Improved Procedure for Palladium-Catalyzed Hiyama Cross-Coupling **Reaction of Aryl Halides with Aryltrimethoxysilanes under Solvent-Free** Conditions

Jin-Heng Li,* Chen-Liang Deng, Ye-Xiang Xie

Key Laboratory of Chemical Biology & Traditional Chinese Medicine Research (Ministry of Education), College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, China

Fax +86(731)8872531; E-mail: jhli@hunnu.edu.cn

Received 6 September 2005; revised 18 October 2005

Abstract: An improved palladium-catalyzed Hiyama cross-coupling reaction is reported. In the presence of PdCl₂(MeCN)₂, P(otol)3 and TBAF, a number of ArX (X = I, Br, Cl) were coupled with ArSi(OMe)₃ efficiently to afford the desired cross-coupled products in moderate to excellent yields. It is noteworthy that this protocol is conducted under relatively low Pd loadings and solvent-free conditions.

Key words: PdCl₂(MeCN)₂, Hiyama cross-coupling reaction, aryl halide, arylsiloxane

The Hivama cross-coupling reaction attracts much attention because its products, biaryls, are useful intermediates in organic synthesis as well as a recurring functional group in a wide range of natural products and other biologically active compounds.¹⁻⁸ Besides these, the siliconderived compounds as alternative reagents are easily available and/or less toxic. Consequently, many efficient and selective palladium catalytic systems for the reactions have been described.^{4–8} However few efficient catalytic systems have been developed for the palladium-catalyzed Hiyama cross-coupling reaction. Generally, the Hiyama reaction is carried out under both high Pd catalyst and phosphine loadings, resulting in high yields for unactivated aryl halides.⁵ For example, 5 to 20 mol% of Pd catalysts are usually required (often 10 mol% Pd) for the coupling of aryl halides with arylsiloxanes when phosphines were used as the ligands. Thus, the development of efficient Hiyama cross-coupling reaction is still significant. Here, we wish to report that the combination of $PdCl_2(MeCN)_2/P(o-tol)_3/TBAF$ is an efficient system for the Hiyama cross-coupling reactions of aryl halides with aryltrimethoxysilanes under solvent-free conditions (Equation 1).

As shown in Table 1, the PdCl₂(MeCN)₂/P(o-tol)₃/TBAF system was efficient for the palladium-catalyzed Hiyama cross-coupling reaction of p-bromotoluene (1a) with phenyltrimethoxysilane (2a). Compared with DeShong's results,5a the reaction performed under solvent-free conditions was more effective than in DMF. Without the aid of any ligands, the coupling of 1a with silane 2a gave a 67% yield of the corresponding product 3 in the presence of 3 mol% of Pd(OAc)₂ and 6 equivalents of TBAF, whereas the yield of **3** was enhanced sharply when a phosphine ligand $[P(o-tol)_3)$ or PPh₃, 6 mol%] was added $[(P(o-tol)_3)$: 94% yield; PPh₃: 90% yield] (entries 1-3). However, De-Shong's results^{5a} showed that only 78% $[P(o-tol)_3)$] or 82% [PPh₃] yield of **3** was observed even in the presence of 10 mol% of Pd(OAc)₂, 20 mol% of the phosphine ligand and 2 equivalents of TBAF when DMF was used as the medium (entries 2 and 3). Other ligands such as Ph₃PO and DABCO⁹ were also investigated, and they were less effective than either $P(o-tol)_3$ or PPh_3 (entries 2–5). A series of Pd catalysts including Pd(OAc)₂, Pd(dba)₂ and $PdCl_2(MeCN)_2$ were then examined. $PdCl_2(MeCN)_2$ turned out to be the best catalyst in term of yields and reaction rates using $P(o-tol)_3$ as the ligand (entries 3, 6 and 7). In the presence of $PdCl_2(MeCN)_2$ (3 mol%), $P(o-tol)_3$ (6 mol%) and TBAF (6 equiv), quantitative yield of 3 was obtained in 40 minutes (entry 7). Identical results were observed when the amount of TBAF was reduced to 3 equivalents (entry 8). It is noteworthy that higher yields of 3 can be achieved smoothly at a loading of 1 mol% Pd. Thus, in the presence of 1 mol% of PdCl₂(MeCN)₂, 2 mol% of P(otol)₃ and 3 equivalents of TBAF, a high yield of **3** was still isolated after 40 minutes (92% yield, entry 9).¹⁰ However, further decreasing loadings of Pd to 0.1 mol% resulted in a rather low yield (entry 10). The results also demonstrated that the reaction could be carried out at room tempera-

$$R = I. Br. Cl$$

$$PdCl_2(MeCN)_2$$

$$(o - tol)_3P$$

$$TBAF \cdot 3H_2O, 80 °C$$

$$F$$



SYNTHESIS 2006, No. 6, pp 0969-0974 Advanced online publication: 27.02.2006 DOI: 10.1055/s-2006-926364; Art ID: F15005SS © Georg Thieme Verlag Stuttgart · New York

ture, and a moderate yield of **3** was obtained after prolonged reaction time (54% yield, entry 11). It is interesting to note that excellent yield of **3** is still obtained in 120 min when 5 mol of **1a** was treated with 10 mol of **2a**, 1 mol% of PdCl₂(MeCN)₂, 2 mol% of P(*o*-tol)₃ and 3 equiv of TBAF (entry 12). Attempts to use KF or CsF in place of TBAF gave rather low yields (entries 13 and 14).

The Hiyama reactions of various aryl halides 1a-1 with silanes 2a-c were carried out smoothly to afford moderate to excellent yields of the corresponding biaryls 4-14 in the presence of PdCl₂(MeCN)₂, P(*o*-tol)₃ and TBAF, and the results are summarized in Table 2. The results showed that the palladium-catalyzed Hiyama reactions tolerated a variety of functional groups, and the yields and rates were based on the substrates. Treatment of aromatic iodides **1b** and **1c** with silane **2a**, respectively, afforded quantitative yields of the corresponding coupled products 4 and 5 in the presence of 1 mol% of PdCl₂(MeCN)₂, 2 mol% of P(otol)₃ and 3 equivalents of TBAF (entries 1 and 2). The reaction of 1c with silane 2a performed at room temperature was also tested, and a moderate yield was still isolated (49% yield after 180 min, entry 3). Under the same reaction conditions, the couplings of aryl bromides 1a and 1df with silanes 2a-d were also proceeded efficiently to give the corresponding cross-coupled products in good to excellent yields (entries 4-10). The efficiency of the PdCl₂(MeCN)₂/P(o-tol)₃/TBAF system for the reactions of the deactivated aryl bromides 1g-j were decreased to some extent, and 3 mol% Pd was required to produce high yields (entries 11–16). It is noteworthy that the couplings of activated aryl chlorides 1k and 1l with silanes, respectively, proceed smoothly in the presence 1 to 3 mol%

 Table 1
 Palladium-Catalyzed Hiyama Cross-Coupling Reaction of p-Bromotoluene (1a) with Phenyltrimethoxysilane (2a)^a

$Me \longrightarrow Br + Si(OMe)_3 \longrightarrow Me \longrightarrow Vert Fried Fr$						
1a	2a	3				
Entry	[Pd]	Ligand	Present work	Present work		
			Time (min)	Yield (%) ^b	Yield (%) ^b	
1	Pd(OAc) ₂	_	540	67	_	
2	Pd(OAc) ₂	PPh ₃	240	90	82	
3	Pd(OAc) ₂	$P(o-tol)_3$	240	94	78	
4	Pd(OAc) ₂	Ph ₃ PO	240	85	_	
5	Pd(OAc) ₂	DABCO	90	41	_	
6	Pd(dba) ₂	$P(o-tol)_3$	30	95	_	
7	PdCl ₂ (MeCN) ₂	$P(o-tol)_3$	40	>99	_	
8 ^d	PdCl ₂ (MeCN) ₂	$P(o-tol)_3$	40	>99	_	
9 ^{d,e}	PdCl ₂ (MeCN) ₂	$P(o-tol)_3$	40	92	_	
10 ^{d,f}	PdCl ₂ (MeCN) ₂	$P(o-tol)_3$	40	12	_	
11 ^{d,g}	PdCl ₂ (MeCN) ₂	$P(o-tol)_3$	720	54	_	
12 ^{d,h}	PdCl ₂ (MeCN) ₂	$P(o-tol)_3$	120	98	_	
13 ^{d,i}	PdCl ₂ (MeCN) ₂	P(o-tol) ₃	120	13	_	
14 ^{d,j}	PdCl ₂ (MeCN) ₂	P(o-tol) ₃	120	18	_	

^a Unless otherwise indicated, the reaction conditions were as follows: **1a** (1 mmol), **2a** (2 mmol), Pd (3.0 mol%), ligand (6.0 mol%), and TBAF·3H₂O (6 equiv) at 80 °C under N₂.

^b Isolated yield.

^c DeShong's reaction conditions: **1a** (5.425 mmol), **2a** (10.983 mmol), Pd (10 mol%), ligand (20 mol%), TBAF·3H₂O (2 equiv), and DMF (40 mL) at 85 °C under N₂ for 1–5 h.

^d TBAF·3H₂O (3 equiv).

e PdCl₂(MeCN)₂ (1 mol%).

^f PdCl₂(MeCN)₂ (0.1 mol%).

^g At room temperature.

^h $\mathbf{1a}$ (5 mmol) and $\mathbf{2a}$ (10 mmol).

ⁱ KF (3 equiv) instead of TBAF for 6 h.

^j CsF (3 equiv) instead of TBAF for 6 h.

PdCl₂(MeCN)₂. For example, the reaction of chloride **1k** with silane **2a** or **2b** afforded the corresponding biaryls **4** and **15** in 90% and 98% yields, respectively, at a loading of 1 mol% Pd (entries 17 and 19). Unfortunately, the couplings of the deactivated aryl chlorides **1m** and **1n** gave low yields in the presence of 3 mol% Pd (entries 21 and 23). Moderate yields were obtained when the loadings of Pd were increased to 10 mol% (entries 22 and 24). As in-

dicated in the earlier report,⁶ CuI might be another better promoter for the Hiyama reaction. However, the yield of **5** was decreased to 10% in the presence of $PdCl_2(MeCN)_2$ (10 mol%), $P(o-tol)_3$ (20 mol%), CuI (0.5 equiv) and TBAF (3 equiv) (entry 25).

Table 2	Palladium-Catalyzed Hiyama	Cross-Coupling Reactions in the	Presence of PdCl ₂ (MeCN) ₂ and P(o-tol) ₃ ^a
---------	----------------------------	---------------------------------	--

Entry	Aryl halide	R'Si(OMe) ₃	Pd (mol%)	Time (min)	Product ^b	Yield (%) ^c
1	O ₂ N-	Si(OMe) ₃	1	45	4	>99
2	1b MeO-	2a 2a 2a	1	45	5	>99
3 ^d	1c 1c	2a	1	180	5	49
4	MeBr	Me — Si(OMe) ₃	1	40	6	79
5	1a 1a	2b MeO- Si(OMe) ₃	1	60	7	81
6	1a	2c O_2N Si(OMe) ₃	1	60	8	90
7	O ₂ N-Br	2d 2a	3	45	4	90
8	1d 1d	2a	1	120	4	91
9	Br	2a	1	45	9	88
10	le	2a	1	50	10	>99
11	1f Br Me	2b	1	120	11	85
12	1g Me Br	2a	3	35	12	98
13	Me 1h Me Me	2a	3	45	13	88
14	1i MeO-	2a	3	35	5	96
15	1j 1j	2b	3	45	7	83
16	1j	2c	3	60	14	80

 Table 2
 Palladium-Catalyzed Hiyama Cross-Coupling Reactions in the Presence of PdCl₂(MeCN)₂ and P(o-tol)₃^a (continued)

Entry	Aryl halide	R'Si(OMe) ₃	Pd (mol%)	Time (min)	Product ^b	Yield (%) ^c
17	O ₂ N-CI	2a	1	90	4	90
18	1k 1k	2a	0.1	420	4	trace
19	1k	2b	1	40	15	98
20) O CI	2a	3	90	8	72
21	11 Me-Cl	2a	3	120	3	19
22	1m 1m	2a	10	1320	3	51
23	MeO	2a	3	1320	5	trace
24	1n 1n	2a	10	1320	5	40
25 ^e	1n	2a	10	1320	5	10

^a Unless otherwise indicated, the reaction conditions were as follows: 1 (1 mmol), 2 (2 mmol), $PdCl_2(MeCN)_2/P(o-tol)_3 (1:2)$, and $TBAF \cdot 3H_2O$ (3 equiv) at 80 °C under N₂.

^b Products are described in the experimental section.

^c Isolated yield.

^d At room temperature.

e CuI (0.5 equiv).

In summary, an improved procedure for the palladiumcatalyzed Hiyama cross-coupling reaction has been developed. In the presence of 1 to 3 mol% of PdCl₂(MeCN)₂, 2 to 6 mol% of $P(o-tol)_3$, and 3 equivalents of TBAF, the couplings of a variety of aryl halides with aryltrimethoxysilanes were carried out smoothly to afford moderate to excellent yields of the corresponding biaryls. Compared with the previous results,⁵ several interesting features are apparent for the present results: First, the reaction is efficient for the deactivated chlorides (entries 14-17, 19 and 20, Table 2). Second, the reaction works well aryl halides bearing different substitutions. Third, the protocol is general because it not only can be conducted under a relatively low palladium catalyst loading (1 to 3 mol% Pd) for aryl iodides, bromides and activated chlorides, but also can be extended to the coupling of deactivated aryl chlorides despite the requirement of high Pd loadings. Finally, no harmful organic solvents such as DMF as the media were required. Further efforts to extend the application of the system to other coupling transformations are underway in our laboratory.

Palladium-Catalyzed Hiyama Cross-Coupling Reaction; General Procedure

A mixture of aryl halide **1** (1 mmol), aryltrimethoxysilane **2** (2 mmol) $PdCl_2(MeCN)_2$ (the indicated amount, Table 2), $P(o-tol)_3$ (the indicated amount, Table 2), and TBAF (3 equiv) was stirred under N₂ at 80 °C for desired time until complete consumption of

starting material as monitored by TLC analysis. After the mixture was diluted with brine, it was extracted with Et₂O. The Et₂O extract was dried (Na₂SO₄) and evaporated. The residue was purified by flash column chromatography (hexane or hexane–EtOAc) to afford the desired coupled products **3–14**.^{4–6,11}

4-Methylbiphenyl (3)⁵

¹H NMR (400 MHz, CDCl₃): δ = 7.58 (t, *J* = 7.6 Hz, 2 H), 7.49 (d, *J* = 8.0 Hz, 2 H), 7.42 (t, *J* = 7.6 Hz, 2 H), 7.31 (t, *J* = 7.6 Hz, 1 H), 7.24 (d, *J* = 8.0 Hz, 2 H), 2.38 (s, 3 H).

¹³C NMR (100 MHz, CDCl₃): δ = 141.1, 138.3, 137.0, 129.5, 128.7, 127.3, 127.2, 127.0, 21.1.

4-Nitrobiphenyl (4)⁵

¹H NMR (400 MHz, CDCl₃): δ = 8.30 (d, *J* = 8.8 Hz, 2 H), 7.74 (d, *J* = 8.8 Hz, 2 H), 7.64 (d, *J* = 6.9 Hz, 2 H), 7.52–7.44 (m, 3 H).

¹³C NMR (100 MHz, CDCl₃): δ = 147.6, 147.2, 138.8, 129.2, 128.9, 127.8, 127.4, 124.1.

4-Methoxybiphenyl (5)⁵

¹H NMR (300 MHz, CDCl₃): δ = 7.54 (t, *J* = 8.4 Hz, 4 H), 7.41 (t, *J* = 7.2 Hz, 2 H), 7.31 (t, *J* = 7.2, 1 H), 6.98 (d, *J* = 6.7, 2 H), 3.85 (s, 3 H).

¹³C NMR (100 MHz, CDCl₃): δ = 159.1, 140.8, 133.7, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3.

4,4'-Dimethylbiphenyl (6)⁵

¹H NMR: (400 MHz, CDCl₃): δ = 7.46 (d, *J* = 8.0 Hz, 4 H), 7.22 (d, *J* = 7.6 Hz, 4 H), 2.37 (s, 6 H).

¹³C NMR (100 MHz, CDCl₃): δ = 138.3, 136.7, 129.4, 126.8, 21.0.

4-Methyl-4'-methoxybiphenyl (7)^{5,6}

¹H NMR (400 MHz, CDCl₃): δ = 7.50 (d, *J* = 8.8 Hz, 2 H), 7.44 (d, *J* = 8.4 Hz, 2 H), 7.22 (d, *J* = 8.0 Hz, 2 H), 6.95 (d, *J* = 8.8 Hz, 2 H), 3.83 (s, 3 H), 2.37 (s, 3 H).

¹³C NMR (100 MHz, CDCl₃): δ = 158.9, 137.9, 136.3, 133.7, 129.4, 127.9, 126.5, 114.1, 55.3, 21.0.

4-Methyl-4'-nitrobiphenyl (8)^{5,6}

¹H NMR (400 MHz, CDCl₃): δ = 8.27 (d, *J* = 8.8 Hz, 2 H), 7.71 (d, *J* = 8.8 Hz, 2 H), 7.53 (d, *J* = 8.4 Hz, 2 H), 7.30 (d, *J* = 7.8 Hz, 2 H), 2.42 (s, 3 H).

¹³C NMR (100 MHz, CDCl₃): δ = 147.5, 146.7, 139.0, 135.7, 129.8, 127.4, 127.1, 124.0, 21.2.

1-Biphenyl-4-ylethanone (9)^{5,6}

¹H NMR (300 MHz, CDCl₃): δ = 8.04 (d, *J* = 8.4 Hz, 2 H), 7.69 (d, *J* = 8.4 Hz, 2 H), 7.64 (d, *J* = 7.6 Hz, 2 H), 7.50–7.40 (m, 3 H), 2.64 (m, 3 H).

¹³C NMR (75 MHz, CDCl₃): δ = 197.8, 145.8, 139.9, 135.8, 128.9, 128.9, 128.2, 127.3, 127.2, 26.7.

Biphenyl (10)⁵

¹H NMR (300 MHz, CDCl₃): δ = 7.59 (d, *J* = 8.4 Hz, 4 H), 7.43 (t, *J* = 7.2 Hz, 4 H), 7.36 (t, *J* = 7.8 Hz, 2 H).

¹³C NMR (75 MHz, CDCl₃): δ = 141.6, 129.1, 127.6, 127.5.

2-Methyl-4'-methoxybiphenyl (11)^{5,6}

¹H NMR (400 MHz, CDCl₃): δ = 7.26–7.22 (m, 6 H), 6.95 (d, J = 8.4 Hz, 2 H), 3.85 (s, 3 H), 2.28 (s, 3 H).

¹³C NMR (100 MHz, CDCl₃): δ = 158.5, 141.5, 135.5, 134.3, 130.3, 130.2, 129.9, 127.0, 125.8, 113.5, 55.3, 20.6.

3,5-Dimethylbiphenyl (12)¹¹

¹H NMR (400 MHz, CDCl₃): δ = 7.59 (d, *J* = 8.4 Hz, 2 H), 7.44– 7.40 (m, 2 H), 7.31–7.28 (m, 1 H), 7.19 (d, *J* = 8.4 Hz, 2 H), 6.98 (d, *J* = 9.2 Hz, 1 H), 2.35 (d, *J* = 8.6 Hz, 6 H).

¹³C NMR (100 MHz, CDCl₃): δ = 141.5, 138.1, 128.9, 128.7, 127.9, 127.2, 127.1, 125.1, 21.4.

2,6-Dimethylbiphenyl (13)¹¹

¹H NMR (400 MHz, CDCl₃): δ = 7.43 (t, *J* = 7.6 Hz, 2 H), 7.36–7.30 (m, 1 H), 7.15–7.11 (m, 5 H), 2.03 (s, 6 H).

¹³C NMR (100 MHz, CDCl₃): δ = 141.1, 136.1, 129.0, 128.8, 128.4, 127.3, 127.0, 126.6, 20.9.

4,4'-Dimethoxybiphenyl (14)^{5,6}

¹H NMR (400 MHz, CDCl₃): δ = 7.46 (d, J = 8.8 Hz, 4 H), 6.94 (d, J = 8.8 Hz, 4 H), 3.83 (s, 6 H).

¹³C NMR (100 MHz, CDCl₃): δ = 158.7, 133.5, 127.7, 114.1, 59.3.

4-Methyl-4'-nitrobiphenyl (15)^{5,6}

¹H NMR (400 MHz, CDCl₃): δ = 8.27 (d, *J* = 8.8 Hz, 2 H), 7.71 (d, *J* = 8.8 Hz, 2 H), 7.53 (d, *J* = 8.4 Hz, 2 H), 7.30 (d, *J* = 7.8 Hz, 2 H), 2.42 (s, 3 H).

¹³C NMR (100 MHz, CDCl₃): δ = 147.5, 146.7, 139.0, 135.7, 129.8, 127.4, 127.1, 124.0, 21.2.

Acknowledgment

We thank the National Natural Science Foundation of China (No. 20202002 and 20572020) and Hunan Provincial Natural Science Foundation of China (No. 05JJ1002) for financial support.

References

- Bringmann, G.; Gunther, C.; Ochse, M.; Schupp, O.; Tasler, S. Progress in the Chemistry of Organic Natural Products, Vol. 82; Herz, W.; Falk, H.; Kirby, G. W.; Moore, R. E., Eds.; Springer: Berlin, 2001, 1–293.
- Hegedus, L. S. Organometallics in Synthesis; Schlosser, M., Ed.; Wiley: Chichester, 2002, 1123.
- (3) For selected Ullmann coupling reactions, see:
 (a) Brongmann, G.; Walter, R.; Weirich, R. Angew. Chem., Int. Ed. Engl. 1990, 29, 977. (b) Zhang, S.; Zhang, D.; Liebeskind, L. S. J. Org. Chem. 1997, 62, 2312. (c) Li, J.-H.; Xie, Y.-X.; Yin, D.-L. J. Org. Chem. 2003, 68, 9867; and references cited therein.
- (4) For selected reviews on the Hiyama cross-coupling reaction, see: (a) Diederich, F.; Stang, P. J. *Metal-Catalyzed Cross-Coupling Reactions*; Wiley-VCH: Weinheim, **1998**.
 (b) Miyaura, N. *Cross-Coupling Reaction*; Springer: Berlin, **2002**. (c) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1317. (d) Horn, K. A. *Chem. Rev.* **1995**, *95*, 1317.
- (5) For selected papers on palladium-phosphine catalytic systems for the Hiyama cross-coupling reaction of siloxanes, see: (a) Mowery, M. E.; DeShong, P. Org. Lett. 1999, 1, 2137. (b) Mowery, M. E.; DeShong, P. J. Org. Chem. 1999, 64, 1684. (c) McElroy, W. T.; DeShong, P. Org. Lett. 2003, 5, 4779. (d) Lee, J.-Y.; Fu, G. C. J. Am. Chem. Soc. 2003, 125, 5616. (e) Koike, T.; Mori, A. Synlett 2003, 1850. (f) Wolf, C.; Lerebours, R. Org. Lett. 2004, 6, 1147. (g) Seganish, W. M.; DeShong, P. J. Org. Chem. 2004, 69, 1137. (h) Lerebours, R.; Wolf, C. Synthesis 2005, 2287.
- (6) For selected papers on palladium-phosphine catalytic systems for the Hiyama cross-coupling reaction of other silanes, see: (a) Hatanaka, Y.; Fukushima, S.; Hiyama, T. Chem. Lett. 1989, 1711. (b) Hatanaka, Y.; Gouda, Y.; Okahara, T.; Hiyama, T. Tetrahedron 1994, 50, 8301. (c) Gouda, K.; Hagiwara, E.; Hatanaka, Y.; Hiyama, T. J. Org. Chem. 1996, 61, 7232. (d) Hagiwara, E.; Gouda, K.; Hatanaka, Y.; Hiyama, T. Tetrahedron Lett. 1997, 38, 439. (e) Denmark, S. C.; Choi, J. U. J. Am. Chem. Soc. 1999, 121, 5821. (f) Mowery, M. E.; DeShong, P. J. Org. Chem. 1999, 64, 3266; and references cited therein. (g) Hirabayashi, K.; Kawashima, J.; Nishihara, Y.; Mori, A.; Hiyama, T. Org. Lett. 1999, 1, 299. (h) Denmark, S. C.; Wu, Z. Org. Lett. 1999, 1, 1495. (i) Hirabayashi, K.; Mori, A.; Kawashima, J.; Suguro, M.; Nishihara, Y.; Hiyama, T. J. Org. Chem. 2000, 65, 5342. (j) Mori, A.; Suguro, M. Synlett 2001, 845. (k) Hoosoi, K.; Nozaki, K.; Hiyama, T. Chem. Lett. 2002, 138. (l) Nakao, Y.; Oda, T.; Sahoo, A. K.; Hiyama, T. J. Organomet. Chem. 2003, 687, 570. (m) Sahoo, A. K.; Oda, T.; Nakao, Y.; Hiyama, T. Adv. Synth. Catal. 2004, 346, 1715. (n) Pierrat, P.; Gros, P.; Fort, Y. Org. Lett. 2005, 7, 697. (o) Jayanth, T. T.; Jeganmohan, M.; Cheng, C.-H. Org. Lett. 2005, 7, 2921. (p) Shindo, M.; Matsumoto, K.; Shishido, K. Synlett 2005, 176. (q) Nakao, Y.; Imanaka, H.; Sahoo, A. K.; Yada, A.; Hiyama, T. J. Am. Chem. Soc. 2005, 127, 6952.
- (7) For a papers on palladium-imidazolium chloride catalytic system for the Hiyama cross-coupling reaction, see: Lee, H. M.; Nolan, S. P. *Org. Lett.* **2000**, *2*, 2053.
- (8) For a papers on β-diimine-palladium catalysts for the Hiyama cross-coupling reaction, see: Domin, D.; Benito-Garagorri, D.; Mereiter, K.; Fröhlich, J.; Kirchner, K. Organometallics 2005, 24, 3957.

Synthesis 2006, No. 6, 969-974 © Thieme Stuttgart · New York

- (9) For papers on DABCO as a ligand for the palladium-catalyzed cross-coupling reactions, see: (a) Li, J.-H.; Liu, W.-J. Org. Lett. 2004, 6, 2809. (b) Li, J.-H.; Zhang, X.-D.; Xie, Y.-X. Synthesis 2005, 804. (c) Li, J.-H.; Liang, Y.; Wang, D.-P.; Liu, W.-J.; Xie, Y.-X.; Yin, D.-L. J. Org. Chem. 2005, 70, 2832.
- (10) Only Pd(OAc)₂ as the Pd source was examined in reference 5a. We also attempted to reuse the PdCl₂(MeCN)₂/P(o-tol)₃/TBAF system, however, only a 48% yield of **3** was isolated in the second run.
- (11) Akiyama, R.; Kobayashi, S. Angew. Chem. Int. Ed. 2001, 40, 3469.