroki–Heck² and Sonogashira³ reactions play important roles in modern synthetic chemistry. The reactions generally proceed in the presence of a homogeneous palladium catalyst, which makes separation and recovery of the catalyst tedious, if not impossible, and might result in unacceptable palladium contamination of the products.

From the standpoint of environmentally benign organic synthesis, the development of highly active and easily reusable immobilized catalysts, and the use of solvent-free reactions instead of organic solvents are of significant interest to chemists. Solid-phase organopalladium metal complexes, having high activity and selectivity, offer several practical advantages in synthetic and industrial chemistry, among which, the ease of separation of the catalyst from the desired reaction products and the ease of recovery and reuse of the catalyst are most important.

Palladacycles have emerged as a promising class of catalysts or catalyst precursors for Pd-catalyzed C–C bond forming reactions such as the Heck–Mizoroki⁴ and Sonogashira⁵ reactions.

To date, many efforts have been made to search for more efficient ligands, the most common ligands used for these coupling reactions being phosphine-based examples.⁶ Since most of the phosphine-based ligands are air and/or moisture-sensitive, phosphine-free ligands such as N-heterocyclic carbenes (NHCs) have been employed.⁷

* Corresponding author. *E-mail address:* m.bakherad@yahoo.com (M. Bakherad). Immobilization methods used to deposit palladium onto heterogeneous solid beds have been studied extensively, and diverse supports such as clay,⁸ carbon nanofiber,⁹ Montmorillonite K-10,¹⁰ magnetic mesoporous silica,¹¹ zeolite,¹² and metal oxides¹³ have been investigated.

Polystyrene-supported palladium catalysts have successfully been used for Heck¹⁴ and Suzuki¹⁵ reactions, and have shown lower levels of palladium leaching during cross-coupling. To date, several palladium complexes on functionalized polystyrene supports have been prepared and successfully used in Sonogashira reactions.¹⁶

Our approach was guided by three imperatives: (1) the support should be easily accessible; (2) the reaction should be carried out using readily available and cheap reagents; and (3) the ligand anchored on the support should be air-stable at room temperature, which should allow its storage with a very long shelf-life in standard bottles.

In continuation of our interest in the development of new ligands for Pd-catalyzed C–C bond forming reactions,¹⁷ we report the synthesis and characterization of a new polystyrene-anchored Pd(II) dithiocarbazate complex catalyst **2**, and illustrate its application in Heck and Sonogashira coupling reactions under aerobic conditions. The catalyst shows high activity in the coupling reactions of various aryl halides. Furthermore, its ease of recovery and excellent recycling efficiency make it an ideal system for coupling reactions. The procedure followed to obtain the catalyst is shown in Scheme 1.

Chloromethylated polystyrene (cross-linked with 2% divinylbenzene, 4–5% Cl content, 1.14–1.40 mmol/g Cl) was treated with

^{0040-4039/\$ -} see front matter © 2012 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.tetlet.2012.08.065





Table 1

Optimization of the conditions for the Heck reaction of iodobenzene with methyl acrylate^a

	+ H ₂ C=/CO ₂ Me	Pd-catalyst 2 base, 70 °C	CO ₂ Me
3 a	4a		5a
Entry	Base	Cat (mol %)	Yield ^b (%)
1	DIPEA ^c	1	87
2	Et ₃ N	1	98
3	Pyridine	1	90
4	Piperidine	1	80
5	Pyrrolidine	1	83
6	КОН	1	81
7	Na ₂ CO ₃	1	75
8	K ₂ CO ₃	1	88
9 ^d	Et ₃ N	1	60
10	Et ₃ N	0.5	90

 $^{\rm a}$ Conditions: iodobenzene (1.0 mmol), methyl acrylate (1.2 mmol), base (1.0 mmol), 5 h, 70 °C.

^b GC yield.

^c Diisopropylethylamine.

^d Reaction at 25 °C.

phenylhydrazine and carbon disulfide in the presence of KOH in DMF at 80 °C to produce the corresponding polystyrene-anchored phenyldithiocarbazate ligand **1**. This was then reacted with PdCl₂(PhCN)₂ in DMF at 80 °C to yield the polystyrene-anchored Pd(II) phenyldithiocarbazate complex **2**. Catalyst **2** was characterized by FT-IR, SEM, and ICP.

The IR spectrum of polystyrene-anchored phenyldithiocarbazate ligand **1** showed a band around 3460 cm^{-1} due to the N–H vibrations. The sharp C–Cl peak (due to $-\text{CH}_2\text{Cl}$ groups) at 1264 cm⁻¹ in the starting polymer was not present or was observed as a weak band after introduction of the phenyldithiocarbazate ligand. The N-content of the resin was calculated to be 2.01% (0.72 mmol/g), which indicated that only 51–63% of the total chlorines had been substituted by phenyldithiocarbazate. The amount of palladium incorporated into the catalyst **2** was determined by inductively coupled plasma (ICP), which gave a value of 0.24 mmol/g for the heterogeneous catalyst.

We applied the polystyrene-anchored Pd(II) phenyldithiocarbazate complex **2** as the catalyst in Heck and Sonogashira reactions. Initial studies were performed on the Heck coupling reaction of iodobenzene (**3a**) with methyl acrylate (**4a**) as a model reaction using complex **2** (1 mol %) as the catalyst at 70 °C over five hours (Table 1). Of the bases screened, Et₃N gave the best result, and the corresponding coupled product **5a** was obtained in 98% GC yield (Table 1, entry 2). The reaction was also studied at 25 °C Table 2

Heck reactions of aryl halides with alkenes using Pd-catalyst 2^a



 a Conditions: aryl halide (1.0 mmol), alkene (1.2 mmol), Pd-catalyst ${\bf 2}$ (0.01 mmol), Et_3N (1.0 mmol), 5 h, 70 °C.

^b GC yield. Isolated yields are given in parentheses.

which was accompanied by extension of the reaction time to 10 h with production of the desired product in 60% yield (entry 9). A lower palladium concentration gave a decreased yield of the product (entry 10).

The optimized conditions were as follows aryl halide (1.0 mmol), alkene (1.2 mmol), Et_3N (1.0 mmol), and polystyreneanchored Pd(II) phenyldithiocarbazate complex **2** (1.0 mol %) under solvent-free conditions at 70 °C for 5 h.

As shown in Table 2, a range of aryl iodides was reacted with methyl acrylate or styrene to give the desired products **5** in excellent yields. The nature of the substituent, either an electron-donating group such as methoxy (entry 4), or an electron-withdrawing group such as Cl or NO₂ (entries 2, 3, and 6) on the phenyl ring of **3** had no significant effect on the reaction outcome. The reactions of iodobenzene and *p*-nitroiodobenzene with styrene gave *trans*-stilbenes **5e** and **5f** in 96% and 98% GC yields, respectively (Table 2, entries 5 and 6).

As expected, aryl iodides were more reactive than aryl bromides, and the substituent effects on the aryl iodides appeared to be less significant than those of the aryl bromides. As shown in Table 2, activated aryl bromides such as *p*-nitrobromobenzene underwent the Heck reaction with methyl acrylate and styrene under similar conditions to afford the corresponding products in 98% and 92% GC yields, respectively (entries 8 and 11), whereas, reaction of *p*-bromoanisole (an unactivated aryl bromide) with methyl acrylate gave product **5d** in 88% GC yield (entry 9).

Another important Pd-catalyzed coupling reaction is the alkynylation of aryl halides, that is, the Sonogashira reaction. The application of this reaction is to be found in the synthesis of numerous natural products including enediyne antibiotics. Thus we investigated the polystyrene-anchored Pd(II) phenyldithiocarbazate complex catalytic system 2 for the copper-free Sonogashira coupling reaction. Since no copper salt was used, the undesired formation of oxidative homocoupling divne products was avoided. We employed the solvent- and copper-free coupling reaction of iodobenzene (1.0 mmol) with phenylacetylene (1.0 mmol) as a model reaction using complex 2 (1 mol %) as the catalyst at room temperature to study the effect of the base on the reaction (Table 3). Among various bases, pyridine was found to be the best (entry 3). The reaction worked well when organic bases were used. Inorganic bases such as KOH, K₂CO₃, and Na₂CO₃ were less effective. A lower palladium concentration gave a decreased yield (entry 9).

Tab	le 3
Opt	imization of the conditions for the Sonogashira reaction of phenylacetylene with
iodo	benzene ^a

Entry	Base	Cat (mol %)	Yield ^b (%)
1	Et ₃ N	1.0	87
2	DIPEA	1.0	85
3	Pyridine	1.0	99
4	Piperidine	1.0	78
5	Pyrrolidine	1.0	93
6	КОН	1.0	65
7	K ₂ CO ₃	1.0	70
8	Na_2CO_3	1.0	50
9	Pyridine	0.5	82

^a Conditions: phenylacetylene (1.0 mmol), iodobenzene (1.0 mmol), base (1.0 mmol), room temperature, 3 h.

^b GC yield.

Table 4

Copper-free Sonogashira reactions of terminal alkynes with aryl halides^a



Entry	R	Х	Y	Product	Yield ^b (%)
1	Ph	I	Н	8a	99 (97)
2	Ph	Ι	4-NO ₂	8b	100 (96)
3	Ph	Ι	3-NO ₂	8c	100 (98)
4	Ph	Ι	4-Cl	8d	97
5	Ph	Ι	4-Br	8e	96
6	Ph	Ι	4-COCH ₃	8f	99
7	Ph	I	$4-OCH_3$	8g	97
8	$n-C_4H_9$	I	Н	8h	90
9	$n-C_4H_9$	I	4-NO ₂	8i	98 (95)
10	$n-C_4H_9$	Ι	$4-OCH_3$	8j	95
11	CH ₂ OH	Ι	Н	8k	94
12	CH ₂ OH	Ι	4-NO ₂	81	98 (96)
13	CH ₂ OH	Ι	$4-OCH_3$	8m	95
14	Ph	Br	Н	8a	96
15	Ph	Br	4-NO ₂	8b	98
16	Ph	Br	3-NO ₂	8c	97 (94)
17	Ph	Br	4-CN	8n	98
18	Ph	Br	4-F	80	94
19	Ph	Br	$4-OCH_3$	8g	94
20	$n-C_4H_9$	Br	Н	8h	93
21	$n-C_4H_9$	Br	4-NO ₂	8i	95 (91)
22	$n-C_4H_9$	Br	$4-OCH_3$	8j	91
23	CH ₂ OH	Br	Н	8k	93
24	CH ₂ OH	Br	4-NO ₂	81	97 (93)
25	CH ₂ OH	Br	4-0CH ₃	8m	95

^a Reaction conditions: aryl halide (1.0 mmol), terminal alkyne (1.0 mmol), Pdcatalyst **2** (0.01 mmol), pyridine (1.0 mmol), 3 h, room temperature, aerobic conditions.

^b GC yield. Isolated yields are given in parentheses.

The heterogeneous catalytic copper-free Sonogashira coupling was also examined with a variety of iodo and bromoarenes under the reaction conditions identified above, which exhibited wide substrate tolerance. Representative results are summarized in Table 4. Reaction of aryl iodides with electron-withdrawing substituents such as nitro and acetoxy (Table 4, entries 2, 3, and 6) with phenylacetylene gave excellent yields of expected products, while aryl iodides with electron-donating groups such as methoxy (entry 7) gave the corresponding coupling product in a slightly lower yield.*p*-Chloroiodobenzene and *p*-bromoiodobenzene also underwent the Sonogashira coupling reaction with phenylacetylene under similar conditions to afford the corresponding biarylacetylenes **8d** and **8e** in good yields (entries 4 and 5). When the less

Table 5

Heck and Sonogashira reactions catalyzed by the recycled catalyst^a

Cycle	Heck yield ^b (%)	Sonogashira yield ^b (%)
1	98	99
2	98	99
3	97	98
4	95	96
5	93	95
	Cycle 1 2 3 4 5	Cycle Heck yield ^b (%) 1 98 2 98 3 97 4 95 5 93

^a Reaction conditions: iodobenzene (1.0 mmol), methyl acrylate (Heck reaction) (1.2 mmol), iodobenzene (1.0 mmol), phenylacetylene (Sonogashira reaction) (1.0 mmol), Pd-catalyst **2** (0.01 mmol), base (1.0 mmol), 70 °C (for Heck reactions), room temperature (for Sonogashira reactions).

^b GC yield.

reactive acetylenes, 1-hexyne, and propargyl alcoho1 were used, the expected coupling products were produced efficiently.

The coupling of *para*-substituted iodobenzenes having nitro and methoxy groups took place with 1-hexyne to give the corresponding products **8i** and **8j** in 98% and 95% GC yields, respectively (entries 9 and 10). The coupling of propargyl alcohol with the more reactive electron-withdrawing *p*-nitroiodobenzene gave an excellent yield of product (entry 12). Under the same conditions, less active, electron-rich *p*-iodoanisole produced a very high 95% GC yield of alkyne **8m** (entry 13).

We next investigated the coupling of various aryl bromides with terminal alkynes. As shown in Table 4, high catalytic activity was observed in the coupling of aryl bromides possessing electrondonating groups such as *p*-bromoanisole (entries 19, 22, and 25). Moreover, *p*-nitrobromobenzene, *m*-nitrobromobenzene, and *p*-bromobenzonitrile having electron-deficient aromatic rings also underwent the Sonogashira coupling reaction with terminal alkynes under similar conditions to afford the corresponding products in excellent yields.

The reusability of the catalyst was tested in reactions of iodobenzene with methyl acrylate (Heck reaction), and iodobenzene with phenyl acetylene (Sonogashira reaction) as representatives in the presence of 1.0 mol % of polystyrene-anchored Pd(II) phenyldithiocarbazate complex **2**. After the first run, the catalyst was separated by filtration, washed thoroughly with ethanol and acetonitrile, and dried at room temperature. The dried catalyst was then reused with a fresh reaction mixture without any further activation. The catalyst could be almost completely recovered and was recycled an additional four times without any significant loss of activity (Table 5).

In conclusion, we have developed a clean and safe protocol for Heck and copper-free Sonogashira reactions catalyzed by polystyrene-anchored Pd(II) phenyldithiocarbazate complex **2** under aerobic conditions. The catalyst shows not only high catalytic activity, but also offers many practical advantages such as air and thermal stability and it can be recycled. The catalyst was used for five consecutive cycles with consistent activity. The excellent catalytic performance and easy preparation and separation of the catalyst make it a valuable heterogeneous system, and potentially a useful alternative to other heterogeneous palladium catalysts.

Preparation of polystyrene-anchored Pd(II) phenyldithiocarbazate complex 2

To a 250 ml round bottom flask equipped with a magnetic stir bar and containing DMF (30 ml) were added chloromethylated polystyrene (2 g, 1.25 mmol/g of Cl), phenylhydrazine (5.0 mmol), KOH (5.0 mmol), and carbon disulfide (5.0 mmol). The mixture was stirred for 10 h at 80 °C and was subsequently filtered and washed thoroughly with DMF, and dried in vacuo for 12 h. Phenyldithiocarbazate-functionalized polymer **1** (2.0 g) was treated with PdCl₂(PhCN)₂ (2.0 g) in DMF, and the mixture heated at 80 °C for 15 h. The resulting bright yellow colored polymer, impregnated with the metal complex, was filtered and washed with MeCN to give the Pd-catalyst **2** (Scheme 1).

General procedure for the Heck reaction

A mixture of aryl halide (1.0 mmol), alkene (1.2 mmol), Pd-catalyst **2** (0.01 mmol), and Et₃N (1.0 mmol) was stirred at 70 °C for 5 h. After completion of the reaction, the mixture was filtered to recover the catalyst. The polymer was washed with EtOH and MeCN, vacuum dried, and reused. After GC analysis, the solvent was removed under vacuum, and the crude product was subjected to silica gel column chromatography using CHCl₃–CH₃OH (98:2) as eluent to afford the pure product.

Compound 5a

¹H NMR (CDCl₃, 300 MHz) δ 3.80 (s, 3H, OMe), 6.44 (d, *J* = 16.1 Hz, 1H), 7.35–7.38 (m, 3H, Ar), 7.52–7.56 (m, 2H, Ar), 7.68 (d, *J* = 16.1Hz, 1H).

Compound 5b

¹H NMR (CDCl₃, 300 MHz) δ 3.83(s, 3H, OMe), 6.31 (d, *J* = 15.9 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 2H, Ar), 7.55 (d, *J* = 8.5 Hz, 2H, Ar), 7.65 (d, *J* = 15.9 Hz, 1H).

General procedure for the Sonogashira coupling reaction

The aryl halide (1.0 mmol) and terminal alkyne (1.0 mmol) were added to a mixture of Pd-catalyst **2** (0.01 mmol) and pyridine (1.0 mmol) in a glass flask with vigorous stirring. The mixture was stirred at room temperature for 3 h under aerobic conditions. The mixture was filtered to recover the catalyst and the polymer was washed with EtOH and MeCN, vacuum dried, and reused. After GC analysis, the solvent was removed under vacuum, and the crude product was subjected to silica gel column chromatography using CHCl₃-CH₃OH (98:2) as eluent to afford the pure product.

Compound 8a

 $^{1}\mathrm{H}$ NMR (CDCl₃, 300 MHz) δ 7.55–7.51 (m, 4H), 7.36–7.29 (m, 6H).

Compound 8b

¹H NMR (CDCl₃, 300 MHz) δ 7.34–7.44 (m, 3H), 7.52–7.58 (m, 2H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.92 (d, *J* = 8.3 Hz, 2H).

Acknowledgement

We are grateful to the Research Council of Shahrood University of Technology for the financial support of this work.

References and notes

- Negishi, E.; de Meijere, A. Handbook of Organopalladium Chemistry for Organic Synthesis; Wiley-Interscience: New York, 2002.
- (a) Heck, R. F. J. Am. Chem. Soc. 1968, 90, 5518; (b) Heck, R. F.; Nolley, J. P. J. Org. Chem. 1972, 37, 2320; (c) Beletskaya, I. P.; Cheprakov, A. V. Chem. Rev. 2000, 100, 3009; (d) Yi, L.; Liebscher, J. Chem. Rev. 2007, 107, 133.
- (a) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *16*, 4467; (b) Negishi, E.; Anastasia, L. *Chem. Rev.* **1979**, 2003, 103; (c) Nicolaou, K. C.; Bulger, P. G.; Sarlah, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 4442; (d) Urgaonkar, S.; Verkade, J. G. *J. Org. Chem.* **2004**, 69, 5752.
- (a) Heck, R. F. Acc. Chem. Res. **1979**, *12*, 146; (b) Crisp, G. T. Chem. Soc. Rev. **1998**, 27, 427; (c) Hagiwara, H.; Sugawara, Y.; Isobe, K.; Hoshi, T.; Suzuki, T. Org. Lett. **2004**, 6, 2325; (d) Deshmukh, R. R.; Rajagopal, R.; Srinivasan, K. V. Chem. Commun. **2001**, *33*, 1544; (e) Whitcombe, N. J.; Hii, K. K. M.; Gibson, S. E. Tetrahedron **2001**, 57, 7449; (f) Yao, Q.; Kinney, E. P.; Yang, Z. J. Org. Chem. **2003**, 68, 7528; (g) Alonso, D. A.; Nájera, C.; Pacheco, M. C. Adv. Synth. Catal. **2002**, 344, 172; (h) Yao, Q.; Kinney, E. P.; Zheng, C. Org. Lett. **2004**, *6*, 2997.
- 5. (a) Herrmann, W. A.; Reisinger, C.-P.; Spiegler, M. J. Organomet. Chem. 1998, 557, 93; (b) McGuinness, D. S.; Cavell, K. J. Organometallics 2000, 19, 741; (c) Bohm, V. P. W.; Herrmann, W. A. Eur. J. Org. Chem. 2000, 3679; (d) Hundertmark, T.; Littke, A. F.; Buchwald, S. L.; Fu, G. C. Org. Lett. 2001, 201, 634, 39; (f) Kollhofer, A.; Plenio, H. Chem. Eur. J. 2003, 1056, 42.
- (a) Phan, N. T. S.; Van Der Sluys, M.; Jones, C. W. Adv. Synth. Catal. 2006, 348, 609; (b) Andersen, N. G.; Keay, B. A. Chem. Rev. 2001, 101, 997; (c) Martin, R.; Buchwald, S. L. Acc. Chem. Res. 2008, 41, 1461.
- (a) Zhang, X.-Q.; Qiu, Y.-P.; Rao, B.; Luo, M.-M. Organometallics **2009**, *28*, 3093;
 (b) Morgan, B. P.; Galdamez, G. A.; Gilliard, R. J., Jr.; Smith, R. C. Dalton Trans. **2009**, 2020; (c) Zhou, Y.-B.; Xi, Z.-X.; Chen, W.-Z.; Wang, D.-Q. Organometallics **2008**, *27*, 5911; (d) Broggi, J.; Clavier, H.; Nolan, S. P. Organometallics **2008**, *27*, 5525; (e) Diebolt, O.; Braunstein, P.; Nolan, S. P.; Cazin, C. S. J. Chem. Commun. **2008**, 3190.
- 8. Datta, K. K. R.; Eswaramoorthy, M.; Rao, C. N. R. J. Mater. Chem. 2007, 17, 613.
- Zhu, J.; Zhou, J.; Zhao, T.; Zhou, X.; Chen, D.; Yuan, W. Appl. Catal. A: Gen. 2009, 352, 243.
- 10. Sidhpuria, K. B.; Patel, H. A.; Parikh, P. A.; Bahadur, P.; Bajaj, H. C.; Jasra, R. V. *Appl. Clay Sci.* **2009**, *42*, 386.
- 11. Li, J.; Zhang, Y.; Han, D.; Gao, Q.; Li, C. J. Mol. Catal. A: Chem. 2009, 298, 31.
- 12. Choi, M.; Lee, D. H.; Ryoo, R. Angew. Chem., Int. Ed. 2009, 48, 3673.
- 13. Pillai, U. R.; Sahle-Demessite, E.; Baiker, A. Green Chem. 2004, 6, 161.
- 14. Phan, N. T. S.; Brown, D. H.; Adams, H.; Spey, S. E.; Styring, P. Dalton Trans. 2004, 1348.
- (a) Phan, N. T. S.; Brown, D. H.; Styring, P. Tetrahedron Lett. 2004, 45, 7915; (b) Byun, J. W.; Lee, Y. S. Tetrahedron Lett. 1837, 2004, 45; (c) Vassylyev, O.; Chen, J.; Panarello, A. P.; Khinast, J. G. Tetrahedron Lett. 2005, 46, 863; (d) Shimizu, K.; Koizumi, S.; Hatamachi, T.; Yoshida, H.; Komai, S.; Kodama, T.; Kitayama, Y. J. Catal. 2004, 228, 141.
- (a) Bakherad, M.; Bahramian, B.; Keivanloo, A.; Kamali, A. T. J. Braz. Chem. Soc. 2009, 20, 907; (b) Bakherad, M.; Bahramian, B.; Isfahani, H. N.; Keivanloo, A.; Doostmohammadi, N. J. Heterocycl. Chem. 2009, 46, 100; (c) Bakherad, M.; Bahramian, B.; Isfahani, H. N.; Keivanloo, A.; Sang, G. Chin. J. Chem. 2009, 27, 353; (d) Datta, A.; Ebert, K.; Plenio, H. Organometallics 2003, 22, 4685; (e) Uozumi, Y.; Kobayashi, Y. Heterocycles 2003, 29, 1255; (f) Lin, C.-A.; Luo, F.-T. Tetrahedron Lett. 2003, 44, 7565; (g) Gonthier, E.; Breinbauer, R. Synlett 2003, 1049.
- (a) Bakherad, M.; Keivanloo, A.; Bahramian, B.; Mihanparast, S. *Tetrahedron Lett.* 2009, *50*, 6418; (b) Bakherad, M.; Keivanloo, A.; Bahramian, B.; Jajarmi, S. *Appl. Cat. A.* 2011, *390*, 135; (c) Bakherad, M.; Keivanloo, A.; Bahramian, B.; Rajaie, M. *Tetrahedron Lett.* 2010, *51*, 33; (d) Bakherad, M.; Keivanloo, A.; Bahramian, B.; Jajarmi, S. *Synlett* 2011, 311; (e) Bakherad, M.; Amin, A. H.; Keivanloo, A.; Bahramian, B.; Raeissi, M. *Tetrahedron Lett.* 2010, *51*, 5653.