

# The First Fluoride-Free Hiyama Reaction of Vinylsiloxanes Promoted by Sodium Hydroxide in Water

Emilio Alacid<sup>a</sup> and Carmen Nájera<sup>a,\*</sup>

<sup>a</sup> Departamento de Química Orgánica, Facultad de Ciencias and Instituto de Síntesis Orgánica (ISO), Universidad de Alicante, Apartado 99, 03080 Alicante, Spain  
Fax: (+34)-965-903-549; e-mail: cnajera@ua.es

Received: June 2, 2006; Accepted: August 7, 2006

Dedicated to Prof. Tamejiro Hiyama on occasion of his 60<sup>th</sup> birthday.

**Abstract:** The first cross-coupling reaction between vinylalkoxysilanes and aryl bromides or chlorides promoted by aqueous sodium hydroxide under fluoride-free conditions to provide styrenes is reported. The reaction is catalyzed by palladium(II) acetate or a 4-hydroxyacetophenone oxime-derived palladacycle either under thermal or microwave heating at 120 °C with low catalyst loading (0.01–1 mol % of palladium) in the presence of tetra-*n*-butylammonium bromide (TBAB) as additive in air. In the case of styryltriethoxysilane, the coupling with aryl or vinyl bromides takes place stereospecifically to give the corresponding stilbenes or dienes, respectively. These mild and simple reaction conditions prevent undesirable polymerization of the products.

**Keywords:** alkenes; cross-coupling; microwave heating; palladacycles; vinylsiloxanes

Palladium-catalyzed cross-coupling reactions are extremely useful processes in chemistry.<sup>[1]</sup> Nowadays, organoboron (Suzuki–Miyaura reaction), organotin (Migita–Kosugi–Stille reaction), organozinc (Negishi reaction) and organosilicon (Hiyama reaction) compounds are the most frequently employed organometallics for C–C bond formation reactions. Among them, silicon-derived compounds are very attractive organometallic nucleophiles for industrial purposes because of their stability, low cost, and accessibility. Different organosilicon reagents, such as alkyl-, fluoro-, chloro-, hydroxy-, and alkoxy-silanes have been used for this carbon-carbon bond forming process.<sup>[2]</sup> Due to the low reactivity of these reagents, generally they need to be activated by the fluoride anion in order to generate a more reactive pentacoordinate silicate anion for the transmetallation step of the aryl- or vinylpalladium intermediates, although

other anionic ligands, such as hydroxide and hydride can also form pentacoordinate silicon intermediates.<sup>[3]</sup>

Siloxanes are the most easily available organosilanes, and have been recently coupled with aryl halides for the synthesis of biaryls using palladium-phosphinous acid complexes (10 mol %) as catalysts and aqueous NaOH.<sup>[4]</sup> Concentrated NaOH (50 %) also promotes this type of Hiyama reaction under solventless conditions when using Pd salts, such as Pd(OAc)<sub>2</sub> or PdCl<sub>2</sub>, and oxime-derived palladacycles **1** and **2** (Fig. 1), which allowed the use of very low catalyst loadings (0.001–0.1 mol % of Pd).<sup>[5]</sup> This procedure can be performed under thermal or microwave heating and allows the reuse of Pd and the isolation of products just by simple ether extraction.

The vinylation reaction of aryl halides has been mainly performed using alkenylstannanes, because alkenylboron reagents are rather unstable. For example, vinylboronic acid has a high tendency to polymerize, and also gives mixtures of Suzuki–Miyaura and Mizoroki–Heck reaction products. Alternatively, potassium trifluorovinylborates can be used for vinylation reactions.<sup>[6]</sup> In general, alkenylsilanes are less active than arylsilanes in the Hiyama reaction. Different types of alkenylsilanes have been used in fluoride-promoted cross-coupling reactions by the groups of Hiyama,<sup>[7]</sup> Denmark,<sup>[8]</sup> and Yoshida,<sup>[9]</sup> although only with aryl iodides due to their low reactivity. In addition, alkenylsiloxanes, such as polyalkenylmethylsiloxanes have shown to be appropriate reagents for the fluoride-promoted alkenylation of aryl iodides.<sup>[10]</sup>

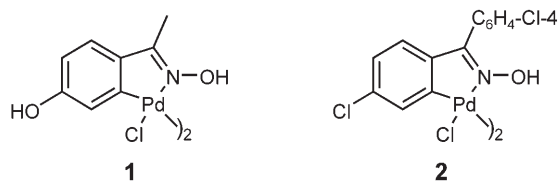
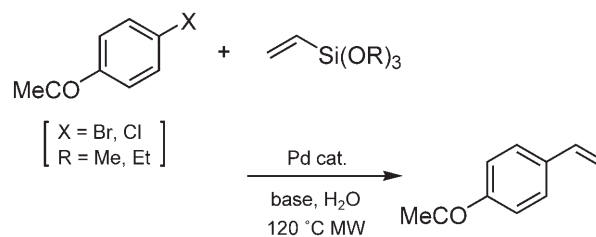


Figure 1.

However, only two procedures describe the use of vinyltrialkoxysilanes as vinyllating agents with aryl bromides and chlorides. Thus, Lee and Nolan have found that activated 4-bromo- and 4-chloroacetophenone can be coupled quantitatively with vinyltrimethoxysilane in the presence of tetra-*n*-butylammonium fluoride (TBAF) using a high loading of Pd(OAc)<sub>2</sub> and an imidazolium salt (3 mol %) as catalyst at 80 °C.<sup>[11]</sup> Recently, the coupling of 4-chloroacetophenone with vinyltrimethoxysilane has been achieved in 95% yield under microwave heating at 110 °C using  $\pi$ -allylpalladium chloride (2.5 mol % of Pd) and *N*-dicyclohexylphosphino-*N*-methylpiperazine as ligand in a THF solution of TBAF.<sup>[12]</sup> We describe here the first fluoride-free coupling of vinylsiloxanes with different aryl halides in water under thermal and microwave conditions.

The initial studies were performed with the cross-coupling of 4-bromo- or 4-chloroacetophenone and vinylsiloxanes (2 equivs.)<sup>[13]</sup> in aqueous NaOH (*ca.* 1 M) under microwave irradiation<sup>[14]</sup> at 120 °C (40–45 W) (Scheme 1 and Table 1). For the cross-coupling of 4-bromoacetophenone and vinyltrimethoxysilane, the use of different Pd sources, such as Pd(OAc)<sub>2</sub>, PdCl<sub>2</sub>, and Pd on charcoal (0.5 mol %) gave 4-acetylstyrene in 97, 87, and 12% yields, respectively, after heating during 10 min (Table 1, entries 1–3). When oxime-derived palladacycles **1** and **2**,<sup>[15]</sup> which have been previously used as precatalysts<sup>[16]</sup> in the cross-coupling of arylsiloxanes,<sup>[5]</sup> were assayed in this vinylation reaction, only the 4-hydroxyacetophenone complex **1** gave a quantitative yield of the corresponding 4-acetoxys-

tyrene (Table 1, entries 4 and 5), whereas the 4,4'-dichlorobenzophenone oxime-derived complex **2** failed. On the other hand, the use of KOH instead of NaOH gave lower yields. (Table 1, compare entries 1 and 6). Alternatively, vinyltriethoxysilane can be used as vinyllating reagent with similar yields (Table 1, compare entries 1 and 7). The Pd loading can be lowered from 0.5 to 0.1 mol % by using tetra-*n*-butylammonium bromide (TBAB) as additive<sup>[17]</sup> (Table 1, entries 8 and 9), whereas, in the absence of TBAB the cross-coupling using the same loading of complex **1** led to a lower yield (Table 1, compare entries 9 and 10). Lower catalyst loading gave a negligible yield of 4-acetoxystyrene (Table 1, entry 11). When 4-chloroacetophenone was cross-coupled with vinyltrimethoxysilane under similar reaction conditions, it was necessary to increase the catalyst loading up to 2 mol % of Pd, the amount of TBAB to 1 equiv. and the irradiation time from 10 to 25 min in order to get reasonable yields of 4-acetoxystyrene (Table 1, entries 12–15). It can be concluded that Pd(OAc)<sub>2</sub> and palladacycle **1**



**Scheme 1.**

**Table 1.** Hiyama reaction of vinylsiloxanes with 4-bromo- and 4-chloroacetophenone under microwave heating: reaction conditions study.<sup>[a]</sup>

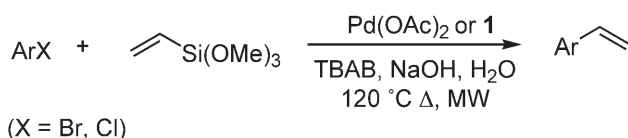
Entry	ArBr	Siloxane	Catalyst (mol % Pd)	Base	TBAB (equivs.)	<i>t</i>	Yield [%] <sup>[b]</sup>
1		CH <sub>2</sub> =CHSi(OMe) <sub>3</sub>	Pd(OAc) <sub>2</sub> (0.5)	NaOH	-	10 min	97 (90)
2			PdCl <sub>2</sub> (0.5)	NaOH	-	10 min	87
3			Pd/C (0.5)	NaOH	-	10 min	12
4			<b>1</b> (0.5)	NaOH	-	10 min	99
5			<b>2</b> (0.5)	NaOH	-	10 min	0
6			Pd(OAc) <sub>2</sub> (0.5)	KOH	-	10 min	66
7		CH <sub>2</sub> =CHSi(OEt) <sub>3</sub>	Pd(OAc) <sub>2</sub> (0.5)	NaOH	-	10 min	90
8		CH <sub>2</sub> =CHSi(OMe) <sub>3</sub>	Pd(OAc) <sub>2</sub> (0.1)	NaOH	0.5	10 min	90
9			<b>1</b> (0.1)	NaOH	0.5	10 min	99
10			<b>1</b> (0.1)	NaOH	-	10 min	71
11			<b>1</b> (0.01)	NaOH	0.5	10 min	6
12		CH <sub>2</sub> =CHSi(OMe) <sub>3</sub>	Pd(OAc) <sub>2</sub> (1)	NaOH	1	10 min	46
13			<b>1</b> (1)	NaOH	1	10 min	48
14			Pd(OAc) <sub>2</sub> (2)	NaOH	1	20 min	60
15			<b>1</b> (2)	NaOH	1	20 min	71 (60)

<sup>[a]</sup> Reaction conditions: aryl or vinyl halide (1 equiv.), vinyltrimethoxysilane (2 equivs.), catalyst (see column), base (2.5 equivs.), TBAB (see column), H<sub>2</sub>O (2 mL/1 mmol), 120 °C (40–45 W, 2–5 bar), with air stream cooling.

<sup>[b]</sup> Determined by <sup>1</sup>H NMR by using diphenylmethane as internal standard. In parenthesis yield after flash chromatography.

are good precatalysts for the NaOH-promoted cross-coupling reaction of vinylsiloxanes with aryl bromides and chlorides using TBAB as additive under microwave irradiation.

For the NaOH-promoted Hiyama cross-coupling reaction between different aryl bromides or chlorides and vinyltrimethoxysilane, either Pd(OAc)<sub>2</sub> or palladacycle **1** were used as precatalyst in the presence of 1 equiv. of TBAB in neat water at 120 °C under microwave and conventional thermal conditions (Scheme 2 and Table 2). The reaction conditions used

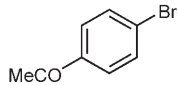
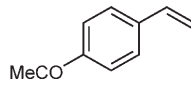
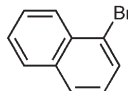
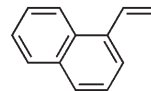
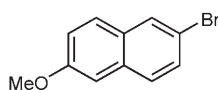
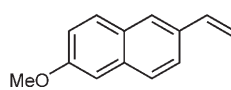
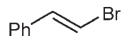
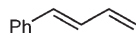
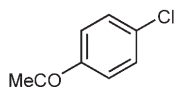
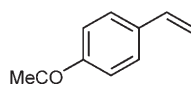
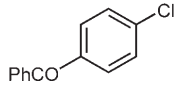
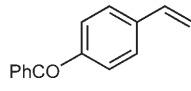


**Scheme 2.**

for 4-bromoacetophenone in the case of the microwave irradiation (0.1 mol % Pd loading) had to be modified for thermal heating (0.5 mol % Pd loading) giving rise to 4-acetylstyrene in good yields, although a reaction time of almost 1 d performed in a pressure tube was necessary (Table 2, entries 1–4). Deactivated 1-bromonaphthalene needed higher Pd loading (1 mol %) and longer reaction time to achieve excellent yields of 1-vinylnaphthalene (Table 2, entries 5–8), whereas 2-bromo-6-methoxynaphthalene showed a higher reactivity (0.5 mol % of Pd), affording 6-methoxy-2-vinylnaphthalene,<sup>[18]</sup> an intermediate for the synthesis of naproxene,<sup>[19]</sup> in good yields (Table 2, entries 9–12). Under similar reaction conditions (*E*)-styryl bromide gave stereospecifically (*E*)-1-phenylbuta-1,3-diene in moderate yields (Table 2, entries 13–16).

Cross-coupling of activated chloroarenes with vinyltrimethoxysilane had to be performed under micro-

**Table 2.** Hiyama reaction of vinyltrimethoxysilane with bromides and chlorides.<sup>[a]</sup>

Entry	ArX	Catalyst (mol % Pd)	Conditions	<i>t</i>	Product	Yield [%] <sup>[b]</sup>
1		Pd(OAc) <sub>2</sub> (0.1)	MW	10 min		90
2		<b>1</b> (0.1)	MW	10 min		99
3		Pd(OAc) <sub>2</sub> (0.5)	Δ	20 h		95 (82)
4		<b>1</b> (0.5)	Δ	20 h		93 (89)
5		Pd(OAc) <sub>2</sub> (1)	MW	20 min		90
6		<b>1</b> (1)	MW	20 min		92
7		Pd(OAc) <sub>2</sub> (1)	Δ	24 h		96
8		<b>1</b> (1)	Δ	24 h		98 (90)
9		Pd(OAc) <sub>2</sub> (0.5)	MW	10 min		80
10		<b>1</b> (0.5)	MW	10 min		91 (83)
11		Pd(OAc) <sub>2</sub> (0.5)	Δ	24 h		64
12		<b>1</b> (0.5)	Δ	24 h		89
13		Pd(OAc) <sub>2</sub> (0.5)	MW	15 min		75
14		<b>1</b> (0.5)	MW	15 min		90 (81)
15		Pd(OAc) <sub>2</sub> (0.5)	Δ	24 h		72 (41)
16		<b>1</b> (0.5)	Δ	24 h		47
17		Pd(OAc) <sub>2</sub> (2)	MW	25 min		60
18		<b>1</b> (2)	MW	25 min		71 (60)
19		Pd(OAc) <sub>2</sub> (2)	MW	25 min		70 (61)
20		<b>1</b> (2)	MW	25 min		65 (54)

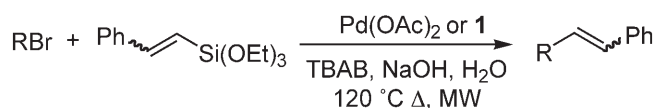
<sup>[a]</sup> Reaction conditions: aryl or vinyl halide (1 equiv.), vinyltrimethoxysilane (2 equivs.), catalyst (see column), NaOH (2.5 equivs.), TBAB (1 equiv.), H<sub>2</sub>O (2 mL/1 mmol), at 120 °C, in a pressure tube for thermal reactions and under 40–45 W irradiation for microwave conditions.

<sup>[b]</sup> Determined by <sup>1</sup>H NMR by using diphenylmethane as internal standard. In parenthesis yield after flash chromatography.

wave irradiation because the cross-coupling under conventional thermal conditions failed. Good yields were obtained in the vinylation of activated 4-chloroacetophenone and 4-chlorobenzophenone by increasing the Pd loading to 2 mol% and the irradiation time to 25 min (Table 2, entries 17–20). Under these reaction conditions the cross-coupling of vinyltrimethoxysilane with deactivated 4-chlorotoluene failed.

In any case, the competition of a Heck reaction to give 2-arylvinylsiloxanes was never observed. The only detected secondary product was the corresponding symmetrical stilbene in less than 2% for aryl bromides and less than 4% for aryl chlorides. The formation of Pd black was observed, as in the previous Hiyama reaction with arylsiloxanes,<sup>[5]</sup> indicating that the real catalyst can also be Pd nanoparticles.

The method was extended to other vinylsiloxanes in order to study the stereochemical outcome of this type of cross-coupling. A 1:2 *Z/E* mixture of styryltriethoxysilane was prepared by hydrosilylation of phenylacetylene with triethoxysilane catalyzed by *in situ* generated (triphenylphosphine)rhodium(I) iodide.<sup>[20]</sup> The coupling of this substituted siloxane with 1-bromonaphthalene in the previous reaction conditions using microwave heating afforded a 1:1.9 mixture of *Z/E* 1-naphthyl-2-phenylethylenes (Scheme 3 and Table 3, entries 1 and 2). When (*E*)-styryl bromide was allowed to react with the styrylsiloxane under the same reaction conditions, a 1:2 mixture of *Z,E* and *E,E* 1,4-diphenylbuta-1,3-dienes was also stereospecifically obtained (Scheme 3 and Table 3, entries 3 and 4). Therefore, it can be concluded



Scheme 3.

ed that this cross-coupling reaction occurred with retention of the configuration of both components.

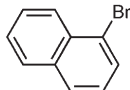
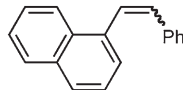
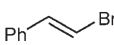
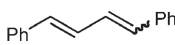
In conclusion, this new NaOH-promoted Hiyama reaction allows the use of vinylsiloxanes as ethylene equivalents. This methodology is an alternative to the Heck reaction and avoids working with ethylene under pressure. This fluoride-free procedure for the cross-coupling reaction between vinylsiloxanes and aryl bromides or chlorides needs a lower Pd loading than other described methods. Ligand-less Pd(OAc)<sub>2</sub> or 4-hydroxyacetophenone oxime-derived palladacycle **1** can be used as precatalyst, the later giving slightly better results. These processes can be performed at 120 °C either under conventional heating in a pressure tube or under microwave irradiation in only 10 to 25 min. In general, aryl chlorides needed higher Pd loadings than aryl bromides and only activated aryl chlorides gave satisfactory results. In the case of styryltriethoxysilane the process took place stereospecifically with 1-naphthyl bromide and (*E*)-styryl bromide to give the corresponding stilbene and butadiene with retention of the configuration of the C=C bonds. This vinylation protocol can be considered the most simple and efficient method described to perform these type of cross-coupling reaction. Further studies about the scope of this procedure are underway.

## Experimental Section

### General Remarks

The reagents and solvents were obtained from commercial sources and were generally used without further purification. Flash chromatography was performed on silica gel 60 (0.040–0.063 mm, Merck). Thin layer chromatography was performed on Polygram<sup>®</sup> SIL G/UV<sub>254</sub> plates. Melting points were determined on a Reichert Thermovar apparatus. Gas chromatographic analyses were performed on an HP-6890 instrument equipped with a WCOT HP-1 fused silica capillary column. IR data were collected on a Nicolet Impact-

Table 3. Hiyama reaction of 1-styryltriethoxysilane with bromides.<sup>[a]</sup>

Entry	RBr	Catalyst (mol % Pd)	<i>t</i>	Product	Yield [%] <sup>[b]</sup>
1		Pd(OAc) <sub>2</sub> (1)	20 min		81 <sup>[c]</sup>
2		<b>1</b> (1)	20 min		89 (83) <sup>[c]</sup>
3		Pd(OAc) <sub>2</sub> (0.5)	20 min		84 <sup>[d]</sup>
4		<b>1</b> (0.5)	20 min		93 (81) <sup>[d]</sup>

<sup>[a]</sup> Reaction conditions: aryl or vinyl halide (1 equiv.), (*Z/E*)-styryltriethoxysilane (2 equivs., 1:2 ratio), catalyst (see column), NaOH (2.5 equivs.), TBAB (1 equiv.), H<sub>2</sub>O (2 mL/1 mmol), at 120 °C under microwave conditions (40–45 Watt).

<sup>[b]</sup> Determined by <sup>1</sup>H NMR by using diphenylmethane as internal standard. In parenthesis, yield after flash chromatography.

<sup>[c]</sup> 1/1.9: *Z/E* ratio.

<sup>[d]</sup> 1/2: *Z/E* ratio.

400D-FT spectrophotometer in  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectra were recorded on a Bruker AC-300 (300 MHz) and, when specified, on a Bruker Advance-DRX-500 (500 MHz). Chemical shifts are reported in ppm using tetramethylsilane (TMS, 0.00 ppm) as internal standard.  $^{13}\text{C}$  NMR spectra were recorded at 75 MHz with  $\text{CDCl}_3$  as the internal reference. EIMS were measured on a Mass Selective Detector G2579 A from Agilent Technologies 5973N in  $m/z$  (rel. intensity in % of base peak). The catalysts were weighed up in an electronic microscale (Sartorius, XM1000P) with a precision of 1  $\mu\text{g}$ . Microwave reactions were performed with a CEM Discover Synthesis Unit in glass vessels (10 mL) sealed with a septum under magnetic stirring. Reaction vessels and stirring bars were washed first with 6M NaOH solution and then with concentrated nitric acid.

### Typical Experimental Procedure for Hiyama Coupling of Aromatic and Vinyl Bromides and Chlorides with Vinylsiloxanes under Microwave Irradiation

A glass tube (10 mL) was charged with the organic halide (0.5 mmol), vinylsiloxane (1 mmol), TBAB (0.5 to 1 mmol, see Tables 1 and 2), Pd salt or palladacycle (see Tables 1 and 2), and  $\text{H}_2\text{O}$  (1 mL). Then an aqueous 50% NaOH solution (0.05 mL, 1.25 mmol) was added dropwise and the tube was sealed with a septum and heated at  $120^\circ\text{C}$  (40–45 W, 4–5 bar) during the time indicated in Tables 1–3 with air stream cooling. After the reaction was stopped, the reaction mixture was cooled to room temperature and extracted with ether ( $5 \times 10$  mL). Then the organic phases were washed successively with 2M NaOH ( $2 \times 20$  mL), 2M HCl (20 mL), and brine ( $2 \times 20$  mL). The ethereal layer was dried ( $\text{MgSO}_4$ ) and evaporated (15 mm Hg). The subsequent residue was purified by flash chromatography on silica gel to give pure alkenes.

### Typical Experimental Procedure for Hiyama Coupling of Aromatic and Vinyl Bromides with Vinylsiloxanes under Thermal Conditions

A mixture of organic halide (1 mmol), vinylsiloxane (2 mmol), TBAB (0.5 to 1 mmol, see Tables 1 and 2) and  $\text{Pd}(\text{OAc})_2$  or palladacycle **1** (see Tables 1 and 2) and  $\text{H}_2\text{O}$  (2 mL) in a 15 mL Ace tube was stirred during 5 min. Then an aqueous 50% NaOH solution (0.1 mL, 2.5 mmol) was added dropwise and the reaction mixture was heated at  $120^\circ\text{C}$  during the time indicated in Table 2. The reaction mixture was cooled to room temperature followed by extractive work up as above.

**4'-Methoxystyrene**:<sup>[21]</sup> Oil;  $R_f=0.63$  (hexane/EtOAc, 10:1); IR (film):  $\nu=3072$  (C=CH), 2929 (CH), 2829 (OMe), 1689, 1601 (C=C)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS):  $\delta=7.35$  (d, 2H,  $J=8.6$  Hz, ArH), 6.86 (d, 2H,  $J=8.6$  Hz, ArH), 6.69 (dd, 1H,  $J=17.6$  Hz and 10.9 Hz, ArC-CH), 5.62 (dd, 1H,  $J=17.6$  and 0.8 Hz, CH- $H_{trans}$ ), 5.13 (dd, 1H,  $J=10.9$  and 0.8 Hz, CH- $H_{cis}$ ), 3.79 (s, 3H,  $\text{CH}_3\text{O}$ );  $^{13}\text{C}$  NMR:  $\delta=159.5$  (ArC-O), 136.4 (CH), 130.6 (ArC), 127.5 (ArCH), 114.0 (ArCH), 111.6 ( $\text{CH}_2$ ), 55.4 ( $\text{CH}_3\text{O}$ ); MS (EI):  $m/z$  (% rel. int.) = 135 ( $\text{M}^+ + 1$ , 9), 134 (100) [ $\text{M}^+$ ], 119 (61), 91 (65).

**4'-Vinylacetophenone**:<sup>[22]</sup> Oil;  $R_f=0.45$  (hexane/EtOAc, 10:1); IR (film):  $\nu=3029$  (C=CH), 2926 (CH), 1683 (C=O),

1611 (C=C), 1265 (CO)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS):  $\delta=7.93$  (d, 2H,  $J=8.4$  Hz, ArH), 7.49 (d, 2H,  $J=8.2$  Hz, ArH), 6.76 (dd, 1H,  $J=17.6$  Hz and 10.9 Hz, ArC-CH), 5.90 (d, 1H,  $J=17.6$  Hz, CH- $H_{trans}$ ), 5.41 (d, 1H,  $J=10.9$  Hz, CH- $H_{cis}$ ), 2.59 [s, 3H,  $\text{CH}_3(\text{C}=\text{O})$ ];  $^{13}\text{C}$  NMR:  $\delta=197.7$  (C=O), 142.2 (ArC), 136.4 (ArC), 136.0 (CH), 128.8, 128.6 (ArCH), 126.4 (ArCH), 116.8 ( $\text{CH}_2$ ), 26.7 ( $\text{CH}_3$ ); MS (EI):  $m/z$  (% rel. int.) = 146 (42) [ $\text{M}^+$ ], 131 (100), 103 (64).

**(E)-1-Phenyl-1,3-butadiene**:<sup>[21]</sup> Oil;  $R_f=0.64$  (pentane/diethyl ether, 10:1); IR (film):  $\nu=3033$  (C=CH), 1678 (C=C), 1601 (CH=CH $_2$ ), 1421 (C-C)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS):  $\delta=7.4$ –7.21 (m, 5H, ArH), 7.38 (d, 1H,  $J=16.8$  Hz, Ar-CH-), 6.83 (dd, 1H,  $J=16.05$  and 10.7 Hz, CH), 6.58 (ddd, 1H,  $J=16.8$ , 10.3 and 10.1 Hz, CH), 5.35 (d, 1H,  $J=16.5$  Hz, CH- $H_{trans}$ ), 5.18 (d, 1H,  $J=10.3$  Hz, CH- $H_{cis}$ );  $^{13}\text{C}$  NMR:  $\delta=137.3$  (CH); 133.0 (ArC), 129.7 (CH), 128.7 (ArCH), 127.7 (ArCH), 126.5 (ArCH), 117.7 ( $\text{CH}_2$ ); MS (EI):  $m/z$  (% rel. int.) = 130 (66) [ $\text{M}^+$ ], 129 (100), 115 (36).

**1-Vinylnaphthalene**:<sup>[21]</sup> Yellow solid; mp  $64$ – $66^\circ\text{C}$ ;  $R_f=0.52$  (hexane); IR (KBr):  $\nu=3054$  (C=CH), 1634, 1596 (C=C)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS):  $\delta=8.11$  (d, 1H,  $J=8.7$  Hz, ArH), 7.84 (d, 1H,  $J=7.17$  Hz, ArH), 7.81 (d, 1H,  $J=8.3$  Hz, ArH), 7.62 (d, 1H, 6.9 Hz, 1H, ArH), 7.52–7.41 (m, 4H, ArH), 5.81 (d, 1H,  $J=17.3$  Hz, CH- $H_{trans}$ ), 5.48 (d, 1H,  $J=10.9$  Hz, CH- $H_{cis}$ );  $^{13}\text{C}$  NMR:  $\delta=135.7$  (ArC), 134.5 (CH), 133.7 (ArC), 131.2 (ArC), 128.6 (ArCH), 128.2 (ArCH), 126.1 (ArCH), 125.8 (ArCH), 123.8 (ArCH), 123.7 (ArCH), 117.2 ( $\text{CH}_2$ ); MS (EI):  $m/z$  (% rel. int.) = 154 (76) [ $\text{M}^+$ ], 153 (100), 152 (56), 76 (59).

**2-Vinyl-6-methoxynaphthalene**:<sup>[21]</sup> White solid; mp  $91$ – $93^\circ\text{C}$ ;  $R_f=0.60$  (hexane/diethyl ether, 10:1); IR (KBr):  $\nu=3054$  (C=CH), 2838 (OMe), 1633, 1597 (C=C), 1482 (C-C), 1258 (C-O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS):  $\delta=7.72$ –7.68 (m, 3H, ArH), 7.62 (d, 1H,  $J=8.5$  Hz, ArH), 7.14 (d, 2H,  $J=8.13$  Hz, ArH), 6.89 (dd, 1H,  $J=17.6$  and 10.9 Hz, CH), 5.85 (d, 1H,  $J=17.6$  Hz, CH- $H_{trans}$ ), 5.29 (d, 1H,  $J=10.9$  Hz, CH- $H_{cis}$ );  $^{13}\text{C}$  NMR:  $\delta=157.7$  (ArC), 136.9 (CH), 134.2 (ArC), 132.9 (ArC), 129.5 (ArCH), 128.8 (ArC), 126.9 (ArCH), 126.1 (ArCH), 123.7 (ArCH), 118.9 (ArCH), 113.0 ( $\text{CH}_2$ ), 105.7 (ArCH), 55.2 (OCH $_3$ ); MS (EI):  $m/z$  (% rel. int.) = 184 (100) [ $\text{M}^+$ ], 169 (17), 141 (50), 115 (19).

**4'-Vinylbenzophenone**:<sup>[23]</sup> White solid; mp  $50$ – $52^\circ\text{C}$ ;  $R_f=0.45$  (hexane/EtOAc, 10:1); IR (KBr):  $\nu=3090$  (C=CH), 1655 (C=O), 1612 (C=C), 1265 (C-O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS):  $\delta=7.77$  (dd, 4H,  $J=8.3$  and 6.39 Hz, ArH), 7.59–7.43 (m, 5H, ArH), 6.81 (dd, 1H, 17.4 and 10.7 Hz, CH), 5.91 (d, 1H,  $J=17.4$  Hz, CH- $H_{trans}$ ), 5.41 (d, 1H,  $J=10.7$  Hz, CH- $H_{cis}$ );  $^{13}\text{C}$  NMR:  $\delta=196.2$  (C=O), 141.5 (ArC), 138.9 (ArC), 137.7 (ArC), 137.2 (CH), 136.7 (ArCH), 136.0 (ArCH), 132.7 (ArCH), 130.1 (ArCH), 126.1 (ArCH), 116.6 ( $\text{CH}_2$ ); MS (EI):  $m/z$  (% rel. int.) = 209 (13) [ $\text{M}^+ + 1$ ], 208 (80) [ $\text{M}^+$ ], 131 (100), 105 (29), 77 (43).

**(E,E)-1,4-Diphenyl-1,3-butadiene**:<sup>[21]</sup> White solid; mp  $152$ – $153^\circ\text{C}$ ;  $R_f=0.25$  (pentane); IR (KBr):  $\nu=3011$  (C=CH), 1604, 1568 (C=C), 1446 (C-C)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta=7.45$  (d, 4H,  $J=8.3$  Hz, ArH), 7.35–7.31 (m, 4H, ArH), 7.23–7.21 (m, 2H, ArH), 6.99 (dd, 2H,  $J=10.4$  and 14.6 Hz, CH), 6.71 (dd, 2H,  $J=14.6$  and 9.1 Hz, CH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta=137.5$  (ArC), 132.9 (CH), 129.3, 128.7 (ArCH), 127.7 (CH), 126.5 (ArCH); MS (EI):  $m/z$  (% rel. int.) = 206 (100) [ $\text{M}^+$ ], 205 (40), 191 (36), 128 (31), 91 (32).

**(E,Z)-1,4-Diphenyl-1,3-butadiene**:<sup>[24]</sup> Colorless oil;  $R_f$  = 0.35 (pentane); IR (KBr):  $\nu$  = 3062, 3026 (C=CH), 1597, 1575 (C=C), 1489, 1446 (C-C)  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 7.40–7.36 (m, 6H, ArH), 7.33–7.20 (m, 5H, ArH and CH), 6.73 (d, 1H,  $J$  = 15.6 Hz,  $\text{CH}_{\text{trans}}$ ), 6.54 (d, 1H,  $J$  = 11.3 Hz,  $\text{CH}_{\text{cis}}$ ), 6.45 (t, 1H,  $J$  = 11.2 Hz, CH);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 137.7, 137.4 (ArC), 134.9 (CH), 130.5, 130.4, 129.2 (ArCH), 128.7 (CH), 128.5, 127.8, 127.1, 126.7 (ArCH), 125.3 (CH); MS (EI):  $m/z$  (% rel. int.) = 206 (100) [ $\text{M}^+$ ], 205 (44), 191 (28), 128 (42), 91 (39).

**(E)-1-Styrylnaphthalene**:<sup>[21]</sup> Colorless oil;  $R_f$  = 0.50 (hexane/EtOAc, 15:1); IR (film):  $\nu$  = 3062, 3026 (C=CH), 1604, 1583 (C=C), 1446 (C-C)  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 8.21 (d, 1H,  $J$  = 8.6 Hz, ArH), 7.91–7.86 (m, 2H, ArH), 7.81 (d, 1H,  $J$  = 8.3 Hz, ArH), 7.76 (d, 1H,  $J$  = 7.1 Hz, ArH), 7.62 (d, 2H,  $J$  = 8.1 Hz, ArH), 7.56–7.47 (m, 3H, ArH), 7.42 (dd, 2H,  $J$  = 7.32 and 7.8 Hz, ArH), 7.32 (dd, 1H, 7.1 and 7.6 Hz, ArH), 7.17 (d, 1H,  $J$  = 15.9 Hz,  $\text{CH}_{\text{trans}}$ );  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 137.7 (ArC), 131.9 (CH), 131.5 (ArC), 128.9, 128.7, 128.1, 127.9, 126.8, 126.2 (ArCH), 125.9 ( $\text{CH}_2$ ), 125.8, 123.9, 123.7 (ArCH); MS (EI):  $m/z$  (% rel. int.) = 230 (96) [ $\text{M}^+$ ], 229 (100), 228 (35), 215 (22), 152 (23).

**(Z)-1-Styrylnaphthalene**:<sup>[25]</sup> Colorless oil;  $R_f$  = 0.57 (hexane/EtOAc, 15:1); IR (film):  $\nu$  = 3054 (C=CH), 1604, 1583 (C=C), 1489 (C-C)  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 8.09 (d, 1H,  $J$  = 7.8 Hz, ArH), 7.88–7.85 (m, 1H, ArH), 7.78 (d, 1H,  $J$  = 7.0 Hz, ArH), 7.50–7.46 (m, 2H, ArH), 7.35–7.33 (m, 2H, ArH), 7.47–7.46 (m, 5H, ArH), 6.85 (d, 1H,  $J$  = 12.1 Hz,  $\text{CH}_{\text{cis}}$ );  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 136.8, 135.3, 133.8, 132.1 (ArC), 129.1, 128.6, 128.5, 128.1, 127.6, 127.2, 126.6, 125.7, 125.0 (ArCH), 126.1, 126.0 (CH); MS (EI):  $m/z$  (% rel. int.) = 230 (91) [ $\text{M}^+$ ], 229 (100), 228 (35), 215 (23), 152 (23).

## Acknowledgements

We thank DGES of the Spanish Ministerio de Educación y Ciencia (MEC) (grant: CTQ2004-00808/BQU), the Generalitat Valenciana (grants: GRUPOS05/11) and the University of Alicante for financial support. E. A. thanks MEC for a predoctoral fellowship.

## References

- [1] For recent reviews, see: a) *Handbook of Organopalladium Chemistry for Organic Synthesis*, (Eds.: E.-I. Negishi, A. de Meijere), Wiley, New York, **2002**; b) *Cross-Coupling Reactions*, (Ed.: N. Miyaura), Springer, Berlin, **2000**; c) *Metal-Catalyzed Cross-coupling Reactions*, 2<sup>nd</sup> edn., (Eds.: F. Diederich, A. de Meijere), Wiley-VCH, Weinheim, **2004**; d) *Transition Metals for Organic Synthesis; Building Block and Fine Chemicals*, 2<sup>nd</sup> edn., (Eds.: M. Beller, C. Bolm), Wiley-VCH, Weinheim, **2004**.
- [2] a) T. Hiyama, in: *Metal-Catalyzed Cross-coupling Reactions*, (Eds.: F. Diederich, P.J. Stang), Wiley-VCH: New York, **1998**, pp. 421–453; b) S. E. Denmark, M. H. Ober, *Aldrichimica Acta* **2003**, *36*, 75–85; c) C. J. Handy, A. S. Manoso, W. T. McElroy, W. M. Seganish, P. DeShong, *Tetrahedron* **2005**, *61*, 12201–12225.
- [3] C. Chuit, R. J. P. Corriu, C. Reye, in: *Chemistry of Hypervalent Compounds*, (Ed.: K.-y. Akiba), Wiley-VCH: New York, **1998**, pp. 81–146.
- [4] a) C. Wolf, R. Lerebours, *Org. Lett.* **2004**, *6*, 1147–1150; b) C. Wolf, R. Lerebours, *Synthesis* **2005**, 2287–2292.
- [5] E. Alacid, C. Nájera, *Adv. Synth. Catal.* **2006**, *348*, 945–952.
- [6] S. Darses, J. P. Genêt, *Eur. J. Org. Chem.* **2003**, 4313–4327.
- [7] a) Y. Hatanaka, T. Hiyama, *J. Org. Chem.* **1988**, *53*, 918–920; b) Y. Hatanaka, K. Goda, T. Hiyama, *J. Organomet. Chem.* **1994**, *465*, 97–100.
- [8] a) S. E. Denmark, J. Y. Choi, *J. Am. Chem. Soc.* **1999**, *121*, 5821–5822; b) S. E. Denmark, D. Wehrli, *Org. Lett.* **2000**, *2*, 565–568; c) S. E. Denmark, D. Wehrli, J. Y. Choi, *Org. Lett.* **2000**, *2*, 2491–2494; d) S. E. Denmark, S. A. Tymonko, *J. Am. Chem. Soc.* **2005**, *127*, 8004–8005; e) S. E. Denmark, W. Pan, *Org. Lett.* **2001**, *3*, 61–64; f) S. E. Denmark, S.-M. Yang, *Org. Lett.* **2001**, *3*, 1749–1752; g) S. E. Denmark, S.-M. Yang, *J. Am. Chem. Soc.* **2002**, *124*, 2102–2103; h) S. E. Denmark, J. D. Baird, *Chem. Eur. J.* **2006**, *12*, 4954–4963.
- [9] a) K. Itami, T. Nokami, J. Yoshida, *J. Am. Chem. Soc.* **2001**, *123*, 5600–5601; b) K. Itami, T. Nokami, Y. Ishimura, K. Mitsudo, T. Kamei, J. Yoshida, *J. Am. Chem. Soc.* **2001**, *123*, 11577–11585.
- [10] a) S. E. Denmark, Z. Wang, *J. Organomet. Chem.* **2001**, *624*, 372–375; b) A. Mori, M. Suguro, *Synlett* **2001**, 845–847.
- [11] H. M. Lee, S. P. Nolan, *Org. Lett.* **2000**, *2*, 2053–2055.
- [12] M. L. Clarke, *Adv. Synth. Catal.* **2005**, *347*, 303–307.
- [13] An excess of vinylsiloxane was used due to partial polymerization during the reaction.
- [14] Microwave reactions were performed with a CEM Discover Synthesis Unit (CEM Corp., Matthews, NC) with a continuous focused microwave power delivery system in glass vessels (10 mL) sealed with a septum under magnetic stirring. The temperature of the reaction mixture inside the vessel was monitored using a calibrated infrared temperature control under the reaction vessel.
- [15] For an account, see: E. Alacid, D. A. Alonso, L. Botella, C. Nájera, M. C. Pacheco, *Chem. Rec.* **2006**, *6*, 124–132.
- [16] Carbapalladacycles decompose under different reaction conditions to give Pd colloids, see, for instance: a) C. S. Consorti, F. R. Flores, J. Dupont, *J. Am. Chem. Soc.* **2005**, *127*, 12054–12065; b) N. T. S. Phan, M. Van Der Sluys, C. W. Jones, *Adv. Synth. Catal.* **2006**, *348*, 609–679.
- [17] It is known that TBAB stabilizes colloidal palladium nanoparticles acting as catalysts in cross-coupling reactions: R. T. Reetz, E. Westermann, *Angew. Chem. Int. Ed.* **2000**, *39*, 165–168.
- [18] This compound has been also prepared by Heck reaction between 6-methoxy-2-bromonaphthalene and ethylene at 140 °C and 20 bar: M. T. Reetz, G. Lohmer, R. Schwickardi, *Angew. Chem. Int. Ed.* **1998**, *37*, 481–483.
- [19] J. Zhang, C. G. Xia, *J. Mol. Catal. A* **2003**, *206*, 59–65, and references cited therein.
- [20] A. Mori, E. Takahisha, Y. Yamamura, T. Kato, A. P. Mudalige, H. Kajiro, K. Hirabayashi, Y. Nishihara, T. Hiyama, *Organometallics* **2004**, *23*, 1755–1765.

- [21] Commercially available.
- [22] D. R. McKean, G. Parrinello, A. F. Renaldo, J. K. Stille, *J. Org. Chem.* **1987**, *52*, 422–424.
- [23] S. Itsuno, K. Ito, *J. Org. Chem.* **1990**, *55*, 3950–3952.
- [24] L.-Y. Yang, *J. Am. Chem. Soc.* **2005**, *127*, 2404–2405.
- [25] J. L. Everett, G. A. R. Kon, *J. Chem. Soc.*, **1948**, 1601–1603.
-