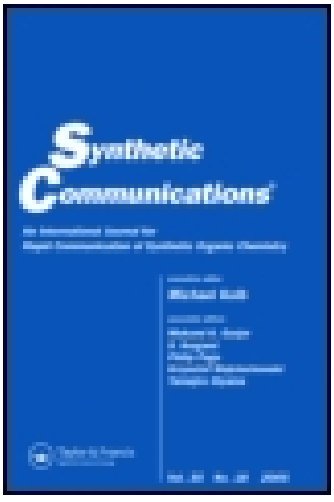


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Suzuki Coupling of 2-Chloroacrylonitrile, Methyl 2-Chloroacrylate, or 2-Chloroprop-1-en-3-ol with Arylboronic Acids Catalyzed by a Palladium-Tetraphosphine Complex

Florian Berthiol [a], Henri Doucet [a] & Maurice Santelli [a]
[a] UMR 6180 CNRS and Université d'Aix-Marseille III, Laboratoire de Synthèse Organique , Faculté des Sciences de Saint Jérôme , Marseille, France
Published online: 16 Feb 2007.

To cite this article: Florian Berthiol , Henri Doucet & Maurice Santelli (2006) Suzuki Coupling of 2-Chloroacrylonitrile, Methyl 2-Chloroacrylate, or 2-Chloroprop-1-en-3-ol with Arylboronic Acids Catalyzed by a Palladium-Tetraphosphine Complex, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 36:20, 3019-3027, DOI: 10.1080/00397910600773866

To link to this article: http://dx.doi.org/10.1080/00397910600773866

Synthetic Communications®, 36: 3019–3027, 2006

ISSN 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910600773866

Suzuki Coupling of 2-Chloroacrylonitrile, Methyl 2-Chloroacrylate, or 2-Chloroprop-1-en-3-ol with Arylboronic Acids Catalyzed by a Palladium-Tetraphosphine Complex

Florian Berthiol, Henri Doucet, and Maurice Santelli
UMR 6180 CNRS and Université d'Aix-Marseille III,
Laboratoire de Synthèse Organique, Faculté des
Sciences de Saint Jérôme, Marseille, France

Abstract: The tetraphosphine all-*cis*-1,2,3,4-*tetrakis*(diphenylphosphinomethyl)cyclopentane (Tedicyp) in combination with $[Pd(C_3H_5)Cl]_2$ affords an efficient catalyst of the coupling of 2-chloroacrylonitrile with arylboronic acids. In the presence of 1% catalyst, the 2-arylacrylonitrile derivatives were obtained in medium to good yields. A variety of substituents such as alkyl, methoxy, fluoro, trifluoromethyl, formyl, or nitro on the arylboronic acid are tolerated. The cross-coupling reactions of methyl 2-chloroacrylate with arylboronic acids give simple access to 2-phenylacrylate derivatives, which are useful precursors for the synthesis of biologically active compounds such as ibuprofen, ketoprofen, and naproxen.

Keywords: Arylboronic acids, catalysis, palladium, tetraphosphine, vinyl chlorides

The palladium-catalyzed Suzuki reaction is one of the most powerful methods for the formation of C–C bonds.[1] In recent years, several palladium catalysts have been successfully used for this reaction, but most of them have not been tested for synthesis of styrene derivatives by coupling of vinyl chlorides with arylboronic acids. In fact, only a few examples of the coupling of vinyl

Received in Poland March 16, 2006

Address correspondence to Henri Doucet, UMR 6180 CNRS and Université d'Aix-Marseille III, "Chirotechnologies: catalyse et biocatalyse," Laboratoire de Synthèse Organique, Faculté des Sciences de Saint Jérôme, Université d'Aix-Marseille III, Avenue Escadrille Normandie-Niemen, 13397, Marseille Cedex 20, France. E-mail: henri.doucet@univ.u-3mrs.fr

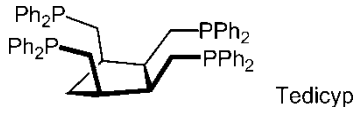


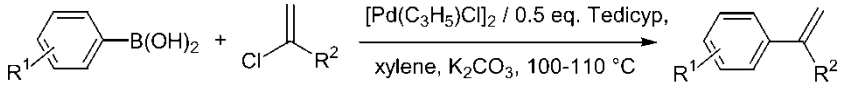
Figure 1. Structure of Tedicyp ligand.

chlorides with arylboronic acids have been reported.[2–9] Vinyl chlorides are less reactive substrates than vinyl bromides or iodides. The most popular ligand for this reaction is triphenylphosphine.[2–4] We found also four examples of the formation of styrene derivatives using vinyl chlorides via Suzuki reaction using other ligands than triphenylphosphine. Good results were obtained using P(*t*Bu)$_3$ as the ligand associated with $Pd_2(dba)_3$ or $PdBr_2(PhCN)_2$; however, with these catalytic systems, 6% of ligands were used.[5,6] Two other monodentate ligands have also been employed successfully for the coupling of vinyl chlorides with arylboronic acids: (*t*-Bu)$_2$P(O H)[7] and a bulky phenanthryl *N*-heterocyclic carbene ligand.[8] To our knowledge, the efficiency of polydentate phosphine ligands for this reaction has not been described; moreover, Suzuki coupling reactions using arylboronic acids with 2-chloroacrylonitrile, methyl 2-chloroacrylate, or 2-chloroprop-1-en-3-ol have not been reported.

To obtain a highly stable palladium catalyst, we have prepared the tetraphosphine ligand, all-*cis*-1,2,3,4-*tetrakis*(diphenylphosphinomethyl)cyclopentane or Tedicyp[10] (Fig. 1). We have already reported several results obtained for Suzuki cross-coupling with aryl halides and arylboronic acids using Tedicyp as ligand.[11] We have also recently reported some results obtained for the coupling of vinyl halides with several arylboronic acids.[12] To further establish the requirements for a successful Suzuki reaction with our catalyst, we herein report on the reaction of 2-chloroacrylonitrile, methyl 2-chloroacrylate, or 2-chloroprop-1-en-3-ol with arylboronic acids.

For this study, based on our previous results,[11,12] xylene was chosen as the solvent and potassium carbonate as the base. The reactions were performed at 100–110°C, under argon, in the presence of a 1:2 ratio of $[Pd(C_3H_5)Cl]_2$/Tedicyp as catalyst.

First, we studied the reactivity of 2-chloroacrylonitrile with arylboronic acids (Scheme 1, Table 1). We observed that, in most cases, the reactions performed



R^1 = H, Me, Ph, OMe, F, CF_3, CHO, NO_2
R^2 = CN, CO_2Me, CH_2OH, CH_2OTHP

Scheme 1.

Table 1. Palladium-catalyzed coupling reactions of arylboronic acids with 2-chloroacrylonitrile, methyl 2-chloroacrylate, or 2-chloroprop-1-en-3-ol (Scheme 1)

Entry	Vinyl chloride	Arylboronic acid	Product	Ratio substrate/catalyst	Yield[a]
1	2-Chloroacrylonitrile	Benzeneboronic acid	**1**	100	79
2	2-Chloroacrylonitrile	4-Methylbenzeneboronic acid	**2**	100	66
3	2-Chloroacrylonitrile	4-Methoxybenzeneboronic acid	**3**	100	74
4	2-Chloroacrylonitrile	4-Methoxybenzeneboronic acid	**3**	100	53[b]
5	2-Chloroacrylonitrile	4-Fluorobenzeneboronic acid	**4**	100	57
6	2-Chloroacrylonitrile	4-Trifluoromethylbenzeneboronic acid	**5**	100	67
7	2-Chloroacrylonitrile	3-Nitrobenzeneboronic acid	**6**	100	34
8	2-Chloroacrylonitrile	3-Formylbenzeneboronic acid	**7**	50	86
9	2-Chloroacrylonitrile	1-Naphthaleneboronic acid	**8**	100	79
10	2-Chloroacrylonitrile	1-Naphthaleneboronic acid	**8**	250	(12)
11	2-Chloroacrylonitrile	2-Methylbenzeneboronic acid	**9**	100	62
12	2-Chloroacrylonitrile	2-Phenylbenzeneboronic acid	**10**	100	78
13	2-Chloroacrylonitrile	2-Methoxybenzeneboronic acid	**11**	100	71
14	2-Chloroacrylonitrile	3-Thiopheneboronic acid	**12**	50	15
15	Methyl 2-chloroacrylate	Benzeneboronic acid	**13**	100	60[c]
16	Methyl 2-chloroacrylate	6-Methoxy-2-naphthylboronic acid	**14**	100	54[c]
17	Methyl 2-chloroacrylate	1-Naphthaleneboronic acid	**15**	100	50[c]
18	2-Chloroprop-1-en-3-ol	4-Methoxybenzeneboronic acid	**16**	100	25[d]
19	2-Chloroprop-1-en-3-ol	4-Fluorobenzeneboronic acid	**17**	100	32[d]

(*continued*)

Table 1. Continued

Entry	Vinyl chloride	Arylboronic acid	Product	Ratio substrate/ catalyst	Yield[a]
20	2-Chloroprop-1-en-3-ol	1-Naphthalene-boronic acid	**18**	100	30[d]
21	2-(2-Chloroallyloxy)-tetrahydropyran	1-Naphthalene-boronic acid	**19**	50	25[d]
22	2-(2-Chloroallyloxy)-tetrahydropyran	1-Naphthalene-boronic acid	**19**	50	(38)[b,d]

Note: Conditions: $[ClPd(C_3H_5)]_2$/Tedicyp = 1:2, 2-chloroacrylonitrile: 2 mmol, arylboronic acid: 1 mmol, K_2CO_3: 2 mmol, xylene, 100°C, 20 h, argon, isolated yields.

[a]Yields in parentheses are GC yields.

[b]0.05 mmol of hydroquinone was added.

[c]Methyl 2-chloroacrylate: 1 mmol, arylboronic acid: 2 mmol, 110°C.

[d]2-Chloroprop-1-en-3-ol or 2-(2-chloroallyloxy)-tetrahydropyran: 1 mmol, arylboronic acid: 2 mmol.

with this vinyl chloride proceed smoothly. Quite similar yields were observed in the presence of electron-poor and electron-rich arylboronic acids. For example, yields of 67% and 74% were obtained respectively for the coupling of 2-chloroacrylonitrile using 4-trifluoromethylbenzeneboronic acid or 4-methoxybenzeneboronic acid employing 1% catalyst (Table 1, entries 3 and 6). Benzeneboronic acid, 4-methylbenzeneboronic acid, 4-fluorobenzeneboronic acid, or 3-formylbenzeneboronic acid gave the 2-arylacrylonitrile derivatives **1**, **2**, **4**, and **7** in 57–86% yields (Table 1, entries 1, 2, 5, and 8). A lower yield was obtained using 3-nitrobenzeneboronic acid as reactant. With this substrate, the formation of side products was observed (Table 1, entry 7). Then, we studied the influence of the presence of *ortho*-substituents on the arylboronic acid on the yield of the reaction. Similar yields to those obtained with *para*-substituted arylboronic acids were obtained using the sterically congested 1-naphthaleneboronic acid, 2-methylbenzeneboronic acid, 2-phenylbenzeneboronic acid, and 2-methoxybenzeneboronic acid with 2-chloroacrylonitrile (Table 1, entries 9–13). We have also investigated this reaction in the presence of the heteroaryl substrate, 3-thiopheneboronic acid, but with this reagent, in the presence of 2% catalyst, a very low yield of product **12** was obtained (Table 1, entry 14). Palladium(II) complexes possess strong thiophilicity. This result suggests that with 3-thiopheneboronic acid, a possible interaction between the sulphur atom and the palladium complex has a poisoning effect.

Methyl 2-chloroacrylate has been reacted with benzeneboronic acid and 1-naphthaleneboronic acid (Table 1, entries 15 and 17). The 2-arylacrylate derivatives **13** and **15** were obtained in 60 and 50% yields respectively using 1% catalyst. Application of this cross-coupling reaction to the synthesis of the

precursor of the nonsteroidal anti-inflammatory agent naproxene is also reported. 6-Methoxy-2-naphthylboronic acid with methyl 2-chloroacrylate gave methyl 2-(6-methoxy-2-naphthyl)acrylate **14** in 54% yield (Table 1, entry 16).

Cross-coupling reactions using 2-chloroprop-1-en-3-ol with arylboronic acids gave the corresponding 2-arylallyl alcohol derivatives **16**–**18** in low yields (25–32%) (Table 1, entries 18–20). Even in the presence of the protected substrate 2-(2-chloroallyloxy)-tetrahydropyran, a low yield of adduct **19** was obtained (Table 1, entries 21 and 22). The oxidative addition to palladium of this nonactivated vinyl chloride is probably very slow.

These results seems to indicate that with this catalyst, as expected, the rate-limiting step for the coupling of arylboronic acid with 2-chloroacrylonitrile, methyl 2-chloroacrylate, or 2-chloroprop-1-en-3-ol is the oxidative addition of the vinyl chloride to the palladium complex.

CONCLUSION

The use of the tetradentate ligand Tedicyp associated to $[ClPd(C_3H_5)]_2$ provides a convenient catalyst for the coupling reaction of 2-chloroacrylonitrile or methyl 2-chloroacrylate with substituted arylboronic acids. A range of functions such as methoxy, fluoro, formyl, nitro, or trifluoromethyl on the arylboronic acid is tolerated. If the function of the arylboronic acids has an influence on the yield of the reaction, their electronic properties have a minor influence. The cross-coupling reaction of 2-chloroprop-1-en-3-ol with arylboronic acids led to the 2-arylprop-1-en-3-ol derivatives in medium yield. As expected, lower turnover numbers were observed for the coupling of these vinyl chlorides than those observed with vinyl bromides such as ethyl 2-bromoacrylate,[12] but in most cases with these substrates the expected arylated adducts were obtained in satisfactory yields with only 1–2% catalyst. We believe that this system compares favorably with the other catalysts that have been reported for the Suzuki reaction with vinyl chlorides. These cross-coupling reactions should give a simple access to nonsteroidal anti-inflammatory agents such as naproxen or ibuprofen. Moreover, 2-chloroacrylonitrile, methyl 2-chloroacrylate, and 2-chloroprop-1-en-3-ol are commercially available, and this is a practical advantage of these reactions.

EXPERIMENTAL

General

Xylene (analytical grade), vinyl chlorides, and arylboronic acids were not purified before use. Potassium carbonate 99+ was used. All reactions were run under argon using vacuum lines in Schlenk tubes in oven-dried glassware. ^1H (300-MHz) and ^{13}C (75-MHz) spectra were recorded in $CDCl_3$ solutions.

Chemical shifts (δ) are reported in parts per million (ppm) relative to $CDCl_3$. Flash chromatographies were performed on silica gel (230–400 mesh).

Preparation of the Pd-Tedicyp Catalyst[10]

An oven-dried 40-mL Schlenk tube equipped with a magnetic stirring bar, under an argon atmosphere, was charged with $[Pd(C_3H_5)Cl]_2$ (4.2 mg, 11.6 μmol) and Tedicyp (20 mg, 23.2 μmol). Anhydrous DMF (2.5 mL) was added, and then the solution was stirred at room temperature for 10 min.

General Procedure

As a typical experiment, the reaction of arylboronic acid (1 or 2 mmol, see Table 1), vinyl chloride (1 or 2 mmol, see Table 1), and K_2CO_3 (0.276 g, 2 mmol) at 100 or 110°C (see Table 1) during 20 h in xylene (4 mL) in the presence of *cis*,*cis*,*cis*-1,2,3,4-*tetrakis*(diphenylphosphinomethyl)cyclopentane–$\frac{1}{2}$ $[PdCl(C_3H_5)]_2$ complex under argon affords the corresponding products after addition of water, extraction with ether or dichloromethane, separation, drying (MgSO4), evaporation, and chromatography on silica gel.

Data

2-Phenylacrylonitrile (1). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.63–7.57$ (m, 2H), 7.46–7.38 (m, 3H), 6.33 (s, 1H), 6.10 (s, 1H).

2-(*p*-Tolyl)acrylonitrile (2). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.48$ (d, $J = 8.0$ Hz, 2H), 7.22 (d, $J = 8.0$ Hz, 2H), 6.27 (s, 1H), 6.03 (s, 1H), 2.34 (s, 3H).

2-(4-Methoxyphenyl)acrylonitrile (3). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.53$ (d, $J = 8.9$ Hz, 2H), 6.92 (d, $J = 8.9$ Hz, 2H), 6.18 (s, 1H), 5.96 (s, 1H), 3.83 (s, 3H).

2-(4-Fluorophenyl)acrylonitrile (4). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.57$ (dd, $J = 8.8$, 5.1 Hz, 2H), 7.09 (t, $J = 8.8$ Hz, 2H), 6.25 (s, 1H), 6.06 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 163.5$ (d, $J_{C\text{-}F} = 250.9$ Hz), 128.5 (d, $^4J_{C\text{-}F} = 3.3$ Hz), 127.7, 127.6 (d, $^3J_{C\text{-}F} = 8.3$ Hz), 121.8, 117.5, 116.0 (d, $^2J_{C\text{-}F} = 22.5$ Hz). Anal. calcd. for C_9H_6FN: C, 73.46; H, 4.11. Found: C, 73.61; H, 4.19.

2-(4-Trifluoromethylphenyl)-acrylonitrile (5). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.73–7.67$ (m, 4H), 6.43 (s, 1H), 6.23 (s, 1H).

2-(3-Nitrophenyl)acrylonitrile (6). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 8.43$ (s, 1H), 8.25 (d, $J = 7.8$ Hz, 1H), 7.93 (d, $J = 7.8$ Hz, 1H), 7.64 (t, $J = 7.5$ Hz, 1H), 6.52 (s, 1H), 6.30 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 148.6$, 134.0, 131.7, 130.9, 130.3, 124.5, 121.1, 120.4, 116.6. Anal. calcd. for $C_9H_6N_2O_2$: C, 62.07; H, 3.47. Found: C, 62.14; H, 3.59.

2-(3-Formylphenyl)acrylonitrile (7). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 10.03$ (s, 1H), 8.06 (t, $J = 1.6$ Hz, 1H), 7.90 (dt, $J = 7.8$, 1.3 Hz, 1H), 7.83 (dt, $J = 7.8$, 1.6 Hz, 1H), 7.59 (t, $J = 7.8$ Hz, 1H), 6.44 (s, 1H), 6.21 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 191.3$, 136.9, 133.3, 131.4, 130.8, 127.8, 129.7, 126.4, 121.8, 117.1. Anal. calcd. for $C_{10}H_7NO$: C, 76.42; H, 4.49. Found: C, 76.60; H, 4.31.

2-(1-Naphthyl)acrylonitrile (8). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 8.12$ (d, $J = 8.3$ Hz, 1H), 7.95–7.87 (m, 2H), 7.63–7.51 (m, 2H), 7.48 (m, 2H), 6.44 (s, 1H), 6.20 (s, 1H).

2-(*o*-Tolyl)acrylonitrile (9). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.35$–7.16 (m, 4H), 6.26 (s, 1H), 6.00 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 135.8$, 133.7, 133.6, 130.8, 129.5, 128.9, 126.4, 123.3, 117.9, 20.0. Anal. calcd. for C_{10}H9 N: C, 83.88; H, 6.34. Found: C, 83.74; H, 6.39.

2-Biphenyl-2-yl-acrylonitrile (10). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.50$–7.30 (m, 9H), 6.07 (s, 1H), 5.90 (s, 1H).

2-(2-Methoxyphenyl)acrylonitrile (11). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.41$ (dd, $J = 7.6$, 1.6 Hz, 1H), 7.35 (td, $J = 7.6$, 1.6 Hz, 1H), 6.98 (td, $J = 7.6$, 1.0 Hz, 1H), 6.93 (d, $J = 8.6$ Hz, 1H), 6.39 (s, 1H), 6.18 (s, 1H), 3.88 (s, 3H).

2-(3-Thienyl)acrylonitrile (12). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.56$ (dd, $J = 3.0$, 1.2 Hz, 1H), 7.37 (dd, $J = 5.2$, 3.0 Hz, 1H), 7.26 (dd, $J = 5.2$, 1.2 Hz, 1H), 6.16 (s, 1H), 5.99 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 135.0$, 127.6, 126.3, 124.9, 124.0, 117.8, 117.6. Anal. calcd. for C_7H_5NS: C, 62.19; H, 3.73. Found: C, 61.94; H, 3.70.

Methyl 2-phenylacrylate (13). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.50$–7.26 (m, 5H), 6.36 (s, 1H), 5.89 (s, 1H), 3.82 (s, 3H).

Methyl 2-(6-methoxy-2-naphthyl)acrylate (14). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.83$ (s, 1H), 7.71 (m, 2H), 7.49 (dd, $J = 8.4$, 1.7 Hz, 1H), 7.12 (m, 2H), 6.39 (s, 1H), 5.98 (s, 1H), 3.93 (s, 3H), 3.84 (s, 3H).

2-Naphthalen-1-yl-acrylic acid methyl ester (15). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.84$ (m, 2H), 7.72 (m, 1H), 7.45 (m, 3H), 7.35 (dd, $J = 7.0$, 1.1 Hz, 1H), 6.71 (s, 1H), 5.88 (s, 1H), 3.71 (s, 3H).

2-(4-Methoxyphenyl)allylalcohol (16). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.40$ (d, $J = 8.7$ Hz, 2H), 6.88 (d, $J = 8.7$ Hz, 2H), 5.38 (s, 1H), 5.25 (q, $J = 1.3$ Hz, 1H), 4.51 (s, 2H), 3.81 (s, 3H).

2-(4-Fluorophenyl)allylalcohol (17). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.41$ (dd, $J = 8.8$, 5.5 Hz, 2H), 7.02 (t, $J = 8.8$ Hz, 2H), 5.40 (s, 1H), 5.32 (s, 1H), 4.49 (s, 2H), 1.89 (s, 1H).

2-(1-Naphthyl)allylalcolol (18). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 8.07$–7.99 (m, 1H), 7.89–7.83 (m, 1H), 7.80 (d, $J = 8.3$ Hz, 1H), 7.52–7.42 (m, 3H), 7.32 (dd, $J = 7.0$, 1.2 Hz, 1H), 5.71 (q, $J = 1.7$ Hz, 1H), 5.26 (q, $J = 1.4$ Hz, 1H), 4.46 (s, 2H), 1.95 (s, 1H).

2-(2-Naphthalen-1-yl-allyloxy)-tetrahydropyran (19). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 8.09$ (m, 1H), 7.87 (m, 1H), 7.78 (d, $J = 8.3$ Hz, 1H), 7.52–7.45 (m, 2H), 7.44 (d, $J = 8.3$ Hz, 1H), 7.33 (dd, $J = 7.0$, 1.2 Hz, 1H), 5.76 (q, $J = 1.8$ Hz, 1H), 5.29 (q, $J = 1.8$ Hz, 1H), 4.76 (t, $J = 3.4$ Hz, 1H), 4.57 (dt, $J = 14.2$ and 1.6 Hz, 1H), 4.32 (dt, $J = 14.2$ and 1.6 Hz, 1H), 4.90–4.75 (m, 1H), 3.50–3.40 (m, 1H), 2.00–1.45 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 145.0$, 138.4, 133.6, 131.5, 128.2, 127.6, 125.8, 125.6, 125.5; 125.4, 125.1, 115.8, 97.8, 69.9, 61.9, 30.4, 25.4, 19.2. Anal. calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.44; H, 7.42.

ACKNOWLEDGMENT

We thank the CNRS for providing financial support.

REFERENCES

1. Suzuki, A. Development of Pd–Cu catalyzed cross-coupling of terminal acetylenes with sp^2-carbon halides. *J. Organomet. Chem.* **2002**, *653* (1–2), 83–90.
2. Chen, C.; Wilcoxen, K.; Strack, N.; McCarthy, J. R. Synthesis of fluorinated olefins via the palladium catalyzed cross-coupling reaction of 1-fluorovinyl halides with organoboranes. *Tetrahedron Lett.* **1999**, *40* (5), 827–830.
3. Organ, M. G.; Cooper, J. T.; Rogers, L. R.; Soleymanzadeh, F.; Paul, T. Synthesis of stereodefined polysubstituted olefins: Sequential intermolecular reactions involving selective, stepwise insertion of Pd(0) into allylic and vinylic halide bonds: The stereoselective synthesis of disubstituted olefins. *J. Org. Chem.* **2000**, *65* (23), 7959–7970.
4. Couty, S.; Barbazanges, M.; Meyer, C.; Cossy, J. Palladium-catalyzed Suzuki-Miyaura coupling reactions involving β,β-dihaloenamides: Application to the synthesis of disubstituted ynamides. *Synlett* **2005** (6), 905–910.
5. Trost, B. M.; Pinkerton, A. B. Formation of vinyl halides via a ruthenium-catalyzed three-component coupling. *J. Am. Chem. Soc.* **2002**, *124* (25), 7376–7389.

6. Thadani, A. N.; Rawal, V. H. Stereospecific synthesis of highly substituted skipped dienes through multifunctional palladium catalysis. *Org. Lett.* **2002**, *4* (24), 4317–4320.
7. Poondra, R. R.; Fischer, P. M.; Turner, N. J. Efficient palladium-catalyzed cross-coupling of chloroalkylidene/arylidene malonates using microwave chemistry. *J. Org. Chem.* **2004**, *69* (20), 6920–6922.
8. Song, C.; Ma, Y.; Chai, Q.; Ma, C.; Jiang, W.; Andrus, M. B. Palladium catalyzed Suzuki–Miyaura coupling with aryl chlorides using a bulky phenanthryl N-heterocyclic carbene ligand. *Tetrahedron* **2005**, *61* (31), 7438–7446.
9. Hesse, S.; Kirsch, G. Palladium-catalyzed C–C bond formation from β-chloroacroleins in aqueous media. *Synthesis* **2001** (5), 755–758.
10. Laurenti, D.; Feuerstein, M.; Pèpe, G.; Doucet, H.; Santelli, M. A new tetratertiary phosphine ligand and its use in Pd-catalyzed allylic substitution. *J. Org. Chem.* **2001**, *66* (5), 1633–1637.
11. Feuerstein, M.; Laurenti, D.; Bougeant, C.; Doucet, H.; Santelli, M. Palladium–tetraphosphine catalysed cross coupling of aryl bromides with arylboronic acids: Remarkable influence of the nature of the ligand. *Chem. Commun.* **2001** (4), 325–326.
12. Berthiol, F.; Doucet, H.; Santelli, M. Synthesis of polysubstituted alkenes by Heck vinylation or Suzuki cross-coupling reactions in the presence of a tetraphosphane palladium catalyst. *Eur. J. Org. Chem.* **2003** (6), 1091–1096.