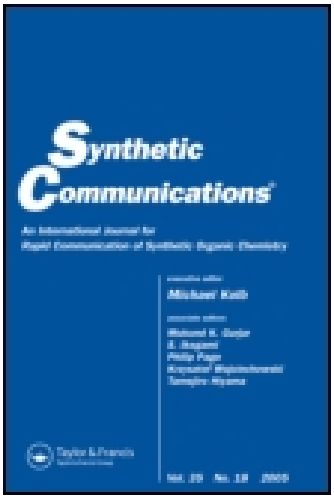

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Suzuki Coupling of Cyclopropylboronic Acid With Aryl Halides Catalyzed by a Palladium-Tetraphosphine Complex

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Suzuki Coupling of Cyclopropylboronic Acid With Aryl Halides Catalyzed by a Palladium–Tetraphosphine Complex

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Abstract: The tetraphosphine all-*cis*-1,2,3,4-*tetrakis*(diphenylphosphinomethyl)-cyclopentane (Tedicyp) in combination with $[Pd(C_3H_5)Cl]_2$ affords a very efficient catalyst for the coupling of cyclopropylboronic acid with aryl bromides and aryl chlorides. Higher reactions rates were observed with aryl bromides than with aryl chlorides; however, even in the presence of 1–0.4% of catalyst, a few aryl chlorides gave the coupling products in good yields. A wide variety of substituents such as alkyl, methoxy, trifluoromethyl, acetyl, benzoyl, formyl, carboxylate, nitro, and nitrile on the aryl halides are tolerated. The coupling reaction of sterically very congested aryl bromides such as bromomesitylene or 2,4,6-triisopropylbromobenzene also proceeds in good yields.

Keywords: Aryl halide, catalysis, cyclopropylboronic acid, palladium, tetraphosphine

The palladium-catalyzed Suzuki reaction is one of the most powerful methods for the formation of C–C bonds.[1] In recent years, several thermally stable palladium catalysts have been successfully used for this reaction, but most

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of these catalysts have not been tested for synthesis of arylcyclopropanes by coupling of aryl halides with cyclopropylboronic acid. The most popular ligand for the reaction of cyclopropylboronic acid derivatives with aryl halides is triphenylphosphine.[2–4] However, the catalyst formed by association of this ligand with palladium complexes is not very efficient in terms of the ratio of substrate/catalyst. We found only three examples of formation of arylcyclopropanes via the Suzuki reaction using ligands other than triphenylphosphine. The best results were obtained with PCy_3 as ligand with $PdOAc_2$; however, with this catalytic system, 10% of ligand and 5% of palladium were used, and moreover very low conversions were obtained with aryl chlorides.[5] Two other monodentate ligands have also been used successfully for the coupling of cyclopropylboronic acids derivatives with aryl iodides or vinyl triflates: P*t*Bu_3 (10 mol%)[6] and PAs_3 (20 mol%).[7] However, to our knowledge, low-catalyst-loading Suzuki reactions using cyclopropylboronic acid with aryl chlorides or bromides 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[8] (Figure 1). We have already reported several results obtained for Suzuki cross-coupling with arylboronic acids using Tedicyp as ligand.[9] We have also reported recently the results obtained for the coupling of primary alkylboronic acids with several arylhalides.[10] To further establish the requirements for a successful Suzuki reaction with our catalyst, we herein report on the reaction of secondary alkylboronic acid with aryl halides.

For this study, based on our previous results,[10] xylene was chosen as the solvent and potassium carbonate as the base. The reactions were performed at 130°C, under argon, in the presence of a ratio 1/2 of $[Pd(C_3H_5)Cl]_2$/Tedicyp as catalyst.

First, we studied the influence of the substituents on the aryl bromide on the reaction rate for the coupling with cyclopropylboronic acid (Scheme 1, Table 1). We observed that in most cases the reactions performed with this secondary alkylboronic acid proceed very smoothly. Quite similar reactions rates were observed in the presence of electron-poor and electron-rich aryl bromides. For example, turnover numbers (TONs) of 320–6100 were obtained in the presence of 4-bromoacetophenone, 4-bromobenzaldehyde, 4-bromobenzophenone, 4-bromonitrobenzene, or 4-trifluoromethylbromobenzene (Table 1, entries 1–12). With electron-rich aryl bromides such as

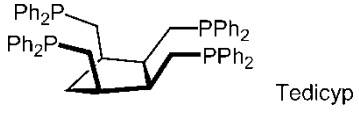
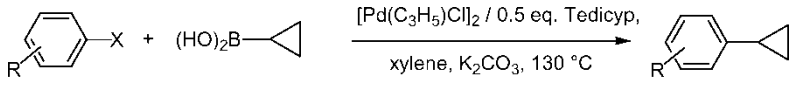


Figure 1. Structure of Tedicyp.



X = Cl, Br

R = Me, *i*-Pr, *t*-Bu, OMe, CF_3, MeCO, PhCO, CHO, CO_2Me, CN, NO_2

Scheme 1.

4-*t*butylbromobenzene, 4-bromotoluene, or 4-bromoanisole TONs of 920, 940, and 280 were obtained respectively (Table 1, entries 13–16, 19, and 20). These results seem to indicate that, with this catalyst, the rate-limiting step for the coupling of cyclopropylboronic acid with aryl bromides is not the oxidative addition of the aryl bromide to palladium.

Then, we studied the influence of the presence of *ortho* substituents on the aryl bromides on the reaction rate. Similar reactions rates were obtained with the *ortho*-substituted 2-bromobenzaldehyde and with the 4-bromobenzaldehyde (Table 1, entries 21 and 22). We also observed that the coupling of 1-bromonaphthalene with cyclopropylboronic acid proceeds in the presence of 0.1% catalyst, in 100% conversion (Table 1, entries 23 and 24). Next, we tried to evaluate the difference of reaction rate between mono- and di-*ortho*-substituted aryl bromides, and we observed that even very hindered aryl bromides could be coupled efficiently with cyclopropylboronic acid. For example, with 2,4,6-trimethylbromobenzene and 2,4,6-triisopropylbromobenzene the aryl cyclopropanes were obtained in 73 and 92% conversion, respectively, in the presence of 0.1 and 1% catalyst (Table 1, entries 25–27).

Then, we investigated this reaction in the presence of heteroaryl bromides. With 4-bromopyridine, 3-bromoquinoline, and 4-bromoisoquinoline, the expected adducts were obtained in good yields in the presence of 1–0.1% catalyst (Table 1, entries 28–33).

Finally, the reactivity of five aryl chlorides was studied (Scheme 1, Table 2). In the presence of electron-poor aryl chlorides such as 4-chloroacetophenone, 4-chlorobenzaldehyde, 4-chlorobenzonitrile, or 4-chloronitrobenzene, the corresponding arylcyclopropanes were obtained in good yields using 1–0.4% catalyst (Table 2, entries 1–6). The reaction also proceeds nicely with the heteroaryl chloride 2-chloroquinoline (Table 2, entries 7 and 8).

These results prompted us to investigate the cross-coupling of a few other secondary alkylboronic acids. However, in all cases with isopropyl-, cyclopentyl-, cyclohexyl-, or cyclooctylboronic acids and iodobenzene or 4-bromobenzophenone as coupling partners, very disappointing results were obtained. The expected adducts were not observed even in the presence of 1–5% catalyst. In some cases, the dimerization of the aryl halides was obtained. We had previously observed that high reactions rates for the

Table 1. Palladium-catalyzed coupling reactions of aryl bromides with cyclopropylboronic acid (Scheme 1)[a]

Entry	Aryl bromide	Product	Ratio substrate/catalyst	Yield[b]
1	4-Bromoacetophenone	**1**	1000	100 (94)
2	4-Bromoacetophenone	**1**	10,000	61
3	Methyl 4-bromobenzoate	**2**	250	100 (95)
4	Methyl 4-bromobenzoate	**2**	1000	90
5	4-Bromobenzaldehyde	**3**	1000	100 (95)
6	4-Bromobenzophenone	**4**	250	100 (93)
7	4-Bromobenzophenone	**4**	1000	56
8	4-Bromobenzonitrile	**5**	1000	98 (92)
9	4-Bromonitrobenzene	**6**	250	100 (94)
10	4-Bromonitrobenzene	**6**	1000	58
11	4-Trifluoromethylbromobenzene	**7**	250	100
12	4-Trifluoromethylbromobenzene	**7**	1000	32
13	4-*t*Butylbromobenzene	**8**	250	100
14	4-*t*Butylbromobenzene	**8**	1000	92 (88)
15	4-Bromotoluene	**9**	250	100
16	4-Bromotoluene	**9**	1000	94
17	6-Methoxy-2-bromonaphthalene	**10**	250	100 (94)
18	6-Methoxy-2-bromonaphthalene	**10**	1000	80
19	4-Bromoanisole	**11**	250	100 (96)
20	4-Bromoanisole	**11**	1000	28
21	2-Bromobenzaldehyde	**12**	250	100 (90)
22	2-Bromobenzaldehyde	**12**	1000	36
23	1-Bromonaphthalene	**13**	250	100
24	1-Bromonaphthalene	**13**	1000	100 (93)
25	2,4,6-Trimethylbromobenzene	**14**	250	100 (91)
26	2,4,6-Trimethylbromobenzene	**14**	1000	73
27	2,4,6-Triisopropylbromobenzene	**15**	100	92 (82)
28	4-Bromopyridine hydrochloride	**16**	100	100 (92)[c]
29	4-Bromopyridine hydrochloride	**16**	250	54[c]
30	3-Bromoquinoline	**17**	250	100 (93)
31	3-Bromoquinoline	**17**	1000	37
32	4-Bromoisoquinoline	**18**	100	100 (93)
33	4-Bromoisoquinoline	**18**	250	60
34	5-Bromo-2-furaldehyde	**19**	100	88 (84)
35	1,4-Dibromobenzene	**20**	100	100[d]

[a]Conditions: $[ClPd(C_3H_5)]_2$/Tedicyp = 1 : 2, aryl bromide: 1 mmol, cyclopropylboronic acid: 2 mmol, K_2CO_3: 2 mmol, xylene, 130°C, 20 h, argon, GC and NMR yields.

[b]Yields in parentheses are isolated.

[c]K_2CO_3: 3 mmol.

[d]Cyclopropylboronic acid: 3 mmol, K_2CO_3: 3 mmol.

coupling of several primary alkylboronic acids with aryl halides could be obtained.[10] We had also observed that isopropenylboronic acid or but-1-en-2-ylboronic acid can be coupled very efficiently with several aryl bromides.[11] The difference of reactivity among these secondary alkylboronic

Table 2. Palladium-catalyzed coupling reaction of aryl chlorides with cyclopropylboronic acid (Scheme 1)[a]

Entry	Aryl bromide	Product	Ratio substrate/catalyst	Yield[b]
1	4-Chloroacetophenone	**1**	100	81 (77)
2	4-Chlorobenzaldehyde	**3**	100	100 (91)
3	4-Chlorobenzaldehyde	**3**	250	26
4	4-Chlorobenzonitrile	**5**	100	100 (90)
5	4-Chlorobenzonitrile	**5**	250	42
6	4-Chloronitrobenzene	**6**	100	60 (56)
7	2-Chloroquinoline	**21**	100	100 (83)
8	2-Chloroquinoline	**21**	250	70

[a]Conditions: $[ClPd(C_3H_5)]_2$/Tedicyp = 1 : 2, aryl chloride: 1 mmol, cyclopropylboronic acid: 2 mmol, K_2CO_3: 2 mmol, xylene, 130°C, 20 h, argon, GC and NMR yields.

[b]Yields in parentheses are isolated.

acids, cyclopropylboronic acid, and primary alkylboronic acids probably comes from both the steric hindrance and the electronic properties of alkylboronic acids.

CONCLUSION

The use of the tetradentate ligand Tedicyp associated to a palladium complex provides a convenient catalyst for the coupling reaction of cyclopropylboronic acid with substituted aryl bromides and aryl chlorides. Both the steric hindrance and the electronic properties of secondary alkylboronic acids seem to have an effect on the reaction. No coupling product was obtained with isopropyl-, cyclopentyl-, cyclohexyl-, or cyclooctylboronic acids and iodobenzene or 4-bromobenzophenone. The complex seems to possess a fine balance of steric and electronic properties that generally allow fast catalytic processes with cyclopropylboronic acid. This secondary alkylboronic acid gave the expected arylcyclopropyl adducts in good yields in the presence of 0.4–0.1% catalyst in most cases, even with sterically congested aryl bromides. As expected, lower TONs were observed for the coupling in the presence of aryl chlorides, but these substrates gave the arylcyclopropyl adducts in satisfactory yields with only 1–0.4% catalyst. We believe that this system compares favorably with the other catalysts that have been reported for this reaction. Because of the high price of palladium, the practical advantage of such low-catalyst-loading reactions can become increasingly important for industrial processes.

EXPERIMENTAL

General

Xylene, analytical grade, was not distilled before use. Potassium carbonate 99+ was used. All reactions were run under argon using vacuum lines in Schlenk tubes in oven-dried glassware. The reactions were followed by GC and NMR for high-boiling-point substrates and by GC for low-boiling-point substrates. ^{1}H (300 MHz) and ^{13}C (75 MHz) spectra were recorded in $CDCl_3$ solutions. Chemical shift (δ) are reported in ppm relative to $CDCl_3$. Flash chromatographies were performed on silica gel (230–400 mesh).

Preparation of the Pd-Tedicyp Catalyst[8]

An oven-dried 40-mL Schlenk tube equipped with a magnetic stirring 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). 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 aryl halide (1 mmol), cyclopropylboronic acid (0.172 g, 2 mmol), and K_2CO_3 (0.276 g, 2 mmol) at 130°C during 20 h in xylene (2 mL) in the presence of *cis*-1,2,3,4-*tetrakis*(diphenylphosphinomethyl)cyclopentane–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 ($MgSO_4$), evaporation, and purification by chromatography on silica gel.

1-Acetyl-4-cyclopropylbenzene (1). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.83$ (d, $J = 7.2$ Hz, 2H), 7.10 (d, $J = 7.2$ Hz, 2H), 2.55 (s, 3H), 1.93 (m, 1H), 1.05 (m, 2H), 0.77 (m, 2H).

4-Cyclopropylbenzoic acid methyl ester (2). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.90$ (d, $J = 8.3$ Hz, 2H), 7.07 (d, $J = 8.3$ Hz, 2H), 3.88 (s, 3H), 1.91 (m, 1H), 1.05 (m, 2H), 0.77 (m, 2H).

4-Cyclopropylbenzaldehyde (3). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 9.93$ (s, 1H), 7.74 (d, $J = 8.3$ Hz, 2H), 7.17 (d, $J = 8.3$ Hz, 2H), 1.95 (m, 1H), 1.07 (m, 2H), 0.79 (m, 2H).

1-Benzoyl-4-cyclopropylbenzene (4). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.76$ (d, $J = 8.3$ Hz, 2H), 7.70 (d, $J = 8.3$ Hz, 2H), 7.56 (t, $J = 7.3$ Hz, 1H), 7.47 (d, $J = 7.3$ Hz, 2H), 7.13 (d, $J = 8.3$ Hz, 2H), 1.96 (m, 1H), 1.07 (m, 2H), 0.80 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 196.2$, 149.7, 137.9, 134.6, 132.0, 130.3, 129.8, 128.1, 125.2, 15.7, 10.3. Anal. calcd. for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.61; H, 6.18.

4-Cyclopropylbenzonitrile (5). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.50$ (d, $J = 8.3$ Hz, 2H), 7.11 (d, $J = 8.3$ Hz, 2H), 1.91 (m, 1H), 1.07 (m, 2H), 0.76 (m, 2H).

1-Cyclopropyl-4-nitrobenzene (6). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 8.10$ (d, $J = 8.8$ Hz, 2H), 7.14 (d, $J = 8.8$ Hz, 2H), 1.99 (m, 1H), 1.13 (m, 2H), 0.81 (m, 2H).

1-Cyclopropyl-4-trifluoromethylbenzene (7). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.58$ (d, $J = 8.1$ Hz, 2H), 7.14 (d, $J = 8.1$ Hz, 2H), 1.93 (m, 1H), 1.03 (m, 2H), 0.73 (m, 2H).

1-*tert*-Butyl-4-cyclopropylbenzene (8). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.48$ (d, $J = 8.0$ Hz, 2H), 7.20 (d, $J = 8.0$ Hz, 2H), 2.03 (m, 1H), 1.49 (s, 9H), 1.09 (m, 2H), 0.85 (m, 2H).

1-Cyclopropyl-4-methylbenzene (9). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.03–6.95$ (m, 4H), 2.35 (s, 3H), 1.85 (m, 1H), 0.93 (m, 2H), 0.64 (m, 2H).

2-Cyclopropyl-6-methoxynaphthalene (10). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.64$ (m, 2H), 7.47 (s, 1H), 7.20–7.10 (m, 3H), 3.91 (s, 3H), 2.03 (m, 1H), 0.99 (m, 2H), 0.79 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 156.9$, 139.0, 132.8, 129.0, 128.7, 126.7, 125.2, 123.7, 118.7, 105.6, 55.2, 15.4, 8.8. Anal. calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.97; H, 6.99.

1-Cyclopropyl-4-methoxybenzene (11). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.05$ (d, $J = 8.0$ Hz, 2H), 6.83 (d, $J = 8.1$ Hz, 2H), 3.80 (s, 3H), 1.88 (m, 1H), 0.91 (m, 2H), 0.64 (m, 2H).

2-Cyclopropylbenzaldehyde (12). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 10.61$ (s, 1H), 7.82 (dd, $J = 7.7$ and 1.5 Hz, 1H), 7.48 (td, $J = 7.5$ and 1.5 Hz, 1H), 7.32 (t, $J = 7.3$ Hz, 1H), 7.15 (d, $J = 7.3$, 1H), 2.64 (m, 1H), 1.08 (m, 2H), 0.80 (m, 2H).

1-Cyclopropylnaphthalene (13). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 8.40$ (d, $J = 8.3$ Hz, 1H), 7.80–6.90 (m, 6H), 1.80 (m, 1H), 1.05 (m, 2H), 0.78 (m, 2H).

2-Cyclopropyl-1,3,5-trimethylbenzene (14). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 6.82$ (s, 2H), 1.65 (m, 1H), 0.97 (m, 2H), 0.52 (m, 2H).

2-Cyclopropyl-1,3,5-triisopropylbenzene (15). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 6.96$ (s, 2H), 3.86 (sept, $J = 7.1$, 2H), 2.87 (sept, 1H), 1.66 (m, 1H), 1.22 (m, 18H), 1.04 (m, 2H), 0.57 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 149.4$, 146.6, 133.9, 120.9, 34.0, 28.8, 24.5, 24.0, 10.3, 8.4. Anal. calcd. for $C_{18}H_{28}$: C, 88.45; H, 11.55. Found: C, 88.61; H, 11.50.

4-Cyclopropylpyridine (16). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 8.04$ (d, $J = 7.5$ Hz, 2H), 7.14 (d, $J = 7.5$ Hz, 2H), 1.97 (m, 1H), 1.18 (m, 2H), 0.90 (m, 2H).

3-Cyclopropylquinoline (17). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 8.79$ (s, 1H), 8.05 (d, $J = 8.5$ Hz, 1H), 7.70 (m, 2H), 7.62 (t, $J = 8.3$ Hz, 1H), 7.48 (t, $J = 8.5$ Hz, 1H), 2.07 (m, 1H), 1.08 (m, 2H), 0.85 (m, 2H).

4-Cyclopropylisoquinoline (18). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 9.13$ (s, 1H), 8.32 (m, 2H), 7.96 (d, $J = 8.1$ Hz, 1H), 7.75 (td, $J = 6.9$ and 1.3 Hz, 1H), 7.61 (td, $J = 6.9$ and 1.3 Hz, 1H), 2.24 (m, 1H), 1.09 (m, 2H), 0.80 (m, 2H).

5-Cyclopropyl-furan-2-carbaldehyde (19). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 9.44$ (s, 1H), 7.15 (d, $J = 3.6$ Hz, 1H), 6.17 (d, $J = 3.6$ Hz, 1H), 1.98 (m, 1H), 1.00 (m, 4H).

1,4-Dicyclopropylbenzene (20). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 6.97$ (s, 4H), 1.84 (m, 2H), 0.92 (m, 4H), 0.65 (m, 4H).

2-Cyclopropylquinoline (21). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 8.00$ (m, 2H), 7.75 (d, $J = 8.5$ Hz, 1H), 7.65 (m, 1H), 7.44 (t, $J = 7.6$ Hz, 1H), 7.15 (d, $J = 8.4$ Hz, 1H), 2.24 (m, 1H), 1.10 (m, 4H).

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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. Wang, X.-Z.; Deng, M.-Z. Cross-coupling reaction of cyclopropylboronic acid with bromoarenes. *J. Chem. Soc. Perkin Trans. 1* **1996**, (22), 2663–2664.
3. Luithle, J. E. A.; Pietruszka, J. Synthesis of enantiomerically pure cyclopropanes from cyclopropylboronic acids. *J. Org. Chem.* **1999**, *64* (22), 8287–8297.
4. Fang, G.-H.; Yan, Z.-J.; Deng, M.-Z. Palladium-catalyzed cross-coupling of stereospecific potassium cyclopropyl trifluoroborates with aryl bromides. *Org. Lett.* **2004**, *6* (3), 357–360.
5. Wallace, D. J.; Chen, C.-Y. Cyclopropylboronic acid: Synthesis and Suzuki cross-coupling reactions. *Tetrahedron Lett.* **2002**, *43* (39), 6987–6990.
6. Rubina, M.; Rubin, M.; Gevorgyan, V. Catalytic enantioselective hydroboration of cyclopropenes. *J. Am. Chem. Soc.* **2003**, *125* (24), 7198–7199.
7. Yao, M.-L.; Deng, M.-Z. Facile approach to 4-substituted 2(5*H*)-furanones. *J. Org. Chem.* **2000**, *65* (16), 5034–5036.
8. 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.
9. 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.
10. Kondolff, I.; Doucet, H.; Santelli, M. Tetraphosphine/palladium catalysed Suzuki cross-coupling reactions of aryl halides with alkylboronic acids. *Tetrahedron* **2004**, *60* (17), 3813–3818.
11. Peyroux, E.; Doucet, H.; Santelli, M. Suzuki cross-coupling reactions between alkenylboronic acids and aryl bromides catalysed by a tetraphosphane-palladium catalyst. *Eur. J. Org. Chem.* **2004**, (5), 1075–1082.