Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

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

Immobilized palladium nanoparticles on silica—starch substrate (PNP—SSS): As a stable and efficient heterogeneous catalyst for synthesis of *p*-teraryls using Suzuki reaction

Ali Khalafi-Nezhad*, Farhad Panahi*

Department of Chemistry, College of Sciences, Shiraz University, Shiraz 71454, Iran

ARTICLE INFO

Article history: Received 12 May 2012 Received in revised form 9 July 2012 Accepted 26 July 2012

Keywords: Palladium nanoparticles Suzuki reaction Heterogeneous catalyst Silica–starch substrate p-Teraryls

1. Introduction

There are many natural products, pharmaceuticals, and advanced materials with biaryl structural units which possess interesting pharmacological or physical properties [1]. p-Terphenyls have received considerable attention, due to their presence as a structural motif in natural products, and their applicability in biological and materials science [2]. Some of the p-terphenyl derivatives such as terphenyllin, terferol, and terprenin have been isolated from the nature. These materials show versatile biological activities and widely used as therapeutic agents [3]. Since, p-terphenyls also possesses unique photophysical characteristics, they widespread applied in material researches including molecular electronics, photonics and chemical sensing [4,5]. For synthesis of *p*-teraryls there are two general methods in the literature. One is the transition metal-catalyzed aryl-aryl coupling reactions and other is cycloaddition reactions using diaryl-substituted open chain precursors [6]. The latter method is limited to specific class of terphenyls and not has widespread structural diversity [7]. Suzuki reaction is the most important and efficient strategy for the construction of polyaryls (biaryls, teraryls, etc.) from aryl halides

ABSTRACT

Immobilized palladium nanoparticles on silica-starch substrate (PNP-SSS) were found to be an efficient reusable catalyst for excellent synthesis of teraryls using Suzuki reaction. The catalytic reactivity of PNP-SSS was examined over a set of substrates, demonstrating that it is reactive toward a variety of functionalities. In this process, the PNP-SSS catalyst can be reused more than six times with almost consistent efficiency and can be recovered by simple filtration.

© 2012 Elsevier B.V. All rights reserved.

and boronic acids [8]. In fact, among aryl—aryl coupling protocols, Suzuki reaction has been widely used as a synthetic strategy in the synthesis of polyaryls, because organoboranes are stable and less toxic in comparison with other aryl nucleophiles such as arylmagnesium bromides, and arylstannyl halides [9].

On the other hand, in the field of palladium reactions, preparation of high performance Pd catalysts and the use of green reaction conditions are two important strategies for the preparation of new Pd catalyst systems, for excellent performing of Pd-catalyzed processes [10]. High performance Pd catalysts are considered, because they allowed the use of aryl chlorides, which are less expensive than aryl bromides or iodides for coupling reactions [11]. This issue is improved not only a cost factor but also is provided a more efficient reaction route for Pd-catalyzed reactions. Moreover, with green chemistry approaches such as using recyclable catalysts and use of less toxic materials as solvents and reagents the synthetic usefulness of these valuable reactions are improved [12].

Pd nanoparticles (Pd-nano) catalyst systems are considered as efficient and green catalysts in Pd-catalyzed process [13]. In Pdnano systems, stability, reactivity and reusability of catalyst are highly depended to type of selected substrate for immobilization of nanoparticles [14]. Silica is a stable substrate for immobilization of Pd nanoparticles, but leaching of metal is unavoidable for this material, so the reactivity of catalyst is decreased after one or two runs [15]. Silica substrate can be modified by organic moieties using





^{*} Corresponding authors.

E-mail addresses: Khalafi@chem.susc.ac.ir (A. Khalafi-Nezhad), panahi@shirazu.ac.ir (F. Panahi).

⁰⁰²²⁻³²⁸X/\$ – see front matter @ 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.jorganchem.2012.07.039

a chemical process to improve its applicability as support in preparation of Pd-nano catalysts. One of the important classes of materials which have been used for stabilization of metal nanoparticles is natural poly hydroxyl compounds. Cellulose, chitosan, gelatin, collagen and starch contain free hydroxyl groups on their backbones, which have the potential for the chelation with transition metals [16]. They also acts as a highly hydroxyl functionalized substrate to catch up and stabilize the Pd nanoparticles by their ligation with hydroxyl groups. Considering to this characteristics they have been used as substrate for preparation of Pd nano catalyst systems. Unfortunately, leaching of Pd, less stability and tedious workup process are main problems with these catalytic systems. However, when these poly hydroxyl substrates are grafted to a stable backbone such as silica, some of the problems can be resolved [17]. Considering to this strategy, we have introduced an efficient heterogeneous catalyst for Heck and copper-free Sonogashira reactions based on immobilization of palladium nanoparticle on silica-starch substrate [18]. In present work we would like to develop the synthetic usefulness of PNP-SSS catalyst by synthesis of some new *p*-teraryls using Suzuki reaction under green conditions.

2. Experimental

Chemicals were purchased from Fluka, Merck and Aldrich chemical companies and used without further purification. The known products were characterized by comparison of their spectral and physical data with those reported in the literature. TEM analvses of the catalyst were performed on a Philips model CM 10 instrument. Inductively Coupled Plasma (ICP) technique (Varian, Vista-pro) was employed for the determination of the amount of immobilized palladium nanoparticles on support. ¹H NMR spectra were recorded on a Bruker Avance 250 MHz spectrometer in CDCl₃ solution with tetramethylsilane (TMS) as an internal standard. FT-IR spectroscopy (Shimadzu FT-IR 8300 spectrophotometer) was employed for characterization of the compounds using KBr pellets. Elemental analyses (CHNS) were performed on a Perkin–Elmer 240-B micro-analyze. Melting points were determined in open capillary tubes in a Barnstead Electrothermal 9100 BZ circulating oil melting point apparatus. The reaction monitoring was accomplished by TLC on silica gel PolyGram SILG/UV254 plates. Column chromatography was carried out on columns of silica gel 60 (70-230 mesh).

2.1. Synthesis of silica chloride (SC)

In a three-necked flask (100 mL) that was equipped with a dropping funnel containing thionyl chloride (SOCl₂, 40 mL), condenser and a gas inlet tube for conducting HCl gas over an adsorbing solution (10% NaOH), 10 g of silica was charged. Thionyl chloride was added drop-wise over a period of 30 min at room temperature. When the addition was completed, the mixture was stirred for 24 h at the refluxing temperature of SOCl₂. Then, the untreated SOCl₂ was removed by distillation. The silica chloride was dried in a vacuum at 90 °C and the resulting grayish powder was stored in a desiccator under vacuum. Based on previous study the amount of chlorosilyl groups on the silica surface was determined about ~0.88 mmol g⁻¹ [18].

2.2. Preparation of silica-starch substrate (SSS)

To a magnetically stirred mixture of silica chloride (5 g) in CHCl₃ (30 mL), potato starch (purchased from Aldrich company) (2 g) and triethyl amine (0.5 mL) were added and refluxed for 12 h. Then, the mixture was filtered and washed with chloroform (2×10 mL) and

water (2 \times 10 mL). After drying in the oven, silica–starch substrate was obtained as a white powder.

2.3. Pd nanoparticles on silica-starch substrate (PNP-SSS)

To a mixture of silica–starch substrate (5 g) in absolute ethanol (30 mL), palladium acetate (0.3 g, 1.3 mmol) was added and stirred 24 h at room temperature. Then, the mixture was filtered and washed with ethanol (3 × 10 mL) and diethyl ether (2 × 10). After drying in a vacuum oven, PNP–SSS catalyst was obtained as a dark solid.

2.4. General procedure for the synthesis of p-teraryls using PNP–SSS catalyst

To a mixture of diarylhalide (1 mmol), aryl boronic acid (2.1 mmol), and NaOH (3 mmol) in 2 mL water, PNP–SSS catalyst (0.05 g) was added and heated in an oil bath at the refluxing temperature of water. The reaction was followed by TLC. After completion of the reaction, the mixture was cooled down to room temperature and filtered and the remaining solid was washed with dichloromethane (3×5 mL) in order to separate catalyst. After the extraction of dichloromethane from water, the organic extract was dried over Na₂SO₄. The products were purified by column chromatography (hexane or hexane/ethyl acetate) to obtain the desired purity.

2.5. General procedure for recycling of the PNP-SSS catalyst

Upon completion of the reaction between 1,4-dichlorobenzene and phenylboronic acid under optimized condition, the reaction mixture was cooled down to room temperature and filtered; the remaining solid was washed with water (2×10) and dichloromethane (3×5 mL) in order to separate catalyst. The reused catalyst was dried in oven at 100 °C and used for next run.

3. Results and discussion

3.1. Catalyst preparation

As shown in Scheme 1, the heterogeneous PNP-SSS catalyst is prepared in three steps. First, activated silica [19] is inverted to silica chloride (SC) based on Firouzabadi et al. producer [20]. Second, SC is reacted with starch in chloroform to obtain silica-starch substrate (SSS). It is noteworthy that, SC is not soluble in all organic solvents and due to this property; it can accept different nucleophiles particularly hydroxyl groups (due to generation of strong Si-O bond) [21]. Considering to this issue, SC is reacted with hydroxyl groups of starch conveniently. However, SC is a moisture capture reagent and its Si-Cl groups can convert to Si-OH groups in the presence of water molecules. So for fine chemical synthesis of SSS we have to use from the fresh SC. Finally, palladium acetate is reduced to Pd nanoparticles with ethanol as reducing agent on SSS to obtain PNP-SSS catalyst. The PNP-SSS catalyst has been fully characterized using some different microscopic and spectroscopic techniques [18].

It is noteworthy that the SSS is a very stable substrate (based on thermal gravimetric analysis it is stable to above 250 °C), because the starch species is connected to silica covalently. SSS is a polyhydroxyl ligand and so it can stabilize the Pd nanoparticles effectively with its hydroxyl groups. When starch reacts with SC it forms a platform on the surface of silica and these organic chains prevents the aggregation of nanoparticles and their separation from the substrate surface. This organic—inorganic hybrid material also provides suitable catalytic sites for reactions in aqueous media. We



Scheme 1. Synthetic route for preparation of PNP-SSS catalyst.

need to point out that, PNP–SSS is a stable, cheap, green and easy handling catalyst for application in Pd-catalyzed reactions.

3.2. PNP–SSS catalyzed Suzuki reaction of phenylboronic acid and 1,4-dihalobenzene (optimization, generality and limitations)

The PNP–SSS catalyzed Suzuki reaction between phenylboronic acid (1a) and 1,4-dichlorobenzene (2a) was chosen as a model reaction to evaluate the effects of solvent, base, temperature and amount of catalyst. Optimization conditions studies are summarized in Table 1.

In our initial selection we used DMF as solvent and K_2CO_3 as base for the reaction between 1,4-dichlorobenzene and phenylboronic acid in the presence of PNP–SSS catalyst, where *p*-

Table 1

Effect of solvent, base, temperature and amount of catalyst on PNP–SSS catalyzed Suzuki reaction of 1,4-chlorobenzene with phenylboronic acid.^a

CI

Ph

	Ph-B(OH) ₂ +				
	1a	2a	Temp	3a	
Entry	Solvent	Base (mmol)	Temp (°C)	Time (h)	Yield (%) ^b
1	DMF	$K_2CO_3(3)$	100	5	61
				12	73
2	DMF:H ₂ O (5:1)	$K_2CO_3(3)$	100	5	71
				12	78
3	DMF:H ₂ O (1:5)	$K_2CO_3(3)$	100	5	79
				12	81
4	H ₂ O	$K_2CO_3(3)$	Reflux	5	88
				12	91
5	H ₂ O	Et ₃ N (4)	Reflux	12	67
6	H ₂ O	NaOH (3)	Reflux	12	91
7	H ₂ O	NaOH (3)	r.t.	24	0
8	H ₂ O	NaOH (3)	Reflux	12	93 ^c
9	H ₂ O	NaOH (3)	Reflux	24	65 ^d
10	H ₂ O	NaOH (4)	Reflux	12	91
11	H ₂ O	NaOH (2)	Reflux	12	85

^a Reaction conditions: 1,4-dichlorobenzene (1 mmol), phenylboronic acid (2.1 mmol), solvent (2 mL).

^b Isolated yield.

^c 0.08 g of catalyst used.

^d 0.03 g of catalyst used.

terphenyl (**3a**) was obtained with 61% isolated yield. We observed that the yield of *p*-terphenyl was enhanced to 71% when some water (Ratio 5:1 of DMF:H₂O) was added to the reaction media (Table 1, entry 2). Additionally, increasing the amount of water (Ratio 1:5 of DMF:H₂O) also increased the yield of product (Table 1, entry 3). Regarding this point, we chose water as solvent for the reaction and interestingly in this condition *p*-terphenyl product was obtained with 88% isolated yield after only 5 h (Table 1, entry 4). It is noteworthy that, in aqueous media not only the yield of product did not deceased but it also increased to some extent, which this may be resulted from organic–inorganic nature of the silica–starch substrate.

When the type of base was changed, it was observed that in the presence of NaOH a good yield of product was obtained (Table 1, entry 6). It is also observed that, the reaction between 1,4-dichlorobenzene and phenylboronic acid did not accomplished at room temperature using PNP–SSS catalyst (Table 1, entry 7). The results showed that, with increasing the amount of catalyst (1.9 mol % per 1 mmol of 1,4-dichlorobenzene), the yield of product did not change much (Table 1, entry 8). While, reducing the amount of catalyst (0.7 per 1 mmol of 1,4-dichlorobenzene) decreased the yield of product (Table 1, entry 9). In according to Table 1, reducing the quantity of base was also affected the reaction yield (entry 11). Thus, as optimum condition, the reaction was carried out under aerobic conditions in refluxing water as green solvent, using NaOH as a cheep base, without the addition of free ligand or any promoting additives.

The results were shown that, under optimized conditions 1,4diiodobenzene react faster than chloride and bromide analogs and gave higher yield of product in more short reaction time (Table 2).

Any product from the reaction of 1,4-diarylfluoride did not observe. Although, the PNP–SSS catalyst is suitable for construction of *p*-teraryls using aryl chlorides, but by use of aryl iodides and aryl bromides the desired *p*-teraryl compound can be synthesized in relatively short reaction time with high efficiency.

After optimization studies, a range of *p*-teraryls were synthesized using PNP–SSS catalyst under optimum conditions (Fig. 1 and Table 3).

Considering to the Table 3 and Fig. 1, this is an efficient approach for one-pot synthesis of *p*-teraryl derivatives based on the Pdcatalyzed Suzuki reaction of aryl boronic acids and diarylhalides. This facile protocol also can be applied to the synthesis of other polyaryls and synthetic compounds with biaryl structural unit. As can be seen in Table 3, by selecting the appropriate boronic acids and diarylhalide a wide range of *p*-teraryls can be synthesized. The reaction between 1,4-dichlorobenzene and phenylboronic acid is resulted the formation of *p*-terphenyl with 91% isolated yield after 5 h (Table 3, entry 1). A similar process allowed the combination of 4-ethylphenylboronic acid with 1,4-dichlorobenzene to provide an excellent yield of the corresponding *p*-terphenyl product (Table 3, entry 2).

The PNP–SSS system is also shown to be most effective in the coupling of diarylhalides with functionalized boronic acids for

Table 2Effect of type of halogen on reaction time and yield of product.^a

Entry	Х	Time/h	Yield (%) ^b
1	Ι	1	97
2	Br	5	92
3	Cl	12	91
4	F	24	0

^a Reaction condition: biarylhalide (1 mmol), phenylboronic acid (2.1 mmol), PNP-SSS (0.05 g), NaOH (3 mmol) and water (2 mL).
 ^b Isolated yield.



Fig. 1. The chemical structure of synthesized *p*-teraryls.

synthesis of symmetrical functionalized *p*-terphenyls (Table 3, entries 3, 4 and 8). These compounds are needed for the applications in synthesis of new polymers and molecules with terphenyl structural units [22]. Thiophenes are found as structural units in a variety of materials such as conductive polymers, organic field effect transistors and organic light emitting diodes [23]. Although, polyaryl compounds incorporating a thiophene moiety are often prepared via a transition metal catalyzed coupling reaction, but there are several limitation for the synthesis of these compounds by thiophene boronic acids in Suzuki reaction [24]. Considering to these points, we decided to synthesis two new *p*-teraryls based on thiophene ring using thiophen-2-yl-2-boronic acid and results were shown that PNP-SSS catalyst also provides efficient and clean condition for synthesis of these compounds (Table 3, entries 9 and 10). Since, naphthalene, phenanthrene and anthracene structural units widely used in design of advanced material for application in organic electronic devices [25], we also synthesized three *p*-teraryls

Table 3



	B(OH) ₂ +	Y PN	P-SSS H ₂ O / I Ref	(1.2 mol%) NaOH lux	Ar R 3a-3m	, Ar
Entry	Ar	R	х	Product	Time (h)	Yield (%) ^{a,b}
1	Ph	Н	Cl	3a	8	91
2	4-Et-Ph	Н	Cl	3b	8	92
3	4–COCH ₃ –Ph	Н	Br	3c	5	92
4	4–CHO–Ph	Н	Br	3d	5	91
5	Ph	CH ₃	Ι	3e	1	96
6	Ph	$C_{6}H_{13}$	I	3f	2	94
7	3,4-F-Ph	CH ₃	Ι	3g	2	96
8	4–COCH ₃ –Ph	C ₆ H ₁₃	Ι	3h	2	93
9	Thiophenyl	CH ₃	Ι	3i	3	89
10	Thiophenyl	$C_{6}H_{13}$	Ι	3j	3	86
11	Naphthyl	CH ₃	Ι	3k	5	89
12	Anthracenyl	CH_3	Ι	31	5	91 ^c
13	Phenanthrenyl	Н	Ι	3m	5	86 ^{c,d}

^a Reaction condition: diarylhalide (1 mmol), phenylboronic acid (2.1 mmol), PNP–SSS (0.05 g), NaOH (3 mmol) and water (2 mL).

^b Isolated yield.

^c Solvent used: DMF:H₂O (1:5) (2 mL).

^d Amount of boronic acid (1 mmol) and aryl halide (2 mmol).

Table 4

Comparison of the results of the synthesis of terphenyl, using SBSAN catalyst with those obtained by the reported catalysts.

	X B(OH) ₂ Ca	atalyst	_ [\mathbb{A}	
x	+	ondition	s		
Entry	Catalyst & conditions	Х	Time (h)	Yield (%)	Ref.
1	PNP—SSS, NaOH,	Cl	12	90	This
	H_2O , reflux	Br	5	92	work
		Ι	1	97	
2	Starch-PNP, NaOAc, DMF/H ₂ O, 80 °C	I	1	90	[16c]
3	Pd Cl ₂ (PPh ₃) ₂ , K ₂ CO ₃ , N ₂ , TBAB, H ₂ O, MW	Br	0.17	92	[29]
4	Silica-supported palladium, K ₂ CO ₃ , dodecane, <i>o</i> -xylene, N ₂ , 110 °C	Br	20	65	[9]
5	Palladium—NHC-containing polymer, NaO ^r Bu, IPA, 80 °C	Cl	8	94	[30]
6	Pd(OAc) ₂ , Na ₂ CO ₃ , H ₂ O/DMF, 60 °C	Br	12	96	[31]
7	LDH-DS-Pd ⁰ , K ₂ CO ₃ , H ₂ O/DMF, 60 °C	Br	3	94	[32]
8	Silica supported palladium-phosphine complex, K ₂ CO ₃ , MeOH/H ₂ O, r.t.	Ι	3	77	[33]



Fig. 2. Synthesis of *o*, *m* and *p*-terphenyl in the presence of PNP–SSS catalyst under optimized conditions.

containing these fragment (Table 3, entries 11, 12 and 13). Thus, our environmentally beginning catalyst system can also provide efficient procedure for the preparation of these materials.

When a fluoro moiety incorporated into an organic molecule its physical, chemical, and biological properties often are dramatically improved [26]. For example, fluorinated aromatics are useful as excellent *n*-type organic materials, because they possess a low barrier to electron injection and a high propensity for electron



Fig. 3. Recyclability of PNP–SSS catalyst in the reaction of 1,4-dichlorobenzene with phenylboronic acid under optimized condition; reaction time is 8 h.



Fig. 4. The TEM image of a) fresh PNP-SSS catalyst and b) reused PNP-SSS catalyst after 6 times.

transporting, so they widely used in organic electronic materials [27]. For this purpose, the development of efficient methods for the synthesis of fluorinated compounds has been considered [28]. One of the efficient protocols for synthesis of this class of compounds is Suzuki reaction. Herein, we also synthesized a new fluorinated *p*-terphenyl using PNP–SSS catalyst (Table 3, entry 7).

In order to show the merit and the reactivity of PNP–SSS catalyst, a comparison with some other reported homogeneous and heterogeneous palladium catalysts for preparation of *p*-terphenyl are presented in Table 4.

As shown in Table 4, our catalyst is superior to some of the previously reported catalysts in terms of reaction condition, reaction time and yield.

We also checked the catalytic activity of PNP–SSS for synthesis of *o*-, *m*- and *p*-terphenyl under optimized conditions. As shown in Fig. 2, for all three dichlorobenzenes, an excellent yield of corresponding products were obtained, indicating that PNP–SSS is efficient for synthesis of three isomers of terphenyls.

3.3. The catalyst recyclability and heterogeneity tests

The recyclability of PNP–SSS catalyst for this protocol is also investigated and the results were shown that, the PNP–SSS catalyst is recovered by simple filtration and reused without remarkable loss of catalytic activity after six times of reusability (Fig. 3).

After five cycles of reusability we also checked the Pd content of PNP–SSS catalyst using ICP analysis and data showed that only 1.2% of the immobilized Pd metal is removed from the silica starch substrate. In one reaction, when the reaction of 1,4-dichlorobenzene and phenylboronic acid was completed the hot filtration was done and ICP analysis was shown that the amount of leached Pd to be less than 0.5%. Also in other experiment the obtained aqueous solution from the filtrate was used as catalyst for the subsequent reaction between 1,4-dichlorobenzene and phenylboronic acid under optimized condition. The amounts of Suzuki reaction products after this process were obtained about 4.5% isolated yield. The TEM image of the catalyst showed that the morphology and size of the catalyst after five times of reusability did not change remarkably (Fig. 4).

These experiments and results are confirmed that the PNP–SSS catalyst provides the high catalytic activity for Suzuki reaction, and not any leached palladium.

4. Conclusion

In conclusion, we have introduced an efficient and clean procedure for the excellent synthesis of teraryls from aryl halides and aryl boronic acids using a heterogeneously catalyzed Suzuki reaction. By use of PNP–SSS catalyst, teraryls were synthesized with high isolated yields under green conditions. Reusability and easy workup were two other advantages of PNP–SSS catalyst in this process. We anticipate that the application of this catalyst can be extended for synthesis of new material using other palladium catalyzed reactions.

Appendix A. Supplementary material

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.jorganchem.2012.07.039.

References

- [1] (a) P. Lloyd-Williams, E. Giralt, Chem. Soc. Rev. 30 (2001) 145–157;
- (b) L. Pu, Chem. Rev. 98 (1998) 2405–2494.
- [2] J.-K. Liu, Chem. Rev. 106 (2006) 2209–2223.
- [3] (a) M. Roberti, D. Pizzirani, M. Recanatini, D. Simoni, S. Grimaudo, A. Di Cristina, V. Abbadessa, N. Gebbia, M. Tolomeo, J. Med. Chem. 49 (2006) 3012–3018;
 (b) T. Finkel, N.J. Holbrook, Nature 408 (2000) 239–247.
- [4] (a) H. Sasabe, Y.-J. Pu, K.-I. Nakayama, J. Kido, Chem. Commun. (2009) 6655–6657;
 (b) A. Goel, V. Kumar, P. Nag, V. Bajpai, B.-j. Kumar, C. Singh, S. Prakash,
- (c) J. Goed, V. Rahar, T. Rag, V. Dapar, D. J. Rahar, C. Shight, S. Flakash,
 R.S. Anand, J. Org. Chem. 76 (2011) 7474–7481;
 (c) J.S. Gasowska, S.J. Cowling, M.C.R. Cockett, M. Hird, R.A. Lewis, E.P. Raynesc,
 I.W. Goodby, I. Mater, Chem. 20 (2010) 299–307.
- [5] (a) B. Chen, U. Baumeister, G. Pelzl, M.K. Das, X. Zeng, G. Ungar, C. Tschierske, J. Am. Chem. Soc. 127 (2005) 16578-16591;
 - (b) R.S. Wright, T.K. Vinod, Tetrahedron Lett. 44 (2003) 7129-7132;
- (c) H. Oka-moto, N. Kawasaki, Y. Kaji, Y. Ku-bozono, A. Fujiwara, M. Yamaji, J. Am. Chem. Soc. 130 (2008) 10470–10471.
- [6] (a) Y. Yamamoto, K. Nunokawa, M. Ohno, S. Eguchi, Synthesis (1996) 949–953;
 (b) M. Modjewski, S.V. Lindeman, R. Rathore, Org. Lett. 11 (2009) 4656–4659;
 (c) L. Li, J. Xiang, C. Xu, Org. Lett. 9 (2007) 4877–4879.
- [7] D.S.B. Daniels, J.M. Brown, M. Gayral, Y. Xu, M.I. Stewart, Synlett (2009) 1387–1390.
- [8] T. Welton, Chem. Rev. 99 (1999) 2071–2083.
- [9] S. Paul, J.H. Clark, Green Chem. 5 (2003) 635-638.
- [10] (a) F. Turksoy, G. Hughes, A.S. Batsanov, Bryce, R. Martin, J. Mater. Chem. 13 (2003) 1554–1557;
 (b) H.-T. Bai, H.-C. Lin, T.-Y. Luh, J. Org. Chem. 75 (2010) 4591–4595;
 (c) D.A. Dickie, A.Y.C. Chan, H. Jalali, H.A. Jenkins, H.-Z. Yu, J.A.C. Clyburne, Chem. Commun. (2004) 2432–2433;
 (d) K. Niknam, A. Gharavi, M.N. Hormozi Nezhad, F. Panahi, M.T. Sharbati, Svnthesis (2011) 1609–1615.
- [11] J. Zhi, D. Song, Z. Li, X. Lei, A. Hu, Chem. Commun. 47 (2011) 10707–10709.
- [11] A. Fihri, M. Bouhrara, B. Nekoueishahraki, J.-M. Basset, V. Polshettiwar, Chem. Soc. Rev. 40 (2011) 5181–5203.
- [13] (a) J.K. Cho, R. Najman, T.W. Dean, O. Ichihara, C. Muller, M. Bradley, J. Am. Chem. Soc. 128 (2006) 6276–6277;
 (b) N. Iranpoor, H. Firouzabadi, S. Motevalli, M. Talebi, J. Organomet. Chem.
- 708–709 (2012) 118–124. [14] L. Wu, B.L. Li, Y.Y. Huang, H.F. Zhou, Y.M. He, Q.H. Fan, Org. Lett. 8 (2006) 3605–3608.
- [15] V. Polshettiwar, C. Len, A. Fihri, Coord. Chem. Rev. 253 (2009) 2599-2626.

- [16] (a) H. Huang, X. Yang, Colloid Surf. A: Physicochem. Eng. Aspects 226 (2003) 77-86; (b) M. Adlim, M.A. Bakar, K.Y. Liew, J. Ismail, J. Mol. Catal. A: Chem. 212 (2004) 141-149;
 - (c) L. Shiyong, Z. Qizhong, J. Huajiang, Chin. J. Chem. 28 (2010) 589-593;
 - (d) H. Wu, C. Wu, O. He, X. Liao, B. Shi, Mater. Sci. Eng. C 30 (2010) 770-776; (e) P. Zhou, H. Wang, J. Yang, J. Tang, D. Sun, W. Tang, Ind. Eng. Chem. Res. 51 (2012) 5743-5748;
 - (f) H. Firouzabadi, N. Iranpoor, A. Ghaderi, Org. Biomol. Chem. 9 (2011) 865-871.
- [17] A.V. Kucherov, N.V. Kramareva, E.D. Finashina, A.E. Koklin, L.M. Kustov, J. Mol. Catal. A: Chem. 198 (2003) 377–389.
- [18] A. Khalafi-Nezhad, F. Panahi, Green Chem, 13 (2011) 2408–2415.
- [19] H. Sharghi, M.H. Beyzavi, M.M. Doroodmand, Eur. J. Org. Chem. (2008) 4126–4138.
- [20] H. Firouzabadi, N. Iranpoor, B. Karimi, H. Hazarkhani, Synlett (2000) 263–265.
- [21] (a) B. Datta, M.A. Pasha, Bull. Korean Chem. Soc. 33 (2012) 2129–2130:
- (b) L. Wu, J. Zhang, L. Fang, C. Yang, F. Yan, Dye. Pigment 86 (2010) 93–96.
 [22] J. Cui, X. Lu, A. Liu, X. Wan, Q. Zhou, Macromolecules 42 (2009) 7678–7688.
- [23] T.S. Skotheim, R.L. Elsenbaumer, J.R. Reynolds (Eds.), Handbook of Conducting
- Polymers, Marcel D., New York, 1998.
- [24] (a) S. Gronowitz, D. Peters, Heterocycles 30 (1990) 645–658;
- (b) J. Malm, B. Rehn, A. Hornfeldt, S.J. Gronowitz, Heterocycl. Chem. 31 (1994) 11-15.
 - (c) R.R. Hark, D.B. Hauze, O. Petrovskaia, M.M. Joullie, Tetrahedron Lett. 35 (1994) 7719-7722;

- (d) B. Andrieu-Malapel, J.-Y. Merour, Tetrahedron 54 (1998) 11079-11094; (e) M. Haddach, J.R. McCarthy, Tetrahedron Lett. 40 (1999) 3109-3112; (f) M. Melucci, G. Barbarella, G. Sotgiu, J. Org. Chem. 67 (2002) 8877-8884.
- [25] (a) K.C. See, C. Landis, A. Sarjeant, H.E. Katz, Chem. Mater. 20 (2008) 3609–3616; (b) H. Suh, Y. Jin, S.H. Park, D. Kim, J. Kim, C. Kim, J.Y. Kim, K. Lee, Macromolecules 38 (2005) 6285-6289;
- (c) Y. Zou, D.D. Young, A. Cruz-Montanez, A. Deiters, Org. Lett. 10 (2008) 4661-4664. [26] T. Lechel, J. Dash, P. Hommes, D. Lentz, H.-U. Reissig, J. Org. Chem. 75 (2010) 726-732.
- [27] T. Okamoto, K. Nakahara, A. Saeki, S. Seki, J.H. Oh, H.B. Akkerman, Z. Bao, Y. Matsuo, Chem. Mater. 23 (2011) 1646–1649.
- [28] (a) C. Isanbor, D. O'Hagan, J. Fluor. Chem. 127 (2006) 303-319; (b) K.L. Kirk, J. Fluor. Chem. 127 (2006) 1013-1029; (c) M. Schlosser, Angew. Chem. Int. Ed. 45 (2006) 5432-5446; (d) D. O'Hagan, Chem. Soc. Rev. 37 (2008) 308–319;
 (e) K. Muller, C. Faeh, F. Diederich, Science 317 (2007) 1881–1886;

- (f) W.K. Hagmann, J. Med. Chem. 51 (2008) 4359–4369.
 [29] L. Bai, J.X. Wang, Y. Zhang, Green Chem. 5 (2003) 615–617.
 [30] X. Zeng, T. Zhang, Y. Qin, Z. Wei, M. Luo, Dalton Trans. (2009) 8341–8348.
 [31] L. Liu, Y. Zhang, B. Xin, J. Org. Chem. 71 (2006) 3994–3997.
- [32] L. Shiyong, Z. Qizhong, J. Zhengneng, J. Huajiang, J. Xuanzhen, Chin. J. Catal. 31 (2010) 557–561.
- [33] W. Chen, P. Li, L. Wang, Tetrahedron 67 (2011) 318-325.