Applied Organometallic Chemistry

Received: 13 February 2008 Revised: 23 March 2008 Accepted: 23 March 2008 Published online in Wiley Interscience:

(www.interscience.com) DOI 10.1002/aoc.1414

Palladium-catalyzed Heck coupling of 2-vinylpyridine with aryl chlorides

Ming Li and Ruimao Hua*

An efficient $PdCl_2(PCy_3)_2$-catalyzed cross-coupling reaction of 2-vinylpyridine with aryl chlorides to afford *trans*-2-styrylpyridines with a variety of functional groups on the benzene ring is described.

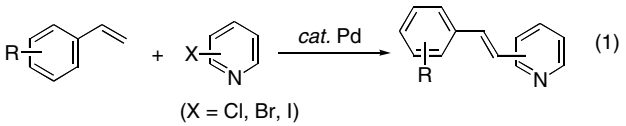
Keywords: aryl chloride; Heck reaction; palladium; 2-vinylpyridine; styrylpyridine

Introduction

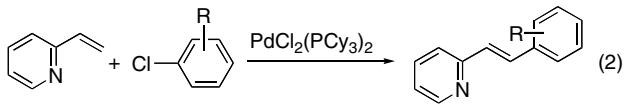
The palladium-catalyzed cross-coupling reaction of aryl halides with alkenes, known as the Heck reaction, is a powerful C–C bond forming process.[1–4] *trans*-Styrylpyridines can be synthesized by the Heck reaction of styrenes with halopyridines (Scheme 1). Although efficient catalytic systems for the Heck reactions of *para*- and *meta*-halopyridines such as 3-iodopyridines and 3-,4-bromopyridines with styrene to afford *trans*-3- or 4-styrylpyridines in good to high yields have been developed,[5–11] reports on the cross-coupling reactions of *ortho*-halopyridines with styrene are few due to the low reactivity of *ortho*-halopyridines under the Heck reaction conditions.[12–14] Only two references have been found in which *trans*-2-styrylpyridine could be obtained by the palladium-catalyzed reaction of styrene (Scheme 1, R = H) with 2-iodopyridine [$Pd(OAc)_2 + 2PPh_3$, in Et_3N at 100 °C for 24 h, 11%],[11] and 2-chloropyridine (oxime-derived palladacycle, in DMF at 160 °C for 30 h, 70%).[12] 2-Bromopyridine showed no reactivity[7,8] or a very low reactivity[5,14] for the similar coupling reaction in the tested catalytic systems. In addition, all the coupling reactions mentioned above were limited to styrene: there have been no reports on the reaction of halopyridines with substituted styrenes so far.

Recently, *trans*-2-styrylpyridine was used as a ligand in metal complexes,[15–17] photoreactive group in polymers,[18–20] and valuable material for the synthesis of physiological and biological active compounds.[21,22] The structural unit of 2-styrylpyridine also exists in biological active compounds.[23,24] Therefore development of an efficient method for the synthesis of *trans*-2-styrylpyridines is interesting and valuable.

Our previous work disclosed that $PdCl_2(PCy_3)_2$ is an efficient catalyst for Sonogashira[25] and Heck[26] cross-coupling reactions of aryl chlorides. In continuation of our interest in applications of $PdCl_2(PCy_3)_2$ as a catalyst in C–C bond formation reaction, in this paper, we report $PdCl_2(PCy_3)_2$-catalyzed cross-coupling reactions of 2-vinylpyridine with aryl chlorides as an alternative efficient catalytic system for the synthesis of *trans*-2-styrylpyridines with a variety of functional groups on the benzene ring (Scheme 2).[27]



Scheme 1. Heck reaction of styrenes with halopyridines.



Scheme 2. Heck reaction of 2-vinylpyridine with aryl chlorides.

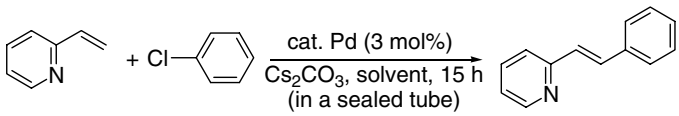
Results and Discussion

The results on examining the catalytic activity of palladium complexes in the reaction of 2-vinylpyridine with chlorobenzene (**1a**) using Cs_2CO_3 as base are described in Table 1. It was found that zero-valent palladium complexes such as $Pd(PPh_3)_4$ and $Pd(dppe)_2$ could not catalyze the cross-coupling reaction in toluene at 130 °C (sealed tube, oil bath temperature): in both cases, only trace amounts of 2-styrylpyridine (**2a**) were detected by GC and GC-MS analyses of the reaction mixture: the starting materials were recovered in almost quantitative yields (Table 1, entries 1 and 2). Palladium(II) complexes such as $PdCl_2(PEt_3)_2$ and $PdCl_2(PPh_3)_2$ showed low catalytic activities under the same reaction conditions to give **2a** in fair yields (Table 1, entries 3 and 4). In the presence of $PdCl_2(CH_3CN)_2$/dppp (1 : 2), **2a** was formed in 38% GC yield (Table 1, entry 5). At a lower reaction temperature (120 °C), $PdCl_2(PCy_3)_2$ catalyzed the coupling reaction to afford **2a** in 38% GC yield (Table 1, entry 6); at 130 °C, it showed a higher catalytic activity to furnish **2a** in 64% GC yield (Table 1, entry 7). The addition of an additional PCy_3 molecule resulted in a significant decrease of the catalytic activity (Table 1, entry 8). Increasing the reaction temperature to 140 °C could significantly enhance the reaction, in this case **2a** was formed in 95% GC yield

* *Correspondence to: Ruimao Hua, Department of Chemistry, Tsinghua University, Innovative Catalysis Program, Key Laboratory of Organic Optoelectronics and Molecular Engineering of Ministry of Education, Beijing 100084, People's Republic of China. E-mail: ruimao@mail.tsinghua.edu.cn*

Department of Chemistry, Tsinghua University, Innovative Catalysis Program, Key Laboratory of Organic Optoelectronics and Molecular Engineering of Ministry of Education, Beijing 100084, People's Republic of China

Table 1. Palladium-catalyzed cross-coupling of 2-vinylpyridine with chlorobenzene under different conditions[a]



1a **2a**

Entry	Catalyst	Solvent	Temperature (°C)	Yield (%)[b]
1	$Pd(PPh_3)_4$	Toluene	130	<5
2[c]	$Pd(dppe)_2$	Toluene	130	<5
3	$PdCl_2(PEt_3)_2$	Toluene	130	26
4	$PdCl_2(PPh_3)_2$	Toluene	130	27
5[d]	$PdCl_2(CH_3CN)_2$ + dppp (1 : 2)	Toluene	130	38
6	$PdCl_2(PCy_3)_2$	Toluene	120	38
7	$PdCl_2(PCy_3)_2$	Toluene	130	64
8	$PdCl_2(PCy_3)_2$ + PCy_3 (1 : 1)	Toluene	130	9
9	$PdCl_2(PCy_3)_2$	Toluene	140	95 (87)
10	$PdCl_2(PCy_3)_2$	*o*-Xylene	140	92
11	$PdCl_2(PCy_3)_2$	DMSO	140	<5
12	$PdCl_2(PCy_3)_2$	Dioxane	140	18

[a] Reactions were carried out with 2-vinylpyridine (0.5 mmol), chlorobenzene (0.6 mmol), Cs_2CO_3 (0.7 mmol) and catalyst (0.015 mmol) in solvent (1.0 ml).
[b] Determined by GC based on 2-vinylpyridine used. Number in parenthesis is isolated yield.
[c] DPPE = 1, 2-bis(diphenylphosphino)ethane.
[d] DPPP = 1, 3-bis(diphenylphosphino)propane.

(Table 1, entry 9), and a similar result could be obtained in *o*-xylene (Table 1, entry 10). In addition, it was disclosed that the effects of solvents were obvious for the present cross-coupling reaction. Whereas our previous reports showed that DMSO and dioxane were good solvents for $PdCl_2(PCy_3)_2$-catalyzed Sonogashira[25] or Heck[26] reactions of aryl chlorides with terminal alkynes or styrenes, respectively, $PdCl_2(PCy_3)_2$ showed a very low catalytic activity when the present cross-coupling reaction was carried out in either DMSO or dioxane (Table 1, entries 11 and 12).

Moreover, it should be noted that the catalytic activity of $PdCl_2(PCy_3)_2$ also depends on the nature of the used bases in the present cross-coupling reaction. The use of K_2CO_3, Bu_3N and pyridine to replace Cs_2CO_3 as bases led to almost no reaction product or low conversions.

Table 2 summarizes the results of the cross-coupling of 2-vinylpyridine with a variety of aryl chlorides in the presence of $PdCl_2(PCy_3)_2$. As can be seen from Table 2, the cross-coupling reactions of 2-vinylpyridine with both neutral and electron-rich (deactivated) aryl chlorides proceeded smoothly at 140 °C to afford the corresponding coupling products in high isolated yields after 10–25 h (Table 2, entries 1–4). Surprisingly, the electron-deficient aryl chlorides, which are commonly considered to be the activated ones in Heck cross-coupling reaction with alkenes, showed a lower reactivity than electron-rich aryl chlorides. For example, the reactions of 2-vinylpyridine with 1,2-dichlorobenzene (**1e**) and 1,4-dichlorobenzene (**1f**) at 140 °C for 25 h afforded the expected cross-coupling products **2e** and **2f** in 56 and 30% yields, respectively (Table 2, entries 5 and 6). Prolonging the reaction time up to 25 h could not increase the yield considerably. Under these conditions, the reactions of 2-vinylpyridine with 2-chlorothiophene (**1g**), methyl 3-chlorobenzoate (**1h**), 4-chlorobenzophenone (**1i**) and 4-chlorobenzaldehyde (**1j**) furnished only small amounts of the desired coupled products; repeating these reactions in the presence of Bu_4NBr as additive, which is considered to be a stabilizer of palladium catalysts in palladium-catalyzed Heck cross-coupling reactions,[28–30] resulted in the formation of products in fair yields (Table 2, entries 7–11).

Since electron-deficient aryl chlorides showed a low reactivity for the cross-coupling reaction with 2-vinylpyridine, we then investigated the reaction using electron-deficient aryl bromides; however the coupled products were also obtained in moderate yields only. For example, methyl 2-bromobenzoate (**1k**) reacted with 2-vinylpyridine to afford the corresponding product **2k** in 46% yield (Scheme 3). When $PdCl_2(PPh_3)_2$ was employed as catalyst, the yield of **2k** was decreased to 15%.

Recently, polypyridyl ligand-coordinated transition metal complexes have been found to have potential applications for synthesizing the functional materials with interesting electrochemical, photochemical and photophysical properties.[31,32]

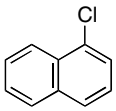
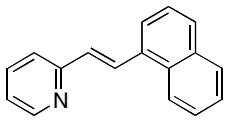
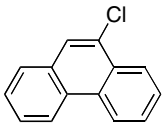
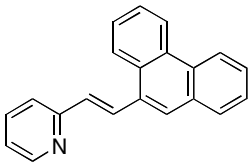
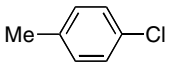
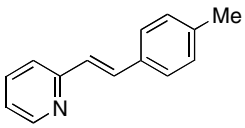
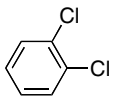
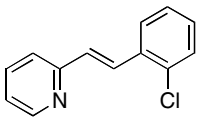
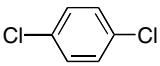
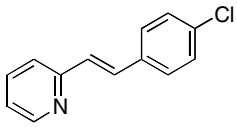
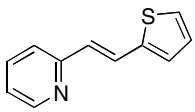
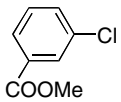
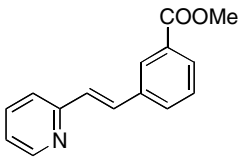
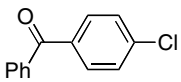
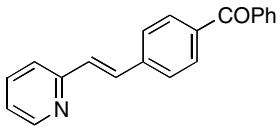
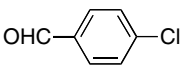
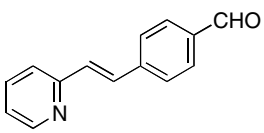
trans-1,2-Di(2-pyridyl)ethene (**2l**) is one of the basic starting materials for preparation of such type of ligands.[33] Therefore, we also examined the cross-coupling reaction of 2-vinylpyridine with 2-bromopyridine (**1l**); unfortunately, **2l** was obtained in only 20% and 16% yields in the presence of $PdCl_2(PCy_3)_2$ and $PdCl_2(PPh_3)_2$, respectively (Scheme 4).

The present cross-coupling reaction of 2-vinylpyridine with aryl chlorides is considered to take place following an essentially similar mechanism to that of the Heck reaction of alkenes with aryl halides, which has been well documented.[34–37] In the present catalyst system, the most likely reducing agent for the reduction of Pd(II) to the crucial catalytically active Pd(0) would be CO_3^{2-}.[38]

Conclusions

In this paper, *trans*-2-styrylpyridines could be obtained by the cross-coupling reaction of 2-vinylpyridine with aryl chlorides in

Table 2. $PdCl_2(PCy_3)_2$-catalyzed cross-coupling of 2-vinylpyridine with aryl chlorides[a]

Entry	Aryl-Cl		Time (h)	Product		Yield (%)[b]
1		**1b**	10		**2b**	70
2		**1b**	25		**2b**	92
3		**1c**	25		**2c**	92
4		**1d**	10		**2d**	78
5		**1e**	25		**2e**	56
6		**1f**	25		**2f**	30
7		**1g**	10		**2g**	<5
8[c]		**1g**	10		**2g**	37
9[c]		**1h**	10		**2h**	34
10[c]		**1i**	10		**2i**	40
11[c]		**1j**	10		**2j**	13

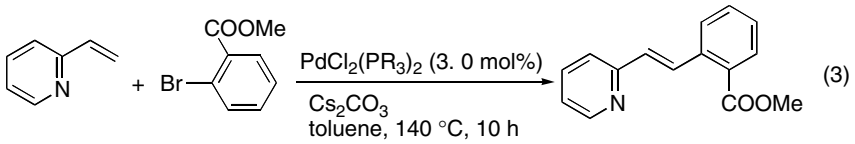
[a] Reactions were carried out with 2-vinylpyridine (1.0 mmol), aryl chloride (1.2 mmol), Cs_2CO_3 (1.3 mmol) and $PdCl_2(PCy_3)_2$ (0.03 mmol) in toluene (2.0 ml) at 140 °C.
[b] Isolated yield based on 2-vinylpyridine used.
[c] Bu_4NBr (10–80%) was added as additive.

the presence of catalytic amounts of $PdCl_2(PCy_3)_2$ in toluene with the use of Cs_2CO_3 as base. The high catalytic activity in the reactions of neutral and electron-rich aryl chlorides is one of the important features of this catalytic system. This catalytic procedure provides a direct and convenient route to *trans*-2-styrylpyridines with various functional groups on the benzene ring.

Experimental Section

General methods

All organic starting materials were analytically pure and used without further purification. ^1H and ^{13}C NMR spectra were recorded on Jeol JNM-ECA300 spectrometers at 300 and 75 MHz,



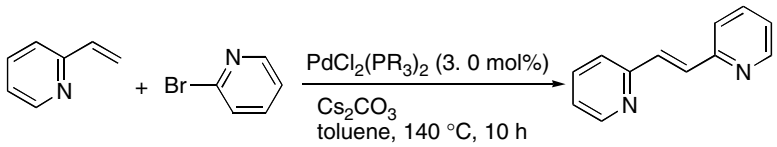
(3)

1k **2k**

R = Cy 46%

Ph 15%

Scheme 3. Heck reaction of 2-vinylpyridine with methyl 2-bromobenzoate.



(4)

1l **2l**

R = Cy 20%

Ph 16%

Scheme 4. Heck reaction of 2-vinylpyridine with 2-bromopyridine.

respectively. ^{1}H chemical shifts (δ) were referenced to TMS and ^{13}C NMR chemical shifts (δ) were referenced to the internal solvent resonance. GC analyses of organic compounds were performed on an Agilent Technologies 1790 GC (with a TC-WAX capillary 25m column) instrument. Mass spectra were obtained on a Hewlett Packard 5890 Series II GC/MS spectrometer with a PEG-25M column. Elemental analyses were obtained with a Flash EA 1112 Element Analyzer in the Institute of Chemistry, Chinese Academy of Sciences.

Typical experimental procedure for the cross-coupling of 2-vinylpyridine with chlorobenzene (1a), affording (*E*)-2-styrylpyridine (2a)

A mixture of 2-vinylpyridine (52.5 mg, 0.5 mmol), **1a** (67.5 mg, 0.60 mmol), Cs_2CO_3 (228.0 mg, 0.7 mmol) and $PdCl_2(PCy_3)_2$ (11.0 mg, 0.015 mmol) in toluene (1.0 ml) under nitrogen in a screw-capped thick-walled Pyrex tube was heated with stirring at 140 °C (oil bath temperature) for 15 h. After cooling, the reaction mixture was diluted with CH_2Cl_2 to 4.0 ml and octadecane (76.2 mg, 0.3 mmol) was added as internal standard for GC analysis. After GC and GC-MS analyses, removing the solvents and volatiles under vacuum, the residue was subjected to preparative TLC isolation (silica gel, eluted with a mixture solvent of ethyl acetate and petroleum ether; 60–90 °C, 1 : 4) to give **2a** as a pale yellow solid (80.0 mg, 0.44 mmol, 87%). The results of GC analysis of the reaction mixture revealed that **2a** was formed in 95% GC yield (Table 1, entry 9).

All cross-coupling products were isolated and gave satisfactory spectral and analytical data. **2a**,[12] **2b**,[39] **2c**,[40] **2d**,[41] **2e**,[42] **2f**,[41] **2g**,[43] **2j**,[18] and **2l**[44] are known compounds which were characterized by ^{1}H, ^{13}C-NMR and mass spectra; **2h, 2i** and **2k** are new compounds, their spectroscopic data are given below.

(E)-2-(3-Methoxycarbonylstyryl)pyridine **2h**

Yellow solid, m.p. 97–98 °C (recrystallization with CH_2Cl_2–cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.61 (d, 1H, J = 3.1 Hz, C*H*N); 8.28 (s, 1H, 1H of benzene ring); 7.95 (d, 1H, J = 7.9 Hz, 1H of benzene ring); 7.74–7.16 (m, 7H, C*H*=C*H*, 3H of pyridinyl and 2H of benzene ring); 3.94 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9 (CO); 155.2 [C_5H_4N, (i)]; 149.7 (C_5H_4N, adjacent to N); 137.0 [C_6H_4, (i), linked CH=CH]; 136.6, 131.6, 131.5, 130.7, 129.2, 129.1, 128.8, 127.9, 122.4(2C) (CH=CH, 5C of benzene ring and 3C of pyridinyl); 52.2 (OCH_3). GCMS *m/z* (% relative intensity): 239 ($M^{\cdot+}$, 33), 238(100), 224(11), 206(11), 178(15), 152(9), 127(2), 104(2), 89(4). Anal. calcd for $C_{15}H_{13}NO_2$: C, 75.31; H, 5.44; N, 5.86. Found: C, 75.01; H, 5.58; N, 5.71.

(E)-2-(4-Benzoylphenylstyryl)pyridine **2i**

Yellow solid, m.p. 142–143 °C (recrystallization with CH_2Cl_2/cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64 (d, 1H, J = 4.1 Hz, C*H*N); 7.85–7.18 (m, 14H, C*H*=C*H*, $C_6H_4COC_6H_5$ and 3H of pyridinyl). ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.1 (CO); 155.0 [C_5H_4N, (i)]; 149.8 (C_5H_4N, adjacent to N); 140.7 [C_6H_4, (i), linked CH=CH]; 137.7, 136.9, 136.7 (2C), 132.4 (2C), 131.6, 130.7 (2C), 130.3, 129.9 (2C), 128.3 (4C), 126.9 (4C), 122.6 (2C) (CH=CH, 17C of benzene ring and 3C of pyridinyl). GCMS*m/z* (% relative intensity): 285 (M^+, 31), 284(100), 207(1), 180(7), 152(5), 12 (2), 105(5), 89(1), 77 (10). Anal. calcd for $C_{20}H_{15}NO$: C, 84.21; H, 5.26; N, 4.91. Found: C, 84.48; H, 5.44; N, 4.75.

(E)-2-(2-Methoxycarbonylstyryl)pyridine **2k**

Yellow viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.61 (d, 1H, J = 4.8 Hz, C*H*N); 8.40 (d, 1H, J = 16.1 Hz, C*H*=CH); 7.95 (d, 1H, J = 7.9 Hz, 1H of benzene ring); 7.73–7.05 (m, 7H, CH=C*H*, 3H of pyridinyl and 3H of benzene ring); 3.93 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.7 (CO); 155.6 [C_5H_4N, (i)]; 149.1(C_5H_4N, adjacent to N), 138.4 [C_6H_4, (i), linked CH=CH]; 136.9, 132.3, 132.2, 130.7, 130.5, 129.0, 127.9, 127.4, 122.3, 121.7 (CH=CH, 5C of benzene ring and 3C of pyridinyl), 52.2 (OCH_3). GCMS *m/z* (% relative intensity): 239 (M^+, 1), 238(4), 224(9), 214(15), 206(3), 180(100), 167(3), 152(8), 127(2), 101(2), 89(4), 77(4). Anal. calcd for $C_{15}H_{13}NO_2$: C, 75.31; H, 5.44; N, 5.86. Found: C, 75.09; H, 5.67; N, 5.70.

Acknowledgments

This project (20573061) was supported by National Natural Science Foundation of China and Specialized Research Fund for the Doctoral Program of Higher Education (20060003079).

References

[1] R. F. Heck, *Acc. Chem. Res.* **1979**, *12*, 146.
[2] G. D. Jr. Daves, A. Hallberg, *Chem. Rev.* **1989**, *89*, 1433.
[3] W. Cabri, I. Candiani, *Acc. Chem. Res.* **1995**, *28*, 2.
[4] I. P. Beletskaya, A. V. Cheprakov, *Chem. Rev.* **2000**, *100*, 3009.
[5] F. Berthiol, M. Feuerstein, H. Doucet, M. Santelli, *Tetrahedron Lett.* **2002**, *43*, 5625.
[6] A. Papp, G. Galbács, Á. Molnár, *Tetrahedron Lett.* **2005**, *46*, 7725.
[7] S. Li, Y. Lin, H. Xie, S. Zhang, J. Xu, *Org. Lett.* **2006**, *8*, 391.
[8] X. Cui, Z. Li, C.-Z. Tao, Y. Xu, J. Li, L. Liu, Q. Guo, *Org. Lett.* **2006**, *8*, 2467.
[9] Ö. Aksin, H. Türkmen, L. Artok, B. Cetinkaya, C. Ni, O. Büyükgüngör, E. Özkal, *J. Organomet. Chem.* **2006**, *691*, 3027.
[10] N. Iranpoor, H. Firouzabadi, R. Azadi, *Eur. J. Org. Chem.* **2007**, 2197.
[11] X. Cui, Y. Zhou, N. Wang, L. Liu, Q.-X. Guo, *Tetrahedron Lett.* **2007**, *48*, 163.
[12] T. Sakamoto, H. Arakida, K. Edo, H. Yamanaka, *Chem. Pharm. Bull.* **1982**, *30*, 3647.
[13] D. A. Alonso, C. Nájera, M. C. Pacheco, *Adv. Synth. Catal.* **2002**, *344*, 172.
[14] V. Polshettiwar, P. Hesemann, J. J. E. Moreau, *Tetrahedron* **2007**, *63*, 6784.
[15] A. Spannenberg, P. Arndt, W. Baumann, V. V. Burlakov, U. Rosenthal, S. Becke, T. Weiss, *Organometallics* **2004**, *23*, 3819.
[16] H.-F. Klein, S. Camadanli, R. Beck, U. Floerke, *Chem. Commun.* **2005**, 381.
[17] X.-F. Shi, Z.-Y. Xing, L. Wu, W.-Q. Zhang, *Inorg. Chim. Acta* **2006**, *359*, 603.
[18] C.-M. Chung, A. Kunita, K. Hayashi, F. Nakamura, K. Saigo, M. Hasegawa, *J. Am. Chem. Soc.* **1991**, *113*, 7316.
[19] W.-S. Kim, D.-K. Ahn, M.-W. Kim, *Macromol. Chem. Phys.* **2004**, *205*, 1932.
[20] M.-W. Kim, S.-H. Hyun, J.-Y. Kong, K.-B. Yoon, L.-S. Park, W.-S. Kim, *J. Ind. Engng Chem.* **2006**, *12*, 261.
[21] G. Zheng, L. P. Dwoskin, A. G. Deaciuc, J. Zhu, M. D. Jones, P. A. Crooks, *Bioorg. Med. Chem.* **2005**, *13*, 3899.
[22] K. J. Wilson, M. B. van Niel, L. Cooper, D. Bloomfield, D. O'Connor, L. R. Fish, A. M. MacLeod, *Bioorg. Med. Chem. Lett.* **2007**, *17*, 2643.
[23] S.-J. Wang, T. S. Sihra *J. Pharmac. Exp. Ther.* **2004**, *309*, 951.
[24] S. Miwatashi, Y. Arikawa, K.-I. Naruo, K. Igaki, Y. Watanabe, H. Kimura, T. Kawamoto, S. Ohkawa, *Chem. Pharm. Bull.* **2005**, *53*, 410.
[25] C. Yi, R. Hua, *J. Org. Chem.* **2006**, *71*, 2535.
[26] C. Yi, R. Hua, *Tetrahedron Lett.* **2006**, *47*, 2573.
[27] There are only two examples on the cross-coupling reaction of 2-vinylpyridine with aryl iodide to give *trans*-2-styrylpyrindines, see ref. 5 and N. Nikbin, M. Ladlow, S. V. Ley, *Org. Process Res. Dev.* **2007**, *11*, 458.
[28] W. A. Herrmann, K. Öfele, D. V. Preysing, S. K. Schneider, *J. Organomet. Chem.* **2003**, *687*, 229.
[29] M. T. Reetz, J. G. de Vries, *Chem. Commun.* **2004**, 1559.
[30] I. Pryjomska-Ray, A. M. Trzeciak, J. Ziółkowski, *J. Mol. Catal. A, Chem.* **2006**, *257*, 3.
[31] V. Balzani, A. Juris, M. Venturi, S. Campagna, S. Serroni, *Chem. Rev.* **1996**, *96*, 759.
[32] J. P. Sauvage, *Acc. Chem. Res.* **1998**, *31*, 611.
[33] C. Richardson, P. J. Steel, D. M. D'Alessandro, P. C. Junk, F. R. Keene, *J. Chem. Soc., Dalton Trans.* **2002**, 2775.
[34] G. T. Crisp, *Chem. Soc. Rev.* **1998**, *27*, 427.
[35] A. Jutand, *Pure Appl. Chem.* **2004**, *76*, 565.
[36] U. Christmann, R. Vilar, *Angew. Chem. Int. Edn* **2005**, *44*, 366.
[37] A. F. Schmidt, A. A. Halaiqa, V. V. Smirnov, *Synlett* **2006**, 2861.
[38] L. G. Quan, M. Lamrani, Y. Yamamoto, *J. Am. Chem. Soc.* **2000**, *122*, 4827.
[39] G. Galiazzo, P. Bortolus, F. Masetti, *J. Chem. Soc., Perkin Trans. 2* **1975**, 1712.
[40] G. G. Aloisi, U. Mazzucato, A. Spalletti, G. Galiazzo, *Z. Phys. Chem. (Munich)* **1982**, *133*, 107.
[41] W. J. Dale, C. M. Ise, *J. Am. Chem. Soc.* **1954**, *76*, 2259.
[42] C. E. Aun, T. J. Clarkson, D. A. R. Happer, *J. Chem. Soc., Perkin Trans. 2*, **1990**, 645.
[43] A. L. Marzinzik, P. Rademacher, *Synthesis* **1995**, 1131.
[44] G. R. Newkome, J. M. Robinson, *Tetrahedron Lett.* **1974**, 691.

