DOI: 10.1002/adsc.200700361

Reusable, Polymer-Supported, Palladium-Catalyzed, Atom-Efficient Coupling Reaction of Aryl Halides with Sodium Tetraphenylborate in Water by Focused Microwave Irradiation

Lin Bai[a,c] and Jin-Xian Wang[a,b,*]

[a] Institute of Chemistry and Department of Chemistry, Northwest Normal University, 805 An Ning Road (E.), Lanzhou 730070, People's Republic of China
Fax: (+86)-931-776-8159; e-mail: wangjx@nwnu.edu.cn
[b] State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, People's Republic of China
[c] Institute of Green Chemistry Experiment and Teaching, Lanzhou City University, Lanzhou 730070, People's Republic of China

Received: July 23, 2007; Revised: November 18, 2007; Published online: January 4, 2008

Supporting information for this article is available on the WWW under http://asc.wiley-vch.de/home/.

Abstract: A rapid and efficient cross-coupling reaction of sodium tetraphenylborate with aryl bromides was carried out in water at 120 °C in the presence of a polymer-supported palladium catalyst and potassium carbonate under focused microwave irradiation. All four phenyl groups of sodium tetraphenylborate participated in the reaction and produced polyfunctional biaryls in excellent yields. The polymeric catalyst can be easily separated from the reaction mixture and reused more than 10 times without showing any decrease in activity.

Keywords: focused microwave heating; polymer-supported palladium; sodium tetraphenylborate; Suzuki cross-coupling; water

Introduction

Homogeneous catalysts have many attractive properties, such as high chemoselectivity, regioselectivity and/or enantioselectivity of the reaction. However, many homogeneous catalytic systems cannot be commercialized because of difficulties associated with separating the products from the catalyst. The Suzuki coupling, which is one of the most commonly used methods for biaryl synthesis, has conventionally been performed by homogeneous palladium catalysts in the presence of various phosphine ligands.[1] Virtually all forms of palladium can be used as precatalysts for the highly active reactions, yet catalyst systems based on ligand-free palladium salts [$Pd(OAc)_2$, $PdCl_2$, etc.] and even Pd/C have attracted increased attention due to their low cost.[2,3] Recently, significant progress in the Suzuki cross-coupling reaction has been made in several key research areas, such as environmentally benign media, the design of recoverable and reusable catalysts, solid-phase synthesis, and the development of synthetic methodology.[4] From both scientific and environmental points of view, development of a new catalytic system and environmentally friendly media for the Suzuki coupling is becoming an area of growing importance.

The major disadvantages of homogeneous catalytic processes are often due to contamination of the products by palladium residues even after the purification step and the impossibility to recover the expensive catalysts for reuse. The development of heterogeneous alternatives where the metal is grafted on inorganic or organic supports has attracted great interest in the past years, because it could combine the advantages of both homogeneous and heterogeneous catalysts in one system.[2,3] It does meet both economical and green chemistry requirements and has proven effective in overcoming these problems.[4,5] Recently, reports have appeared on the Suzuki coupling with palladium loaded on magnesium-lanthanum mixed oxides,[6] γ-Al_2O_3,[7] and mesoporous silica.[8] Several approaches to immobilize palladium catalysts on polymer supports have been described in the literature, the most common is polystyrene (cross-linked with divinylbenzene), which can bear different functional groups.[4a,c,d,5] The polystyrene-supported palladium catalysts can be seen as a borderline class of catalysts, which retain the advantages of homogeneous catalysts while securing the ease of recovery and work-up of heterogeneous catalysts. These catalysts are also advantageous in as much as contamination of the products by the phosphine ligand is avoid. The palladium complex supported on polystyrene resin has indeed achieved excellent results in the Suzuki cross-coupling reaction of arylboronic acids with aryl halides or triflates.[9–12] The polystyrene-supported palladium catalysts were stable to heat and air and were reused multiple times with no significant decrease in activity. However, it was demonstrated that in many cases, the polymeric catalysts lose the palladium, which leaches under the reaction conditions from the surface into the solution because the reaction was carried out in organic solvents (such as DMF, dioxane, toluene, etc.) and the polymeric catalysts are broken by vigorous, long-lasting stirring.

Water has clear advantages as an environmentally friendly solvent alternative in organic synthesis due to its low cost, non-flammability, non-toxicity, and the fact that it is a renewable resource. In addition, the use of water in combination with hydrophilic homogeneous metal catalysts offers the potential to easily separate and recycle the metal catalyst from organic product streams.[4a] With its high dielectric constant, water is also potentially a very useful solvent for the microwave-assisted Suzuki cross-coupling reaction.[13,14] Thus, we were interested to see if the combination of the polystyrene-supported palladium catalyst and water alone as a solvent would show improved activity and stability of the catalyst in microwave-promoted cross-coupling reactions. By using this method it is possible to shorten the reaction time and decreased leaching of the catalyst occurs in water.

The unique advantage associated with sodium tetraphenylborate, unlike boronic acid or ester and other reagents, is that it can react with 4 equivalents of electrophilic reagents. From both economical concerns and increased environmental awareness, this is an atom economical reaction in organic synthesis.[15] Despite this obvious advantage, only a few reactions involving Ph_4BNa for C–C bond formation have been reported.[13a,16,17] The known cross-coupling reaction of Ph_4BNa with 4 equivalents of aryl halide involves homogeneous palladium catalysts [$Pd(OAc)_2$, $PdCl_2$] and with electrophilic coupling reagents such as iodo- (and bromo-)benzoic acids, *p*-iodonitrobenzene, and allyl bromide;[16] 2-bromopyridine, 5-bromoindole;[17] *p*-bromoacetophenone, *p*-bromobenzoic acid and *p*-bromomethoxybenzene with no transition-metal catalyst being used under focused microwave irradiation conditions.[13a] Thus, to expand the scope and reactivity of Ph_4BNa, the development of new and efficient catalytic protocols is necessary.

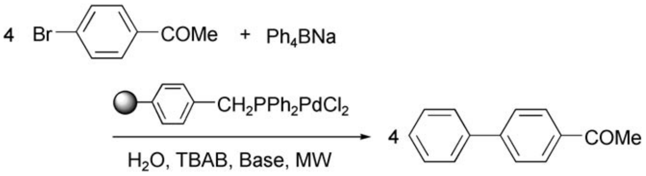
We have also reported the efficiency of the polystyrene-supported palladium-catalyzed Suzuki cross-coupling of aryl bromides (1 equiv.) with Ph_4BNa (1 equiv.) using toluene-H_2O (10:1) as a co-solvent under microwave irradiation conditions.[18] Herein, we report the PS-supported, Pd(II)-catalyzed, heterogeneous reaction of Ph_4BNa with 4 equivs. of aryl bromides in water using our methodology. The reaction is performed in a focused microwave synthesis system so that it is possible to control the temperature, pressure, microwave power, and reaction times very easily and with a high degree of reproducibility.

Results and Discussion

As a starting point for the development of our microwave-mediated methodology and the economical reaction in water, we initially studied the microwave-promoted coupling of 4-bromoacetophenone with Ph_4BNa for optimizing reaction conditions, and the effects of base, reaction time, temperature on the yield of the coupling reaction are summarized in Table 1.

The effect of bases on the reaction was significant (Table 1, entries 1–6), because the desired cross-coupling products were not obtained in any noticeable amounts in the absence of bases. A comparative reactivity study of bases in the reaction showed that K_2CO_3, K_3PO_4, and Na_2CO_3 proved to be more effec-

Table 1. Optimized conditions *via* the coupling of 4-bromoacetophenone with Ph_4BNa.[a]



Entry	Base [mmol]	Time [min]	*T* [°C]	Yield [%][b]
1	Na_2CO_3 (3.5)	15	120	90
2	K_2CO_3 (3.5)	15	120	95
3	K_3PO_4 (3.5)	15	120	91
4	NaOH (3.5)	15	120	78
5	KF (3.5)	15	120	84
6	KF/Al_2O_3 (3.5)	15	120	90
7	K_2CO_3 (3.5)	15	110	87
8	K_2CO_3 (3.5)	15	125	94
9	K_2CO_3 (3.5)	15	130	90
10	K_2CO_3 (2.5)	15	120	82
11	K_2CO_3 (3.0)	15	120	90
12	K_2CO_3 (4.0)	15	120	94
13	K_2CO_3 (3.5)	12	120	81
14	K_2CO_3 (3.5)	14	120	91
15	K_2CO_3 (3.5)	16	120	94

[a] *Reaction conditions:* *p*-$CH_3COC_6H_4Br$ (1.0 mmol), Ph_4BNa (0.25 mmol), TBAB (0.3 mmol), PS-supported Pd(II) catalyst (corresponding to 1 mol% palladium), and water (2 mL); microwave irradiation at 10 W.

[b] Yield of isolated products (average of two runs).

tive for this coupling. Considering the economical and environmental advantages, we chose K_2CO_3 as the base. The quantity of K_2CO_3 was also found to be important (Table 1, entries 2, 10–12). A 3.5 mmol of K_2CO_3 in 2 mL water worked most efficiently. The highest yield of 4-acetylbiphenyl can be obtained at 120 °C after 15 min microwave heating (Table 1, entries 2, 3–15).

We have also investigated the effects of solvent and phase-transfer catalyst (PTC) on a representative reaction: the coupling of 2-bromonaphthalene with Ph_4BNa (Scheme 1).

Water is potentially a very useful solvent with its high dielectric constant for the microwave-assisted, Suzuki-type coupling reaction of aryl halides with phenylboronic acid.[13] In our previous report,[18] the reaction could not couple in water using PS-supported Pd(II) as catalyst under an improved reflux domestic microwave oven. Toluene-H_2O or benzene-H_2O was found to be an effective solvent for the reaction. However, aryl bromides cannot completely couple with all four phenyl groups of Ph_4BNa. The corresponding biaryl products were isolated in good yields, using a stoichometric ratio of the two reagents of 1:1, respectively.

The Discover single-mode focused microwave system is a new device designed for synthesis. It can be operate at elevated pressure and temperature using sealed vessels. The focused microwave system is able to raise the temperature from ambient to 250 °C (pressure is close to 300 psi). In our initial efforts, we screened the representative reaction of 2-bromonaphthalene (4 equivs.) as a example with Ph_4BNa (1 equivs.) using benzene-H_2O and toluene-H_2O as solvents under focused microwave irradiation (Table 2, entries 1 and 2). Unfortunately, these solvents failed to promote formation of the corresponding atom-efficient cross-coupling products in high yields. The experiments proved that the polymeric catalyst along with K_2CO_3 in water at 120 °C were the ideal reagent combination affording high conversions of the atom-efficient products. The PS-supported Pd(II) catalyst was activated in water at high temperature under focused microwave irradiation.

Similar to classical PTC reaction conditions, under solid-liquid PTC conditions with the use of microwaves the role of the catalyst is very important. For the Suzuki reaction it has been found that, in the absence of a PTC, the reaction proceeds very slowly or not at all. During investigation of the effect of PTC on the reaction of aryl bromide with Ph_4BNa, quaternary ammonium salts such as tetrabutylammonium chloride (TBAC), tetrabutylammonium bromide (TBAB), benzyltrimethylammonium chloride (BTMAC), benzyltriethylammonium chloride (BTEAC), cetyltrimethylammonium bromide (CTMAB), and polyethylene glycol (PEG) were used. The best yields, for the representative reaction, were obtained in the presence of TBAB as catalyst (Table 3).

Table 2. Effect of solvents on the coupling of 2-bromonaphthalene with Ph_4BNa.[a]

Entry	Solvents	Yield [%][b]
1	Benzene-H_2O (5 mL-1 mL)	48
2	Toluene-H_2O (5 mL-1 mL)	32
3	H_2O (2 mL)	93
4	Ethanol-H_2O (5 mL-1 mL)	82
5	Solvent-free	40

[a] *Reaction conditions:* 2-bromonaphthalene (1.0 mmol), Ph_4BNa (0.25 mmol), K_2CO_3 (3.5 mmol), TBAB (0.3 mmol), PS-supported Pd(II) catalyst (corresponding to 1 mol% palladium); microwave irradiation at 120 °C for 15 min.

[b] Yield of isolated products.

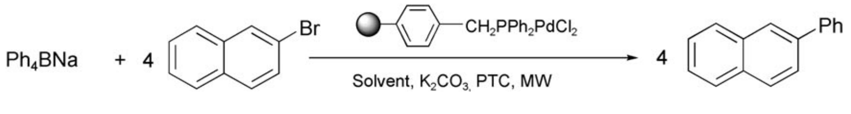
The PS-supported Pd(II) catalyst with a Pd/P ratio of 1/1 was prepared by the procedure described previously,[18] using a Merrifield resin with 2% divinylbenzene under ultrasound conditions. The activity of the PS-supported Pd(II) catalyst for the Suzuki reactions of aryl bromide with sodium tetraphenylborate in water was first measured on a representative reaction (Scheme 1). Our catalysts were stable for more than 5 years at least when stored in air at 20 °C. They were

Table 3. Effect of PTC on the coupling of 2-bromonaphthalene with Ph_4BNa.[a]

Entry	Phase-transfer catalyst	Yield [%][b]
1	TBAC	86
2	TBAB	93
3	BTMAC	65
4	BTEAC	78
5	CTMAB	74
6	PEG-400	73
7	PEG-1000	53
8	None	36

[a] *Reaction conditions:* 2-bromonaphthalene (1.0 mmol), Ph_4BNa (0.25 mmol), K_2CO_3 (3.5 mmol), PTC (0.3 mmol), PS-supported Pd(II) catalyst (corresponding to 1 mol% palladium), and water (2 mL); microwave irradiation at 120 °C for 15 min.

[b] Yield of isolated products.



Scheme 1.

reused more than 10 times without any decrease in activity: the polymeric catalyst was placed into the reaction vessel, which was heated with reactants at 120 °C for 15 min under microwave irradiation. The polymeric catalyst was filtered and washed with solvent. The same catalyst was recycled, carrying out the identical reaction ten times. The isolated yields of purified product are showed in Table 4.

Table 4. Recycling of polymer-supported Pd(II) catalyst.[a]

Entry	PS-supported Pd(II)	Yield [%]
1	fresh	93
2	recycle 1	91
3	recycle 2	92
4	recycle 3	91
5	recycle 4	90
6	recycle 5	92
7	recycle 6	93
8	recycle 7	91
9	recycle 8	93
10	recycle 9	92

[a] *Reaction conditions:* 2-bromonaphthalene (1.0 mmol), Ph_4BNa (0.25 mmol), K_2CO_3 (3.5 mmol), TBAB (0.3 mmol), PS-supported Pd(II) catalyst (corresponding to 1 mol% palladium), and water (2 mL); microwave irradiation at 120 °C for 15 min.

The polymeric catalyst holding the concentration of palladium at 1 mol% gives very high activity in the coupling of aryl bromide with Ph_4BNa in the presence of a phase-transfer catalyst, K_2CO_3, and in water under focused microwave irradiation at 120 °C. The catalyst was found to be insensitive to high temperature, and filtration of the catalyst followed by evaporation of the extracted solvent yielded almost pure biaryls since neither the phosphine ligand nor the palladium metal contaminated the products.

To evaluate the activity of the PS-supported Pd(II) catalyst we also investigated the influence of simple (classic) homogeneous or heterogeneous Pd catalysts on the representative reaction under the applied conditions. It can be seen in Table 5 that the polymeric-catalyst is almost the same as $Pd(OAc)_2$ in terms of activity. To us the polymeric catalyst appeared to be most convenient, since it can be recovered and reused as shown in the above investigations.

Under the optimized reaction conditions, various aryl bromides, including some heterocyclic species can react with Ph_4BNa providing cross-coupling products (**2a–t**) in excellent yields. From the results shown in Table 6, it can be seen that a wide array of aryl bromides containing an electron-withdrawing group or an electron-donating group were efficiently coupled to provide the corresponding biaryl products in excellent isolated yields. The aryl bromides can completely couple with all four phenyl groups of Ph_4BNa.

Table 5. Comparative experiments with simple Pd catalysts on the representative reaction.[a]

Entry	Pd catalyst	Yield [%][e]
1	PS-supported Pd(II)[b]	93
2	$PdCl_2$[c]	82
3	$Pd(OAc)_2$[c]	94
4	Pd/C[d]	85

[a] *Reaction conditions:* 2-bromonaphthalene (1.0 mmol), Ph_4BNa (0.25 mmol), K_2CO_3 (3.5 mmol), TBAB (0.3 mmol), and water (2 mL); microwave irradiation at 120 °C for 15 min.

[b] PS-supported Pd(II) catalyst (corresponding to 1 mol% palladium).

[c] 1 mmol% Pd salt.

[d] 1 mmol% Pd/C.

[e] Yield of isolated products.

Conclusions

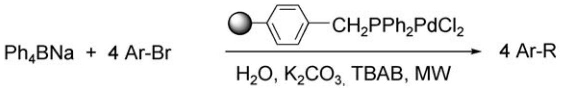
We have developed a reliable, highly efficient method for the synthesis of biaryls in excellent yields that involves the use of water as solvent under focused microwave irradiation. The coupling of microwave technology with water, polymer-supported palladium catalyst and solid-liquid PTC conditions constitutes a new and especially efficient, powerful and attractive method. Particularly valuable features of this methodology are its superiority from the point of view of yield, atom economics, short reaction time, broad substrate scopes, as well as an environmentally more friendly synthesis than the reported methods. From a synthetic perspective, these results open new possibilities for exploiting the cross-coupling reaction, since sodium tetraphenylborate is a cheap and easily available starting material in place of phenylboronic acid as a phenylating agent.

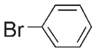
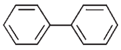
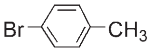
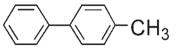
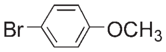
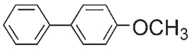
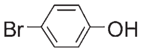
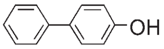
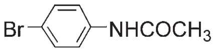
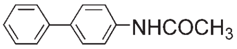
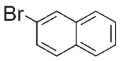
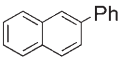
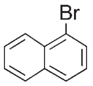
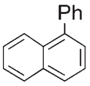
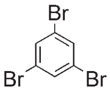
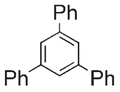
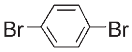
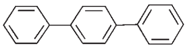
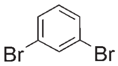
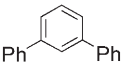
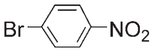
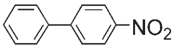
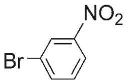
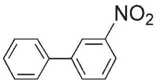
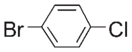
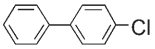
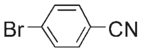
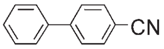
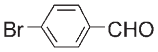
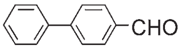
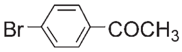
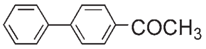
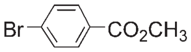
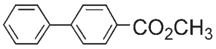
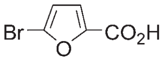
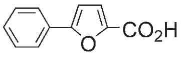
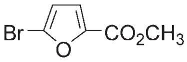
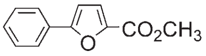
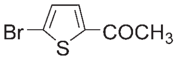
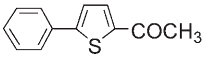
Experimental Section

The melting points were determined on a WRS-1 A digital melting point apparatus. IR spectra were measured for KBr discs using an Alpha Centauri FT-IR spectrophotometer. ^1H NMR spectra were recorded on a Mercury plus 400 MHz spectrometer in $CDCl_3$ with TMS as an internal standard. ^{13}C NMR spectra were obtained at 100 MHz in $CDCl_3$ with TMS as an internal standard using a Mercury plus 400 MHz spectrometer. EI-MS were measured on an HP5988A mass spectrometer.

Microwave reactions were conducted using a CEM Focused Microwave™ Synthesis System (CEM Corp., Matthews, NC). The machine consists of a continuous focused microwave power delivery system with operator selectable power output from 0 to 300 W. The pressure control system uses a load cell for an indirect measurement of the reaction vessel contents. The load cell is connected to a 10-mL vessel and senses changes in the external deflection of the septa on

Table 6. Cross-coupling of aryl bromides with sodium tetraphenylborate.[a]



Entry	Ar-Br	Products[b]		T [°C]/Time[min]	Yield [%][c]
1			**2a**[18,19]	120/18	90
2			**2b**[18,20]	120/18	91
3			**2c**[18,20]	120/20	89
4			**2d**[18,21]	120/20	88
5			**2e**[18,22]	120/18	92
6			**2f**[18,23]	120/15	93
7			**2g**[18,19]	120/15	89
8			**2h**[18,19]	120/20	87
9			**2i**[18,19]	120/20	92
10			**2j**[18,19]	120/20	90
11			**2k**[18,19]	120/15	92
12			**2l**[26]	120/15	88
13			**2m**[18,20]	120/15	91
14			**2n**[18,21]	120/15	94
15			**2o**[18,19]	120/15	92
16			**2p**[18,19]	120/15	95
17			**2q**[18,24]	120/15	92
18			**2r**[18,25]	120/15	91
19			**2s**[18]	120/15	92
20			**2t**[18,26]	120/15	95

[a] *Reaction conditions:* aryl bromides (1.0 mmol), Ph_4BNa (0.25 mmol), K_2CO_3 (3.5 mmol), PS-supported Pd(II) catalyst (corresponding to 1 mol% palladium), H_2O (2 mL).

[b] All products were characterized by melting point, IR, ^1H NMR, ^{13}C NMR and MS.

[c] Average of isolated yields based on two runs.

top of the sealed pressure vessel. The sensor housing incorporates a capture and release mechanism to secure the reaction in the cavity. Pressure is programmable from 0–300 psi (0–21 bar). The temperature control system uses a non-contact, infrared sensor to measure temperature. It is located below the microwave cavity floor and measures the temperature on the bottom of the vessel. The sensor is vessel volume independent and is used in a feedback loop with the on-board computer to control the temperature rise rate and control point of the vessel contents. Temperature is programmable from 25–250 °C. All experiments were performed using a stirring option whereby the contents of the vessel are stirred by means of a rotating magnetic plate located below the floor of the microwave cavity and a Teflon-coated magnetic stir bar in the vessel.

Typical Procedure for the Synthesis of Biaryls

In a 10-mL glass tube were placed aryl bromide (1.0 mmol), Ph_4BNa (0.25 mmol), K_2CO_3 (3.5 mmol), PS-supported Pd(II) (corresponding to 1 mol% palladium), TBAB (0.3 mmol), 2 mL H_2O, and a magnetic stir bar. The vessel was sealed with a septum and placed into the microwave cavity. Microwave irradiation of 10 W was used, the temperature being ramped from room temperature to 120 °C. Once 120 °C was reached, the reaction mixture was held at this temperature for 15 min. After cooling the mixture to room temperature, the reaction vessel was opened and the contents poured into a separating funnel. Ethyl acetate-acetone (5:1 v/v, 10 mL) was added and the organic material was dissolved. The mixture was filtered, and polymeric catalyst was extracted twice with ethyl acetate-acetone (5 mL × 2). The water layer was separated and the organic phase was washed with saturated NaCl (5 mL). The organic phase was dried over anhydrous $MgSO_4$. The solvent was removed by evaporation under reduced pressure to afford the biaryls. The product was recrystallized from 95% ethanol or purified by column chromatography on silica gel using petroleum ether-ethyl acetate (30:1 v/v) as the eluent to give the analytically pure product.

All products are known compounds. The compounds were characterized by melting point, IR, ^1H NMR, ^{13}C NMR and MS, and in agreement with already published data.

Supporting Information

Details of the characterization of all compounds can be founded in the Supporting Information.

Acknowledgements

The work is supported by the National Natural Science Foundation of China (NO. 20272047, 20572086) and the Gansu Natural Science Foundation of China (NO. 3ZS061 A25–059, 3ZS051 A25–001).

References

[1] a) S. Kotha, K. Lahiri, D. Kashinath, *Tetrahedron* **2002**, *58*, 9633–9695; b) A. F. Littke, G. C. Fu, *Angew. Chem. Int. Ed.* **2002**, *41*, 4176–4211; c) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457–2483.

[2] N. T. S. Phan, M. Van Der Sluys, C. W. Jones, *Adv. Synth. Catal.* **2006**, *348*, 609–679.

[3] a) F.-X. Felpin, T. Ayad, S. Mitra, *Eur. J. Org. Chem.* **2006**, 2679–2690; b) L. Yin, J. Liebscher, *Chem. Rev.* **2007**, *107*, 133–173.

[4] a) L. Bai, J.-X. Wang, *Curr. Org. Chem.* **2005**, *9*, 535–553; b) J. Hassan, M. Sévignon, C. Gozzi, E. Schulz, M. Lemaire, *Chem. Rev.* **2002**, *102*, 1359–2469; c) Y. Uozumi, *Top. Curr. Chem.* **2004**, *242*, 77–112; d) C. A. McNamara, M. J. Dixon, M. Bradley, *Chem. Rev.* **2002**, *102*, 3275–3300; e) S. Bräse, J. H. Kirchhoff, J. Köbberling, *Tetrahedron* **2003**, *59*, 885–939.

[5] a) N. E. Leadbeater, M. Marco, *Chem. Rev.* **2002**, *102*, 3217–3274; b) S. Schweizer, J.-M. Becht, C. Le Drian, *Adv. Synth. Catal.* **2007**, *349*, 1150–1158; c) S. Schweizer, J.-M. Becht, C. Le Drian, *Org. Lett.* **2007**, 9, 377–380.

[6] A. Cwik, Z. Hell, F. Figueras, *Org.Biomol. Chem.* **2005**, *3*, 4307–4309.

[7] D. Kudo, Y. Masui, M. Onaka, *Chem. Lett.* **2007**, *36*, 918–919.

[8] R. Sayah, K. Glegota, E. Framery, V. Dufaud, *Adv. Synth. Catal.* **2007**, 349, 373–381.

[9] S.-B. Jang, *Tetrahedron Lett.* **1997**, *38*, 1793–1796.

[10] I. Fenger, C. L. Drian, *Tetrahedron Lett.* **1998**, *39*, 4287–4290.

[11] K. Inada, N. Miyaura, *Tetrahedron* **2000**, *56*, 8661–8664.

[12] B. Atrash, J. Reader, M. Bradley, *Tetrahedron Lett.* **2003**, *44*, 4779–4782.

[13] a) N. E. Leadbeater, M. Marco, *Angew. Chem. Int. Ed.* **2003**, *42*, 1407–1409; b) N. E. Leadbeater, M. Marco, *J. Org. Chem.* **2003**, *68*, 5660–5667; c) N. E. Leadbeater, M. Marco, *J. Org. Chem.* **2003**, *68*, 888–892; d) N. E. Leadbeater, M. Marco, *Org. Lett.* **2002**, *4*, 2973–2976; e) R. K. Arvela, N. E. Leadbeater, *Org. Lett.* **2005**, *7*, 2101–2104.

[14] a) L. Bai, J.-X. Wang, Y. M. Zhang, *Green Chem.* **2003**, *5,* 615–617; b) L. Bai, J.-X. Wang, *Chin. Chem. Lett.* **2004**, *15*, 286–287.

[15] a) B. M. Trost, *Science* **1991**, *254*, 1471; b) P. T. Anastas, J. C. Warner, *Green Chemistry: Theory and Practice*, Oxiford University Press, Oxford, **1998**.

[16] N. A. Bumagin, V. V. Bykov, *Tetrahedron* **1997**, *53*, 14437–14450.

[17] D. Villemin, M. J. Gomez-Escalonilla, J.-F. Saint-Clair, *Tetrhedron Lett.* **2001**, *42*, 635–637.

[18] L. Bai, Y. M. Zhang, J.-X. Wang, *QSAR Comb. Sci.* **2004**, *23*, 857–882.

[19] R. C. Weast, (Ed.), *CRC Handbook of Chemistry and Physics*, 63rd edn., CRC Press, Boca Raton, Florida, **1982**.

[20] G. W. Kabalka, L. Wang, R. M. Pagni, C. M. Hair, V. Namboodiri, *Synthesis* **2003**, 217–222.

[21] J. P. Wolfe, R. A. Singer, B. H. Yang, S. L. Buchwald, *J. Am. Chem. Soc.* **1999**, *121*, 9550–9561.

[22] M. Z. A. Badr, M. M. Aly, A. M. Fahmy, *J. Org. Chem.* **1981**, *46*, 4784–4787.

[23] M. A. Tius, *Tetrahedron Lett.* **1981**, *22*, 3335–3338.

[24] C. G. Blettner, W. A. Konig, W. Stenzel, T. Schotten, *J. Org. Chem.* **1999**, *64*, 3885–3890.

[25] M.-G. Liu, K.-F. Tong, G.-F. Luo, Q.-B. Liao, S.-L. Fu, *Chin. J. Org. Chem.* **2000**, *20*, 198–201.

[26] J. Hassan, C. Hathroubi, C. Gozzi, M. Lemaire, *Tetrahedron* **2001**, *57*, 7845–7855.