Palladium–Tetraphosphine Complex Catalysed Heck Reaction of Vinyl Bromides with Alkenes: A Powerful Access to Conjugated Dienes

Mhamed Lemhadri,[a] Ahmed Battace,[a] Florian Berthiol,[a] Touriya Zair,[b] Henri Doucet,*[c] Maurice Santelli*[a]

[a] Laboratoire de Synthèse Organique, Faculté des Sciences de Saint Jérôme, UMR 6180 CNRS, Université d'Aix-Marseille III, Avenue Escadrille Normandie-Niemen, 13397 Marseille Cedex 20, France
Fax +33(4)91983865; E-mail: m.santelli@univ-cezanne.fr

[b] Laboratoire de Chimie Organique Appliquée, Faculté des Sciences, Université Moulay Ismail, BP 4010, Beni M'mhammed, 50000 Meknes, Morocco

[c] Institut Sciences Chimiques de Rennes, UMR 6226 CNRS-, Université de Rennes 'Catalyse et Organometalliques', Campus de Beaulieu, 35042 Rennes, France
Fax +33(2)23236939; E-mail: henri.doucet@univ-rennes1.fr

Received 17 December 2007

Abstract: A wide variety of 1,3-dienes have been prepared by the Heck vinylation of vinyl bromides using $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$/*cis*,*cis*,*cis*-1,2,3,4-tetrakis[(diphenylphosphino)methyl]cyclopentane (Tedicyp) as the catalyst precursor. Both α- and β-substituted vinyl bromides undergo the Heck reaction with functionalised alkenes such as acrylates, enones, styrenes or a vinyl sulfone, and also with nonfunctionalised alkenes such as dec-1-ene, leading stereoselectively, in most cases, to the corresponding *E*- or *E*,*E*-1,3-dienes in good yields. Furthermore, this catalyst can be used at low loading for several reactions.

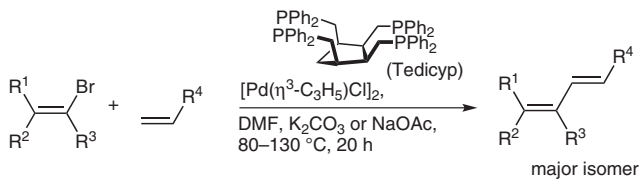
Key words: catalysis, palladium, tetraphosphine, alkenes, vinyl bromides

The palladium-catalysed so-called Heck reaction is one of the most powerful methods for the formation of carbon–carbon bonds; however, most of the results described so far have been for such reactions performed using aryl halides.[1] The use of vinyl halides to prepare 1,3-dienes has attracted less attention.[2,3] In fact, in many cases, 1,3-dienes are actually prepared by cross-coupling of organometallic vinyl derivatives [metal = MgX,[4] ZnX,[5] SnR_3,[6] $B(OR)_2$[7]] with vinyl halides. The major drawback of these reactions is that they require the preparation of the organometallic derivatives and also provide either an organometallic compound or a salt (MX) as byproduct. The direct coupling of vinyl halides with alkenes, especially at low catalyst loadings, would provide a cost-effective and environmentally attractive procedure for the preparation of 1,3-dienes (only HX as byproduct). In general, these couplings have been performed using palladium catalysts associated with the triphenylphosphine ligand. However, the efficiency of palladium associated with triphenylphosphine as the catalyst precursor is generally low in terms of the substrate-to-catalyst ratio. In recent years, several more stable and efficient palladium catalysts have been successfully used for Heck reactions, but most of the results which have been described with these catalysts were obtained for the coupling of aryl halides.[3] Relatively few results have been reported for vinyl halides.[8] One of the most active catalysts for such substrates is a sulfur-containing palladacycle.[8a] With this catalytic system, the coupling of β-bromostyrene with methyl acrylate allowed formation of the corresponding conjugated diene in a high turnover number (TON) of 9000, but in moderate yields (18% and 40%). Tris(dibenzylideneacetone)dipalladium(0) (1 mol%) associated with the electron-rich and sterically hindered phosphine ligand tri-*tert*-butylphosphine efficiently promotes the reaction of 2-bromobut-2-ene with styrene in 89% yield.[8b] Recently, the coupling of a 2-bromoacrylate with a 1,1-disubstituted alkene using palladium(II) acetate (3 mol%) and tri-2-tolylphosphine (6 mol%) as the catalytic system was described. This reaction allowed the stereoselective synthesis of a 1,3-diene, which is a precursor of a marine natural product, in 84% yield.[8c]

Several results have been reported for the coupling of vinyl halides with alkenes, however, the influence of substituents on the vinyl halides on the reaction yields and rates, and also couplings with functionalised alkenes, has not been studied in detail. Thus, an effective and selective method for this reaction, especially using high substrate/catalyst ratios, is still subject to significant improvements.

The coordination of ligands on palladium has an important effect on the rates and selectivities of catalysed reactions. In order to find more efficient palladium catalysts we have prepared the tetradentate phosphine ligand, *cis*,*cis*,*cis*-1,2,3,4-tetrakis[(diphenylphosphino)methyl]cyclopentane[9] (Tedicyp, Scheme 1). The presence of these four phosphines close to the metal centre appears to increase the stability of the catalyst and prevents the formation of 'palladium black'. We have recently reported several results[10] obtained in allylic substitution reactions,[11] Suzuki,[12a] Sonogashira[12b] or Negishi couplings,[13] C–H activation/functionalisation of furans[14a] or thiophenes,[14b] and also for the Heck vinylation,[15] using Tedicyp as ligand. We have also reported some preliminary results for the Heck reaction using vinyl bromides and alkenes.[16] Here, in order to further establish the requirements for a successful Heck reaction using vinyl halide derivatives, we wish to report on the reaction of α- or β-

SYNTHESIS 2008, No. 7, pp 1142–1152
Advanced online publication: 06.03.2008
DOI: 10.1055/s-2008-1032124; Art ID: Z29107SS



Scheme 1

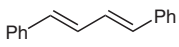
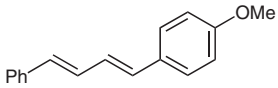
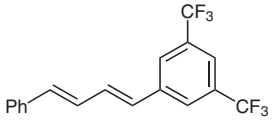
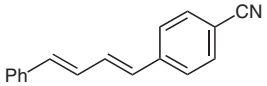
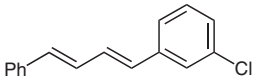
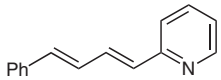
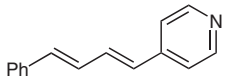
substituted vinyl bromides with a variety of alkenes such as acrylates, enones, a vinyl sulfone, simple alkenes or styrene derivatives using Tedicyp as the ligand at moderate to very low catalyst loading.

First, we investigated the Heck reaction of β-bromostyrene with several alkenes in the presence of the system $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$/Tedicyp (Schemes 1 and 2, Tables 1– 3). For this study, based on previous results,[15] *N*,*N*-dimethylformamide was chosen as the solvent and potassium carbonate or sodium acetate as the base. The reactions were performed at 80–130 °C under argon. Table 1 discloses the results obtained using styrene derivatives as the vinylation reactant. In Table 2, the influence of functional groups on the alkene has been studied. Table 3 describes the Heck reaction of β-bromostyrene with simple alkenes such as dec-1-ene or cyclic alkenes.

In the presence of styrene derivatives and β-bromostyrene, the reactions required 0.01–0.1 mol% catalyst in order to obtain high yields of products (Table 1). For example, the coupling of styrene, 3,5-bis(trifluoromethyl)styrene or 3-chlorostyrene gave the (*E*,*E*)-1,4-diarylbuta-1,3-dienes **1**, **3** and **5** with high regio- and stereoselectivities, in high TONs of 4300, 3700 and 2500, and also in good yields (Table 1, entries 1, 2, 5, 6, 9 and 10). An electron-donating substituent on the aryl ring of styrene such as a *para*-methoxy group slightly decreased the reaction rate (TON 640) (Table 1, entries 3 and 4). This catalyst is also highly active for the coupling of β-bromostyrene with the heteroarylalkenes 2- and 4-vinylpyridine (Table 1, entries 11–14). A higher reaction rate was observed with 4-vinylpyridine (TON 7000) than with 2-vinylpyridine (TON 550). This difference of reactivity could result from a possible interaction between the nitrogen atom of 2-vinylpyridine and the palladium complex, which might have a retarding effect on the reaction rate.

Next, we examined the influence of several functional groups on the alkene, such as an ester, ketone, aldehyde or sulfone group, on the reaction rate for the coupling with β-bromostyrene (Table 2). The reaction with *n*-butyl acrylate can be performed with as little as 0.001% catalyst, leading to butyl (*E*,*E*)-5-phenylpenta-2,4-dienoate (**8**) in good yield and with high stereoselectivity (Table 2, entries 1 and 2). For this vinylation reaction, a very high TON of 66000 was obtained. The first attempts using conjugated enones, such as but-3-en-2-one or pent-1-en-3-one, as reactants were unsuccessful (Table 2, entries 3 and 6). This is probably due to a fast polymerisation of these enones under the reaction conditions. Commercially available alk-1-en-3-ones are often stabilised with 0.5%

Table 1 Palladium–Tedicyp Complex Catalysed Heck Reaction of β-Bromostyrene with Styrene Derivatives[a] (Scheme 1)

Entry	Alkene	Ratio substrate/catalyst	Product[b]	Yield[c] (%)
1	styrene	1000	**1** 	(95)
2	styrene	10000		43
3	4-methoxystyrene	250	**2** 	100 (88)
4	4-methoxystyrene	1000		64
5	3,5-bis(trifluoromethyl)styrene	1000	**3** 	100 (90)
6	3,5-bis(trifluoromethyl)styrene	10000		25
7	4-cyanostyrene	250	**4** 	100 (82)
8	4-cyanostyrene	1000		65
9	3-chlorostyrene	1000	**5** 	100 (87)
10	3-chlorostyrene	10000		37
11	2-vinylpyridine	250	**6** 	100 (86)
12	2-vinylpyridine	1000		55
13	4-vinylpyridine	1000	**7** 	100 (91)
14	4-vinylpyridine	10000		70

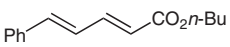
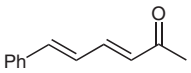
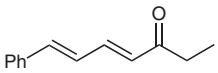
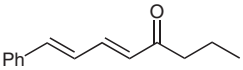
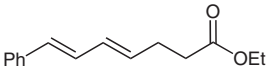
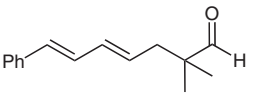
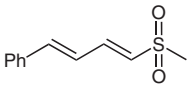
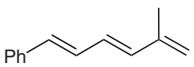
[a] Reaction conditions: β-bromostyrene (1 equiv), alkene (2 equiv), K_2CO_3 (2 equiv), DMF, 130 °C, 20 h.
[b] *E*,*E*-Isomers were obtained selectively (>95%).
[c] GC or NMR yields. Isolated yields are in parentheses.

hydroquinone. We had previously observed that, for Heck reactions with aryl halides, the addition of 8% hydroquinone to the reaction mixture led to the arylation of such enones to give the corresponding (*E*)-1-arylalk-1-en-3-ones in high yields and TONs.[15e] The addition of hydroquinone probably reduces the rate of polymerisation or decomposition of these enones. Using this additive, in the presence of β-bromostyrene, the expected (*E*,*E*)-1-phenylalka-1,3-dien-5-ones **9**–**11** were obtained with high stereoselectivities and in high yields using as little as 0.1–1 mol% catalyst (Table 2, entries 4, 5, and 7–10). Ethyl pent-4-enoate and 2,2-dimethylpent-4-enal also gave the expected *E*,*E*-1,3-dienes **12** and **13** in moderate to good yields (Table 2, entries 11–14). With these substrates, the formation of traces of side products arising from the migration of the double bond was observed. Methyl vinyl sulfone was also found to be a suitable reactant for the preparation of the conjugated diene (Table 2, entries 15 and 16); the *E*,*E*-1,3-diene **14** was obtained in 81% yield employing 1 mol% catalyst. On the other hand, when 2-methylbut-3-en-2-ol was used, an unexpected reaction was observed. With this substrate a dehydration occurred to give the conjugated triene **15** as the major product, but in moderate yield (Table 2, entries 17 and 18).

Then, we performed some reactions using simple linear, branched or cyclic alkenes (Schemes 1 and 2, Table 3). The vinylation of β-bromostyrene performed in the presence of dec-1-ene led to the *E*,*E*-1,3-diene **16** in 44% selectivity (Table 3, entries 1 and 2). In the course of this reaction, the formation of several other isomers occurs due to partial migration of the double bond of dec-1-ene. On the other hand, the reaction of β-bromostyrene with the sterically congested 3,3-dimethylbut-1-ene led to the product **17** with a very high regio- and stereoselectivity in favour of the *E*,*E*-1,3-diene and in good yield (Table 3, entry 3).

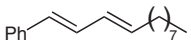
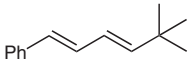
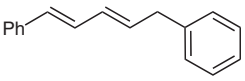
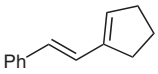
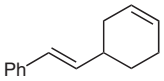
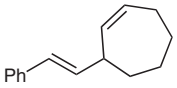
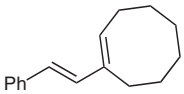
Several reactions were also performed using cyclic alkenes, namely, cyclopentene, cyclohexene, cycloheptene and cyclooctene, as the coupling partners (Scheme 2, Table 3, entries 5–9). Cyclohexene and cycloheptene led to the *E*-1,5- and *E*-1,4-dienes **20** and **21** with 94 and 80% selectivity, respectively. With these two substrates, partial migration of the carbon–carbon double bond of the cycloalkene occurs. Such migration has been previously reported.[2h] A suitable conformation of the palladium intermediate is necessary for the β-elimination step of the catalytic cycle. These suitable conformations can be favoured by partial migration of the double bond of the cycloalkene. On the other hand, cyclopentene and cy-

Table 2 Palladium–Tedicyp Complex Catalysed Heck Reaction of β-Bromostyrene with Functionalised Alkenes[a] (Scheme 1)

Entry	Alkene	Ratio substrate/catalyst	Product[b]	Yield[c] (%)
1	*n*-butyl acrylate	10000	**8** 	100 (95)[d]
2	*n*-butyl acrylate	100000		(66)[d]
3	but-3-en-2-one	250		0
4	but-3-en-2-one	250	**9** 	100 (75)[e]
5	but-3-en-2-one	1000		49[e]
6	pent-1-en-3-one	250		0
7	pent-1-en-3-one	250	**10** 	100 (77)[e]
8	pent-1-en-3-one	1000		88[e]
9	hex-1-en-3-one	100	**11** 	100 (79)[e]
10	hex-1-en-3-one	250		52[e]
11	ethyl pent-4-enoate	250	**12** 	100 (66)
12	ethyl pent-4-enoate	1000		67
13	2,2-dimethylpent-4-enal	100	**13** 	100 (64)
14	2,2-dimethylpent-4-enal	250		47
15	methyl vinyl sulfone	100	**14** 	100 (81)
16	methyl vinyl sulfone	250		33
17	2-methylbut-3-en-2-ol	250	**15** 	100 (48)[f]
18	2-methylbut-3-en-2-ol	1000		63[f]

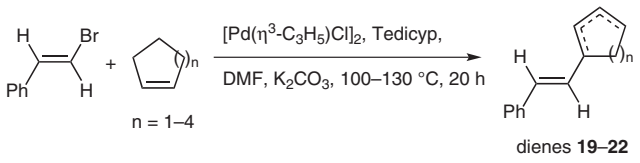
[a] Reaction conditions: β-bromostyrene (1 equiv), alkene (2 equiv), NaOAc (2 equiv), DMF, 110 °C, 20 h.
[b] *E*,*E*-Isomers were obtained selectively (>95%).
[c] GC or NMR yields. Isolated yields are in parentheses.
[d] K_2CO_3 (2 equiv) was used as base, at 130 °C.
[e] Hydroquinone (8%) was added to the reaction mixture.
[f] Reaction temperature: 80 °C.

Table 3 Palladium–Tedicyp Complex Catalysed Heck Reaction of β-Bromostyrene with Linear, Branched or Cyclic Alkenes[a] (Schemes 1 and 2)

Entry	Alkene	Ratio substrate/catalyst	Product		Yield[b] (%)
1	dec-1-ene	1000	**16**		(68)[c]
2	dec-1-ene	10000			40[c]
3	3,3-dimethylbut-1-ene	250	**17**		100 (79)[d]
4	allylbenzene	100	**18**		98 (82)[e]
5	cyclopentene	1000	**19**		100 (88)[d,f]
6	cyclohexene	1000	**20**		100 (84)[d,g]
7	cycloheptene	10000	**21**		92 (81)[h,i]
8	cyclooctene	1000	**22**		100 (93)[j]
9	cyclooctene	10000			54[j]

[a] Reaction conditions: β-bromostyrene (1 equiv), alkene (2 equiv), K_2CO_3 (2 equiv), DMF, 130 °C, 20 h.
[b] GC or NMR yields. Isolated yields are in parentheses.
[c] Mixture of isomers; selectivity in favour of (*E*,*E*)-dodeca-1,3-dienylbenzene: 44%.
[d] Reaction performed in an autoclave.
[e] Mixture of isomers; selectivity in favour of (*E*,*E*)-1,5-diphenylpenta-1,3-diene: 55%.
[f] Mixture of isomers; selectivity in favour of (*E*)-1-styrylcyclopentene: 55%.
[g] Mixture of isomers; selectivity in favour of (*E*)-4-styrylcyclohexene: 94%.
[h] Mixture of isomers; selectivity in favour of (*E*)-3-styrylcycloheptene: 80%.
[i] Reaction temperature: 100 °C.
[j] Mixture of isomers; selectivity in favour of (*E*)-1-styrylcyclooctene: 93%.

clooctene led mainly to the expected *E*-1,3-dienes **19** and **22** (Table 3, entries 5, 8 and 9). It should be noted that a very high selectivity of 93% in favour of *E*-1,3-diene **22** was obtained from cyclooctene. Moreover, most of the reactions with these nonfunctionalised linear or cyclic alkenes were performed using as little as 0.1 mol% catalyst.



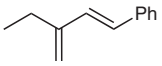
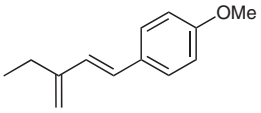
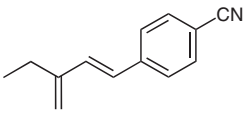
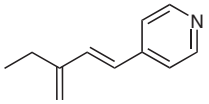
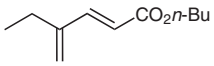
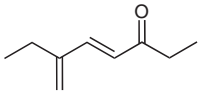
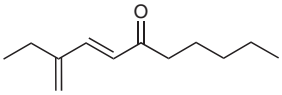
Scheme 2

Next, we studied the formation of 1,3-dienes using four alternative bromoalkenes: 2-bromobut-1-ene, 3-bromobut-3-en-1-ol, 1-bromo-2-methylprop-1-ene and 2-bromo-3-methylbut-2-ene (Tables 4– 7). With the α-substituted vinyl bromide, 2-bromobut-1-ene, several reactions were performed using styrene derivatives (Table 4, entries 1–5). With styrene, 4-methoxystyrene, 4-cyanostyrene or 4-vinylpyridine, the *E*-1,3-dienes **23**–**26** were obtained selectively in moderate to good yields using 0.4 mol% catalyst (Table 4, entries 1–3 and 5). A higher reaction rate and TON of 2500 was obtained with the electron-poor alkene *n*-butyl acrylate (Table 4, entries 6 and 7). Using pent-1-en-3-one or oct-1-en-3-one, the reactions gave a simple access to the expected *E*-1,3-dien-5-ones **28** and **29**. Again, with these unstable substrates, a small amount of hydroquinone had to be added to the reaction mixture in order to reduce the polymerisation side reaction (Table 4, entries 8–11).

The other α-substituted vinyl bromide, 3-bromobut-3-en-1-ol, in the presence of *n*-butyl acrylate, styrene, pent-1-en-3-one or oct-1-en-3-one also selectively gave the expected *E*-1,3-dienes **30**–**33** (Table 5). However, with this vinyl bromide slightly lower yields were generally obtained than for 2-bromobut-1-ene. This is due to the formation of minor side products.

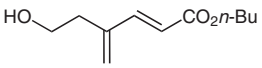
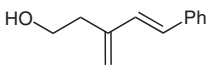
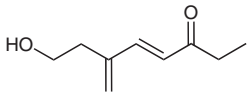
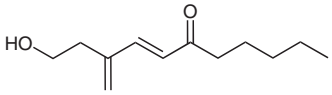
With the β,β-disubstituted vinyl bromide, 1-bromo-2-methylprop-1-ene, results similar to those for 2-bromobut-1-ene were obtained, indicating a minor influence of the position of the alkyl substituents on the bromoalkene on reaction rates (Table 6). Four alkenes were employed: *n*-butyl acrylate, styrene, 4-cyanostyrene and 4-vinylpyridine. In all cases, using only 0.4 mol% catalyst, the *E*-1,3-

Table 4 Palladium–Tedicyp Complex Catalysed Heck Reaction of 2-Bromobut-1-ene[a] (Scheme 1)

Entry	Alkene	Ratio substrate/catalyst	Product[b]		Yield[c] (%)
1	styrene	250	**23**		(58)
2	4-methoxystyrene	250	**24**		(76)
3	4-cyanostyrene	250	**25**		(83)
4	4-cyanostyrene	1000			75
5	4-vinylpyridine	250	**26**		(69)
6	*n*-butyl acrylate	1000	**27**		92 (80)
7	*n*-butyl acrylate	10000			25
8	pent-1-en-3-one	100	**28**		100 (64)[d]
9	pent-1-en-3-one	250			47[d]
10	oct-1-en-3-one	100	**29**		100 (71)[d]
11	oct-1-en-3-one	250			33[d]

[a] Reaction conditions: 2-bromobut-1-ene (1 equiv), alkene (2 equiv), K_2CO_3 (2 equiv), DMF, 80 °C, 20 h.
[b] *E*-Isomers were obtained selectively (>95%).
[c] GC or NMR yields. Isolated yields are in parentheses.
[d] NaOAc (2 equiv) was used as base, and hydroquinone (8%) was added to the reaction mixture.

Table 5 Palladium–Tedicyp Complex Catalysed Heck Reaction of 3-Bromobut-3-en-1-ol[a] (Scheme 1)

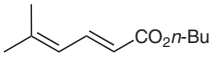
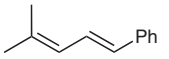
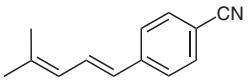
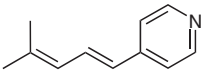
Entry	Alkene	Ratio substrate/catalyst	Product[b]		Yield[c] (%)
1	*n*-butyl acrylate	1000	**30**		(76)
2	styrene	100	**31**		(45)
3	pent-1-en-3-one	1000	**32**		77 (62)[d]
4	oct-1-en-3-one	250	**33**		62 (41)[d]

[a] Reaction conditions: 3-bromobut-3-en-1-ol (1 equiv), alkene (2 equiv), K_2CO_3 (2 equiv), DMF, 130 °C, 20 h.
[b] *E*-Isomers were obtained selectively (>95%).
[c] GC or NMR yields. Isolated yields are in parentheses.
[d] NaOAc (2 equiv) was used as base, at 110 °C, and hydroquinone (8%) was added to the reaction mixture.

dienes **34**–**37** were obtained in good yields and with high regio- and stereoselectivities.

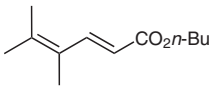
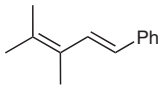
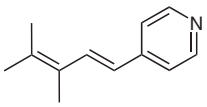
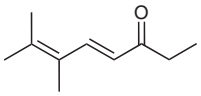
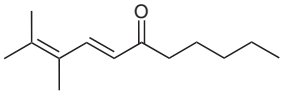
These results were confirmed by the reactivity of the trisubstituted vinyl bromide, 2-bromo-3-methylbut-2-ene (Table 7). An acrylate, styrenes and enones have been successfully employed to give the *E*-1,3-dienes **38**–**42** in high yields and TONs of 200–850. Again, these TONs and yields are very similar to those obtained with 2-bromobut-1-ene or 1-bromo-2-methylprop-1-ene. It should be noted that, in the literature, relatively few examples of coupling reactions of trisubstituted vinyl halides with alkenes have been reported.[17] Therefore, the Heck reaction represents a simple and powerful method for the preparation of such compounds.

Table 6 Palladium–Tedicyp Complex Catalysed Heck Reaction of 1-Bromo-2-methylprop-1-ene[a] (Scheme 1)

Entry	Alkene	Ratio substrate/catalyst	Product[b]	Yield[c] (%)
1	*n*-butyl acrylate	250	**34** 	100 (89)
2	*n*-butyl acrylate	1000		73
3	styrene	250	**35** 	(78)
4	4-cyanostyrene	250	**36** 	(75)
5	4-vinylpyridine	250	**37** 	(85)

[a] Reaction conditions: 1-bromo-2-methylprop-1-ene (1 equiv), alkene (2 equiv), K_2CO_3 (2 equiv), DMF, 100 °C, 20 h.
[b] *E*-Isomers were obtained selectively (>95%).
[c] GC or NMR yields. Isolated yields are in parentheses.

Table 7 Palladium–Tedicyp Complex Catalysed Heck Reaction of 2-Bromo-3-methylbut-2-ene[a] (Scheme 1)

Entry	Alkene	Ratio substrate/catalyst	Product[b]	Yield[c] (%)
1	*n*-butyl acrylate	250	**38** 	82
2	styrene	250	**39** 	88
3	4-vinylpyridine	250	**40** 	92
4	pent-1-en-3-one	1000	**41** 	57[d]
5	oct-1-en-3-one	1000	**42** 	62[d]

[a] Reaction conditions: 2-bromo-3-methylbut-2-ene (1 equiv), alkene (2 equiv), K_2CO_3 (2 equiv), DMF, 100 °C, 20 h.
[b] *E*-Isomers were obtained selectively (>95%).
[c] Isolated yields.
[d] NaOAc (2 equiv) was used as base, at 110 °C, and hydroquinone (8%) was added to the reaction mixture.

In summary, in the presence of the palladium–Tedicyp complex, the Heck reaction of vinyl bromides can be performed with a wide variety of alkenes such as acrylates, enones, styrene derivatives, sulfones or simple linear and cyclic alkenes. Moreover, both α- and β-substituted vinyl bromides can be employed, and relatively similar TONs are obtained indicating a minor steric effect of the vinyl bromide substituents on the reaction rate. A wide range of *E*- and *E*,*E*-1,3-dienes have been selectively prepared in good yields. The high levels of regio- and stereoselection for most of the reactions, as well as the functional group tolerance, are worthy of note. Most of these reactions can be performed with as little as 0.01–1 mol% catalyst. To date, few other catalytic systems have achieved this objective. Due to the high price of palladium, the practical advantage of such low catalyst loadings is increasingly important for industrial processes.

DMF analytical grade (99%) was not distilled before use. K_2CO_3 and NaOAc (99+%) were used. All reactions were run under argon using vacuum lines, in Schlenk tubes with oven-dried glassware. ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on a Bruker Avance DPX-300 spectrometer in $CDCl_3$ solution. Chemical shifts (δ) are reported in ppm relative to $CDCl_3$. Elemental analyses were performed on a Thermo Finnigan EA 1112 apparatus. Flash chromatography was performed on silica gel (230–400 mesh).

Palladium–Tedicyp Complex Catalyst[9]

An oven-dried 40-mL Schlenk tube equipped with a magnetic stirrer bar, under argon atmosphere, was charged with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (4.2 mg, 11.6 μmol) and Tedicyp (20 mg, 23.2 μmol).

Anhyd DMF (2.5 mL) was added, then the solution was stirred at r.t. for 10 min. This catalyst solution was used directly for the catalysed reactions.

Butyl (*E*,*E*)-5-Phenylpenta-2,4-dienoate (8) (Table 2, Entry 2); Typical Procedure

The reaction of β-bromostyrene (1.83 g, 10 mmol), *n*-butyl acrylate (2.56 g, 20 mmol) and K_2CO_3 (2.8 g, 20 mmol) in anhyd DMF (10 mL) in the presence of the palladium–Tedicyp complex (0.0001 mmol) under argon at 130 °C for 20 h afforded the corresponding product **8**, after extraction with CH_2Cl_2 (20 mL), concentration and flash cromatography (pentane–Et_2O, 1:1); yield: 1.52 g (66%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 7.4 Hz, 2 H), 7.45–7.25 (m, 4 H), 6.89 (m, 2 H), 5.98 (d, *J* = 15.3 Hz, 1 H), 4.15 (t, *J* = 6.6 Hz, 2 H), 1.65 (m, 2 H), 1.40 (m, 2 H), 0.94 (t, *J* = 7.4 Hz, 3 H).

(*E*,*E*)-1,4-Diphenylbuta-1,3-diene (1) (Table 1, Entry 1)

The reaction of β-bromostyrene (1.83 g, 10 mmol), styrene (2.08 g, 20 mmol) and K_2CO_3 (2.80 g, 20 mmol) with the palladium complex (0.01 mmol) at 130 °C afforded **1**; yield: 1.96 g (95%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40 (d, *J* = 8.2 Hz, 4 H), 7.30 (t, *J* = 7.6 Hz, 4 H), 7.20 (t, *J* = 7.6 Hz, 2 H), 6.92 (m, 2 H), 6.63 (m, 2 H).

(*E*,*E*)-1-(4-Methoxyphenyl)-4-phenylbuta-1,3-diene (2) (Table 1, Entry 3)

The reaction of β-bromostyrene (1.83 g, 10 mmol), 4-methoxystyrene (2.68 g, 20 mmol) and K_2CO_3 (2.80 g, 20 mmol) with the palladium complex (0.04 mmol) at 130 °C afforded **2**; yield: 2.08 g (88%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50–7.20 (m, 7 H), 7.02–6.75 (m, 4 H), 6.65 (d, *J* = 8.2 Hz, 2 H), 3.85 (s, 3 H).

(*E*,*E*)-1-[3,5-Bis(trifluoromethyl)phenyl]-4-phenylbuta-1,3-diene (3) (Table 1, Entry 5)

The reaction of β-bromostyrene (0.183 g, 1 mmol), 3,5-bis(trifluoromethyl)styrene (0.480 g, 2 mmol) and K_2CO_3 (0.280 g, 2 mmol) with the palladium complex (0.001 mmol) at 130 °C afforded **3**; yield: 0.308 g (90%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.85–7.25 (m, 8 H), 7.09 (dd, *J* = 15.1, 10.6 Hz, 1 H), 6.95 (dd, *J* = 15.1, 10.6 Hz, 1 H), 6.78 (d, *J* = 15.0 Hz, 1 H), 6.67 (d, *J* = 15.0 Hz, 1 H).

(*E*,*E*)-1-(4-Cyanophenyl)-4-phenylbuta-1,3-diene (4) (Table 1, Entry 7)

The reaction of β-bromostyrene (0.183 g, 1 mmol), 4-cyanostyrene (0.260 g, 2 mmol) and K_2CO_3 (0.280 g, 2 mmol) with the palladium complex (0.004 mmol) at 130 °C afforded **4**; yield: 0.190 g (82%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65–7.25 (m, 9 H), 7.07 (dd, *J* = 14.9, 10.6 Hz, 1 H), 6.98 (dd, *J* = 14.8, 10.6 Hz, 1 H), 6.78 (d, *J* = 15.1 Hz, 1 H), 6.67 (d, *J* = 14.8 Hz, 1 H).

(*E*,*E*)-1-(3-Chlorophenyl)-4-phenylbuta-1,3-diene (5) (Table 1, Entry 9)

The reaction of β-bromostyrene (0.183 g, 1 mmol), 3-chlorostyrene (0.277 g, 2 mmol) and K_2CO_3 (0.280 g, 2 mmol) with the palladium complex (0.001 mmol) at 130 °C afforded **5**; yield: 0.209 g (87%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50–7.15 (m, 9 H), 6.97 (m, 2 H), 6.75–6.55 (m, 2 H).

2-[(*E*,*E*)-4-Phenylbuta-1,3-dienyl]pyridine (6) (Table 1, Entry 11)

The reaction of β-bromostyrene (0.183 g, 1 mmol), 2-vinylpyridine (0.210 g, 2 mmol) and K_2CO_3 (0.280 g, 2 mmol) with the palladium complex (0.004 mmol) at 130 °C afforded **6**; yield: 0.178 g (86%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.57 (d, *J* = 4.1 Hz, 1 H), 7.62 (td, *J* = 7.5, 1.7 Hz, 1 H), 7.45 (d, *J* = 8.2 Hz, 2 H), 7.43–7.20 (m, 5 H), 7.10 (dd, *J* = 7.4, 4.9 Hz, 1 H), 6.98 (dd, *J* = 15.5, 10.7 Hz, 1 H), 6.78 (d, *J* = 15.8 Hz, 1 H), 6.72 (d, *J* = 15.5 Hz, 1 H).

4-[(*E*,*E*)-4-Phenylbuta-1,3-dienyl]pyridine (7) (Table 1, Entry 13)

The reaction of β-bromostyrene (0.183 g, 1 mmol), 4-vinylpyridine (0.210 g, 2 mmol) and K_2CO_3 (0.280 g, 2 mmol) with the palladium complex (0.001 mmol) at 130 °C afforded **7**; yield: 0.188 g (91%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.53 (d, *J* = 6.0 Hz, 2 H), 7.45 (d, *J* = 8.2 Hz, 2 H), 7.35 (t, *J* = 7.6 Hz, 2 H), 7.30–7.20 (m, 3 H), 7.12 (dd, *J* = 15.5, 10.2 Hz, 1 H), 6.94 (dd, *J* = 15.5, 10.2 Hz, 1 H), 6.77 (d, *J* = 15.5 Hz, 1 H), 6.57 (d, *J* = 15.5 Hz, 1 H).

Butyl (*E*,*E*)-5-Phenylpenta-2,4-dienoate (8) (Table 2, Entry 2)

See typical procedure.

(*E*,*E*)-6-Phenylhexa-3,5-dien-2-one (9) (Table 2, Entry 4)

The reaction of β-bromostyrene (0.183 g, 1 mmol), but-3-en-2-one (0.140 g, 2 mmol), hydroquinone (0.009 g, 0.08 mmol) and NaOAc (0.164 g, 2 mmol) with the palladium complex (0.004 mmol) at 110 °C afforded **9**; yield: 0.129 g (75%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40 (d, *J* = 7.7 Hz, 2 H), 7.35–7.17 (m, 4 H), 6.90 (d, *J* = 16.5 Hz, 1 H), 6.81 (dd, *J* = 15.7, 9.6 Hz, 1 H), 6.19 (d, *J* = 15.7 Hz, 1 H), 2.25 (s, 3 H).

(*E*,*E*)-7-Phenylhepta-4,6-dien-3-one (10) (Table 2, Entry 7)

The reaction of β-bromostyrene (0.183 g, 1 mmol), pent-1-en-3-one (0.164 g, 2 mmol), hydroquinone (0.009 g, 0.08 mmol) and NaOAc (0.164 g, 2 mmol) with the palladium complex (0.004 mmol) at 110 °C afforded **10**; yield: 0.143 g (77%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 7.7 Hz, 2 H), 7.38–7.27 (m, 4 H), 6.95 (d, *J* = 16.5 Hz, 1 H), 6.86 (dd, *J* = 15.7, 9.6 Hz, 1 H), 6.29 (d, *J* = 15.7 Hz, 1 H), 2.60 (q, *J* = 7.7 Hz, 2 H), 1.14 (t, *J* = 7.7 Hz, 3 H).

(*E*,*E*)-8-Phenylocta-5,7-dien-4-one (11) (Table 2, Entry 9)

The reaction of β-bromostyrene (0.183 g, 1 mmol), hex-1-en-3-one (0.188 g, 2 mmol), hydroquinone (0.009 g, 0.08 mmol) and NaOAc (0.164 g, 2 mmol) with the palladium complex (0.01 mmol) at 110 °C afforded **11**; yield: 0.158 g (79%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 7.7 Hz, 2 H), 7.38–7.25 (m, 4 H), 6.97 (d, *J* = 16.5 Hz, 1 H), 6.88 (dd, *J* = 15.7, 9.6 Hz, 1 H), 6.30 (d, *J* = 15.7 Hz, 1 H), 2.59 (q, *J* = 7.7 Hz, 2 H), 1.70 (m, 2 H), 0.99 (t, *J* = 7.7 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.6, 142.3, 141.0, 136.0, 129.7, 128.9, 128.8, 127.2, 126.8, 42.6, 17.8, 13.8.

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.79; H, 8.01.

Ethyl (*E*,*E*)-7-Phenylhepta-4,6-dienoate (12) (Table 2, Entry 11)

The reaction of β-bromostyrene (0.183 g, 1 mmol), ethyl pent-4-enoate (0.256 g, 2 mmol) and NaOAc (0.164 g, 2 mmol) with the palladium complex (0.004 mmol) at 110 °C afforded **12**; yield: 0.152 g (66%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36 (d, *J* = 7.7 Hz, 2 H), 7.27 (t, *J* = 7.7 Hz, 2 H), 7.19 (t, *J* = 7.7 Hz, 1 H), 6.73 (dd, *J* = 15.8, 10.4 Hz, 1 H), 6.44 (d, *J* = 15.8 Hz, 1 H), 6.24 (dd, *J* = 15.1, 10.4 Hz, 1 H), 5.80 (dt, *J* = 15.1, 6.8 Hz, 1 H), 4.14 (q, *J* = 7.7 Hz, 2 H), 2.45 (m, 4 H), 1.18 (t, *J* = 7.7 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.9, 137.4, 132.9, 131.5, 130.9, 128.9, 128.5, 127.2, 126.2, 60.4, 33.9, 28.1, 14.2.

Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.04; H, 8.03.

(*E*,*E*)-2,2-Dimethyl-7-phenylhepta-4,6-dienal (13) (Table 2, Entry 13)

The reaction of β-bromostyrene (0.183 g, 1 mmol), 2,2-dimethylpent-4-enal (0.224 g, 2 mmol) and NaOAc (0.164 g, 2 mmol) with the palladium complex (0.01 mmol) at 110 °C afforded **13**; yield: 0.137 g (64%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.53 (s, 1 H), 7.40 (d, *J* = 7.7 Hz, 2 H), 7.31 (t, *J* = 7.7 Hz, 2 H), 7.19 (t, *J* = 7.7 Hz, 1 H), 6.75 (dd, *J* = 15.8, 10.4 Hz, 1 H), 6.49 (d, *J* = 15.8 Hz, 1 H), 6.27 (dd, *J* = 15.1, 10.4 Hz, 1 H), 5.74 (dt, *J* = 15.1, 6.8 Hz, 1 H), 2.32 (d, *J* = 7.8 Hz, 2 H), 1.11 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.8, 137.3, 134.1, 131.3, 129.1, 128.7, 128.6, 127.4, 126.2, 46.3, 40.4, 21.3.

Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.31; H, 8.57.

[(*E*,*E*)-4-(Methylsulfonyl)buta-1,3-dienyl]benzene (14) (Table 2, Entry 15)

The reaction of β-bromostyrene (0.183 g, 1 mmol), methyl vinyl sulfone (0.212 g, 2 mmol) and NaOAc (0.164 g, 2 mmol) with the palladium complex (0.01 mmol) at 110 °C afforded **14**; yield: 0.169 g (81%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 7.7 Hz, 2 H), 7.40–7.30 (m, 4 H), 6.99 (d, *J* = 15.3 Hz, 1 H), 6.81 (dd, *J* = 15.5, 10.8 Hz, 1 H), 6.48 (d, *J* = 15.3 Hz, 1 H), 2.98 (s, 3 H).

[(*E*,*E*)-5-Methylhexa-1,3,5-trienyl]benzene (15) (Table 2, Entry 17)

The reaction of β-bromostyrene (0.183 g, 1 mmol), 2-methylbut-3-en-2-ol (0.172 g, 2 mmol) and NaOAc (0.164 g, 2 mmol) with the palladium complex (0.004 mmol) at 80 °C afforded the corresponding dehydrated product **15**; yield: 0.081 g (48%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40 (d, *J* = 7.7 Hz, 2 H), 7.31 (t, *J* = 7.7 Hz, 2 H), 7.19 (t, *J* = 7.7 Hz, 1 H), 6.84 (dd, *J* = 15.5, 9.4 Hz, 1 H), 6.57 (d, *J* = 15.5 Hz, 1 H), 6.45 (d, *J* = 15.3 Hz, 1 H), 5.40 (dd, *J* = 15.3, 9.4 Hz, 1 H), 5.03 (s, 1 H), 5.01 (s, 1 H), 1.91 (s, 3 H).

(*E*,*E*)-Dodeca-1,3-dienylbenzene (16) (Table 3, Entry 1)

The reaction of β-bromostyrene (1.83 g, 10 mmol), dec-1-ene (2.80 g, 20 mmol) and K_2CO_3 (2.80 g, 20 mmol) with the palladium complex (0.01 mmol) at 130 °C afforded a mixture of product **16** with other regio- and stereoisomers in 68% (1.65 g) isolated yield and in 44% selectivity in favour of **16**.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50–7.15 (m, 5 H), 6.75 (dd, *J* = 10.9, 15.7 Hz, 1 H), 6.43 (d, *J* = 15.7 Hz, 1 H), 6.19 (dd, *J* = 10.9, 15.1 Hz, 1 H), 5.82 (dt, *J* = 15.1, 7.0 Hz, 1 H), 1.50–1.15 (m, 12 H), 1.15 (m, 2 H), 0.88 (t, *J* = 6.8 Hz, 3 H).

[(*E*,*E*)-5,5-Dimethylhexa-1,3-dienyl]benzene (17) (Table 3, Entry 3)

The reaction of β-bromostyrene (1.83 g, 10 mmol), 3,3-dimethylbut-1-ene (1.68 g, 20 mmol) and K_2CO_3 (2.80 g, 20 mmol) with the palladium complex (0.04 mmol) at 130 °C in an autoclave afforded **17**; yield: 1.47 g (79%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36 (d, *J* = 8.2 Hz, 2 H), 7.29 (t, *J* = 7.6 Hz, 2 H), 7.18 (t, *J* = 7.6 Hz, 1 H), 6.74 (dd, *J* = 15.5, 10.0 Hz, 1 H), 6.45 (d, *J* = 15.7 Hz, 1 H), 6.14 (dd, *J* = 15.5, 10.0 Hz, 1 H), 5.84 (d, *J* = 15.4 Hz, 1 H), 1.05 (s, 9 H).

(*E*,*E*)-1,5-Diphenylpenta-1,3-diene (18) (Table 3, Entry 4)

The reaction of β-bromostyrene (1.83 g, 10 mmol), allylbenzene (2.36 g, 20 mmol) and K_2CO_3 (2.80 g, 20 mmol) with the palladium complex (0.1 mmol) at 130 °C afforded a mixture of product **18** with other regio- and stereoisomers in 82% (1.81 g) isolated yield and in 55% selectivity in favour of **18**.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30–7.15 (m, 10 H), 6.80 (dd, *J* = 15.0, 10.2 Hz, 1 H), 6.51 (d, *J* = 15.0 Hz, 1 H), 6.29 (dd, *J* = 15.0, 10.2 Hz, 1 H), 6.01 (dt, *J* = 15.0, 7.5 Hz, 1 H), 3.51 (d, *J* = 7.5 Hz, 2 H).

(*E*)-1-Styrylcyclopentene (19) (Table 3, Entry 5)

The reaction of β-bromostyrene (1.83 g, 10 mmol), cyclopentene (1.36 g, 20 mmol) and K_2CO_3 (2.80 g, 20 mmol) with the palladium complex (0.01 mmol) at 130 °C in an autoclave afforded a mixture of product **19** with other regio- and stereoisomers in 88% (1.50 g) isolated yield and in 55% selectivity in favour of **19**.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 8.2 Hz, 2 H), 7.39–7.25 (m, 3 H), 7.04 (d, *J* = 16.0 Hz, 1 H), 6.43 (d, *J* = 16.0 Hz, 1 H), 5.89 (m, 1 H), 2.65–2.40 (m, 4 H), 2.00 (quin, *J* = 7.5 Hz, 2 H).

(*E*)-4-Styrylcyclohexene (20) (Table 3, Entry 6)

The reaction of β-bromostyrene (1.83 g, 10 mmol), cyclohexene (1.50 g, 20 mmol) and K_2CO_3 (2.80 g, 20 mmol) with the palladium complex (0.01 mmol) at 130 °C in an autoclave afforded a mixture of product **20** with other regio- and stereoisomers in 84% (1.55 g) isolated yield and in 94% selectivity in favour of **20**.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40 (d, *J* = 8.2 Hz, 2 H), 7.35–7.15 (m, 3 H), 6.43 (d, *J* = 16.0 Hz, 1 H), 6.26 (dd, *J* = 16.0, 7.1 Hz, 1 H), 5.73 (m, 2 H), 2.55–1.45 (m, 7 H).

(*E*)-3-Styrylcycloheptene (21) (Table 3, Entry 7)

The reaction of β-bromostyrene (1.83 g, 10 mmol), cycloheptene (1.64 g, 20 mmol) and K_2CO_3 (2.80 g, 20 mmol) with the palladium complex (0.001 mmol) at 100 °C afforded a mixture of product **21** with other regio- and stereoisomers in 81% (1.60 g) isolated yield and in 80% selectivity in favour of **21**.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.28 (m, 4 H), 7.22 (t, *J* = 7.5 Hz, 1 H), 6.44 (d, *J* = 15.8 Hz, 1 H), 6.28 (dd, *J* = 15.8, 7.3 Hz, 1 H), 5.83 (dt, *J* = 11.2, 5.1 Hz, 1 H), 5.69 (dd, *J* = 11.2, 4.5 Hz, 1 H), 3.17 (m, 1 H), 2.30–1.40 (m, 8 H).

(*E*)-1-Styrylcyclooctene (22) (Table 3, Entry 8)

The reaction of β-bromostyrene (1.83 g, 10 mmol), cyclooctene (1.78 g, 20 mmol) and K_2CO_3 (2.80 g, 20 mmol) with the palladium complex (0.01 mmol) at 130 °C afforded a mixture of product **22** with other regio- and stereoisomers in 93% (1.97 g) isolated yield and in 93% selectivity in favour of **22**.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40 (d, *J* = 7.7 Hz, 2 H), 7.29 (t, *J* = 7.2 Hz, 2 H), 7.17 (t, *J* = 7.2 Hz, 1 H), 6.74 (d, *J* = 16.2 Hz, 1 H), 6.47 (d, *J* = 16.2 Hz, 1 H), 5.86 (t, *J* = 8.3 Hz, 1 H), 2.51 (m, 2 H), 2.25 (m, 2 H), 1.70–1.40 (m, 8 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.3, 138.0, 133.8, 132.2, 128.5, 126.8, 126.1, 125.1, 30.4, 28.6, 27.4, 26.9, 26.0, 24.3.

Anal. Calcd for $C_{16}H_{20}$: C, 90.51; H, 9.49. Found: C, 91.30; H, 9.37.

[(*E*)-3-Ethylbuta-1,3-dienyl]benzene (23) (Table 4, Entry 1)

The reaction of 2-bromobut-1-ene (0.135 g, 1 mmol), styrene (0.208 g, 2 mmol) and K_2CO_3 (0.280 g, 2 mmol) with the palladium complex (0.004 mmol) at 80 °C afforded **23**; yield: 0.092 g (58%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 7.7 Hz, 2 H), 7.31 (t, *J* = 7.2 Hz, 2 H), 7.19 (t, *J* = 7.2 Hz, 1 H), 6.82 (d, *J* = 16.1 Hz, 1 H), 6.57 (d, *J* = 16.1 Hz, 1 H), 5.12 (s, 1 H), 5.07 (s, 1 H), 2.36 (q, *J* = 7.3 Hz, 2 H), 1.15 (t, *J* = 7.3 Hz, 3 H).

1-[(*E*)-3-Ethylbuta-1,3-dienyl]-4-methoxybenzene (24) (Table 4, Entry 2)
The reaction of 2-bromobut-1-ene (0.135 g, 1 mmol), 4-methoxystyrene (0.268 g, 2 mmol) and K_2CO_3 (0.280 g, 2 mmol) with the palladium complex (0.004 mmol) at 80 °C afforded **24**; yield: 0.143 g (76%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34 (d, *J* = 8.7 Hz, 2 H), 6.86 (d, *J* = 8.7 Hz, 2 H), 6.70 (d, *J* = 16.2 Hz, 1 H), 6.53 (d, *J* = 16.2 Hz, 1 H), 5.07 (s, 1 H), 5.01 (s, 1 H), 3.80 (s, 3 H), 2.34 (q, *J* = 7.3 Hz, 2 H), 1.15 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.1, 147.8, 130.2, 129.1, 127.5, 127.2, 114.1, 114.0, 55.3, 24.7, 12.8.

Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.71; H, 8.68.

4-[(*E*)-3-Ethylbuta-1,3-dienyl]benzonitrile (25) (Table 4, Entry 3)
The reaction of 2-bromobut-1-ene (0.135 g, 1 mmol), 4-cyanostyrene (0.260 g, 2 mmol) and K_2CO_3 (0.280 g, 2 mmol) with the palladium complex (0.004 mmol) at 80 °C afforded **25**; yield: 0.152 g (83%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 8.5 Hz, 2 H), 7.48 (d, *J* = 8.5 Hz, 2 H), 6.90 (d, *J* = 16.4 Hz, 1 H), 6.55 (d, *J* = 16.4 Hz, 1 H), 5.22 (s, 1 H), 5.19 (s, 1 H), 2.36 (q, *J* = 7.3 Hz, 2 H), 1.16 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.1, 142.0, 134.8, 132.4, 126.7, 125.9, 119.0, 117.7, 110.3, 24.5, 12.6.

Anal. Calcd for $C_{13}H_{13}N$: C, 85.21; H, 7.15. Found: C, 85.43; H, 7.06.

4-[(*E*)-3-Ethylbuta-1,3-dienyl]pyridine (26) (Table 4, Entry 5)
The reaction of 2-bromobut-1-ene (0.135 g, 1 mmol), 4-vinylpyridine (0.210 g, 2 mmol) and K_2CO_3 (0.280 g, 2 mmol) with the palladium complex (0.004 mmol) at 80 °C afforded **26**; yield: 0.110 g (69%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.52 (d, *J* = 6.4 Hz, 2 H), 7.26 (d, *J* = 6.4 Hz, 2 H), 6.99 (d, *J* = 16.4 Hz, 1 H), 6.47 (d, *J* = 16.4 Hz, 1 H), 5.23 (s, 1 H), 5.20 (s, 1 H), 2.34 (q, *J* = 7.3 Hz, 2 H), 1.16 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.8, 147.0, 145.0, 135.7, 125.1, 120.8, 118.1, 24.4, 12.5.

Anal. Calcd for $C_{11}H_{13}N$: C, 82.97; H, 8.23. Found: C, 82.99; H, 8.31.

Butyl (*E*)-4-Ethylpenta-2,4-dienoate (27) (Table 4, Entry 6)
The reaction of 2-bromobut-1-ene (0.135 g, 1 mmol), *n*-butyl acrylate (0.256 g, 2 mmol) and K_2CO_3 (0.280 g, 2 mmol) with the palladium complex (0.001 mmol) at 80 °C afforded **27**; yield: 0.146 g (80%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32 (d, *J* = 15.9 Hz, 1 H), 5.93 (d, *J* = 15.9 Hz, 1 H), 5.36 (s, 1 H), 5.33 (s, 1 H), 4.15 (t, *J* = 6.8 Hz, 2 H), 2.24 (q, *J* = 7.3 Hz, 2 H), 1.65 (m, 2 H), 1.42 (m, 2 H), 1.11 (t, *J* = 7.3 Hz, 3 H), 0.94 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.3, 146.6, 146.1, 122.0, 117.9, 64.3, 30.7, 24.3, 19.1, 13.7, 12.3.

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.61; H, 10.08.

(*E*)-6-Ethylhepta-4,6-dien-3-one (28) (Table 4, Entry 8)
The reaction of 2-bromobut-1-ene (0.135 g, 1 mmol), pent-1-en-3-one (0.164 g, 2 mmol), hydroquinone (0.009 g, 0.08 mmol) and NaOAc (0.164 g, 2 mmol) with the palladium complex (0.01 mmol) at 80 °C afforded **28**; yield: 0.088 g (64%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.18 (d, *J* = 16.3 Hz, 1 H), 6.19 (d, *J* = 16.3 Hz, 1 H), 5.39 (s, 1 H), 5.36 (s, 1 H), 2.61 (q, *J* = 7.5 Hz, 2 H), 2.24 (q, *J* = 7.5 Hz, 2 H), 1.11 (m, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 201.5, 146.5, 144.3, 125.8, 122.7, 33.7, 24.3, 12.3, 8.2.

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.30; H, 10.07.

(*E*)-2-Ethyldeca-1,3-dien-5-one (29) (Table 4, Entry 10)
The reaction of 2-bromobut-1-ene (0.135 g, 1 mmol), oct-1-en-3-one (0.206 g, 2 mmol), hydroquinone (0.009 g, 0.08 mmol) and NaOAc (0.164 g, 2 mmol) with the palladium complex (0.01 mmol) at 80 °C afforded **29**; yield: 0.128 g (71%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.21 (d, *J* = 16.3 Hz, 1 H), 6.22 (d, *J* = 16.3 Hz, 1 H), 5.43 (s, 1 H), 5.40 (s, 1 H), 2.60 (t, *J* = 7.5 Hz, 2 H), 2.27 (q, *J* = 7.5 Hz, 2 H), 1.75–0.78 (m, 12 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 202.0, 147.3, 145.2, 126.9, 123.5, 41.3, 32.3, 25.1, 24.8, 23.2, 14.7, 13.1.

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.87; H, 11.34.

Butyl (*E*)-4-(2-Hydroxyethyl)penta-2,4-dienoate (30) (Table 5, Entry 1)
The reaction of 3-bromobut-3-en-1-ol (0.151 g, 1 mmol), *n*-butyl acrylate (0.256 g, 2 mmol) and K_2CO_3 (0.280 g, 2 mmol) with the palladium complex (0.001 mmol) at 130 °C afforded **30**; yield: 0.151 g (76%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29 (d, *J* = 16.0 Hz, 1 H), 5.92 (d, *J* = 16.0 Hz, 1 H), 5.48 (s, 1 H), 5.41 (s, 1 H), 4.15 (t, *J* = 7.5 Hz, 2 H), 3.76 (t, *J* = 7.5 Hz, 2 H), 2.52 (t, *J* = 7.5 Hz, 2 H), 1.64 (m, 2 H), 1.41 (m, 2 H), 0.93 (t, *J* = 7.5 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.1, 145.9, 141.0, 125.0, 118.7, 64.4, 60.8, 34.9, 30.7, 19.1, 13.7.

Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.79; H, 9.26.

(*E*)-3-Methylene-5-phenylpent-4-en-1-ol (31) (Table 5, Entry 2)
The reaction of 3-bromobut-3-en-1-ol (0.151 g, 1 mmol), styrene (0.208 g, 2 mmol) and K_2CO_3 (0.280 g, 2 mmol) with the palladium complex (0.01 mmol) at 130 °C afforded **31**; yield: 0.078 g (45%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 7.4 Hz, 2 H), 7.31 (t, *J* = 7.4 Hz, 2 H), 7.23 (t, *J* = 7.4 Hz, 1 H), 6.81 (d, *J* = 16.2 Hz, 1 H), 6.60 (d, *J* = 16.2 Hz, 1 H), 5.26 (s, 1 H), 5.14 (s, 1 H), 3.82 (t, *J* = 6.5 Hz, 2 H), 2.64 (t, *J* = 6.5 Hz, 2 H).

(*E*)-6-(2-Hydroxyethyl)hepta-4,6-dien-3-one (32) (Table 5, Entry 3)
The reaction of 3-bromobut-3-en-1-ol (0.151 g, 1 mmol), pent-1-en-3-one (0.164 g, 2 mmol), hydroquinone (0.009 g, 0.08 mmol) and NaOAc (0.164 g, 2 mmol) with the palladium complex (0.001 mmol) at 110 °C afforded **32**; yield: 0.096 g (62%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.18 (d, *J* = 16.0 Hz, 1 H), 6.22 (d, *J* = 16.0 Hz, 1 H), 5.53 (s, 1 H), 5.46 (s, 1 H), 3.77 (t, *J* = 7.5 Hz, 2 H), 2.62 (q, *J* = 7.5 Hz, 3 H), 2.54 (t, *J* = 7.5 Hz, 2 H), 1.12 (t, *J* = 7.5 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 201.2, 143.6, 141.4, 126.4, 125.6, 60.8, 34.8, 33.9, 8.1.

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.21; H, 9.04.

(*E*)-2-(2-Hydroxyethyl)deca-1,3-dien-5-one (33) (Table 5, Entry 4)

The reaction of 3-bromobut-3-en-1-ol (0.151 g, 1 mmol), oct-1-en-3-one (0.206 g, 2 mmol), hydroquinone (0.009 g, 0.08 mmol) and NaOAc (0.164 g, 2 mmol) with the palladium complex (0.004 mmol) at 110 °C afforded **33**; yield: 0.080 g (41%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.17 (d, *J* = 16.0 Hz, 1 H), 6.21 (d, *J* = 16.0 Hz, 1 H), 5.52 (s, 1 H), 5.45 (s, 1 H), 3.76 (t, *J* = 7.5 Hz, 2 H), 2.59 (t, *J* = 7.5 Hz, 2 H), 2.52 (t, *J* = 7.5 Hz, 2 H), 1.61 (m, 2 H), 1.30 (m, 4 H), 0.88 (t, *J* = 7.5 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 201.1, 143.8, 141.4, 126.5, 125.7, 60.8, 40.7, 34.8, 31.4, 23.9, 22.4, 13.9.

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.56; H, 10.31.

Butyl (*E*)-5-Methylhexa-2,4-dienoate (34) (Table 6, Entry 1)

The reaction of 1-bromo-2-methylprop-1-ene (0.135 g, 1 mmol), *n*-butyl acrylate (0.256 g, 2 mmol) and K_2CO_3 (0.280 g, 2 mmol) with the palladium complex (0.004 mmol) at 100 °C afforded **34**; yield: 0.162 g (89%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54 (dd, *J* = 11.7, 15.2 Hz, 1 H), 5.97 (d, *J* = 11.7 Hz, 1 H), 5.75 (d, *J* = 15.2 Hz, 1 H), 4.15 (t, *J* = 6.8 Hz, 2 H), 1.88 (s, 3 H), 1.86 (s, 3 H), 1.65 (m, 2 H), 1.40 (m, 2 H), 0.94 (t, *J* = 7.3 Hz, 3 H).

[(*E*)-4-Methylpenta-1,3-dienyl]benzene (35) (Table 6, Entry 3)

The reaction of 1-bromo-2-methylprop-1-ene (0.135 g, 1 mmol), styrene (0.208 g, 2 mmol) and K_2CO_3 (0.280 g, 2 mmol) with the palladium complex (0.004 mmol) at 100 °C afforded **35**; yield: 0.123 g (78%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 7.7 Hz, 2 H), 7.29 (t, *J* = 7.2 Hz, 2 H), 7.17 (t, *J* = 7.2 Hz, 1 H), 6.99 (dd, *J* = 15.5, 11.0 Hz, 1 H), 6.41 (d, *J* = 15.5 Hz, 1 H), 5.99 (d, *J* = 11.0 Hz, 1 H), 1.86 (s, 3 H), 1.84 (s, 3 H).

4-[(*E*)-4-Methylpenta-1,3-dienyl]benzonitrile (36) (Table 6, Entry 4)

The reaction of 1-bromo-2-methylprop-1-ene (0.135 g, 1 mmol), 4-cyanostyrene (0.260 g, 2 mmol) and K_2CO_3 (0.280 g, 2 mmol) with the palladium complex (0.004 mmol) at 100 °C afforded **36**; yield: 0.138 g (75%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 7.5 Hz, 2 H), 7.42 (d, *J* = 7.5 Hz, 2 H), 7.08 (dd, *J* = 15.5, 10.9 Hz, 1 H), 6.38 (d, *J* = 15.5 Hz, 1 H), 6.01 (d, *J* = 10.9 Hz, 1 H), 1.87 (s, 3 H), 1.86 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.7, 140.0, 132.3, 129.2, 127.5, 126.3, 125.1, 119.2, 109.7, 26.4, 18.7.

Anal. Calcd for $C_{13}H_{13}N$: C, 85.21; H, 7.15. Found: C, 85.35; H, 7.01.

4-[(*E*)-4-Methylpenta-1,3-dienyl]pyridine (37) (Table 6, Entry 5)

The reaction of 1-bromo-2-methylprop-1-ene (0.135 g, 1 mmol), 4-vinylpyridine (0.210 g, 2 mmol) and K_2CO_3 (0.280 g, 2 mmol) with the palladium complex (0.004 mmol) at 100 °C afforded **37**; yield: 0.135 g (85%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.51 (m, 2 H), 7.17 (dd, *J* = 11.0, 15.5 Hz, 1 H), 7.15 (m, 2 H), 6.32 (d, *J* = 15.5 Hz, 1 H), 6.02 (d, *J* = 11.0 Hz, 1 H), 1.88 (s, 3 H), 1.87 (s, 3 H).

Butyl (*E*)-4,5-Dimethylhexa-2,4-dienoate (38) (Table 7, Entry 1)

The reaction of 2-bromo-3-methylbut-2-ene (0.149 g, 1 mmol), *n*-butyl acrylate (0.256 g, 2 mmol) and K_2CO_3 (0.280 g, 2 mmol) with the palladium complex (0.004 mmol) at 100 °C afforded **38**; yield: 0.161 g (82%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 15.5 Hz, 1 H), 5.77 (d, *J* = 15.5 Hz, 1 H), 4.15 (t, *J* = 6.8 Hz, 2 H), 1.95 (s, 3 H), 1.86 (s, 3 H), 1.78 (s, 3 H), 1.65 (m, 2 H), 1.40 (m, 2 H), 0.94 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.2, 143.4, 141.5, 125.9, 115.4, 64.0, 30.8, 22.5, 20.9, 19.2, 14.0, 13.7.

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.61; H, 10.04.

[(*E*)-3,4-Dimethylpenta-1,3-dienyl]benzene (39) (Table 7, Entry 2)

The reaction of 2-bromo-3-methylbut-2-ene (0.149 g, 1 mmol), styrene (0.208 g, 2 mmol) and K_2CO_3 (0.280 g, 2 mmol) with the palladium complex (0.004 mmol) at 100 °C afforded **39**; yield: 0.152 g (88%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51 (m, 2 H), 7.48 (d, *J* = 15.9 Hz, 1 H), 7.25 (m, 3 H), 6.35 (d, *J* = 15.9 Hz, 1 H), 1.96 (s, 3 H), 1.88 (s, 6 H).

4-[(*E*)-3,4-Dimethylpenta-1,3-dienyl]pyridine (40) (Table 7, Entry 3)

The reaction of 2-bromo-3-methylbut-2-ene (0.149 g, 1 mmol), 4-vinylpyridine (0.210 g, 2 mmol) and K_2CO_3 (0.280 g, 2 mmol) with the palladium complex (0.004 mmol) at 100 °C afforded **40**; yield: 0.159 g (92%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.50 (d, *J* = 5.1 Hz, 2 H), 7.47 (d, *J* = 15.9 Hz, 1 H), 7.25 (d, *J* = 5.1 Hz, 2 H), 6.35 (d, *J* = 15.9 Hz, 1 H), 1.95 (s, 3 H), 1.87 (s, 6 H).

(*E*)-6,7-Dimethylocta-4,6-dien-3-one (41) (Table 7, Entry 4)

The reaction of 2-bromo-3-methylbut-2-ene (0.149 g, 1 mmol), pent-1-en-3-one (0.164 g, 2 mmol), hydroquinone (0.009 g, 0.08 mmol) and NaOAc (0.164 g, 2 mmol) with the palladium complex (0.001 mmol) at 110 °C afforded **41**; yield: 0.087 g (57%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 15.9 Hz, 1 H), 6.11 (d, *J* = 15.9 Hz, 1 H), 2.60 (q, *J* = 7.4 Hz, 2 H), 1.97 (s, 3 H), 1.88 (s, 3 H), 1.79 (s, 3 H), 1.12 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 201.8, 142.6, 141.1, 126.2, 123.8, 34.1, 22.7, 20.9, 14.1, 8.5.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.69; H, 10.41.

(*E*)-2,3-Dimethylundeca-2,4-dien-6-one (42) (Table 7, Entry 5)

The reaction of 2-bromo-3-methylbut-2-ene (0.149 g, 1 mmol), oct-1-en-3-one (0.206 g, 2 mmol), hydroquinone (0.009 g, 0.08 mmol) and NaOAc (0.164 g, 2 mmol) with the palladium complex (0.001 mmol) at 110 °C afforded **42**; yield: 0.120 g (62%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 15.9 Hz, 1 H), 6.09 (d, *J* = 15.9 Hz, 1 H), 2.54 (t, *J* = 7.4 Hz, 2 H), 1.96 (s, 3 H), 1.87 (s, 3 H), 1.78 (s, 3 H), 1.62 (m, 2 H), 1.30 (m, 4 H), 0.88 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 201.5, 142.7, 141.1, 126.2, 124.0, 41.1, 31.5, 24.3, 22.7, 22.5, 21.0, 14.1, 13.9.

Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.17; H, 11.29.

Acknowledgment

We thank CNRS for financial support.

References

(1) For reviews on the Heck reaction, see: (a) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009. (b) Whitcombe, N. J.; Hii, K. K. M.; Gibson, S. E. *Tetrahedron* **2001**, *57*, 7449. (c) Littke, A. F.; Fu, G. C. *Angew. Chem. Int. Ed.* **2002**, *41*, 4176. (d) Farina, V. *Adv. Synth. Catal.* **2004**, *346*, 1553.

(2) For examples of Heck reactions with vinyl halides, see: (a) Dieck, H. A.; Heck, R. F. *J. Org. Chem.* **1975**, *40*, 1083. (b) Patel, B. A.; Heck, R. F. *J. Org. Chem.* **1978**, *43*, 3898. (c) Patel, B. A.; Kao, L.-C.; Cortese, N. A.; Minkiewicz, J. V.; Heck, R. F. *J. Org. Chem.* **1979**, *44*, 918. (d) Kao, L.-C.; Stakem, F. G.; Patel, B. A.; Heck, R. F. *J. Org. Chem.* **1982**, *47*, 1267. (e) Fischetti, W.; Mak, T.; Stakem, F. G.; Kim, J.-I.; Rheingold, A. L.; Heck, R. F. *J. Org. Chem.* **1983**, *48*, 948. (f) Mitsudo, T.-A.; Fischetti, W.; Heck, R. F. *J. Org. Chem.* **1984**, *49*, 1640. (g) Jeffery, T. *Tetrahedron Lett.* **1985**, *26*, 2667. (h) Larock, R. C.; Gong, W. H. *J. Org. Chem.* **1989**, *54*, 2047. (i) Jeffery, T. *J. Chem. Soc., Chem. Commun.* **1991**, 324. (j) Lu, X.; Huang, X.; Ma, S. *Tetrahedron Lett.* **1992**, *33*, 2535. (k) Jeffery, T. *Tetrahedron Lett.* **1993**, *34*, 1133. (l) Zhang, X.-p.; Schlosser, M. *Tetrahedron Lett.* **1993**, *34*, 1925. (m) Crisp, G. T.; Glink, P. T. *Tetrahedron* **1994**, *50*, 2623. (n) Voigt, K.; von Zezschwitz, P.; Rosauer, K.; Lansky, A.; Adams, A.; Reiser, O.; de Meijere, A. *Eur. J. Org. Chem.* **1998**, 1521. (o) Fayol, A.; Fang, Y.-Q.; Lautens, M. *Org. Lett.* **2006**, *8*, 4203.

(3) For examples of efficient catalyst precursors for Heck reactions, see: (a) Herrmann, W. A.; Brossmer, C.; Öfele, K.; Reisinger, C.; Riermeier, T.; Beller, M.; Fisher, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1844. (b) Herrmann, W. A.; Brossmer, C.; Reisinger, C.; Riermeier, T.; Öfele, K.; Beller, M. *Chem. Eur. J.* **1997**, *3*, 1357. (c) Ohff, M.; Ohff, A.; van der Boom, M. E.; Milstein, D. *J. Am. Chem. Soc.* **1997**, *119*, 11687. (d) Bergbreiter, D.; Osburn, P.; Liu, Y.-S. *J. Am. Chem. Soc.* **1999**, *121*, 9531. (e) Gai, X.; Grigg, R.; Ramzan, M. I.; Sridharan, V.; Collard, S.; Muir, J. E. *Chem. Commun.* **2000**, 2053. (f) Gibson, S.; Foster, D. F.; Cole-Hamilton, D. J.; Eastham, G. R.; Tooze, R. P. *Chem. Commun.* **2001**, 779. (g) Alonso, D. A.; Najera, C.; Pacheco, M. C. *Adv. Synth. Catal.* **2002**, *344*, 172. (h) Takenaka, K.; Uozumi, Y. *Adv. Synth. Catal.* **2004**, *346*, 1693. (i) Cui, X.; Li, Z.; Tao, C.-Z.; Xu, Y.; Li, J.; Liu, L.; Guo, Q.-X. *Org. Lett.* **2006**, *8*, 2467. (j) Yoon, M. S.; Ryu, D.; Kim, J.; Ahn, K. H. *Organometallics* **2006**, *25*, 2409.

(4) (a) Negishi, E.; Takahashi, T.; Baba, S.; Van Horn, D. E.; Okukado, N. *J. Am. Chem. Soc.* **1987**, *109*, 2393. (b) Ramiandrasoa, P.; Brehon, B.; Thivet, A.; Alami, M.; Cahiez, G. *Tetrahedron Lett.* **1997**, *38*, 2447.

(5) (a) Williams, D. R.; Kammler, D. C.; Donnell, A. F.; Goundry, W. R. F. *Angew. Chem. Int. Ed.* **2005**, *44*, 6715. (b) Conway, J. C.; Quayle, P.; Regan, A. C.; Urch, C. J. *Tetrahedron* **2005**, *61*, 11910.

(6) For recent examples of the synthesis of dienes via Stille coupling, see: (a) Reginato, G.; Gaggini, F.; Mordini, A.; Valacchi, M. *Tetrahedron* **2005**, *61*, 6791. (b) Sorg, A.; Siegel, K.; Brückner, R. *Chem. Eur. J.* **2005**, *11*, 1610.

(7) For recent examples of the synthesis of dienes via Suzuki coupling, see: (a) Molander, G. A.; Felix, L. A. *J. Org. Chem.* **2005**, *70*, 3950. (b) Batsanov, A. S.; Knowles, J. P.; Whiting, A. *J. Org. Chem.* **2007**, *72*, 2525.

(8) (a) Gruber, A. S.; Zim, D.; Ebeling, G.; Monteiro, A. L.; Dupont, J. *Org. Lett.* **2000**, *2*, 1287. (b) Littke, A. F.; Fu, G. C. *J. Am. Chem. Soc.* **2001**, *123*, 6989. (c) Fürstner, A.; Aïssa, C.; Chevrier, C.; Tepl, F.; Nevado, C.; Tremblay, M. *Angew. Chem. Int. Ed.* **2006**, *45*, 5832.

(9) Laurenti, D.; Feuerstein, M.; Pèpe, G.; Doucet, H.; Santelli, M. *J. Org. Chem.* **2001**, *66*, 1633.

(10) Doucet, H.; Santelli, M. *Synlett* **2006**, 2001.

(11) Feuerstein, M.; Laurenti, D.; Doucet, H.; Santelli, M. *Chem. Commun.* **2001**, 43.

(12) (a) Feuerstein, M.; Laurenti, D.; Bougeant, C.; Doucet, H.; Santelli, M. *Chem. Commun.* **2001**, 325. (b) Feuerstein, M.; Berthiol, F.; Doucet, H.; Santelli, M. *Org. Biomol. Chem.* **2003**, *1*, 2235.

(13) Kondolff, I.; Doucet, H.; Santelli, M. *Organometallics* **2006**, *25*, 5219.

(14) (a) Battace, A.; Lemhadri, M.; Zair, T.; Doucet, H.; Santelli, M. *Organometallics* **2007**, *26*, 472. (b) Battace, A.; Lemhadri, M.; Zair, T.; Doucet, H.; Santelli, M. *Adv. Synth. Catal.* **2007**, *349*, 2507.

(15) (a) Feuerstein, M.; Doucet, H.; Santelli, M. *J. Org. Chem.* **2001**, *66*, 5923. (b) Berthiol, F.; Doucet, H.; Santelli, M. *Eur. J. Org. Chem.* **2003**, 1091. (c) Berthiol, F.; Doucet, H.; Santelli, M. *Tetrahedron Lett.* **2004**, *45*, 5633. (d) Battace, A.; Lemhadri, M.; Zair, T.; Doucet, H.; Santelli, M. *Synthesis* **2006**, 3495. (e) Lemhadri, M.; Doucet, H.; Santelli, M. *Synlett* **2006**, 2935. (f) Berthiol, F.; Doucet, H.; Santelli, M. *Tetrahedron* **2006**, *62*, 4372. (g) Berthiol, F.; Doucet, H.; Santelli, M. *Appl. Organomet. Chem.* **2006**, *20*, 855. (h) Battace, A.; Feuerstein, M.; Lemhadri, M.; Zair, T.; Doucet, H.; Santelli, M. *Eur. J. Org. Chem.* **2007**, 3122. (i) Fall, Y.; Doucet, H.; Santelli, M. *Tetrahedron Lett.* **2007**, *48*, 3579.

(16) Berthiol, F.; Doucet, H.; Santelli, M. *Synlett* **2003**, 841.

(17) (a) Kim, J.-I. I.; Patel, B. A.; Heck, R. F. *J. Org. Chem.* **1981**, *46*, 1067. (b) Hodgson, D. M.; Fleming, M. J.; Stanway, S. J. *J. Am. Chem. Soc.* **2004**, *126*, 12250. (c) Molander, G. A.; Felix, L. A. *J. Org. Chem.* **2005**, *70*, 3950.