

Homo-coupling of Aryl Iodide and Bromide Catalyzed by Immobilized Palladium with a Bidentate Nitrogen Ligand

CHEN, Xiaofang^a(陈孝芳) WANG, Lei^{*,a,b}(王磊)

^a Department of Chemistry, Huaibei Coal Teacher College, Huaibei, Anhui 235000, China

^b State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

The immobilized palladium onto organic-inorganic hybrid material, which contains bidentate nitrogen ligands, was a very effective catalyst for homo-coupling of aryl iodide and bromide. The protocol involved the use of *N,N*-dimethylacetamide as a solvent, and *n*-tributylamine as a base. The reaction generated the corresponding homo-coupling products in good to excellent yields at low catalyst loading (0.20 mol%). Furthermore, the silica-supported palladium catalyst could be recovered and recycled by a simple filtration of the reaction solution and used for five consecutive trials without loss of its activity.

Keywords homo-coupling, aryl halide, immobilization of palladium, organic-inorganic hybrid material, *N,N'*-bidentate ligand

Introduction

As we all know, substituted biaryls are important building blocks for the syntheses of many pharmaceutical and agrochemical compounds.¹ Among the various known methods to synthesize biaryl, the Ullmann-type reaction is the typical synthetic route.² Because the Cu promoted biaryl formation reactions need a strict condition, such as high temperature, stoichiometric amounts of Cu, it is essential to develop more efficient catalyst instead of Cu to catalyze the Ullmann-type reaction. Recently, much more attention has been paid to Pd-catalyzed homo-coupling reactions of aryl halide.³ It is true that palladium is a very efficient catalyst to catalyze this type of reaction under mild reaction conditions. In 2003, Tanaka *et al.*⁴ used PdCl₂(PhCN)₂ as a catalyst and tetrakis(dimethylamino)ethylene (TDAE) as a ligand to accomplish the Ullmann-type homo-coupling reaction with good to excellent yields of desired products, and Tang *et al.*⁵ described a successful use of cyclopalladated complexes of tertiary arylamines as a catalyst for the Ullmann-type reaction with high yields of products. Other reports of palladacycles containing phosphine,⁶ sulfur⁷ were also very effective. According to the reported literature, silica immobilized palladium catalyst is very popular, because of facilitating both the isolation and recycling of the catalyst by filtration, and providing environmentally cleaner processes.⁸ As a part of our program aiming at developing selective and environmentally friendly methodologies using organic-inorganic hybrid material supported catalysts for the

preparation of fine chemicals and in continuation of our interest in exploring novel synthetic strategies for the carbon-carbon and carbon-heteroatom bond formation reactions,⁹ herein, we wish to report an efficient and recyclable silica immobilized palladium catalyst and its application to the Ullmann-type reaction (Scheme 1). This *N,N'*-bidentate ligand with two potential coordination sites offers certain advantages since it is known for a transition metal complex that an additional coordination site in the ligand as a stabilizing group during the course of a metal-mediated reaction can improve the catalytic efficiency of the complex.¹⁰ When it was proceeding under the optimized reaction conditions for the Ullmann-type reactions of aryl iodide and bromide, the reactions generated the corresponding biaryls in good to excellent yields. It is important to note that the silica-supported Pd catalyst could be recovered and recycled by a simple filtration of the reaction solution and used for 5 consecutive trials without significant loss of its activity.

Results and discussion

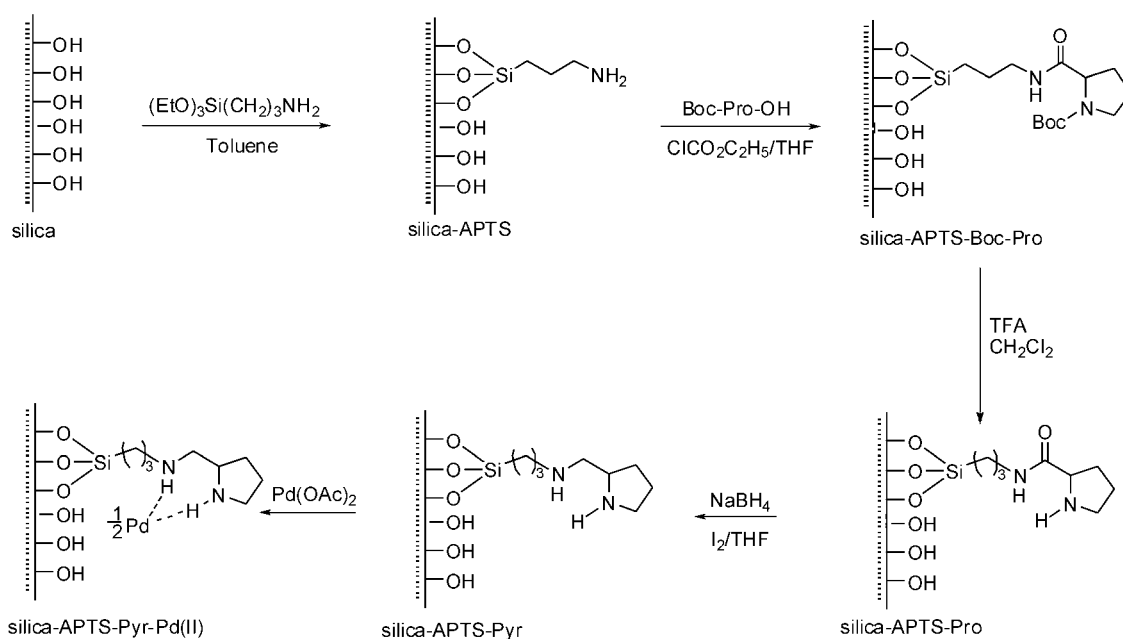
The synthesis of the organic-inorganic hybrid material immobilized Pd catalyst was illustrated in Scheme 1. It was readily prepared through a multi-step procedure. The silica gel (100–200 mesh, from Aldrich) was reacted with (3-aminopropyl)trimethoxysilane in dry toluene at 120 °C for 24 h to afford the 3-aminopropyl functionalized silica gel (silica-APTS). The obtained silica-APTS was then reacted with Boc-*L*-proline in the

* E-mail: leiwang@hbcnc.edu.cn; Tel.: 0086-0561-3802069; Fax: 0086-0561-03090518

Received February 10, 2009; revised April 20, 2009; accepted June 18, 2009.

Project supported by the National Natural Science Foundation of China (No. 20772043), and the Key Project of Science and Technology of the Ministry of Education of China (No. ZD2007005–1).

Scheme 1



presence of stoichiometric amounts of ethyl chloroformate as peptide coupling reagent ($\text{ClCOOC}_2\text{H}_5$) and triethylamine in THF to generate the silica-APTS-Boc-Pro, and following deprotection of Boc group procedure in CF_3COOH and CH_2Cl_2 (V/V, 1/1) resulted in the corresponding silica-APTS-Boc. The generated silica-APTS-Boc was reduced to the corresponding silica-APTS-Pyr by $\text{NaBH}_4\text{-I}_2$ in THF solution, which was next reacted with $\text{Pd}(\text{OAc})_2$ in acetone at room temperature to provide the final silica-supported catalyst, silica-APTS-Pyr-Pd(II) in good yields.

The assignments of infrared (IR) absorption bands for the functionalized silica gel samples, silica-APTS, silica-APTS-Boc-Pro, silica-APTS-Pro and silica-APTS-Pyr were made by comparison with the IR spectra of palladium complexes silica-APTS-Pyr-Pd(II). The results are listed in Table 1. The magnitude of $\Delta\nu$ [$\nu_{\text{N-H}}$ (silica-APTS-Pyr) $-\nu_{\text{N-H}}$ (silica-APTS-Pyr-Pd(II))] was found to be 108 cm^{-1} , indicating the coordination effect of bidentate nitrogen ligand with palladium. The CHN analysis data confirmed that the organic functionalization took place with the intended ligands (analysis of the pure silica prior to modification showed only negligible amounts of carbon and nitrogen). The elemental analysis data in Table 1 showed that for silica-APTS, the loading was readily quantified via CHN microanalysis and found to be 0.512 mmol/g of $\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ based on the nitrogen percentage. The palladium metal amount of silica-APTS-Pyr-Pd(II) was found to be $w = 2.20\%$ based on atomic absorption spectroscopy (AAS) analysis, also indicating the coordination number of bidentate nitrogen ligand with palladium (2 : 1).

In our initial screening experiments, the Ullmann-type reaction of 4-iodobenzene catalyzed by silica-APTS-Pyr-Pd(II) catalyst was chosen as the model reac-

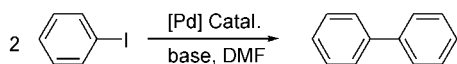
Table 1 IR and microanalysis of functionalized silica and silica-immobilized palladium catalyst

Sample	FT-IR (KBr) ν/cm^{-1}				Microanalysis ^a
	Si—O	C—H	N—H	C=O	N/wt%
silica-APTS	1096	2947	3472, 3395	—	0.72
silica-APTS-Boc-Pro	1088	2945	3464	1670, 1649	—
silica-APTS-Pro	1091	2949	3464, 3283	1671	0.39
silica-APTS-Pyr	1101	2937	3330	—	0.40
silica-APTS-Pyr-Pd(II)	1082	2941	3222	—	—

^a CHN microanalysis results.

tion. When we searched for a homo-coupling protocol of 4-iodobenzene, we observed that 4-iodobenzene could react in the presence of 0.20 mol% of silica-APTS-Pyr-Pd(II) catalyst and 2 equiv of triethylalcohol amine in DMF at $120\text{ }^\circ\text{C}$ to afford the desired homo-coupling product in 43% yield (Table 2, Entry 5). Encouraged by this result, we continued our research to improve the yield of product by the optimization of reaction conditions. We tested several different bases for the Ullmann-type reactions catalyzed by silica-APTS-Pyr-Pd(II) in *N,N*-dimethylformamide (DMF). *n*- Bu_3N was found to be the most effective base. Other bases, such as K_2CO_3 , *t*-BuOK, pyridine, dicyclohexylamine, and triethylalcohol amine were substantially less effective (Table 2, Entries 2–6).

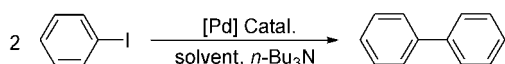
We then turned our attention to investigate the effect of solvent on the homo-coupling reaction of 4-iodobenzene catalyzed by silica-APTS-Pyr-Pd(II). Noteworthy is that the choice of DMA (*N,N*-dimethylacet-

Table 2 Effect of base on the Ullmann-type reaction^a

Entry	Base	Yield ^b /%
1	<i>n</i> -Bu ₃ N	86
2	Pyridine	23
3	Dicyclohexylamine	51
4	K ₂ CO ₃	18
5	Triethylalcohol amine	43
6	<i>t</i> -BuOK	15

^a 4-Iodobenzene (2.00 mmol), silica-APTS-Pyr-Pd(II) catalyst (containing Pd 0.002 mmol), base (2.00 mmol), in DMF (2.0 mL) at 120 °C for 12 h. ^b Isolated yield.

amide) as the solvent was crucial, and 93% isolated yield of the desired product was provided (Table 3, Entry 1). Indeed, when another solvent, such as DMF, DMSO (dimethyl sulfoxide), toluene, or dioxane was used instead of DMA, desired homo-coupling products were obtained in lower yields (Table 3, Entries 2–5). However, only trace amount of desired homo-coupling product was observed during the reaction in C₂H₅OH (Table 3, Entry 6).

Table 3 Effect of solvent on the Ullmann-type reaction^a

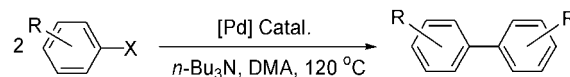
Entry	Solvent (Temperature/°C)	Yield ^b /%
1	DMA (120)	93
2	DMF (120)	86
3	DMSO (140)	81
4	C ₆ H ₅ CH ₃ (110)	72
5	Dioxane (100)	36
6	C ₂ H ₅ OH (80)	trace

^a 4-Iodobenzene (2.00 mmol), silica-APTS-Pyr-Pd(II) catalyst (containing Pd 0.002 mmol), *n*-Bu₃N (2.00 mmol), solvent (2.0 mL) at the temperature indicated in Table 3 for 12 h. ^b Isolated yield.

During the course of our further optimization of the reaction conditions, when using a 0.20 mol% loading of silica-APTS-Pyr-Pd(II), the reactions were generally completed in a matter of hours, but the time, as expected, was inversely proportional to the temperature. A reaction temperature of 120 °C was found to be optimal. Thus, the optimized reaction conditions for this Ullmann-type reaction are silica-APTS-Pyr-Pd(II) (0.20 mol%), *n*-Bu₃N (2 equiv.) in DMA at 120 °C for 12 h.

We have investigated the reactions using a variety of aryl iodides, and aryl bromides as the substrates under the optimized reaction conditions and the results are listed in Table 4. Electron-neutral, electron-rich and electron-poor aryl iodides, as well as electron-poor aryl bromides reacted very well to generate the correspond-

ing homo-coupling products in excellent yields under the standard reaction conditions (Table 4, Entries 1–10). For electron-neutral and electron-rich aryl bromides, moderate yields of the desired products were obtained (Table 4, Entries 11–13). However, when 2-bromopyridine was used, only 42% of coupling product was isolated (Table 4, Entry 14).

Table 4 Silica-APTS-Pyr-Pd(II) catalyzed Ullmann-type reaction^a

Entry	Substrate	Product	Yield ^b /%
1	C ₆ H ₅ I	C ₆ H ₅ C ₆ H ₅	93
2	<i>p</i> -CH ₃ OC ₆ H ₄ I	(<i>p</i> -CH ₃ OC ₆ H ₄) ₂	90
3	<i>p</i> -CH ₃ C ₆ H ₄ I	(<i>p</i> -CH ₃ C ₆ H ₄) ₂	92
4	<i>m</i> -NCC ₆ H ₄ I	(<i>m</i> -NCC ₆ H ₄) ₂	91
5	<i>p</i> -O ₂ NC ₆ H ₄ I	(<i>p</i> -O ₂ NC ₆ H ₄) ₂	95
6	<i>m</i> -O ₂ NC ₆ H ₄ I	(<i>m</i> -O ₂ NC ₆ H ₄) ₂	91
7	<i>p</i> -NCC ₆ H ₄ Br	(<i>p</i> -NCC ₆ H ₄) ₂	84
8	<i>p</i> -O ₂ NC ₆ H ₄ Br	(<i>p</i> -O ₂ NC ₆ H ₄) ₂	83
9	<i>p</i> -CH ₃ COC ₆ H ₄ Br	(<i>p</i> -CH ₃ COC ₆ H ₄) ₂	80
10	<i>m</i> -NCC ₆ H ₄ Br	(<i>m</i> -NCC ₆ H ₄) ₂	82
11	C ₆ H ₅ Br	C ₆ H ₅ C ₆ H ₅	76
12	<i>p</i> -CH ₃ C ₆ H ₄ Br	(<i>p</i> -CH ₃ C ₆ H ₄) ₂	74
13	<i>p</i> -CH ₃ OC ₆ H ₄ Br	(<i>p</i> -CH ₃ OC ₆ H ₄) ₂	73
14			42

^a Aryl halide (2.00 mmol), silica-APTS-Pyr-Pd(II) catalyst (containing Pd 0.002 mmol), *n*-Bu₃N (2.00 mmol) in DMA (2.0 mL) at 120 °C for 12 h. ^b Isolated yield.

The recyclability of silica-APTS-Pyr-Pd(II) was also surveyed. After reaction, the solution was vacuum filtered using a sintered glass funnel and washed with CH₂Cl₂ (3 mL × 2), Et₂O (3 mL × 2), C₂H₅OH (3 mL × 2), and hexane (3 mL × 2), respectively. After being dried to constant weight, it could be reused directly without further purification. The silica-APTS-Pyr-Pd(II) could be recovered and recycled for 5 consecutive trials without loss of its activity (Figure 1).

Conclusion

We have developed an efficient and economic catalyst system for the Ullmann-type reaction by using silica-APTS-Pyr-Pd(II) catalyst containing a bidentate nitrogen ligand in DMA. The homo-coupling reactions of aryl iodide and aryl bromide generated the corresponding coupling products in good to excellent yields in the standard reaction conditions. Furthermore, silica-APTS-Pyr-Pd(II) could be recovered and recycled by a simple filtration of the reaction solution and used for 5 consecutive trials without decreases in activity.

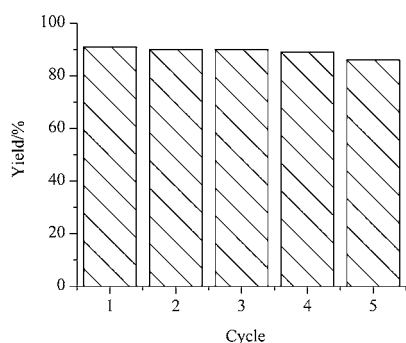


Figure 1 Yields obtained with recycled silica-APTS-Pyr-Pd(II) (for the model reaction of 4-iodobenzene used as substrate under standard reaction conditions).

Experimental

Physical measurements and materials

Melting points were recorded on a WRS-2B melting point apparatus and uncorrected. All ^1H NMR spectra were recorded on a Bruker 300 MHz FT-NMR spectrometer. Chemical shifts were given as δ values with reference to tetramethylsilane (TMS) as an internal standard. IR spectra were obtained by using a Nicolet NEXUS 470 spectrophotometer. Products were purified by flash column chromatography on 230–400 mesh silica gel, SiO_2 .

The chemicals were purchased from commercial suppliers (Aldrich, USA and Shanghai Chemical Company, China) and used without purification prior to use.

Activation of silica^{9j}

10.0 g of silica (100–200 mesh, Aldrich) were introduced in a round-bottomed flask equipped with a reflux condenser, 80 mL of concentrated H_2SO_4 and 15 mL of HNO_3 were added and the mixture was heated in an oil-bath at 140 °C for 24 h. The solution was filtered and the white powder was washed with distilled water until neutral pH was attained. The solid was again washed with acetone, methanol and dichloromethane, respectively, and dried under vacuum at 140 °C for 48 h.

Typical procedure for preparation of silica-APTS^{9j}

In a 50 mL three-neck round-bottomed flask with a Dean-Stark trap, 20 mL of anhydrous toluene, 3.0 g of activated silica obtained from the above procedure and 10 mL of 3-aminopropyltri(ethoxy)silane were added successively. The solution was refluxed for 24 h, then filtered and the solid was washed with acetone and dichloromethane, respectively, dried under reduced pressure at 60 °C overnight. Thus 3.36 g of silica-ATPS was obtained. IR (KBr) ν : 1096 (Si—O), 2947 (C—H), 3472 (N—H), 3395 (N—H) cm^{-1} . The loading was readily quantified via CHN microanalysis and found to be 0.512 mmol/g of aminopropyl groups based on the nitrogen percentage.

Typical procedure for preparation of silica-APTS-Boc-Pro¹⁶

Boc-*L*-proline (301 mg, 1.4 mmol) and triethylamine (141 mg, 1.4 mmol) were dissolved in THF (10 mL). The resulting solution was cooled to 0 °C, and ethyl chloroformate (154 mg, 1.4 mmol) was added to the solution dropwise in 10 min. After the solution was stirred for 30 min, the 3-aminopropyl functionalized silica gel (2.735 g, loading: 0.512 mmol/g of aminopropyl groups) was added, then the resulting mixture was stirred at 0 °C for 1 h, at room temperature for another 16 h, and finally refluxed for 3 h. After cooling down to the room temperature, the mixture was filtered and washed with THF, EtOH, and ethyl acetate, respectively, and then dried in vacuum. Thus 2.931 g of silica-ATPS-Boc-Pro were obtained. IR (KBr) ν : 1088 (Si—O), 2945 (C—H), 1670 (C=O), 1649 (C=O), 3464 (N—H) cm^{-1} . The loading was readily quantified via CHN microanalysis and found to be 0.336 mmol/g based on the nitrogen percentage.

Typical procedure for preparation of silica-APTS-Pyr^{16,17}

In a 10 mL round-bottomed flask was introduced successively 5 mL of CF_3COOH and 5 mL of CH_2Cl_2 , then the mixture was stirred smoothly. After silica-APTS-Boc-Pro (2.700 g) was added to the solution, the resulting mixture was stirred for 2.5 h in an ice-bath. The solution was filtered and the solid was washed with CH_2Cl_2 , dried in vacuum to give the corresponding deprotection product of silica-APTS-Boc-Pro, silica-APTS-Pro (2.502 g). IR (KBr) ν : 1091 (Si—O), 2949 (C—H), 1671 (C=O), 3464 (N—H), 3283 (N—H) cm^{-1} .

In a 50 mL round-bottomed flask were introduced successively the obtained silica-APTS-Boc-Pro (2.5 g), NaBH_4 (127 mg) and 25 mL of anhydrous THF, then the mixture was cooled to 0 °C overnight. After a solution of iodine (160 mg) in THF (5 mL) was added, the solution was refluxed for 48 h. After the mixture was cooled to room temperature, it was filtered out and washed with THF, EtOH and ethyl acetate, respectively, then dried till constant weight under reduced pressure. The organic-inorganic hybrid material silica-APTS-Pyr was obtained (2.405 g). The loading was readily quantified via CHN microanalysis and found to be 0.332 mmol/g based on the nitrogen percentage. IR (KBr) ν : 1101 (Si—O), 2937 (C—H), 3330 (N—H) cm^{-1} .

Typical procedure for preparation of silica-APTS-Pyr-Pd(II) catalyst^{9j}

In a small Schlenk tube, $\text{Pd}(\text{OAc})_2$ (56 mg, 0.25 mmol) was dissolved in acetone (10 mL), then the above-functionalized silica was added (1.147 g) in one portion under nitrogen atmosphere at 0 °C with stirring for 10 h. The solution was filtered and the solid was washed with acetone, EtOH, respectively, then dried under reduced pressure at room temperature overnight, leading to a light yellow powder, silica-APTS-Pyr-Pd(II) catalyst (1.163 g). IR (KBr) ν : 1082 (Si—O), 2941 (C—

H), 3222 (N—H) cm^{-1} . The palladium metal amount of this silica gel supported complex was found to be $w = 2.20\%$ based on AAS analysis.

General procedure for the Ullmann-type reaction

Under nitrogen atmosphere, an oven-dried round-bottomed flask was charged with silica-APTS-Pyr-Pd(II) (15 mg, containing 0.20% mmol of Pd, loading: $w = 2.20\%$), *n*-Bu₃N (372 mg, 2.0 mmol), aryl halide (2.0 mmol) and DMA (2.0 mL). The reaction mixture was stirred at 120 °C for 12 h. After cooling to room temperature, the reaction mixture was vacuum filtered using a sintered glass funnel and washed with CH₂Cl₂ (5.0 mL \times 2). The combined organic materials were dried over Na₂SO₄, filtered, concentrated, and the residue was purified by flash chromatography on silica gel to give the desired homo-coupling product.

The recyclability of silica-APTS-Pyr-Pd(II) catalyst

After reaction, the mixture was vacuum filtered using a sintered glass funnel and washed with CH₂Cl₂ (3 mL \times 2), Et₂O (3 mL \times 2), C₂H₅OH (3 mL \times 2), and hexane (3 mL \times 2), respectively. After being dried in an oven, they could be reused directly without further purification.

Biphenyl: White solid, m.p. 66–68 °C (lit.¹¹ 70 °C); ¹H NMR (CDCl₃, 300 MHz) δ : 7.61 (d, $J = 7.8$ Hz, 4H), 7.48 (t, $J = 7.5$ Hz, 4H), 7.39 (t, $J = 7.4$ Hz, 2H); IR (KBr) ν : 3033, 1479, 1169, 728 cm^{-1} .

4,4'-Dimethoxybiphenyl: White solid, m.p. 179–180 °C (Lit.¹¹ 176–178 °C); ¹H NMR (CDCl₃, 300 MHz) δ : 7.49 (d, $J = 8.8$ Hz, 4H), 6.98 (d, $J = 8.6$ Hz, 4H), 3.84 (s, 6H); IR (KBr) ν : 2975, 1499, 1248, 1041 825 cm^{-1} .

4,4'-Dimethylbiphenyl: White solid, m.p. 119–120 °C (Lit.¹² 121 °C); ¹H NMR (CDCl₃, 300 MHz) δ : 7.49 (d, $J = 8.1$ Hz, 4H), 7.26 (d, $J = 7.8$ Hz, 4H), 2.39 (s, 6H); IR (KBr) ν : 2915, 1501, 1113, 804 cm^{-1} .

4,4'-Diacetylbiphenyl: White solid, m.p. 192–193 °C (Lit.¹³ 190–192 °C); ¹H NMR (CDCl₃, 300 MHz) δ : 8.08 (d, $J = 8.4$ Hz, 4H), 7.74 (d, $J = 8.1$ Hz, 4H), 2.69 (s, 6H); IR (KBr) ν : 1680, 1604, 1273, 819 cm^{-1} .

3,3'-Dicyanobiphenyl: White solid, m.p. 197–199 °C (Lit.¹⁴ 200–201 °C); ¹H NMR (CDCl₃, 300 MHz) δ : 7.96 (s, 2H), 7.91 (d, $J = 6.3$ Hz, 2H), 7.82 (d, $J = 6.3$ Hz, 2H), 7.71 (d, $J = 6.6$ Hz, 2H); IR (KBr) ν : 2228, 1470, 787, 687 cm^{-1} .

4,4'-Dinitrobiphenyl: Yellow solid, m.p. 234–236 °C (Lit.¹⁵ 240 °C); ¹H NMR (CDCl₃, 300 MHz) δ : 8.37 (d, $J = 8.7$ Hz, 4H), 7.77 (d, $J = 8.7$ Hz, 4H); IR (KBr) ν : 1599, 1512, 1342, 859 cm^{-1} .

3,3'-Dinitrobiphenyl: Yellow solid, m.p. 198–200 °C (Lit.¹⁸ 200 °C); ¹H NMR (CDCl₃, 300 MHz) δ : 7.52 (t, $J = 1.5$ Hz, 2H), 7.35 (d, $J = 8.1$ Hz, 2H), 7.04 (d, $J = 7.5$ Hz, 2H), 6.77 (t, $J = 8.0$ Hz, 2H); IR (KBr) ν : 3079, 1525, 1349, 1103, 857, 699 cm^{-1} .

4,4'-Dicyanobiphenyl: White solid, m.p. 233–235 °C (Lit.¹¹ 234–235 °C); ¹H NMR (CDCl₃, 300 MHz) δ : 7.78 (d, $J = 8.1$ Hz, 4H), 7.67 (d, $J = 8.4$ Hz, 4H); IR

(KBr) ν : 2226, 1604, 1180, 818 cm^{-1} .

2,2'-Bipyridyl: White solid, m.p. 68–70 °C (Lit.¹¹ 70–71 °C); ¹H NMR (CDCl₃, 300 MHz) δ : 8.69–8.68 (m, 2H), 8.42–8.38 (m, 2H), 7.87–7.82 (m, 2H), 7.32–7.29 (m, 2H); IR (KBr) ν : 1579, 1452, 1250, 1040, 757 cm^{-1} .

References

- (a) Fanta, P. E. *Synthesis* **1974**, 9.
(b) Fanta, P. E. *Chem. Rev.* **1964**, 64, 613.
(c) Sainsbury, M. *Tetrahedron* **1980**, 36, 3327.
(d) Bringmann, G.; Walter, R.; Weirich, R. *Angew. Chem., Int. Ed. Engl.* **1990**, 29, 977.
- (a) Ullmann, F. *Chem. Ber.* **1903**, 36, 2389.
(b) Zhang, S.; Zhang, D.; Liebeskind, L. S. *J. Org. Chem.* **1997**, 62, 2312.
(c) Hauser, F. M.; Gauuan, P. J. F. *Org. Lett.* **1999**, 1, 671.
- (a) Venkatraman, S.; Li, C. J. *Org. Lett.* **1999**, 1, 1133.
(b) Mukhopadhyay, S.; Rothenberg, G.; Wiener, H.; Sasson, Y. *Tetrahedron* **1999**, 55, 14763.
(c) Mukhopadhyay, S.; Rothenberg, G.; Gitis, D.; Wiener, H.; Sasson, Y. *J. Chem. Soc.* **1999**, 2, 2481.
(d) Hennings, D.; Iwama, T.; Rawal, V. H. *Org. Lett.* **1999**, 1, 1205.
(e) Hassan, J.; Penalva, V.; Lavenot, L.; Gozzi, C.; Lemaire, M. *Tetrahedron* **1998**, 54, 13793.
(f) Amii, H.; Kohda, M.; Seo, M.; Uneyama, K. *Chem. Commun.* **2003**, 1752.
- Kuroboshi, M.; Waki, Y.; Tanaka, H. *J. Org. Chem.* **2003**, 68, 3938.
- Li, Q.; Nie, J.; Yang, F.; Zheng, R.; Zou, G.; Tang, J. *Chin. J. Chem.* **2004**, 22, 419.
- Luo, F. T.; Jeevanandam, A.; Basu, M. K. *Tetrahedron Lett.* **1998**, 39, 7939.
- Silveira, P. B.; Lando, V. R.; Dupont, J.; Monteiro, A. L. *Tetrahedron Lett.* **2002**, 43, 2327.
- (a) Kirschnig, A.; Monenschein, H.; Wittenberg, R. *Angew. Chem., Int. Ed.* **2001**, 40, 650.
(b) Clapham, B.; Reger, T. S.; Janda, K. D. *Tetrahedron* **2001**, 57, 4637.
- (a) Wang, M.; Li, P.; Wang, L. *Eur. J. Org. Chem.* **2008**, 2255.
(b) Li, P.; Wang, L.; Zhang, Y. *Tetrahedron* **2008**, 64, 10825.
(c) Li, P.; Wang, L.; Zhang, Y.; Wang, G. *Tetrahedron* **2008**, 64, 7633.
(d) Liu, H.; Wang, L.; Li, P. *Synthesis* **2008**, 2405.
(e) Wu, Q.; Wang, L. *Synthesis* **2008**, 2007.
(f) Miao, T.; Wang, L. *Synthesis* **2008**, 363.
(g) Wang, Z.; Wang, L.; Li, P. *Synthesis* **2008**, 1367.
(h) Li, P.; Wang, L. *Tetrahedron* **2007**, 63, 5455.
(i) Miao, T.; Wang, L. *Tetrahedron Lett.* **2007**, 48, 95.
(j) Li, H.; Wang, L.; Li, P. *Synthesis* **2007**, 1635.
(k) Li, P.; Wang, L. *Adv. Synth. Catal.* **2006**, 348, 681.
(l) Wang, Z.; Wang, L.; Yan, J. *Chin. J. Chem.* **2008**, 26, 1721.
(m) Zhang, L.; Wang, L. *Chin. J. Chem.* **2006**, 24, 1605.
- (a) Reetz, M. T.; Waldvogel, S. R.; Goddard, R. *Tetrahedron Lett.* **1997**, 38, 5967.

- (b) Jung, I. G.; Son, S. U.; Park, K. H.; Chung, K. C.; Lee, J. W.; Chung, Y. K. *Organometallics* **2003**, 4715.
- (c) Kostas, I. D.; Steele, B. R.; Terzis, A.; Amosova, S. V. *Tetrahedron* **2003**, 59, 3467.
- 11 Abiraj, K.; Srinivasa, G.; Channe, G. D. *Tetrahedron Lett.* **2004**, 45, 2081.
- 12 Zincke, T. *Chem. Ber.* **1871**, 4, 396.
- 13 Richard, H. W.; Gerald, L. M. *J. Polym. Sci. Part A: Polym. Chem.* **1963**, 1, 217.
- 14 Cahiez, G.; Chaboche, C.; Mahuteau-Betzer, F.; Ahr, M. *Org. Lett.* **2005**, 7, 1943.
- 15 Padmanabhau, S.; Gavaskar, K. V.; Triggle, D. J. *Synth. Commun.* **1996**, 26, 3109.
- 16 Yan, J.; Wang, L. *Chirality* **2009**, 15, 413.
- 17 McKennon, M. J.; Meyers, A. I.; Drauz, K.; Schwarm, M. J. *Org. Chem.* **1993**, 58, 3568.
- 18 Ullmann, F.; Bielecki, J. *Chem. Ber.* **1901**, 34, 2174.

(E0902104 Chen, J.)