Suzuki cross-coupling of aryl halides with phenylboronic acid catalysed by an amidoxime fibres-nickel(0) complex

Zhi-Chuan Wu, Ye-Neng Lu, Yi-Ming Ren, Zhi-Ming Chen and Ting-Xian Tao*

Department of Biochemical Engineering, Anhui Polytechnic University, Wuhu, 241000, P. R. China

---

Amidoxime fibres–nickel(0) complexes [Ni(0)–AOFs] were synthesised by combining a Ni^{2+}-solution with amidoxime fibres and reduced by NaH_2PO_2. The Ni(0)–AOFs are inexpensive phosphine-free recyclable heterogeneous catalysts for the Suzuki coupling reaction of aryl halides with phenylboronic acid to provide the corresponding biphenyls in high yields. The heterogeneous catalyst can be readily recovered by simple filtration and reused several times without significant loss of activity.

Keywords: Ni(0)–AOFs, Suzuki reaction, amidoxime fibres, heterogeneous catalyst

---

The transition metal-catalysed Suzuki cross-coupling reaction is an efficient methods for the construction of C–C bonds.[1–6] The Suzuki reaction has been widely used in the synthesis of natural products, pharmaceutical intermediate and useful materials containing aryl–aryl bonds.[7–12] Various efficient Pd catalyst precursors have been developed that allow aryl iodides, bromides, triflates and chlorides to be effectively coupled with aryl boronic acids under mild reaction conditions.[13–17] Ni-based catalysts have also been successfully used for the Suzuki reaction of aryl chlorides.[18–21] Most of the Ni-based catalysts are homogeneous and always have phosphine ligands.[22–24] Although they have a high catalytic activity and selectivity, homogeneous nickel catalysts are difficult to separate, reuse and the phosphine ligands are harmful to environment. To solve this problem, various heterogeneous nickel catalysts have been developed.[25–28] Modified fibres research has become widespread.[29–32] Previously, we have described the Suzuki reactions of aryl bromides catalysed by an amidoxime fibre–palladium^{II} complex.[33] The use of amidoxime fibres (AOFs)–nickel complex in catalysing the Suzuki reactions was discovered during this experimental study.

We report here an efficient preparation of AOFs–nickel complexes and their application as heterogeneous catalysts for the Suzuki cross-coupling reaction under ambient conditions.

Firstly, the Ni(0)–AOFs was characterised. Figure 1 shows SEM patterns of the AOFs (Fig. 1a), Ni(II)–AOFs (Fig. 1b), Ni(0)–AOFs before (Fig. 1c), after reaction (Fig. 1d) and after recycling five times (Fig. 1e). Before the preparation, the amidoxime fibres and the Ni(II)–AOFs were cylindrical and the surface was very smooth, showing unique fibrous texture (Fig. 1a and 1b). The presence of Ni was confirmed by EDS (Fig. 2a) on the surface of Ni(II)–AOFs. Before the Suzuki cross-coupling reaction, the Ni(0)–AOFs showed a crude surface with a lot of irregularly shaped particles. The particle size was about 300 nm (Fig. 1c), and the presence of Ni was confirmed by EDS (Fig. 2b) in the surface. Figure 1d shows the Ni(0)–AOFs after the reaction. The morphology of the Ni in Ni(0)–AOFs surface had changed after the reaction and the amount of the highly active granular Ni had reduced. The unique fibrous texture was clearly displayed in Fig. 1e. Most of the highly active granular Ni had disappeared after the recycling. This might be the reason for the low yield in the last recycling reaction (Table 4, Run 5).

Figure 3 shows the XRD patterns of AOFs (Fig. 3a), Ni(0)–AOFs(Fig. 3b) and Ni(0)–AOFs (Fig. 3c). The XRD results indicated that the diffraction peaks centered at 18.6° [33] resulted from AOFs (Fig. 3a and 3b), and there were no characteristic diffraction peaks for Ni. After the reduction reaction, characteristic diffraction peaks of Ni disappeared at 46.2° and indicated amorphous structure. Combining with analysis of SEM, it indicated small particle size of Ni(0) and poor crystallinity.

The Ni(0)–AOFs were then used in the Suzuki cross-coupling reaction to check their catalytic activity. The coupling between iodobenzene and phenylboronic acid was chosen as the model reaction. Initially, a single solvent such as DMF, EtOH, and H_2O was studied. As shown in Table 1, single solvents gave low yields for the reaction (Table 1, entries 1–3). However, high yields were obtained (Table 1, entries 4 and 5) after we adopted an organic/aqueous co-solvent. The value of the co-solvent may be attributed to the good solubility of the organic reactants and the inorganic base.

Next, we examined the effects of bases on the Suzuki reaction in EtOH/H_2O. Organic and inorganic bases including Et_3N, NaOH, KOH, $NaHCO_3$, Na_2CO_3, $K_3PO_4{\cdot}3H_2O$ and K_2CO_3 were investigated (Table 2, entries 2–7). As shown in Table 2, K_2CO_3 was the best base for the reaction giving a high yield. The results showed that the best amount of K_2CO_3 was 2 equiv. to iodobenzene (Table 2, entry 10). A low yield was obtained without any base or by using a strong base (Table 2, entries 1–3). Under the optimised reaction conditions, the effect of the amount of the Ni(0)–AOFs was examined. Various amounts of Ni(0)–AOFs were used to catalyse the coupling between iodobenzene and phenylboronic acid. The purified yield showed that the best amount of Ni(0)–AOFs was 6 mol% to iodobenzene (Table 2, entry 10). The yield was not increased when more amount of Ni(0)–AOFs was added.

Finally, the coupling of various aryl iodides and aryl bromides with phenylboronic acid catalysed by AOFs–nickel(0) complex were investigated (Table 3). All of the aryl iodides were converted to the corresponding biphenyls in high yields (Table 3, entries 1–8). However, the yield obtained from 2-iodobenzoic acid was lower than the others possibly be due to steric effects (Table 3, Entry 6). The yields from the aryl bromides were slightly lower than the aryl iodides. Nevertheless, aryl bromides substituted by electron-withdrawing substituents in the *para*-position increased the reactivity and the corresponding products were obtained in high yields (Table 3, entries 11–13).

The recycling performance of Ni(0)–AOFs was investigated in the reaction of iodobenzene and phenylboronic acid. Ni(0)–AOFs was filtered from the reaction, washed with hot ethanol and water, and reused in a subsequent reaction. The data listed in Table 4 show that Ni(0)–AOFs could be reused four times without significant loss of catalytic activity.

In conclusion, Ni(0)–AOFs are polymer-supported and inexpensive catalysts, which exhibit good catalytic activity in promoting the Suzuki reaction of aryl halides with phenylboronic acid. The reaction has a wide functional group tolerance. Furthermore, the catalyst can be reused four times without significant loss of catalytic activity. The results imply that the Ni–AOFs catalyst may be a potential alternative for the construction of the aryl–aryl moiety.

---

* Correspondent. E-mail: tingxiantao@yahoo.cn

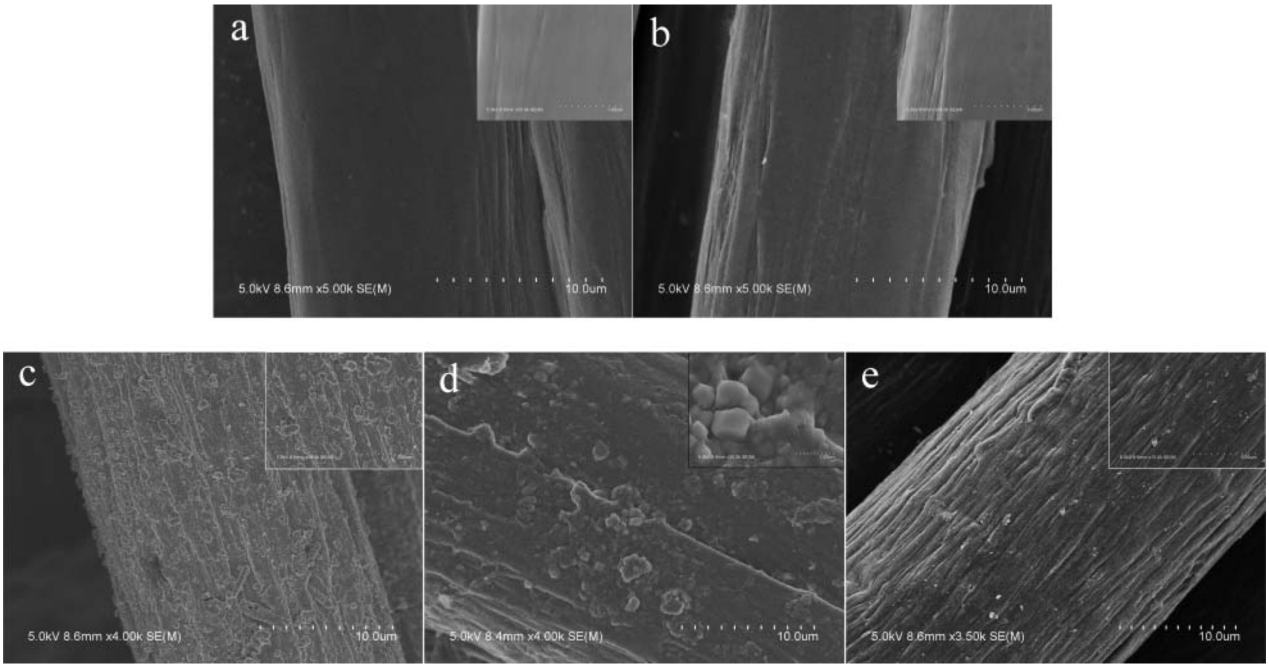


Fig. 1 SEM patterns of the AOFs (a); Ni(II)–AOFs (b); Ni(0)–AOFs before reaction (c); after reaction (d); after recycling five times (e).

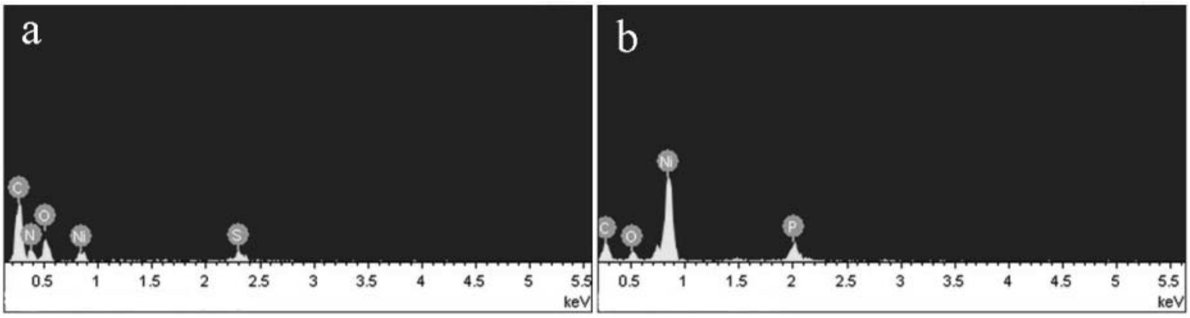


Fig. 2 Energy spectrum diagram of Ni(II)–AOFs (b) and Ni(0)–AOFs.

Experimental

The polyacrylonitrile (PAN) fibres were provided by the Jilin Carbon Co., Ltd. (Jilin, China). Reagents were obtained from commercial sources and were used without further purification. All products were known compounds and were identified by comparing their melting points and ^{1}H NMR with those reported in the literature.

A Hitachi S-4800 field-emission scanning electron microscope equipped with an energy dispersive spectrometer was employed to examine the morphologies of the samples. The sample fibres were pressed into disks to examine their phase structures using a Philips X’ Pert PRO SUPER (XRD) with CuKα radiation in step-scan mode. The tests were performed with an accelerating voltage of 40 kV and a current of 50 mA, as well as a scanning step size of 0.02° and a step time of 0.2 s (the XRD profiles were recorded from 10 to 80°). ^{1}HNMR spectra were obtained with Bruker ARX-300 spectrometer.

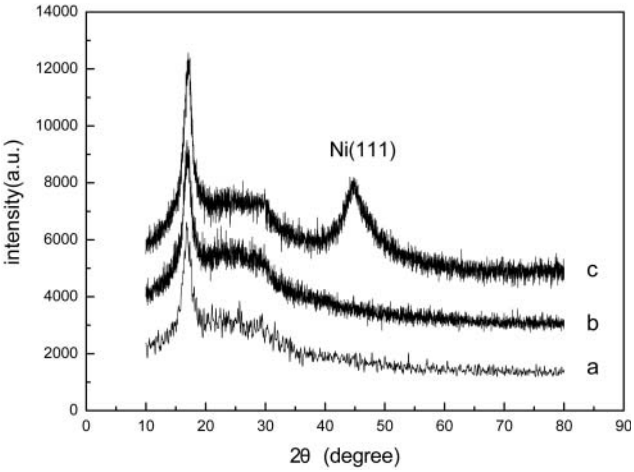
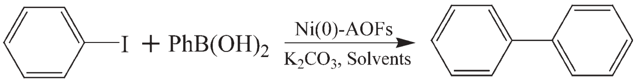


Fig. 3 XRD patterns of AOFs (a) Ni(II)–AOFs (b), and Ni(0)–AOFs (c).

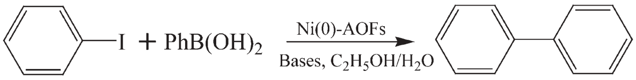
Table 1 The effect of solvents on the Ni(0)–AOFs catalysed Suzuki reaction[a]



Entry	Solvents	Yield/%[b]
1	C_2H_5OH	/
2	H_2O	17
3	DMF	/
4	C_2H_5OH/H_2O (1: 1)	87
5	C_2H_5OH/H_2O (2: 1)	98
6	DMF/H_2O (1: 1)	16
7	DMF/H_2O (2: 1)	10

[a] Reaction conditions: iodobenzene (10.0 mmol), phenylboronic acid (11.0 mmol), Ni(0)–AOFs (6 mol%), K_2CO_3 (11.0 mmol), reaction time (4 h), heating reflux, solvent (30 mL).
[b] Isolated yield.

Table 2 The effect of various bases on the Ni(0)–AOFs catalysed Suzuki reaction[a]



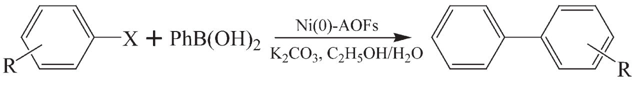
Entry	Base (base: iodobenzene /mol:mol)	Yield/%[b]
1	no base (/)	/
2	KOH(2:1)	<1
3	NaOH (2:1)	6
4	Et_3N (2:3)	15
5	$NaHCO_3$ (2:1)	95
6	Na_2CO_3 (1:1)	94
7	$K_3PO_4·3H_2O$ (2:3)	78
8	K_2CO_3 (1:2)	80
9	K_2CO_3 (1:1)	90
10	K_2CO_3 (2:1)	98, 41[c], 80[d], 98[e], 98[f]
11	K_2CO_3 (3:1)	98

[a] Reaction conditions: iodobenzene (10.0 mmol), phenylboronic acid (11.0 mmol), Ni(0)–AOFs (6 mol%), C_2H_5OH: H_2O (V/V = 2) 30 mL, reaction time (4 h), heating reflux

[b] Isolated yield.

[c] Ni(0)–AOFs: 3 mol%. [d] Ni(0)–AOFs: 4.5 mol%. [e] Ni(0)–AOFs: 7.5 mol%. [f] Ni(0)–AOFs: 9 mol%.

Table 3 Effect of substituent groups on the Ni(0)–AOFs catalysed Suzuki reaction[a]



1 **2**

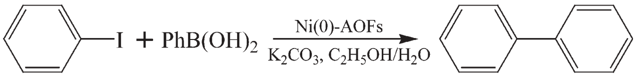
X=I, Br

Entry	R	X	Time/h	Products	Yield/%[b]
1	H	I	4	**2a**	98
2	4-H_3CO	I	4	**2b**	95
3	4-CH_3	I	4	**2c**	90
4	4-H_2N	I	4	**2d**	87
5	4-O_2N	I	4	**2e**	92
6	2-COOH	I	4	**2f**	75
7	3-COOH	I	4	**2g**	89
8	4-COOH	I	4	**2h**	96
9	H	Br	8	**2a**	91
10	4-CH_3	Br	8	**2c**	54
11	4-CH_3CO	Br	8	**2i**	92
12	4-COOH	Br	8	**2h**	94
13	4-O_2N	Br	8	**2e**	90
14	4-H_2N	Br	8	**2d**	48
15	3-CH_3O	Br	8	**2j**	28

[a] Reaction conditions: aryl halides (10.0 mmol), phenylboronic acid (11.0 mmol), Ni(0)–AOFs (6 mol%), C_2H_5OH:H_2O (V/V = 2) 30 mL, reaction time, heated under reflux.

[b] Isolated yield.

Table 4 Effect of reusability of catalyst on the Ni(0)–AOFs catalysed Suzuki reaction[a]



Run	Yield/%[b]
1	98
2	95
3	90
4	80
5	40

[a] Reaction conditions: iodobenzene (10.0 mmol), phenylboronic acid (11.0 mmol), Ni(0)–AOFs (6 mol%), K_2CO_3 (11.0 mmol), C_2H_5OH/H_2O (V/V = 2) 30 mL, reaction time (4 h), heated under reflux.

[b] Isolated yield.

Preparation of the catalyst

The PAN fibres (1 g) were immersed in NH_2OH aqueous solution (200 mL, 1 mol L^{-1}) at 65 °C for 1.5 h. The resultant fibres (AOFs) were filtered off, washed with distilled water several times and dried.[33] Subsequently, the AOFs (0.4 g) and $NiSO_4$-solution (30 mL, 0.15 mol L^{-1}) were stirred at 25 °C for 6 h and then filtered. The Ni^{II}–AOFs were washed by distilled water several times and reduced with NaH_2PO_2 (50 mL, 0.2 mol $L^{-1)}$, Finally the grey fibres [Ni(0)–AOFs] were dried at room temperature in air (Scheme 1).

The AOFs–nickel(0) complex was dissolved in a nitric acid solution (50 mL, 50% HNO_3). The content of Ni(0)–AOFs surface was obtained by using a titration analysis method to measure the concentration of Ni^{2+}-solution. It was 7.5 mmol $g^{-1.}$

Coupling reactions

A solution of phenylboronic acid (11 mmol), aryl iodide (10 mmol) and K_2CO_3 (20 mmol) in EtOH (30 mL, EtOH: H_2O = 2: 1) was treated with Ni(0)–AOFs (6 mol%) at room temperature. After the mixture was stirred and refluxed for 4 h, the catalyst was separated by filtration, washed with hot ethanol and distilled water, and dried at room temperature, and reused in a next cycle. The filtrate was cooled, and products were precipitated as white scaly crystals. The the solid product was filtered, dried, and recrystallised from EtOH–H_2O to afford the pure product.

Biphenyl (**2a**): White solid, m.p. 70–71 °C (lit.[33] 70–71 °C), ^1H NMR (300 MHz, $CDCl_3$): δ 7.32 (t, *J* = 7.5 Hz, 2H), 7.42(t, *J* = 7.5 Hz, 4H), 7.58 (d, *J* = 6.9 Hz, 4H).

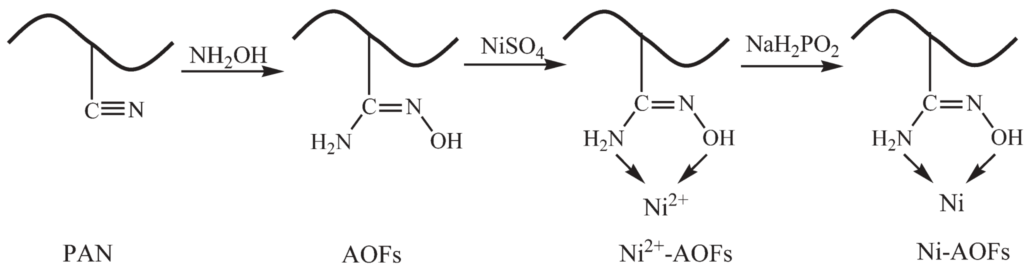
4-Methoxybiphenyl (**2b**): White solid, m.p. 88–90 °C (lit.[33] 88–90 °C), ^1H NMR (300 MHz, $CDCl_3$): δ 3.82 (s, 3H), 6.96 (d, *J* = 8.4 Hz, 2H), 7.28–7.31 (m, 1H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.50–7.55 (m, 4H).

4-Methylbiphenyl (**2c**): Colourless solid, m.p. 45–47 °C (lit.[33] 45–48 °C), ^1HNMR (300 MHz, $CDCl_3$): δ 2.37 (s, 3H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.27–7.32 (m, 1H), 7.38–7.43 (m, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.55–7.58 (m, 2H).

4-Aminobiphenyl (**2d**): Brown solid, m.p. 52–54 °C (lit.[33] 52–54 °C), ^1H NMR (300 MHz, $CDCl_3$): δ 3.72 (br s, 2H), 6.75 (d, *J* = 8.4 Hz, 2H), 7.25–7.28 (m, 1H), 7.36–7.43 (m, 4H), 7.53 (d, *J* = 9.0 Hz, 2H).

4-Nitrobiphenyl (**2e**): Pale yellow solid, m.p. 114–115 °C (lit.[33] 114–115 °C), ^1H NMR (300 MHz, $CDCl_3$): δ 7.41–7.51 (m, 3H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 9.0 Hz, 2H), 8.26 (d, *J* = 9.0 Hz, 2H).

2-Phenylbenzoic acid (**2f**): White solid, m.p. 110–113 °C (lit.[8] 110–113 °C), ^1H NMR (300 MHz, $CDCl_3$) 7.96 (d, *J* = 7.8 Hz, 1H), 7.60–7.55 (m, 1H), 7.46–7.36 (m, 7H).



Scheme 1 Synthesis of Ni(0)–AOFs.

3-Phenylbenzoic acid (**2g**): White solid, m.p. 164–166 °C (lit.[8] 164–168 °C), ^{1}H NMR (300 MHz, DMSO): δ 7.41–7.45 (m, 1H), 7.53 (t, J = 7.8 Hz, 6.9 Hz, 2H), 7.63 (t, J = 7.8 Hz, 2H), 7.72 (d, J = 7.2 Hz, 2H), 7.96 (t, J = 8.7 Hz, 8.1 Hz, 2H), 8.21 (s, 1H).

4-Phenylbenzoic acid (**2h**): White solid, m.p. 223–225 °C (lit.[8] 223–226 °C), ^{1}H NMR (300 MHz, DMSO): δ 7.39–7.52 (m, 3H), 7.73 (d, J = 6.9 Hz, 2H), 7.79 (d, J = 8.4 Hz, 2H), 8.03 (d, J = 8.4 Hz, 2H).

4-Acetylbiphenyl (**2i**): White solid, m.p. 118–120 °C (lit.[33] 118–123 °C), ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.62 (s, 3H), 7.38–7.48 (m, 3H), 7.60–7.68 (m, 4H), 8.02 (d, J = 8.4 Hz, 2H).

3-Methoxybiphenyl (**2j**): Pale yellow liquid, refractive index: 1.6070–1.6090 (lit.[33] refractive index: 1.6070–1.6100), ^{1}H NMR (300 MHZ, $CDCl_3$) δ 3.89 (s, 3H), 6.93–6.95 (d, J = 7.86, 1H), 7.18–7.24 (dd, J_1 = 10.86, J_2 = 7.65, 2H), 7.37–7.40 (d, 2H), 7.45–7.50 (t, J = 7.15, 2H), 7.62–7.65 (d, J = 7.23, 2H).

This research was supported by the National Natural Science Foundation of China (Nos. 21171003, 20771002, 21101002).

Received 28 March 2013; accepted 13 May 2013
Paper 1301863   doi: 10.3184/174751913X13726940260318

References

1 N. Miyaura, T. Yanagi and A. Suzuki, *Synth. Commun.*, 1981, **11**, 513.
2 N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457.
3 D.A. Safin and M.G. Babashkina, *Catal. Lett.*, 2009, **130**, 679.
4 T. Zell, M. Feierabend, B. Halfter and U. Radius, *J. Organomet. Chem.*, 2011, **696**, 1380.
5 Y. He and C. Cai, *Catal. Commun.*, 2011, **12**, 678.
6 F.E. Negrete, S.H. Ortega and D.M. Morales, *Inorg. Chim. Acta.*, 2012, **387**, 58.
7 B.H. Lipshutz, J.A. Sclafani and P.A. Blomgren, *Tetrahedron*, 2000, **56**, 2139.
8 G.K. Rao, A. Kumar, J. Ahmed and A.K. Singh, *Chem. Commun.*, 2010, **46**, 5954.
9 D.D.L. Martins, L.C.S. Aguiar and O.A.C. Antunes, *J. Organomet. Chem.*, 2011, **696**, 2845.
10 C. Tan, F.S. Liu, D.S. Shen, T. Cheng and Z.Z. Zhou, *Catal. Lett.*, 2011, **141**, 1332.
11 J. Wang, C.J. Yang, H.N. Peng, Y.S. Deng and X.C. Gao, *Synth. Commun.*, 2011, **41**, 832.
12 L. Wan and C. Cai, *Catal. Commun.*, 2012, **24**, 105.
13 S.S. Soomro, F.L. Ansari, K. Chatziapostolou and K. Köhler, *J. Catal.*, 2010, **273**, 138.
14 R. Rossi, F. Bellina and M. Lessi, *Tetrahedron*, 2011, **67**, 6969.
15 Y. Zhu, W.B. Yi and C. Cai, *Catal. Commun.*, 2011, **15**, 118.
16 M.M. Zhang, J.C. Guan, B.S. Zhang, D.S. Su, C.T. Williams and C.H. Liang, *Catal. Lett.*, 2012, **142**, 313.
17 M. Kim, E. Heo, A. Kim, J.C. Park, H. Song and K.H. Park, *Catal. Lett.*, 2012, **142**, 588.
18 N.E. Leadbeater and S.M. Resouly, *Tetrahedron*, 1999, **55**, 11889.
19 Z.Y. Tang and Q.S. Hu, *J. Am. Chem. Soc.*, 2004, **126**, 3058.
20 V.B. Phapale and D.J. Cardenas, *Chem. Soc. Rev.*, 2009, **38**, 1598.
21 L. Martín, E. Molins and A. Vallribera, *Tetrahedron*, 2012, **68**, 6517.
22 Z.Y. Tang, S. Spinella and Q.S. Hu, *Tetrahedron Lett.*, 2006, **47**, 2427.
23 M.M. Tamish and R. Karvembu, *Inorg. Chem. Commun.*, 2012, **25**, 30.
24 C. Chen and L.M. Yang, *Tetrahedron Lett.*, 2007, **48**, 2427.
25 B.H. Lipshutz, *Adv. Synth. Catal.*, 2001, **343**, 313.
26 B.H. Lipshutz, B. Frieman and C.T. Lee, *Chem. Asian. J.*, 2006, **1**, 417.
27 B.H. Lipshutz, T. Butler and E. Swift, *Org. Lett.*, 2008, **10**, 697.
28 A.M. Oertel, V. Ritleng and M.J. Chetcuti, *Organometallics*, 2012, **31**, 2829.
29 J. Liu, Y.L. Tian, Y.J. Chen, J.Y. Liang, L.F. Zhang and H. Fong, *Mater. Chem. Phys.*, 2010, **122**, 548.
30 H.Y. Wu, Q.H. Hu, L.Q. Zhang, H. Fong and M. Tian, *Mater. Lett.*, 2012, **84**, 5.
31 L.F. Zhang, X.X. Wang, Y. Zhao, Z.T. Zhu and H. Fong, *Mater. Lett*., 2012, **68**, 133.
32 L.F. Zhang, J. Luo, T.J. Menkhaus, H. Varadaraju, Y.Y. Sun and H. Fong, *J. Membrane. Sci.*, 2011, **369**, 499.
33 Z.C. Wu, Y. Huang, Y.N. Lu, T.X. Tao and Z. Zhang, *Catal. Commun.*, 2012, **29**, 158.