

Palladium-Catalyzed Hydrophenylation of Alkynes with Sodium Tetraphenylborate under Mild Conditions

Hanxiang Zeng and Ruimao Hua*

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

ruimao@mail.tsinghua.edu.cn

Received September 19, 2007



In an aqueous solution of acetic acid, PdCl₂(PPh₃)₂ showed high catalytic activity for the hydrophenylation of both terminal and internal alkynes with sodium tetraphenylborate (NaBPh₄) under mild conditions, affording phenyl alkenes in moderate to excellent yields.

Introduction

Catalytic hydroarylation of multiple carbon-carbon bonds is an important method for constructing complex molecules from relatively simple precursors. Although transition metal complex¹ or Lewis acid² catalyzed hydroarylations by direct activation of a C-H bond of arenes have been intensively studied, most research so far has focused only on the electron-rich arenes, and the control of regioselectivity is still difficult. The use of organoheteroatom compounds has also been described in hydroarylation with high selectivity, such as diphenylantimony chloride³ and tetraphenyltin.⁴ In particular, arylboron drew a lot of attention recently, due to its high functional group compatibility, ready availability, and stability. Miyaura and coworkers reported the first rhodium-catalyzed addition of arylboronic acid to α,β -unsaturated ketones in 1997.⁵ After that, great effort was made in this rhodium-catalyzed asymmetric 1,4addition by applying a variety of appropriate chiral ligands.⁶ The hydroarylation of alkynes with arylboronic acid has also

558 J. Org. Chem. **2008**, 73, 558–562

been described,⁷ and the reaction has been extended to the arylative cyclization of alkyne-tethered olefins and aldehydes.⁸ However, the reaction of hydroarylation with sodium tetraphenylborate, which is a stable and inexpensive phenylating reagent, has rarely been reported.⁹ In this paper, we wish to develop an efficient palladium-catalyzed hydrophenylation of alkynes with sodium tetraphenylborate under mild conditions.

Results and Discussion

The reaction of 1-octyne (**1a**) with sodium tetraphenylborate was first investigated to optimize reaction conditions, and a variety of acids and palladium catalysts were examined (Table 1). When a mixture of **1a** (0.5 mmol), NaBPh₄ (0.5 mmol), and PdCl₂(PPh₃)₂ (0.005 mmol) was stirred at room temperature in glacial acetic acid or H₂O for 6 h (entries 1 and 2), only a small

⁽¹⁾ Selected examples: (a) Jia, C.; Piao, D.; Oyamada, J.; Lu, W.; Kitamura, T.; Fujiwara, Y. *Science* **2000**, *287*, 1992–1995. (b) Lim, Y.-G.; Lee, K.-H.; Koo, B. T.; Kang, J.-B. *Tetrahedron Lett.* **2001**, *42*, 7609–7612. (c) Tsukada, N.; Mitsuboshi, T.; Setoguchi, H.; Inoue, Y. J. Am. Chem. Soc. **2003**, *125*, 12102–12103. (d) Karshtedt, D.; Bell, A. T.; Tilley, T. D. Organometallics **2004**, *23*, 4169–4171.

⁽²⁾ Selected examples: (a) Yamaguchi, M.; Kido, Y.; Hayashi, A.;
Hirama, M. Angew. Chem., Int. Ed. Engl. 1997, 36, 1313–1315. (b)
Yonehara, F.; Kido, Y.; Yamaguchi, M. Chem. Commun. 2000, 1189–1190. (c) Reetz, M. T.; Sommer, K. Eur. J. Org. Chem. 2003, 3485–3496.

⁽³⁾ Matoba, K.; Motofusa, S.-i.; Cho, C. S.; Ohe, K.; Uemura, S. J. Organomet. Chem. **1999**, 574, 3–10.

⁽⁴⁾ Ohe, T.; Uemura, S. Tetrahedron Lett. 2002, 43, 1269–1271.

⁽⁵⁾ Sakai, M.; Hayashi, H.; Miyaura, N. Organometallics 1997, 16, 4229-4231.

⁽⁶⁾ Selected examples: (a) Takaya, Y.; Ogasawara, M.; Hayashi, T. J. Am. Chem. Soc. **1998**, 120, 5579–5580. (b) Takaya, Y.; Ogasawara, M.; Hayashi, T. Tetrahedron Lett. **1999**, 40, 6957–6961. (c) Hayashi, T.; Senda, T.; Takaya, Y.; Ogasawara, M. J. Am. Chem. Soc. **1999**, 121, 11591–11592. (d) Senda, T.; Ogasawara, M.; Hayashi, T. J. Org. Chem. **2001**, 66, 6852–6856. (e) Hayashi, T.; Ueyama, K.; Tokunaga, N.; Yoshida, K. J. Am. Chem. Soc. **2003**, 125, 11508–11509. (f) Otomaru, Y.; Kina, A.; Shintani, R.; Hayashi, T. Tetrahedron: Asymmetry **2005**, 16, 1673–1679. (g) Chen, F.-X.; Kina, A.; Hayashi, T. Org. Lett. **2006**, 8, 341–344.

^{(7) (}a) Hayashi, T.; Inoue, K.; Taniguchi, N.; Ogasawara, M. J. Am. Chem. Soc. **2001**, *123*, 9918–9919. (b) Shirakawa, E.; Takahashi, G.; Tsuchimoto, T.; Kawakami, Y. Chem. Commun. **2001**, 2688–2689.

^{(8) (}a) Shintani, R.; Okamoto, K.; Otomaru, Y.; Ueyama, K.; Hayashi, T. J. Am. Chem. Soc. **2004**, 127, 54–55. (b) Shintani, R.; Tsurusaki, A.; Okamoto, K.; Hayashi, T. Angew. Chem., Int. Ed. **2005**, 44, 3909–3912.

^{(9) (}a) Cho, C. S.; Uemura, S. J. Organomet. Chem. 1994, 465, 85–92.
(b) Cho, C. S.; Motofusa, S.-i.; Ohe, K.; Uemura, S. J. Org. Chem. 1995, 60, 883–888.

TABLE 1. Reaction of 1-Octyne (1a) with SodiumTetraphenylborate^a

<i>n</i> -C ₆ H	13 + NaBPh ₄	$\xrightarrow{cat.}_{cid, H_2O, r.t.} \xrightarrow{n-C_6H_{13}}_{H_1}H$	<i>n</i> -C ₆ H + ⊦	H ₁₃ H
	1a	2a		3a
			yield	
entry	catalyst (mol %)	acid (equiv to 1a)	$(\%)^{b}$	2a:3a ^c
1^d	PdCl ₂ (PPh ₃) ₂ (1.0)	HOAc	<5	
2^e	PdCl ₂ (PPh ₃) ₂ (1.0)		<5	
3	PdCl ₂ (PPh ₃) ₂ (1.0)	HOAc (1.0)	65	94:6
4	PdCl ₂ (PPh ₃) ₂ (1.0)	HOAc (2.0)	80	95:5
5	PdCl ₂ (PPh ₃) ₂ (3.0)	HOAc (2.0)	98	93:7
6 ^f	PdCl ₂ (PPh ₃) ₂ (3.0)	HOAc (2.0)	49	96:4
7	PdCl ₂ (PPh ₃) ₂ (3.0)	<i>p</i> -nitrobenzoic acid (2.0)	67	96:4
8^g	PdCl ₂ (PPh ₃) ₂ (3.0)	HCl(aq)	0	
9	PdCl ₂ (PCy ₃) ₂ (3.0)	HOAc (2.0)	6	>99:1
10	Pd(OAc) ₂ (3.0)	HOAc (2.0)	12	>99:1
11	PdCl ₂ (3.0)	HOAc (2.0)	17	57:43
12	$PdCl_2(3.0) + PPh_3(6.0)$.0) HOAc (2.0)	13	>99:1
13	Pd(PPh ₃) ₄ (3.0)	HOAc (2.0)	33	97:3
14	NiCl ₂ (PPh ₃) ₂ (3.0)	HOAc (2.0)	0	
15^{h}	NiCl ₂ (dppp) (3.0)	HOAc (2.0)	7	>99:1

^{*a*} Unless otherwise noted, reactions were carried out using 0.5 mmol of **1a** and 0.5 mmol of NaBPh₄ with acid and catalyst in 1.0 mL of H₂O in a sealed tube at room temperature for 6 h. ^{*b*} Total GC yield. ^{*c*} Determined by GC. ^{*d*} In 1.0 mL of acetic acid. ^{*e*} In 1 mL of deionized water. ^{*f*} 0.5 equiv of NaBPh₄. ^{*g*} In 1.0 mL of 36% HCl. ^{*h*} dppp = 1,3-bis(diphenylphophino) propane.

amount of 2a was formed (confirmed by GC-MS). In an aqueous solution of acetic acid (0.5 mmol), however, the reaction was significantly improved to give the hydrophenylation product in 65% GC yield with perfect regioselectivity in favor of the Markovnikov adduct 2a (entry 3). Increasing the amount of acid or catalyst loading was found to further promote the reaction (entries 3-5), and the highest yield of adducts was obtained by the use of 3.0 mol % PdCl₂(PPh₃)₂ and 2.0 equiv of acetic acid (entry 5). Decreasing the amount of NaBPh₄ to 0.5 equiv resulted in lower yield of only 49% (entry 6), which means that only one phenyl group was efficiently utilized under this condition. Other acids were also tested in our study. The use of p-nitrobenzoic acid gave somewhat lower yield (67%, entry 7), whereas the catalyst completely lost its activity in concentrated aqueous hydrocholoric acid and all of the starting materials were recovered. This was possibly caused by the strong affinity of chloride ion to the palladium. In addition, we employed other palladium or nickel catalysts, but none of them displayed good activity (entries 9-15). It should also be noted that the PPh₃ ligand seems to have a great influence on the selectivity, since the use of PdCl₂ apparently did not favor the Markovnikov adduct (entry 11) and the addition of PPh₃ did not promote the reaction but changed the selectivity (entry 12).

In order to assess the scope of this process, we have examined the hydrophenylation of several terminal and internal alkynes under the optimized condition indicated in entry 5 of Table 1. The results are summarized in Table 2. As expected, 1-heptyne (**1b**) showed similar reactivity as **1a** to furnish **2b** in 87% yield (entry 1). However, in the cases of phenylacetylene (**1c**) and 5-chloropent-1-yne (**1d**), the corresponding adducts **2c** and **2d** were isolated in somewhat low yields (entries 2 and 3). It should be noted that the C–Cl bond of **1d** was intact.

Under the same reaction conditions, the hydrophenylation of internal alkynes also took place smoothly at room temperature to give *cis*-adducts. For example, dialkylated acetylene **1e**, **1f**,

TABLE 2. PdCl₂(PPh₃)₂-Catalyzed Reaction of Alkynes with Sodium Tetraphenylborate^a

R'-	——R" + NaBPh ₄ - 1.0 equiv	PdCl (3.0 HOA r.t. fo	2(PPh ₃) ₂ mol%) R Ac, H ₂ O Ph or 6 h	R' R" +		ξ" Ph
entry	alkyne		main product	у	ield (%) ^b	2:3 ^c
1	<i>n-</i> C₅H ₁₁ ── ─ 1k)	n-C ₅ H ₁₁ Ph	2b	87	91:9
2	Ph-== 10	;	Ph Ph	2c	51	86:14
3	Cl 1c	I		/—Cl 2d	42	90:10
4	C ₂ H ₅ C ₂ H ₅	1e	C ₂ H ₅ C ₂ H ₅ Ph H	5 2e	61	_
5	<i>n</i> -C ₃ H ₇	1f	n-C ₃ H ₇ Ph H	H ₇ 2f	84	_
6	<i>n</i> -C ₄ H ₉ <i>n</i> -C ₄ H ₉	1g	n-C ₄ H ₉ Ph H	H ₉ 2g	86	_
7	PhPh	1h	Ph Ph Ph H	2h	>99	_
8 C	сн₃оос——соосн	C ₃1i		осн ₃ 2і	81	
9	CH₃— — Ph	1j	CH ₃ Ph Ph H 2i (44%)		Ph Ph (31%)	
10	сн₃- = соосн	3 1k		DCH ₃ 2k	95	>99:1

^{*a*} Reactions were carried out using alkyne (1.0 mmol), NaBPh₄ (1.0 mmol), HOAc (2.0 mmol), and PdCl₂(PPh₃)₂ (0.03 mmol) in H₂O (2.0 mL) in a sealed tube at room temperature for 6 h. ^{*b*} Isolated yield. ^{*c*} Determined by GC.

TABLE 3. Reaction of Diphenylacetylene (1h) with Sodium Tetraphenylborate^a

		PdCl ₂ (PPh ₃) ₂ (3.0 mol%)	01-	
	$1n + NaBPn_4$	HOAc, H ₂ O	20	
	amount of NaBPh4	temp	time	yield
entry	(equiv to 1h)	(°C)	(h)	$(\%)^{b}$
1	0.33	rt	6	58
2	0.33	rt	24	71
3	0.33	50	12	96
4	0.25	50	12	75

^{*a*} Reactions were carried out using **1h** (1.0 mmol), NaBPh₄ as indicated in the table, HOAc (2.0 mmol), and PdCl₂(PPh₃)₂ (0.03 mmol) in H₂O (2.0 mL in a sealed tube. ^{*b*} Isolated yield based on **1h** used.

and 1g reacted with NaBPh₄ to afford the trisubstituted alkenes 2e, 2f, and 2g in good to high yields (entries 4–6), and the hydrophenylation of diphenylacetylene (1h) afforded the corresponding adduct 2h in quantitative yield (entry 7). Furthermore, the reaction of electron-deficient internal alkyne 1i gave the adduct 2i in 81% yield (entry 8). As for the unsymmetrical internal alkynes, the regioselectivity depends on the nature of substitutents. In the case of 1-phenylpropyne (1j), the two *cis*adducts 2j and 3j were isolated in 44% and 31% yields, respectively (entry 9). However, the use of methyl but-2-ynoate (1k) resulted in the formation of methyl 3-phenyl-2-butenoate $(2\mathbf{k})$ in excellent yield and regioselectivity, indicating that the phenyl group was almost exclusively introduced at the position β to the ester group (entry 10).

Although the reaction of 2-methylbut-3-yn-2-ol (11) with sodium tetraphenylborate at room temperature afforded a complicated mixture, in which the formation of corresponding adduct could be determined by GC and GC-MS, when the same reaction was performed at 50 °C for 12 h, interestingly, (*E*)-2-methyl-4-phenyl-buta-1,3-diene (4) was obtained in 75% isolated yield (eq 1). These results indicated that, in contrast to linear terminal alkynes, the use of sterically congested 11 resulted in selective formation of the *anti*-Markovnikov adduct, which underwent dehydration to give 4 under the reaction conditions. Since many alkynols are relatively easy to access, this process could be used as a practical method for the synthesis of conjugated dienes.



However, when 2-phenylbut-3-yn-2-ol (**1m**) was employed, no expected products of dehydration could be obtained, and the corresponding Markovnikov adduct **2m** and *trans anti*-Markovnikov adduct **3m** were isolated in low yields (eq 2). Likewise, as a result of the steric hindrance of substituents, the formation of the *anti*-Markovnikov adduct was favored.

The hydrophenylations of 1,3-diynes were also examined, and the reactions took place smoothly under the same conditions. The conversion of 1,4-bis(trimethylsilyl)buta-1,3-diyne (**5a**) was almost quantitative, affording both singly and doubly phenylated products **6** and **7** in 85% and 13% yields, respectively (eq 3). In the case of 1,4-diphenylbuta-1,3-diyne (**5b**), the reaction gave three doubly phenylated products that were isolated in 85% as a mixture (eq 4). Attempts to separate these adducts were not successful, and only **8** was isolated in analytical purity with low yield (15%).



SCHEME 1. Proposed Mechanism for

Palladium(II)-Catalyzed Hydrophenylation of Alkynes with NaBPh₄



 TABLE 4. Palladium-Catalyzed Reactions of Alkynes with Sodium Tetraphenylborate^a

		PdCl ₂ (PPh ₃) ₂ (3.0 mol%) R R	" R' /	२
к—=	——R° + NaBPn ₄ · 0.33 equiv 1	HOAc, H ₂ O Ph H 50 °C for 12 h 2	I Ph I 3	H
entry	y alkyne	main adduct	yield(%) ^b	2:3°
1	1a	2a	51	92:8
2	<i>n</i> -C ₅ H ₁₁ COOR 1n	Et $n - C_5 H_{11}$ COOEt Ph H	87	92:8
3	PhCOOE 10	Et Ph COOEt Ph H	>99	>99:1
4	<i>n</i> -C₄H ₉ ────Ph 1p	n-C₄H₃ Ph Ph H	70	66:34 ^d
		20		

^{*a*} Reactions were carried out using alkyne (1.0 mmol), NaBPh₄ (0.3 mmol), HOAc (2.0 mmol), and PdCl₂(PPh₃)₂ (0.03 mmol) in H₂O (2.0 mL) in a sealed tube at 50 °C for 12 h. ^{*b*} Isolated yield based on alkyne used. ^{*c*} Determined by GC. ^{*d*} Determined by ¹H NMR.

In previous reports on the hydrophenylation of alkenes with NaBPh₄⁹ and coupling reaction of NaBPh₄ with aryl halides,¹⁰ usually only one or two phenyl groups could be transferred. As shown in Table 2, entry 7, the reaction of diphenylacetylene (**1h**) with NaBPh₄ afforded the adduct **2h** in quantitative yield. In order to explore the possibility for further efficient transfer of phenyl groups in NaBPh₄, we examined the reaction of **1h** with 0.33 or 0.25 equiv of NaBPh₄ again under different conditions. As summarized in Table 3, either increasing reaction temperature or prolonging reaction time could promote the reaction, and a satisfactory result could be achieved when the reaction was performed at 50 °C for 12 h with 0.33 equiv of NaBPh₄, indicating that at most three phenyl groups could be efficiently utilized (entries 3 and 4).

To demonstrate the generality and efficiency of the above process, we carried out the reaction of 0.33 equiv of NaBPh₄ with several other alkynes at 50 °C (Table 4). Although the reaction of **1a** with 0.33 equiv of NaBPh₄ afforded adducts in 51% yield (entry 1), similar to the result by using 0.5 equiv of

⁽¹⁰⁾ Wang, J.-X.; Yang, Y.; Wei, B. Synth. Commun. 2004, 34, 2063–2069.

NaBPh₄ at room temperature as indicated in entry 6 of Table 1, the internal alkynes underwent the hydrophenylation smoothly to give corresponding products in good to high yields (entries 2-4). Both yields of adducts and the selectivities of reactions are comparable to the results summarized in Table 2.

It is known that NaBPh₄ can react with acetic acid to give Ph_3B , benzene, and sodium acetate, and Ph_3B can be further hydrolyzed into di- and monophenylboronic acid.⁹ Therefore, we also examined the reactivity of Ph_3B and $PhB(OH)_2$ with alkyne at room temperature. As shown in eqs 5 and 6, the reactions of **1h** with Ph_3B or $PhB(OH)_2$ also afforded **2h** in moderate yields.



On the basis of the above observations, we proposed a possible mechanism for the present hydrophenylation in Scheme 1. It includes the oxidative addition of the C–B bond to Pd(0) species to give intermediate B^{11} and selective insertion of alkyne into Pd–C to give C. Hydrolysis of C followed by reductive elimination of the C–C bond finally gives the hydrophenylating products and regenerates the Pd(0) species. Ph₃B, Ph₂B(OH), and PhB(OH)₂ should be the possible phenylating intermediates in the reaction system.

The results obtained in this work can be rationally explained by this proposed mechanism: (1) the formation of benzene was found in all the reactions confirmed by GC and GC-MS, and thus only three phenyl groups in NaBPh₄ could be maximally efficiently used; (2) the dominant formation of Markovnikovtype adduct in the hydrophenylation of terminal alkynes is due to the selective insertion of a terminal alkyne (R = H) into Pd-C bonds with the R' group away from the metal center to give the less steric repulsion intermediate C; (3) the regioselectivity of the phenyl group attached to the position β to the ester group in the reactions of propiolates **1k**, **1n**, and **1o** (R = COOR'') is possibly resulted from the interaction of palladium and ester group.¹²

In addition, the careful analyses of the reaction mixture indicated in entry 5 of Table 1 disclosed the formation of monoand diphenylboronic acids, and we have also successfully isolated PhB(OH)₂ from the reaction mixture and found that PhB(OH)₂ is in equilibrium with triphenylboroxin in CDCl₃ (eq 7).¹³ Moreover, as shown in eq 8, the reaction of **1a** in D₂O afforded selectively deuterated product **2a**-*d*, which again confirmed the *cis*-type addition manner. These findings gave direct evidence to support our proposed mechanism. More interestingly, in Hayashi's Rh-catalyzed hydroarylation system, a similar reaction as eq 8 gave the product with deuterium incorporated at the ortho position of the phenyl group, which was caused by 1,4-rearrangement of rhodium in intermediate $C.^{7a}$ Larock has also reported similar behavior in the Pd-catalyzed reaction of alkynes and aryl iodide.¹⁴ However, possibly as a result of milder reaction conditions, no migration was observed in the present catalysis system.



Conclusions

In summary, we have developed a palladium-catalyzed hydrophenylation of alkynes with sodium tetraphenylborate with improved utilization efficiency of the reagent. From a synthetic point of view, the present catalytic procedure to produce arylalkenes has advantages over other methods in that it took place in an aqueous solution under mild conditions with high regio- and stereoselectivity and several functional groups were tolerated.

Experimental Section

Typical Procedure for Hydrophenylation of 1-Octyne (1a) with Sodium Tetraphenylborate To Afford 2-Phenyloct-1-ene¹⁵ (2a) (Table 1, entry 5). A mixture of 1-octyne (1a) (74.0 µL, 0.5 mmol), NaBPh₄ (171.1 mg, 0.5 mmol), HOAc (58.0 µL, 1.0 mmol), PdCl₂(PPh₃)₂ (10.5 mg, 0.015 mmol), and H₂O (1.0 mL) was stirred under nitrogen in a sealed tube at room temperature for 6 h. After reaction, the mixture was first subjected to a short silica column chromatography (ca. 5 cm of silica gel, eluted with CH₂Cl₂) to remove the water. Then octadecane (92.5 mg, 0.36 mmol) was added in the elution as internal standard for GC analysis. After GC and GC-MS analysis, the solvents and volatiles were removed under vacuum, and the residue was then subjected to preparative TLC isolation (silica, eluted with petroleum ether). Compound 2a was obtained in 84.7 mg (0.45 mmol, 90%) as a yellow oil. The result of GC analysis of the reaction mixture revealed that 2a and 3a were formed in a total of 98% yield with a ratio of 93:7. Data for 2a: ¹H NMR (300 MHz, CDCl₃) δ 7.39-7.21 (m, 5H), 5.24 (d, 1H, J = 1.5 Hz), 5.03 (d, 1H, J = 1.5 Hz), 2.48 (t, 2H, J = 7.4Hz), 1.48–1.23 (m, 8H), 0.86 (t, 3H, J = 6.9 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 148.8, 141.5, 128.2, 127.2, 126.1, 112.0, 35.4, 31.7, 29.1, 28.3, 22.7, 14.1; GC-MS m/z 188 (M⁺).

Hydrophenylation of Diphenylacetylene (1h) with Sodium Tetraphenylborate To Afford Triphenylethene (2h)¹⁶ at Elevated Temperature (Table 3, entry 3). A mixture of diphenyl-

⁽¹¹⁾ Oxidative addition of a carbon-boron bond to Pd(0) has so far been proposed in several cases: (a) Ohe, T.; Ohe, K.; Uemura, S.; Sugita, N. J. Organomet. Chem. **1988**, 344, C5. (b) Cho, C. S.; Uemura, S. J. Organomet. Chem. **1994**, 465, 85–92. (c) Cho, C. S.; Motofusa, S.-i.; Ohe, K.; Uemura, S. J. Org. Chem. **1995**, 60, 883–888.

⁽¹²⁾ The interaction of carbonyl group and transition metal complex has been previously reported in catalyzed 1,4-additions. See refs 5 and 8.

⁽¹³⁾ For review, see: Lappert, M. F. Chem. Rev. 1956, 56, 959-1064.

⁽¹⁴⁾ Tian, Q.; Larock, C. L. Org. Lett. 2000, 2, 3329-3332.

⁽¹⁵⁾ Yoshida, K.; Hayashi, T. J. Am. Chem. Soc. 2003, 125, 2872–2873.
(16) Song, C. E.; Jung, D.-u.; Choung, S. Y.; Roh, E. J.; Lee, S.-g.; Angew. Chem., Int. Ed. 2004, 43, 6183–6185.

acetylene (**1h**) (178.2 mg, 1.0 mmol), NaBPh₄ (112.9 mg, 0.33 mmol), HOAc (116.0 μ L, 2.0 mmol), PdCl₂(PPh₃)₂ (21.0 mg, 0.03 mmol), and H₂O (2.0 mL) was heated in a sealed tube under nitrogen at 50 °C for 12 h. After reaction, the mixture was first subjected to a short silica column chromatography (ca. 5 cm of silica gel, eluted with CH₂Cl₂) to remove the water. The elution was condensed and subjected to GC and GC-MS analysis. After that, the solvents and volatiles were removed under vacuum, and the residue was then subjected to preparative TLC isolation (silica, eluted with petroleum ether). Compound **2h** was obtained in 245.9 mg (0.96 mmol, 96%) as a pale yellow oil. **Data for 2h**: ¹H NMR

(300 MHz, CDCl₃) δ 7.33–6.95 (m, 16H); $^{13}\mathrm{C}$ NMR (75 MHz, CDCl₃) δ 143.4, 142.5, 140.3, 137.3, 130.3, 129.5, 128.6, 128.2, 128.1, 127.9, 127.6, 127.5, 127.4, 126.7; GC-MS m/z 256 (M⁺).

Acknowledgment. This project (20573061) was supported by National Natural Science Foundation of China.

Supporting Information Available: General method, characterization data and charts of ¹H and ¹³C NMR for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

JO7020554