Journal of Organometallic Chemistry 693 (2008) 3692–3696

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

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

Synthesis and catalytic applications of sulfonate β-ketoimine and β-diimine in the Suzuki reaction in aqueous phase

Xuming Guo, Jin Zhou, Xiaoyan Li, Hongjian Sun *

School of Chemistry and Chemical Engineering, Shandong University, Shanda Nanlu 27, Jinan 250100, People's Republic of China

ARTICLE INFO

Article history:
Received 4 August 2008
Received in revised form 27 August 2008
Accepted 29 August 2008
Available online 8 September 2008

Keywords:
Suzuki reaction
Aryl bromide
Aryl boric acid
β-Ketoimine
β-Diimine
Palladium chloride

ABSTRACT

A series of sulfonated β-ketoimine and β-diimine compounds were synthesized and characterized. As supporting ligands they were used in the Suzuki cross-coupling reaction in aqueous phase with $PdCl_2$ as catalyst. The new catalytic system can tolerate a wide range of substrates.

1. Introduction

The homogeneous palladium-catalyzed cross-coupling reaction of aryl halides with aryl boronic acids in the presence of base, the Suzuki reaction, has become an important method for generating carbon–carbon bond, in particular for a convenient formation of biaryls, because of its higher stability, wide range functional group tolerance in the reaction partners [1–10]. Most of these reactions were performed in traditional organic solvents and resulted in considerable environmental pollution. Therefore, the replacement of organic solvents by water has received remarkable attention in catalysis. Some water-soluble catalysts for the Suzuki reaction have been developed [11–17]. But most of the water-soluble catalysts are palladium complexes with polar oder ionic phosphorus-ligand [18].

Instead of phosphorus-containing ligands, some nitrogen-containing ligands in combination with palladium compounds were used in the Suzuki reaction. A family of sulfonamide-based palladium complexes and phenylhydrazine-based palladacycles have been applied in the Suzuki reaction [19]. Liu et al. found that the cylcopalladated complex $[Pd(Cl)(\kappa^2N,C\text{–}CH_2C_6H_2(Me)_2\text{-}CH{=}NC_6H_3(Pr^i)_2)_2$ is an excellent catalyst for Suzuki crossing-coupling reactions in aqueous medium under aerobic conditions [20]. Zhang et al. developed a $Pd(OAc)_2$/guanidine aqueous system for the room-temperature Suzuki cross-coupling reaction with good to excellent yields and high turnover numbers [21].

β-Ketomine and β-diimine can be also used as supporting ligands in the olefin polymerization [22,23]. Kirchner reported an efficient synthesis of *N*,*N*′-diaryl and dialkyl β-diimines with the central carbon atom as part of five- and six-membered ring systems. At the same time, the catalytic activity of palladium(II) compounds with these ligands has been studied in *N*-methyl-2-pyrrolidone as a solvent for C–C coupling reactions [24].

In this paper we report on the synthesis, characterization and some applications of β-ketomines and β-diimines as supporting ligands in the palladium-catalyzed Suzuki reaction in aqueous phase. Reaction conditions were optimized for catalytic performance. This catalytic system was also examined using different substrates.

2. Results and discussion

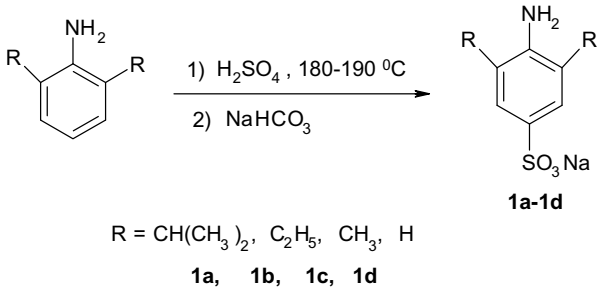
2.1. Synthesis of sulfonated β-ketoimines and β-diimines

2,6-Dialkyl anilines were sulfonated at 180–190 °C with concentrated sulfuric acid in yields of 65–75% (Scheme 1) [25,26].

The condensation of acetylacetone with the sulfonated 2,6-dialkyl anilines (**1a**–**d**) in the ratio of 1:1.1 in the presence of catalytic amounts of formic acid affords β-ketoimines (**2a**–**d**) in yields of 80–90% (Scheme 2). The sulfonated β-diimines (**3a**–**d**) were obtained by reaction of sulfonated anilines (**1a**–**d**) with acetylacetone (2:1.05) in the presence of hydrochloric acid in yields of 60–65%

* Corresponding author. Tel.: +86 531 88361350; fax: +86 531 88564464.
E-mail address: hjsun@sdu.edu.cn (H. Sun).

0022-328X/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2008.08.038



Scheme 1.

Table 1
Ligand optimization in aqueous Suzuki coupling reaction[a]

Entry	Ligand	L:Pd	Yield[b] (%)
1	No		46
2	**2c**	1:1	92[c]
3	**2c**	1:1	96
4	**2c**	1.5:1	81
5	**3a**	1:1	93
6	**3a**	1.5:1	73

[a] Reaction conditions: 1.0 mmol bromobenzene, 1.5 mmol phenylboronic acid, 1% Pd, 80 °C, 2 ml water, 1.5 mmol KOH, 0.5 mmol tetrabutylammonium bromide.
[b] GC yield after 2 h.
[c] Under aerobic conditions.

(Scheme 3). The formation of β-ketoimines (**2a**–**d**) and β-diimines (**3a**–**d**) were monitored by UV-spectroscopy using the C=N absorption band of the β-ketoimines (**2a**–**d**) at 317 nm which is separated from that of the anilines (at about 250 nm). Similarly, for the C=N group in the β-diimines the UV-absorption is shifted to 343 nm (**3a**–**d**) from that of 250 nm for the anilines (**1a**–**d**).

All β-ketoimine and β-diimine compounds were characterized by IR, ^{1}H NMR, MS, and elemental analysis. The molecular and crystal structure of the β-diimine **3b** was determined through X-ray diffraction [27].

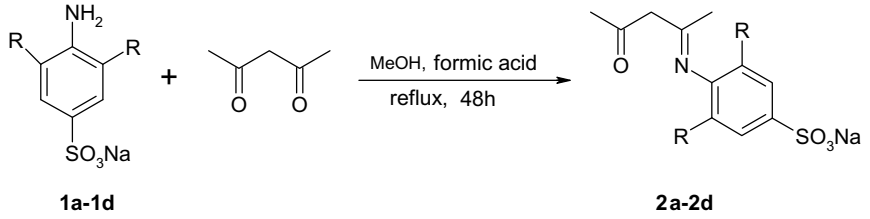
2.2. The Suzuki reaction

The reaction of bromobenzene with phenyl boronic acid in aqueous phase was selected to study the catalytic conditions (Scheme 4). The results are collected in Table 1. The yields with the ratio of ligand/palladium (1:1) are higher than those with a ratio (1.5:1) (Table 1, entry 4 and 3; entry 6 and 5). This conclusion is consistent with the catalytic system of phosphine ligands where the yields under aerobic conditions are lower than under inert atmosphere (N_2) (Table 1, entry 2 and 3) [28–30].

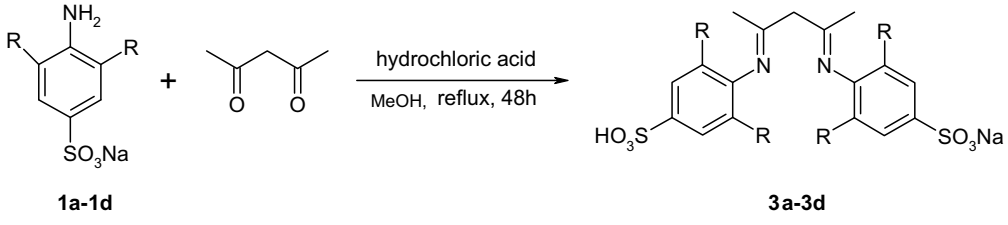
In these catalytic conditions the presence of tetrabutylammonium bromide (TBAB) is crucial, possibly because it not only acts as phase-transfer agent, but also forms $PhB(OH)_3^-Bu_4N^+$ [31–33].

Under same catalytic conditions, different bases were investigated in the experiments (Table 2). Here potassium hydroxide gave the best catalytic result. K_2CO_3, an effective base for the cyclopalladated-imine catalyst in the Suzuki reaction [34], proved to be slightly inferior to KOH, leading to a 92% isolated yield (Table 2, entry 5). Na_2CO_3 and $NaHCO_3$ are slightly inferior to K_2CO_3 (Table 2, entry 1 and 2). Other bases such as KO^{t}Bu, $N(CH_2CH_3)_3$, NaOMe, and NaOAc, proved to be less effective for the cross-coupling of bromobenzene with phenylboronic acid (Table 2, entries 3, 6–8).

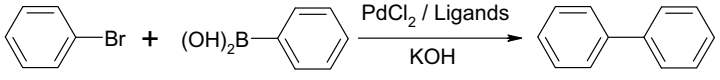
In Table 3 the results with different ligands are compared. We observed that the coupling of bromobenzene and phenylbornic acid in the presence of 1 mol% of $PdCl_2$ and KOH in water at 80 °C without any supporting ligand, gave 42% isolated yield (Table 3, entry 1). The addition of the β-ketoimine or the β-diimine ligands in the catalytic system remarkably improved the yields (Table 3, entries 2–9). With different substitutents in 2, 6-positions of the phenyl ring different trends of the sulfonated Pd/β-ketoimine system and the sulfonated Pd/β-diimine system were observed. For the sulfonated Pd/β-ketoimine system, ligand **2c** gave the highest yield (Table 3, entry 4); while ligand **3a** brought the highest



Scheme 2.



Scheme 3.



Scheme 4.

Table 2
Effect of base in water Suzuki coupling reaction[a]

Entry	Base	Yield[b] (%)
1	Na_2CO_3	76
2	$NaHCO_3$	84
3	$K(O^tBu)$	35
4	KOH	96
5	K_2CO_3	92
6	$N(CH_2CH_3)_3$	33
7	NaOMe	29
8	NaOAc	31

[a] Reaction conditions: 1.0 mmol bromobenzene, 1.5 mmol phenylboronic acid, 1% $PdCl_2$, 1% 2c, 80 °C, 2 ml water, 1.5 mmol base, 0.5 mmol tetrabutylammonium bromide (TBAB).
[b] GC yield after 2 h.

Table 3
Influence of ligands on the palladium-catalyzed Suzuki reaction of bromobenzene with phenylboronic acid[a]

Entry	Ligand	Yield[b]
1	No L	42[c]
2	**2a**	91
3	**2b**	93
4	**2c**	96
5	**2d**	87
6	**3a**	93
7	**3b**	90
8	**3c**	88
9	**3d**	84

[a] Reaction conditions: 1.0 mmol bromobenzene, 1.5 mmol phenylboric acid, 80 °C, 2 ml water, 1.5 mmol base, 0.5 mmol tetrabutylammonium bromide,
[b] Isolated yields, all reactions were monitored by GC, yields are average of two runs.
[c] A large amount of palladium black was observed.

yield (Table 3, entry 6) for the sulfonated Pd/β-diimine system. We conclude that both steric and electronic effects of these ligands play a role in the catalytic system. A detailed analysis of these trends is presently not feasible. In the Pd/β-diimine system steric effects are decisive, because ligand **3a** with the more bulky *iso*-propyl groups gives superior yields.

From Table 4 we conclude that the palladium-catalyzed Suzuki reaction with the sulfonated β-ketoimines and β-diimines as supporting ligands can not only be carried out in neat water but also in mixed media such as H_2O/CH_3CN, H_2O/C_2H_5OH, H_2O/CH_3COCH_3 giving high yields (Table 4, entries 1–3, 8–9). Surprisingly, with smaller amounts of catalyst (less than 0.05 mol%) the addition of TBAB is not essential (Table 4, entries 5–6, 10–12). In these cases the prolonged reaction times and/or raised reaction temperatures are needed in order to increase the yields. Moreover, no palladium black appeared as by-product. Under optimized conditions (0.01 mol% catalyst/100 °C/without TBAB) the Suzuki reaction with the supporting ligand **2c** could be completed after 9 h with 95% yield (Table 4, entry 7).

With the optimized conditions, we screened a representative range of aryl halides for the reaction (Scheme 5). The results are summarized in Table 5.

As illustrated in Table 5, the palladium catalyst with the sulfonated β-ketoimines and β-diimines ligands for the Suzuki reaction

Table 4
Aqueous Suzuki coupling reaction of bromobenzene and phenylboronic acid[a]

Entry	*L* (mol%)	Solvent (1:1)	TBAB (equiv.)	*t* (h)	Yield[b]
1	**2c** (0.1)	H_2O/CH_3CN	0.5	3	95
2	**2c** (0.1)	H_2O/C_2H_5OH	0.5	3	95
3	**2c** (0.1)	H_2O/CH_3COCH_3	0.5	3	94
4	**2c** (0.05)	H_2O	0.5	3	96
5	**2c** (0.03)	H_2O		6	78
6	**2c** (0.03)	H_2O		3	96[c]
7	**2c** (0.01)	H_2O		9	95[c]
8	**3a** (0.1)	H_2O/CH_3CN	0.5	3	94
9	**3a** (0.05)	H_2O/CH_3CN	0.5	3	93
10	**3a** (0.05)	H_2O		3	91
11	**3a** (0.03)	H_2O		6	72
12	**3a** (0.03)	H_2O		2	92[c]

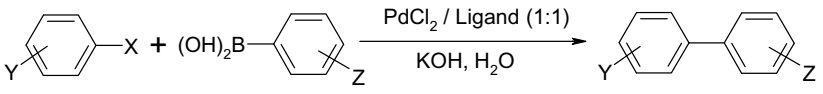
[a] Reaction conditions: 1.0 mmol bromobenzene, 1.5 mmol phenylboronic acid, 80 °C, 2 ml solvent, 1.5 mmol base.
[b] Isolated yields, all reactions were monitored by GC, yields are average of two runs.
[c] At 100 °C.

Table 5
Suzuki coupling reactions of arylbromides with various arylboronic acids[a]

Entry	X	Y	Z	*t* (h)	Yield(%)[b]
1	Br	H	H	3	93[c]
2	Br	H	4-Me	3	97
3	Br	H	4-OMe	2	95
					93[c]
4	Br	H	4-Cl	2	97
5	Br	4-Me	H	6	95
6	Br	4-Me	4-Me	4	95
7	Br	4-Me	4-OMe	3	94
8	Br	4-Me	4-Cl	4	94
					92[c]
9	Br	4-OMe	H	4	90
10	Br	4-OMe	4-Me	5	94
11	Br	4-OMe	4-OMe	4	93
12	Br	4-OMe	4-Cl	3	92
					91[c]
13	Br	4-COMe	H	3	99
					96[c]
14	Br	2-CHO	4-Me	2	99
15	Br	2-CHO	H	2	98
					96[c]
16	Br	3-NO_2	H	2	96
17	Br	3-NO_2	4-Me	3	99
					96[c]
18	Br	4-C_6H_5	H	5	90
19	Br	1-naphthalene	H	5	95
20	Br	4-NH_2	H	3	98
21	Br	2-NH_2	H	3	98
22	Cl	2-NO_2	H	12	89[d]
23	Cl	4-NO_2	4-CH_3	9	90[d]
24	Cl	H	H	24	33[d]

[a] Reaction conditions: 1.0 mmol bromobenzene, 1.5 mmol phenylboronic acid, 0.03 mol% $PdCl_2$/complex **2c**, 100 °C, 2 ml water, 1.5 mmol KOH.
[b] Isolated yields, all reactions were monitored by GC, yields are average of two runs.
[c] 0.03 mol% $PdCl_2$/**3a** complex.
[d] TBAB (0.1 equiv.) as the additive. 1.0 mol% complex was used.

proved exceptionally active. Regardless of phenyl halides and phenyl boronic acids with the electron-donating or electron-withdraw-



Scheme 5.

ing groups in different positions of the phenyl rings, these catalytic systems always gave good to excellent yields of products. The catalytic combinations tolerate a wide range of sensitive functional groups, such as CHO, NO_2, OMe, Me, NH_2, Cl, and COMe in both substrates. Even without TBAB addition the Suzuki reaction could be catalyzed by less than 0.05 mol% catalyst without by-product or palladium black. It is also worthy to be mentioned that the system is effective for the coupling of un-activated aryl chlorides (Table 5, entries 22–23), but more catalyst and a small amount of TBAB were required to improve the yield. The coupling of chlorobenzene with phenyl boronic acid gave moderate yield (Table 5, entry 24).

3. Conclusion

In conclusion, a series of water-soluble sulfonated β-ketoimine and β-diimine ligands were synthesized and characterized. As supporting ligands they can be used in the palladium-catalyzed Suzuki reaction of phenyl bromide and phenyl boronic acid in the presence of TBAB in aqueous phase. This catalytic system tolerates a wide range of substrates, including not only phenyl halides but also phenyl boronic acids. These results provide environmentally benign preparations of diaryl compounds. Further studies on the reaction mechanism with this catalytic system and further applications are currently under investigation.

4. Experimental

4.1. Synthesis of sulfonated 2,6-dialkyl anilines (*1a–d*)

The sulfonated 2,6-dialkyl anilines (**1a–d**) were prepared according to the literature [25,26].

4.2. Synthesis of the β-ketoimines (*2a–d*)

*Synthesis of **2a**:* A mixture of sulfonated 2,6-diisopropyl aniline (**1a**) (5.58 g, 20 mmol) and acetylacetone (2.20 g, 22 mmol) in refluxing anhydrous methanol (40 ml) was kept stirring, and 0.3 ml of formic acid was added to the reaction solution. Ultraviolet spectra were recorded to monitor the reaction process. When the 317 nm peak reached its maximum, the reaction was stopped. After cooling, anhydrous ether was added dropwise to the reaction solution until a white solid appeared. Stirring was continued at room-temperature until a large amount of white solid had formed. Filtration and evaporation of the solvent afforded **2a** as a white solid (6.50 g, 90%). ^{1}H NMR (300 MHz, D_2O): δ 7.58 (s, 2H, Ar), 5.30 (s, 1H, CH), 2.79–2.93 (heptet, J = 6.9, 2H, CH), 1.96 (s, 3H, CH_3), 1.54 (s, 3H, CH_3), 1.11–1.13 (d, J = 6.9, 6H, CH_3), 0.99–1.01 (d, J = 6.9, 6H, CH_3). MS (APCI-MS): m/z: 338.4 $[M-Na]^-$. Elemental Anal. Calc. for $C_{17}H_{24}NNaO_4S$ (361.44 g/mol): C: 56.49%; H: 6.69%; N: 3.88%. Found: C: 56.36; H: 6.60; N: 3.91%.

Compounds **2b**, **2c**, and **2d** were obtained with the same method as for **2a**.

*Compound **2b***: ^{1}H NMR (300 MHz, D_2O): δ 7.49 (s, 2H, Ar), 5.29 (s, 1H, CH), 2.46–2.38 (q, J = 7.2 Hz, 4H, CH_3), 2.12 (s, 3H, CH_3), 1.54 (s, 3H, CH_3), 1.10–0.98 (t, J = 7.2 Hz, 6H, CH_3). MS (APCI-MS): m/z: 310.3 $[M-Na]^-$. Elemental Anal. Calc. for $C_{15}H_{20}NNaO_4S$ (333.38 g/mol): C: 54.04; H: 6.05; N: 4.20. Found: C: 53.98%; H: 5.99%; N: 4.10%.

*Compound **2c***: ^{1}H NMR (300 MHz, D_2O): δ7.50 (s, 2H, Ar), 5.34 (s, 1H, CH), 2.13 (s, 6H, CH_3), 1.99 (s, 3H, CH_3), 1.16 (s, 3H, CH_3). MS (APCI-MS): m/z: 282.1 $[M-Na]^-$. Elemental Anal. Calc. for $C_{13}H_{16}NNaO_4S$ (305.33 g/mol): C: 51.14; H: 5.28; N: 4.59. Found: C: 51.32; H: 5.28; N: 4.75%.

*Compound **2d***: ^{1}H NMR (300 MHz, D_2O): δ *7.66–7.63* (d, J = 8.7Hz, 2H, Ar), 7.16–7.13 (d, J = 8.7 Hz, 2H, Ar), 5.217 (s, 1H, CH), 1.92 (s, 6H, CH_3). MS (APCI-MS): m/z: 254.1 $[M-Na]^-$. Elemental Anal. Calc. for $C_{11}H_{12}NNaO_4S$ (277.28 g/mol): C: 47.65; H: 4.36; N: 5.05. Found: C: 47.48; H: 4.28; N: 5.10%.

4.3. Synthesis of the β-diimines (*3a–d*)

*Synthesis of **3a**:* A mixture of sulfonated 2,6-diisopropyl aniline (**1a**) (5.58 g, 20 mmol) and acetylacetone (1.05 g, 10.5 mmol) in anhydrous methanol was stirred under reflux (40 ml). 0.82 ml of concentrated HCl (10 mmol) was added dropwise. The reaction was monitored by recording UV spectra. When the 343 nm peak reached its maximum, the reaction was stopped. After cooling, anhydrous ether was added dropwise until a small amount of white solid had formed. Stirring was continued at room-temperature until precipitation was complete, filtration and evaporation of the remaining solvent afforded **3a** as a white solid (3.60 g, 59%). ^{1}H NMR (300 MHz, D_2O): δ7.41 (s, 4H, Ar), 4.21 (s, 1H, CH), 2.65–2.58 (heptet, J = 6.6 Hz, 4H, CH), 2.56 (s, 6H, CH_3), 0.94–0.92 (d, J = 6.6 Hz, 12H, CH_3), 0.74–0.71 (d, J = 6.6 Hz, 12H, CH_3). MS (APCI-MS): m/z: 577.5 ($[M-Na]^-$, 100%), 288.4 ($[M-Na-H]/2$, 42%). Elemental Anal. Calc. for $C_{29}H_{41}N_2Na_2O_6S_2$ (600.78 g/mol): C: 57.98; H: 6.88; N: 4.66. Found: C: 57.92; H: 6.48; N: 4.65%.

Compound **3b**, **3c**, and **3d** were obtained with the same method as for **3a**.

*Compound **3b***: ^{1}H NMR (300 MHz, D_2O): δ7.28 (s, 4H, Ar), 4.133 (s, 1H, CH), 2.53 (s, 6H, CH_3), 2.16 (q, J = 7.5 Hz, 8H, CH_2), 0.82-0.77 (t, J = 7.5 Hz, 12H, CH_3), MS (APCI-MS): m/z: 521.2 ($[M-Na]^-$, 48%), 260.1 ($[M-Na-H]/2$, 100%). Elemental Anal. Calc. for $C_{25}H_{33}N_2Na_2O_6S_2$ (544.67 g/mol): C: 55.13; H: 6.11; N: 5.14. Found: C: 55.26; H: 6.00; N: 5.50%.

*Compound **3c***: ^{1}H NMR (300 MHz, D_2O): δ7.20 (s, 4H, Ar), 4.06 (s, 1H, CH), 2.52 (s, 6H, CH_3), 1.79 (s, 12H, CH_3), MS (APCI-MS): m/z: 465.0 ($[M-Na]^-$, 25%), 232.1 ($[M-Na-H]/2$, 100%). Elemental Anal. Calc. for $C_{21}H_{25}N_2Na_2O_6S_2$ (488.56 g/mol): C: 51.63; H: 5.16; N: 5.73. Found: C: 51.88; H: 5.19; N: 6.00%.

*Compound **3d***: ^{1}H NMR (300 MHz, D_2O): δ7.74–7.71 (d, 2H, J = 7,8Hz, Ar), 7.33–7.30 (d, 2H, J = 7.8, Ar), 5.52 (s, 1H, CH), 2.36 (s, 6H, CH_3). MS (APCI-MS): m/z: 409.1 ($[M-Na]^-$, 65%), 204.1 ($[M-Na-H]/2$, 100%). Elemental Anal. Calc. for $C_{17}H_{17}N_2Na_2O_6S_2$ (432.45 g/mol): C: 47.22; H: 3.96; N: 6.48. Found: C: 47.38; H: 4.20; N: 6.59%.

4.4. General procedure for the Suzuki coupling reaction

Under nitrogen, a round bottom flask equipped with a reflux condenser, was charged with bromobenzene (0.157 g, 1 mmol), phenyl boronic acid (0.183 g, 1 mmol), KOH (0.0842 g, 1.5 mmol), a stock solution of 2 c/$PdCl_2$ complex in water (0.001 M, 1 ml), and 1 ml water. The mixture was stirred in a preheated 100 °C oil bath for 3 h, and then allowed to cool to room-temperature. After the addition of water (8 ml) and extraction with ether (3×10 ml), the organic phase was dried over $MgSO_4$, filtered, passed over silica gel by flash chromatography and analyzed by GC and GC-MS. All products were characterized by NMR [35].

Acknowledgements

This work was supported by NSFC No. 20372042 and the Science Foundation of Shandong Y2006B18.

References

[1] N. Miyaura, T. Yanagi, A. Suzuki, Syn. Commun. 11 (1981) 513.
[2] N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457.
[3] S.P. Stanforth, Tetrahedron 54 (1998) 263.
[4] A. Suzuki, J. Organomet. Chem. 576 (1999) 147.
[5] A. Suzuki, J. Organomet. Chem. 653 (2002) 83.

[6] N. Miyaura, Top. Curr. Chem. 219 (2002) 11.
[7] A.F. Littke, G.C. Fu, Angew. Chem. Int. Ed. 41 (2002) 4176.
[8] R.B. Bedford, C.S.J. Cazin, D. Holder, Coord. Chem. Rev. 248 (2004) 2283.
[9] F. Bellina, A. Carpita, R. Rossi, Synthesis (2004) 2419.
[10] A.C. Frisch, M. Beller, Angew. Chem. Int. Ed. 44 (2005) 674.
[11] R.K. Arvela, N.E. Leadbeater, M.S. Sangi, V.A. Williams, P. Granados, R.D. Singer, J. Org. Chem. 70 (2005) 161.
[12] J. Gil-Moltó, S. Karlström, C. Nájera, Tetrahedron 61 (2005) 12168.
[13] N.E. Leadbeater, M. Marco, J. Org. Chem. 68 (2003) 888.
[14] C.G. Blettner, W.A. König, W. Stenzel, T. Schotten, J. Org. Chem. 64 (1999) 3885.
[15] D.N. Korolev, N.A. Bumagin, Tetrahedron Lett. 46 (2005) 5751.
[16] J.P. Genet, A. Linquist, E. Blart, V. Mourie's, M. Savignac, M. Vaultier, Tetrahedron Lett. 36 (1995) 1443.
[17] G.A. Molander, B. Biolatto, J. Org. Chem. 68 (2003) 4302.
[18] K.H. Shaughnessy, R.S. Booth, Org. Lett. 3 (2001) 2757.
[19] N.S.C. Ramesh Kumar, I. Victor Paul Raj, A. Sudalai, J. Mol. Cat. A: Chem. 269 (2007) 218.
[20] C.L. Chen, Y.H. Liu, S.M. Peng, S.T. Liu, Tetrahedron Lett. 46 (2005) 521.
[21] S.H. Li, Y.J. Lin, J.G. Cao, S.B. Zhang, J. Org. Chem. 72 (2007) 4067.
[22] J. Feldman, S.J. Mclain, A. Parthasarathy, W.J. Marshall, J.C. Calabrese, S.D. Arthur, Organometallics 16 (1997) 1514.
[23] C. Wang, S. Friedrich, T.R. Younkin, R.T. Li, R.H. Grubbs, D.A. Bansleben, M.W. Day, Organometallics 17 (1998) 3149.
[24] D. Domin, D. Benito-Garagorri, K. Mereiter, J. Fröhlich, K. Kirchner, Organometallics 24 (2005) 3957.
[25] A. Courtin, H.R. Tobel, P. Doswald, Helv. Chim. Acta 61 (1978) 3079.
[26] F. Kanetani, H. Yamaguchi, Bull. Chem. Soc. Jpn. 54 (1981) 3048.
[27] X.M. Guo, Q.B. Wang, K. Harms, H. Sun, J. Acta Cryst. E63 (2007) m2316.
[28] A.F. Littke, C. Dai, G.C. Fu, J. Am. Chem. Soc. 122 (2000) 4020.
[29] J.F. Hartwig, M. Kawatsura, S.I. Hauck, K.H. Shaughnessy, L.M. Alcazar-Roman, J. Org. Chem. 64 (1999) 5575.
[30] K.H. Shaughnessy, R.S. Booth, Org. Lett. 3 (2001) 2757.
[31] T. Jeffery, Tetrahedron Lett. 35 (1994) 3051.
[32] D. Badone, M. Baroni, R.A. Cardamone, I.U. Guzzi, J. Org. Chem. 62 (1997) 7170.
[33] L. Botella, C. Náera, Angew. Chem. Int. Ed. 41 (2002) 179.
[34] H. Weissman, D. Milstein, Chem. Commun. (1999) 1901.
[35] (1) Biphenyl δ 7.59–7.57 (m, 4H), 7.44–7.40 (m, 4H), 7.35–7.30 (m, 2H). (2) 4-Methylbiphenyl δ 7.54 (d, J = 8.1 Hz, 2H), 7.45 (d, J = 8.1 Hz, 2H), 7.37 (t, J = 7.8 Hz, 2H), 7.27 (t, J = 8.4 Hz, 1H), 7.19 (d, J = 7.8 Hz, 2H), 2.34 (s, 3H). (3) 4-Methoxybiphenyl δ 7.57–7.52 (m, 4H), 7.42 (t, J = 7.2 Hz, 2H), 7.30 (t, J = 7.2 Hz, 1H), 6.98 (d, J = 9.0 Hz, 2H), 3.85 (s, 3H). (4) 2-Methylbiphenyl δ 7.43–7.35 (m, 2H), 7.34–7.27 (m, 3H), 7.26–7.18 (m, 4H), 2.27 (s, 3H). (5) 4-Acetylbiphenyl δ 8.04 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.7 Hz, 2H), 7.62 (d, J = 8.7 Hz, 2H), 7.55–7.30 (m, 3H), 2.64 (s, 3H). (6) 4-Chlorobiphenyl δ 7.68–7.33 (m 9H). (7) 2-biphenylcarbaldehyde δ 9.98 (s, 1H), 8.03 (d, J = 7.80 Hz, 1H), 7.67–7.61 (m, 1H), 7.52–7.36 (m, 7H). (8) 3-Nitrobiphenyl δ 8.43 (s, 1H), 8.18 (d, J = 8.10 Hz, 1H), 7.90 (d, J = 7.80 Hz, 1H), 7.62–7.56 (m, 3H), 7.51–7.39 (m, 3H). (9) *p*-Terphenyl δ 7.68–7.55 (m, 8H), 7.48–7.44 (m, 4H), 7.38–7.33 (m, 2H). (10) 4-Aminobiphenyl δ 7.52 (d, J = 7.2 Hz, 2H), 7.48–7.35 (m, 4H), 7.25 (t, J = 7.2 Hz, 1H), 6.71 (d, J = 8.7 Hz, 2H), 3.66 (s, 2H). (11) 4, 4′-Dimethoxybiphenyl δ 7.47 (d, J = 9.0 Hz, 4H), 6.95 (d, J = 9.0 Hz, 4H), 3.83 (s, 6H). (12) 4-Methoxy-4′-methylbiphenyl δ 7.50 (d, J = 8.7 Hz, 2H), 7.45 (d, J = 7.8 Hz, 2H), 7.22 (d, J = 7.8 Hz, 2H), 6.96 (d, J = 8.7 Hz, 2H), 3.83 (s, 3H), 2.38 (s, 3H). (13) 4-Methylbiphenyl-2′-carbaldehyde δ 9.98 (s, 1H), 8.00 (d, J = 7.8 Hz, 1H), 7.60 (t, J = 7.5 Hz, 1H), 7.44(s, J = 7.8 Hz, 1H), 7.41 (d, J = 7.5 Hz, 1H), 7.25 (s, 4H), 2.41 (s, 3H). (14) 4-Chloro-4′-methoxybiphenyl δ 7.51–7.46 (m, 4H), 7.39 (d, J = 8.7 Hz, 2H), 6.98 (d, J = 8.7 Hz, 2H), 3.86 (s, 3H). (15) 4-Nitro-4-methylbiphenyl δ 8.25 (d, J = 8.7 Hz, 2H), 7.72 (d, J = 8.7 Hz, 2H), 7.53 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 2.42 (s, 3H). (16) 2-Aminobiphenyl δ 7.42–7.38 (m, 4H), 7.36–7.28 (m, 1H), 7.12 (t, J = 7.8 Hz, 2H), 6.80 (t, J = 7.8 Hz, 1H), 6.72 (d, J = 7.8 Hz, 1H), 3.58 (s, 2H). (17) 2-Nitro-4'-methylbiphenyl δ 8.43 (s, 1H), 8.16 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 7.8 Hz, 1H), 7.58 (t, J = 7.8 Hz, 1H), 7.52 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 7.8 Hz, 2H), 2.42 (s, 3H). (18) 4-Methyl-4′-methylbiphenyl δ 7.45 (d, J = 7.8 Hz, 4H), 7.20 (d, J = 7.8 Hz, 4H). (19) 4-Chloro-4′-methylbiphenyl δ 7.50–7.42 (m, 4H), 7.37 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H). (20) 1-phenylnaphthalene δ 7.81–7.71 (m, 3H), 7.41–7.29 (m, 9H).