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Recoverable Homogeneous Palladium(0) Catalyst for Cross-Coupling Reactions of Arenediazonium Salts with Potassium Organotrifluoroborates: Detection of Catalytic Intermediates by Electrospray Ionization Mass Spectrometry

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Fifteen-membered triolefinic macrocyclic palladium(0) complex **1**, (*E,E,E*)-1-ferrocenylsulfonyl-6,11-bis[(4-methylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-trienepalladium(0), is an active and recoverable catalyst for Suzuki–Miyaura cross-couplings between arenediazonium salts and potassium organotrifluoroborates. The reactions were performed under aerobic conditions at room temperature and without added base. Use of electrospray ionization mass spectrometry (ESI-MS) allowed the direct detection and identification of several intermediates, which furthers the study of the mechanistic aspects of the Suzuki–Miyaura reaction.

Introduction

Palladium(0)-catalysed cross-couplings between aryl or heteroaryl compounds and boron derivatives (the Suzuki–Miyaura reaction) represent a useful synthetic method because of their broad applicability and the simplicity of the experimental procedure.[1] Because this method represents one of the most versatile ways to prepare biaryl and heterobiaryl derivatives found in biologically active compounds, ligands and other materials such as polymers, considerable efforts have been devoted to improve the catalytic process. This work has resulted in the design of highly active palladium catalysts and also in the development of recoverable catalysts, which considerably reduces costs.

Heterogenation of a palladium catalyst permits its easy recovery from a reaction mixture by simple filtration. A homogeneous catalyst, however, should allow more efficient molecular interactions, which results in increased reactivity, and so it would be desirable to develop a homogeneous reaction in which the catalyst could easily be separated from the products and recycled. To this end, we have prepared air- and moisture-stable azamacrocyclic triolefinic palladium(0) complex **1**[2] (Figure 1), which has been found to be an active and recoverable catalyst in several C–C bond formation reactions.[3]

The most commonly used electrophilic coupling partners in Suzuki–Miyaura reactions are aryl or vinyl halides or triflates, with boronic acids or esters as their second coupling counterparts. In order to broaden the scope of this reaction, new, more efficient alternatives are being sought. An interesting alternative for the electrophilic partner of this reaction is to use arenediazonium salts, which have demonstrated their potential in many cross-couplings and especially in Suzuki–Miyaura reactions.[4] Arenediazonium salts present several advantages over aryl halides in that they can easily be synthesized from the inexpensive aromatic amines[5] and they are more reactive than the corresponding aryl halides.The reactions can usually be carried out at low temperatures and without the need for bases or additives.

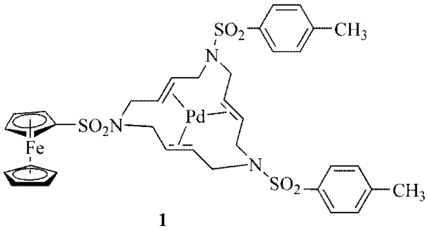

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Figure 1. Structure of azamacrocyclic triolefinic palladium(0) complex **1**.

Another area in which Suzuki–Miyaura reactions remain underdeveloped is in the search for alternatives to organoboron coupling partners. Among the most promising alternatives to boron reagents are potassium organotrifluoroborates,[6] which are easily prepared by treatment of commercially available organoboronic acids or esters with aqueous KHF_2.[7] Organotrifluoroborates can be prepared simply and in large quantities and, unlike most organoboronic compounds, are completely air- and moisture-stable. The fact that they are monomeric species makes their stoichiometric determination highly reliable. Potassium aryl- and alkenyltrifluoroborates have been efficiently coupled with arenediazonium salts by Genêt et al.,[4b,4d,4h] with the more typical aryl and heteroaryl halides and triflates by Mo-

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lander et al.[8] and with aryl chlorides by Buchwald et al.[9] Recently, Kabalka et al.[10] and Leadbeater et al.[11] have reported the enhancement of cross-couplings between organotrifluoroborates and aryl halides by microwave heating.

In this paper we present palladium(0) complex **1** as an efficient and recoverable catalyst in cross-coupling reactions between arenediazonium salts and potassium organotrifluoroborates. To the best of our knowledge there has to date been no general study of cross-coupling reactions between arenediazonium salts and organotrifluoroborates with recovery of the catalyst, although an attempt to recycle the catalytic system in couplings between arenediazonium salts and phenyl- or vinyltrifluoroborate through the use of ionic liquids as a reaction medium was described last year by Mastrorilli et al.[4p] That study demonstrated that by working with a 20% excess of arenediazonium salt (with respect to the organotrifluoroborate) it was possible to recycle the catalytic solution, but the yield obtained in the first run (72%) was lower than that achieved when working with an excess of potassium trifluoroborate (93%), whereas only a moderate yield of 46% was obtained on the second catalytic run.

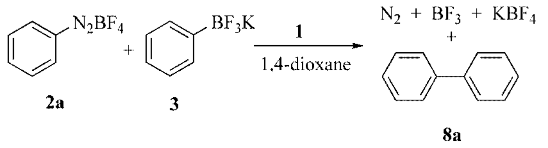
To investigate the mechanistic aspects of the cross-coupling reaction between these two partners further, we conducted electrospray ionization mass spectrometry (ESI-MS)[12] analysis directly on solution mixtures. ESI-MS is a soft ionization technique that offers the capability to transfer ions into the gas phase without inducing undesirable side reactions; this permits the trapping and identification of short-lived intermediates in organometallic catalytic cycles, with the compositions of ESI-generated ions often closely reflecting those found in solution.[13]

Results and Discussion

Suzuki–Miyaura Reactions

In a previous study of Suzuki–Miyaura cross-couplings between iodobenzene and benzeneboronic acid in the presence of palladium(0) complex **1**, a 70% yield of biphenyl was obtained and 95% of the catalyst was recovered by column chromatography.[3a] When we tried to extend the methodology to more demanding substrates, however, the corresponding biphenyls were obtained in only moderate yields and the Pd^0 complex was decomplexed and impossible to recover. We assumed that decomplexation of the palladium(0) complex, with the subsequent loss of the catalyst because of the precipitation of black palladium in the reaction mixture, was due to the high temperatures required for the cross-coupling reaction. Since we had demonstrated that Pd^0 complex **1** is an excellent recoverable catalyst with high activity for Mizoroki–Heck reactions of diazonium salts at room temperature,[3b] we decided to try cross-couplings between arenediazonium salts and boronic acids. After some experimentation we were able to find optimal reaction conditions[14] to afford the corresponding biphenyls in good yields, but once again, it was not possible to recover the catalyst at the end of the process. At this point we decided to exploit the advantages of organotrifluoroborates, as discussed in the Introduction. Reaction conditions were optimized through the use of the cross-coupling between benzenediazonium tetrafluoroborate (**2a**) and potassium phenyltrifluoroborate (**3**) as a model system (Table 1). 1,4-Dioxane was selected as the most efficient of a range of solvents that we tested. An excess of potassium phenyltrifluoroborate (**2a**/**3**, 1:1.2) permitted us to follow the reaction through the evolution of nitrogen gas.

Table 1. Optimization of the cross-coupling reaction between **2a** and **3**.[a]



Entry	Catalyst **1** [%]	*T* [°C]	*t* [h]	**2a**/1,4-dioxane [M]	Yield of **8a** [%]	Recovery of **1**[b] [%]
1	5	r.t.	17	0.043	63	100
2	5	50	3	0.043	45	88
3	10	r.t.	22	0.043	62	100
4	5	r.t.	17	0.043	60	100
5	5	r.t.	17	0.167	55	92

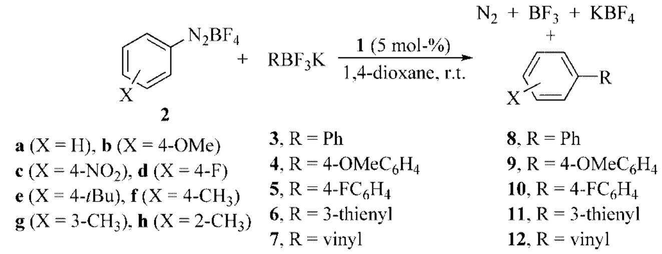
[a] Reactions were carried out with a **2a**/**3** molar ratio of ca. 1:1.2 in 1,4-dioxane until the evolution of N_2 had ceased. [b] Isolated by column chromatography on silica gel.

Temperature was an important factor in providing high yields of biphenyl and quantitatively recovering the catalyst. Working at room temperature allowed us to obtain the best results (compare Entries 1 and 2) although reaction times were no shorter than 15 h. By increasing the load of Pd^0 complex **1** from 5 to 10 mol-% did not improve the results (Entry 3). The experiments reported in Entries 1, 2, and 3 were run under inert atmospheric conditions and in anhydrous 1,4-dioxane, but the results were similar when the reaction was carried out in an open vessel and without anhydrous conditions (Entry 4). This last entry was particularly interesting as reactions in the presence of the robust palladium(0) catalyst **1** were thus practical under aerobic conditions in commercially available nondegassed solvents. In order to test whether decomposition of the arenediazonium salt could be a cause of the moderate yields of **8a**, diazonium salt **2a** was added progressively to the reaction mixture at 0.5 equiv. per hour until 2 equiv. with respect to counterpart **3** was reached, but the results were not improved upon.[15] Further adjustment of the solution concentrations provided better results at higher dilutions (compare Entries 1 and 5).

To test the scope of these conditions, different arenediazonium tetrafluoroborates **2b**–**h** were then coupled with several potassium organotrifluoroborates **3**–**7** (Table 2).

As a general trend, the cross-coupled products were obtained in moderate-to-good yields. Palladium(0) complex **1** seems only to be moderately active in this kind of process,

Table 2. Suzuki–Miyaura reactions between arenediazonium tetrafluoroborates and potassium organotrifluoroborates.[a]



Entry	Ar-N_2BF_4 **2**	RBF_3K	*t* [h]	Product	Yield [%]	Recovery of **1**[b] [%]
1	**2b**	**3**	17	**8b**	63	100
2	**2c**	**3**	17	**8c**	69	100
3	**2d**	**3**	20	**8d**	35	100
4	**2e**	**3**	16	**8e**	43	100
5	**2f**	**3**	19	**8f**	39	100
6	**2g**	**3**	19	**8g**	30	100
7	**2h**	**3**	19	**8h**	23	100
8	**2a**	**4**	19	**9a**[c]	43	100
9	**2f**	**4**	18	**9f**	40	100
10	**2a**	**5**	17	**10a**[d]	54	100
11	**2b**	**5**	17	**10b**	42	100
12	**2a**	**6**	19	**11a**	24	97
13	**2b**	**6**	19	**11b**	24	96
14	**2c**	**7**	3	**12c**	60	100
15[e]	**2e**	**7**	3.5	**12e**	43	95
16[e]	**2b**	**7**	3	**12b**	41	95
17[e]	**2f**	**7**	3.5	**12f**	36	96

[a] Reactions were carried out under aerobic conditions with 1 equiv. of **2**, 1.2 equiv. of RBF_3K and 5 mol-% of Pd^0 complex **1** in 1,4-dioxane (ca. 0.043 M) at room temperature and until the evolution of N_2 had ceased. [b] Palladium(0) complex **1** was recovered by column chromatography on silica gel in Entries 1–14 and by precipitation and further filtration from the reaction mixture in Entries 15–17 (see Experimental Section for details). [c] Compound **9a** is the same as compound **8b**, which are the products of two different Suzuki–Miyaura cross-coupling reactions as a function of the reactant in which the substituent (OMe) is found. [d] Compound **10a** is the same as compound **8d**, which are the products of two different Suzuki–Miyaura cross-coupling reactions as a function of the reactant in which the substituent (F) is found. [e] A mixture of isomers of double arylation of potassium vinyltrifluoroborate was obtained together with the desired products; 21% yield for Entry 15, 1% yield for Entry 16 and 12% yield for Entry 17.

but the most remarkable fact was that complex **1** was quantitatively recovered at the end of the reaction with its reutilization in subsequent runs being possible. Potassium vinyltrifluoroborate (**7**) (Entries 14–17) demonstrated a high reactivity over that of aryltrifluoroborates since the reaction times were around 3 h, but yields of derivatives **12** were also only moderate. In part, this is due to the competitive double arylation process that provides mixtures of isomers. Table 2 shows that the electronic nature of the substituents in the arenediazonium salts did not have significant effects either on the yields or on the recovery of the catalyst, but that steric effects of substituents in the *ortho* positions (compare Entries 5 and 7) in the arenediazonium salts did seem to be the cause of the reduced yields.

ESI Mass Spectrometric Study

In 1994 Canary et al.[16] used electrospray ionization mass spectrometry to study Suzuki–Miyaura coupling reactions between pyridyl halides and phenylboronic acids and identified both oxidative addition and transmetallation intermediates, which confirms their involvement in the catalytic cycle. Later, Moreno-Mañas, Aramendía et al.[17] studied self-coupling reactions of areneboronic acids by the same mass spectrometry technique. No mechanistic investigations into Suzuki–Miyaura cross-couplings involving arenediazonium salts had previously been performed. Therefore, we conducted an electrospray ionization mass spectrometry study to seek experimental support to validate the postulated Suzuki–Miyaura mechanism, which is thought to involve a sequence consisting of an oxidative addition, transmetallation and reductive elimination.[1b,18] The experimental details for ESI mass spectrometry are specified in the Experimental Section and the results are summarized in Table 3 and Figure 2, Figure 3 and Figure 4. The identification of the species detected by ESI-MS was aided by comparison between the observed and calculated isotope distribution patterns: in this case peaks due to species containing palladium were easily detected by the characteristic isotope distribution of the metal.

We first used ESI-MS to monitor the reaction between an equimolar amount of benzenediazonium tetrafluoroborate (**2a**) and Pd^0 complex **1** in 1,4-dioxane at room temperature. After the evolution of nitrogen gas had ceased, the mixture was injected into the mass spectrometer for analysis and a cluster centred at $m/z = 946$ corresponding to oxidative addition intermediate **I** with the predicted isotope pattern was detected (Table 3, Entry 1; Figure 2). Potassium phenyltrifluoroborate (**3**) was then added to the previously formed mixture and samples were taken every 10 min and injected into the mass spectrometer for analysis until the reaction was complete. Unfortunately, no intermediate involving the other aryl partner was observed, but when the reaction was complete, the oxidative addition peak had disappeared and a peak corresponding to the potassium adduct of Pd^0 complex **1** ($m/z = 908$) was detectable, at least demonstrating the recovery of the catalyst (Entry 2). The same oxidative addition intermediate and behaviour was observed in a previous ESI-MS study of the Heck reaction with arenediazonium salts in the presence of macrocyclic palladium(0) complex **1**.[3b,3d]

Because transmetallation intermediates have not been observed, we decided to study the mechanism of the cross-coupling in the presence of a more common Pd^0 catalyst such as $Pd_2(dba)_3$. We initially studied the $Pd_2(dba)_3$-catalysed cross-coupling reaction between 4-$CH_3PhN_2BF_4$ (**2f**) and potassium phenyltrifluoroborate (**3**) (Table 3, Entries 3 and 4; Figure 3). The ESI mass spectrum of the solution generated from a mixture of 20 mol-% of $Pd_2(dba)_3$ and 4-methylbenzenediazonium tetrafluoroborate (**2f**) in 1,4-dioxane showed several clusters corresponding to cationic oxidative addition intermediate **II**, such as $m/z = 431$, 472 and

Table 3. Electrospray mass spectral data for reaction mixtures.[a]

Entry	Reaction mixtures	*t* [min]	Identified species[b]
1	**2a** + Pd^0 complex **1**	30	*m*/*z* = 943–952 (946) (**I**)
2	**2a** + Pd^0 complex **1** + **3**	10, 20, 60	10 min *m*/*z* = 943–952 (946) (**I**)
			20 min *m*/*z* = 943–952 (946) (**I**)
			60 min (reaction completed): *m*/*z* = 905–914 (908) [**1** + K]$^+$
3	**2f** + $Pd_2(dba)_3$	30, 80	*m*/*z* = 428–437 (431) $[CH_3Ph–Pd(dba)]^+$ (**IIa**)
			m/*z* = 469–478 (472) $[CH_3Ph–Pd(dba) + CH_3CN]^+$ (**IIb**)
			m/*z* = 662–671 (665) $[CH_3Ph–Pd(dba)_2]^+$ (**IIc**)
4	**2f** + $Pd_2(dba)_3$ + **3**	30, 60	*m*/*z* = 506–515 (509) $[CH_3Ph–Pd(dba)–Ph + H]^+$ (**IIIa**)
			m/*z* = 547–556 (550) $[CH_3Ph–Pd(dba)–Ph + CH_3CN + H]^+$ (**IIIb**)
			m/*z* = 520–529 (523) $[CH_3Ph–Pd(dba)–CH_3Ph + H]^+$ (**IVa**)
			m/*z* = 561–570 (564) $[CH_3Ph–Pd(dba)–CH_3Ph + CH_3CN + H]^+$ (**IVb**)
5	**2a** + $Pd_2(dba)_3$	30	*m*/*z* = 648–657 (651) $[Ph–Pd(dba)_2]^+$ (**V**)
6	**2a** + $Pd_2(dba)_3$ + **5**	30, 60	*m*/*z* = 492–501 (495) $[Ph–Pd(dba)–Ph + H]^+$ (**VIa**)
			m/*z* = 533–542 (536) $[Ph–Pd(dba)–Ph + CH_3CN + H]^+$ (**VIb**)
			m/*z* = 510–519 (513) $[FPh–Pd(dba)–Ph + H]^+$ (**VIIa**)
			m/*z* = 551–560 (554) $[FPh–Pd(dba)–Ph + CH_3CN + H]^+$ (**VIIb**)

[a] The HPLC mobile phase is CH_3CN/H_2O (70:30). [b] Reported *m*/*z* values are from the lowest to the highest mass in the isotope envelopes of the clusters; values in brackets correspond to the most abundant peak. Unidentified ions in the spectra have not been included.

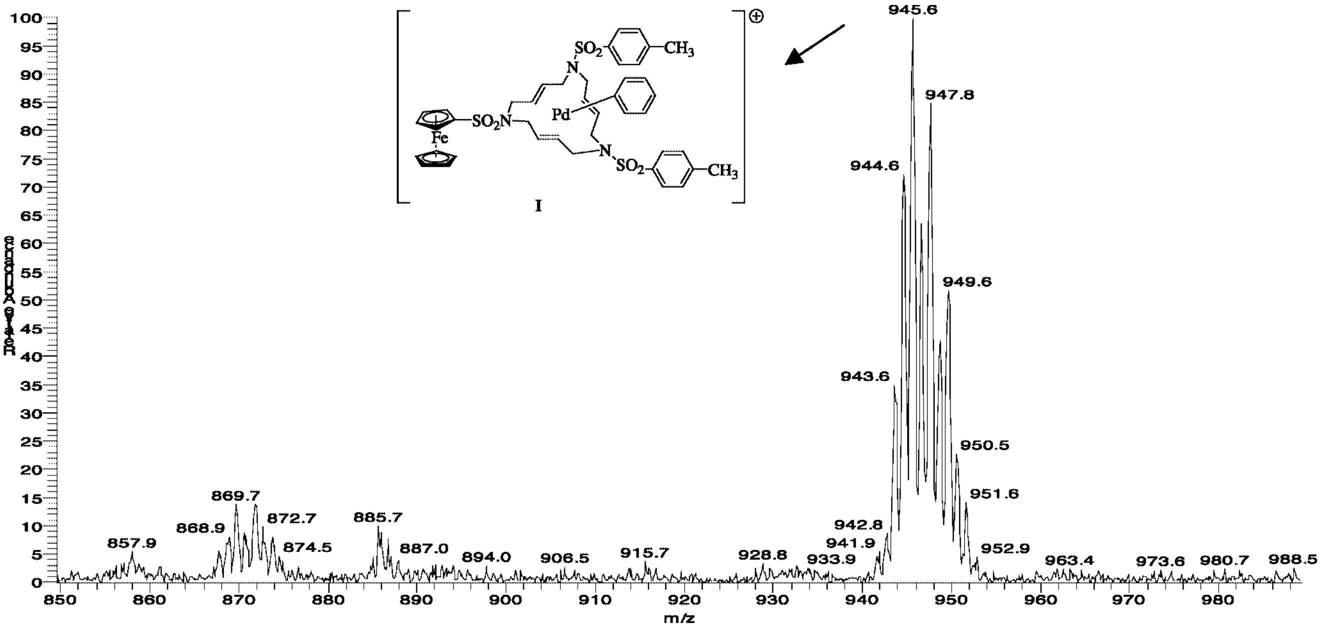


Figure 2. ESI(+) mass spectra of an equimolar mixture of benzenediazonium tetrafluoroborate (**2a**) and palladium(0) complex **1** in 1,4-dioxane.

665 corresponding to $[CH_3Ph-Pd(dba)]^+$ (**IIa**), $[CH_3Ph–Pd(dba) + CH_3CN]^+$ (**IIb**) and $[CH_3Ph–Pd(dba)_2]^+$ (**IIc**), respectively (Entry 3). After 80 min, the above mixed solution was again injected into the mass spectrometer but no changes were observed in the mass spectrum. Afterwards, 1.2 equiv. of potassium phenyltrifluoroborate (**3**) was added to the previously formed mixture, and protonated species corresponding to diaryl Pd^{II} intermediates **III** were observed at *m*/*z* = 509 $[CH_3Ph–Pd(dba)–Ph + H]^+$ (**IIIa**) and *m*/*z* = 550 $[CH_3Ph–Pd(dba)–Ph + CH_3CN + H]^+$ (**IIIb**) (Entry 4). In some of these cross-couplings, byproducts arising mainly from homocoupling of the starting materials were observed along with the expected biaryl derivatives.[4h,4p] In our experiments, traces of homocoupled products $CH_3Ph–PhCH_3$ and Ph–Ph, together with biaryl **8f**, were detected by GC–MS. In accordance with this, the ESI mass spectrum also showed two clusters centred at *m*/*z* = 523 $[CH_3Ph–Pd(dba)–CH_3Ph + H]^+$ (**IVa**) and *m*/*z* = 564 $[CH_3Ph–Pd(dba)–CH_3Ph + CH_3CN + H]^+$ (**IVb**), corresponding to protonated diaryl Pd^{II} intermediate **IV**, which gave rise to the homocoupled product 4,4′-methylbiphenyl (Entry 4). However, we did not observe any intermediate corresponding to the homocoupling of the trifluoroborate derivative. Analogous experiments were performed under stoichiometric conditions [1 equiv. of $Pd_2(dba)_3$ with respect to **2f**] and afforded data similar to those observed under catalytic conditions. Running the reaction with all components gave no new data of interest.

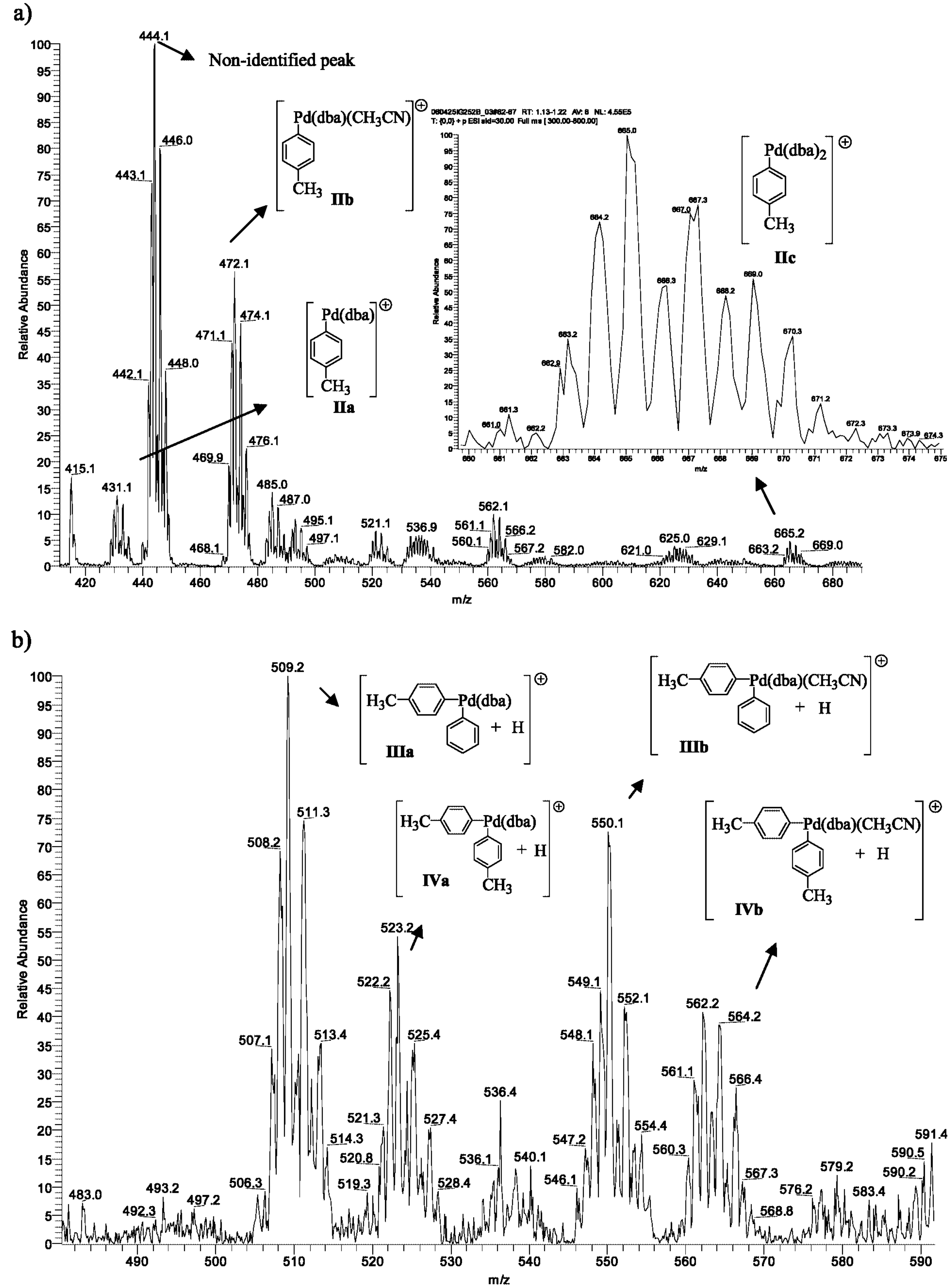


Figure 3. ESI(+) mass spectra of 1,4-dioxane solutions of: a) 4-methylbenzenediazonium tetrafluoroborate (**2f**) and $Pd_2(dba)_3$ (20 mol%) after mixing for 30 min, and b) 4-methylbenzenediazonium tetrafluoroborate (**2f**), $Pd_2(dba)_3$ (20 mol%) and $PhBF_3K$ (**3**), after mixing for 60 min. The HPLC mobile phase is CH_3CN/H_2O (70:30).

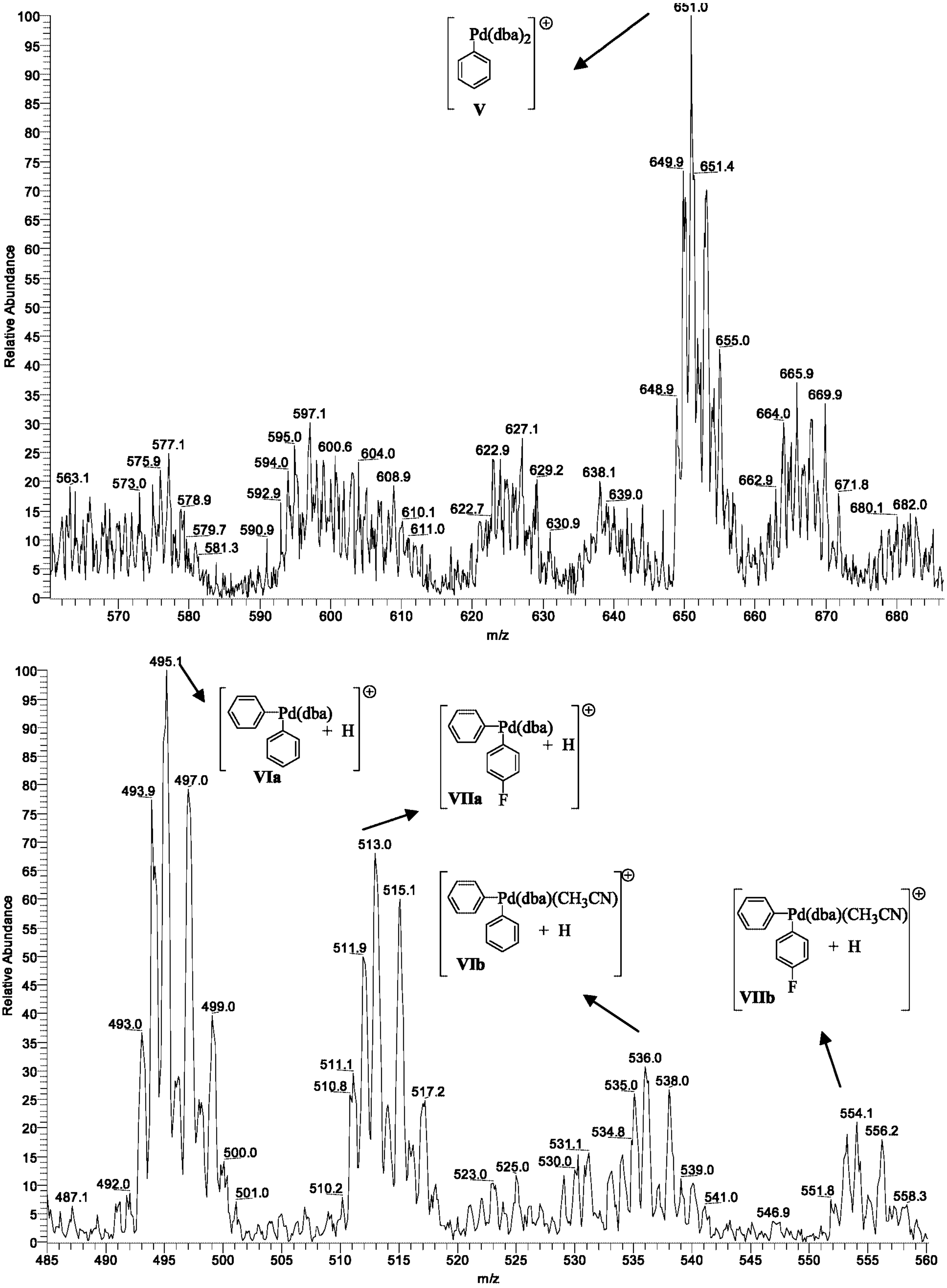
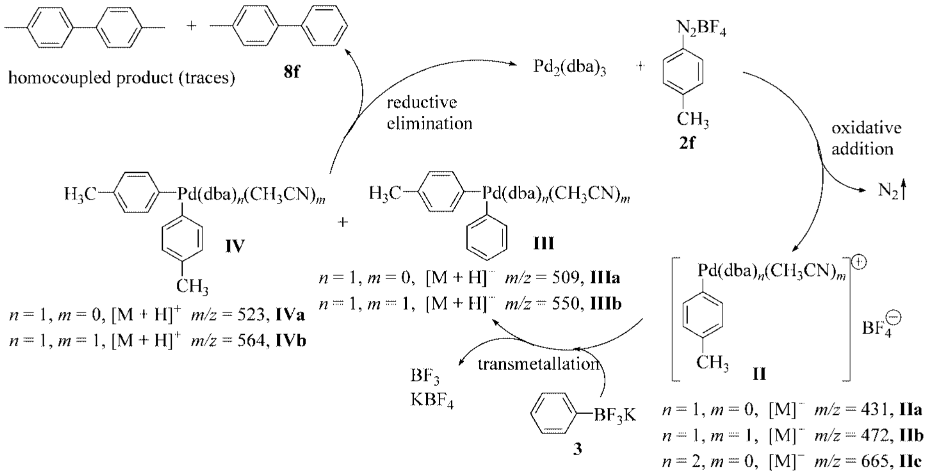


Figure 4. ESI(+) mass spectra of 1,4-dioxane solutions of: a) benzenediazonium tetrafluoroborate (**2a**) and $Pd_2(dba)_3$ (20 mol%) after mixing for 30 min, and b) benzenediazonium tetrafluoroborate (**2a**), $Pd_2(dba)_3$ (20 mol%), and 4-$FPhBF_3K$ (**5**), after mixing for 60 min. The HPLC mobile phase is CH_3CN/H_2O (70:30).



Scheme 1. Proposed catalytic cycle for Suzuki–Miyaura cross-couplings between arenediazonium salts and potassium organotrifluoroborates.

In order to confirm the formation of Pd^{II} intermediates detected in the experiments reported in Entries 3 and 4, analogous experiments were carried out with two different substrates: benzenediazonium tetrafluoroborate (**2a**) and potassium 4-fluorophenyltrifluoroborate (**5**) in the presence of the same $Pd_2(dba)_3$ catalytic system. Entries 5 and 6 in Table 3 and Figure 4 show the observed clusters, which are the same kind of intermediates that were detected in Entries 3 and 4. Oxidative addition intermediate **V** and diaryl Pd^{II} transmetallated intermediates **VI** and **VII** were also detected by ESI-MS.

Scheme 1 shows a proposed catalytic cycle that is based on the ESI-MS results for the Suzuki–Miyaura reaction with arenediazonium salts and potassium organotrifluoroborates. The scheme shows the intermediates intercepted by ESI-MS in the specific case of cross-coupling between 4-methylbenzenediazonium tetrafluoroborate (**2f**) and potassium phenyltrifluoroborate (**3**).

Conclusions

In conclusion, air- and moisture-stable palladium(0) complex **1** is an active and recoverable catalyst for Suzuki–Miyaura reactions between arenediazonium salts and potassium aryl-, heteroaryl- and vinyltrifluoroborates, and can be used to form the corresponding biaryls, heterobiaryls and styrenes in moderate-to-good yields. Catalyst **1** is easily recovered from the reaction mixture either by column chromatography on silica gel or by precipitation and further filtration.

An ESI-MS study of cross-couplings between arenediazonium salts and aryltrifluoroborates in the presence of $Pd_2(dba)_3$ has allowed the identification of some intermediate organometallic species involved in the catalytic cycle, including those that give rise to homocoupling products. This ESI-MS study provides experimental support to validate the proposed mechanism of the Suzuki–Miyaura reaction.

Experimental Section

General: Palladium(0) complex **1** has previously been synthesized and characterized in our laboratories.[3b] Arenediazonium tetrafluoroborates **2a**–**h** were generally prepared from commercially available aromatic amines by published methods.[5b] The salts can be stored for several weeks at –20 °C. Potassium organotrifluoroborates **3**–**7** were prepared by literature procedures.[4g,4h,7] ^1H NMR spectra were recorded at 200 MHz with Me_4Si as an internal standard. Chemical shifts are given in δ units. EI mass spectra were recorded at 70 eV.

Biphenyl 8a – General Procedure for the Suzuki–Miyaura Reaction: A solution of benzenediazonium tetrafluoroborate (**2a**, 0.066 g, 0.34 mmol), potassium phenyltrifluoroborate (**3**, 0.076 g, 0.41 mmol) and Pd^0 catalyst **1** (0.015 g, 0.017 mmol) in 1,4-dioxane (8 mL) was stirred at room temperature for 17 h until N_2 gas evolution ceased. Dichloromethane (10 mL) was added to the reaction mixture, the organic layer was washed with saturated NaCl aqueous solution (15 mL) and H_2O (2×15 mL), dried with anhydrous sodium sulfate and the solvents evaporated. The residue was purified by column chromatography on silica gel (hexanes/ethyl acetate, 9:1) to give biphenyl (**8a**). Further elution (hexanes/ethyl acetate, 7:3) gave quantitative recovery of **1**.

Biphenyl (8a): Colourless solid. Yield: 0.034 g (63%). M.p. 69–71 °C (ref.[19] 71 °C). ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 7.22–7.48 (m, 6 H), 7.50–7.62 (m, 4 H) ppm. GC–MS: *m/z* (%) = 154 (100) $[M]^+$, 76 (79).

The following compounds were prepared and isolated by the General Procedure. Their analytical data were identical to those reported: **8b**–**8c**,[8f] **8d**,[19] **8e**–**8h**,[4j] **9f**,[8f] **10b**,[20] **11a**–**11b**,[21] **12c**.[19] Compounds **12e**,[22] **12b**,[23] and **12f**[19] were prepared by the General Procedure but were purified by bulb-to-bulb distillation. The residue from the distillation was dissolved in dichloromethane and after the addition of hexanes palladium(0) complex **1** precipitated and was quantitatively recovered by simple filtration.

4-Methoxybiphenyl (8b): Colourless solid. Yield: 0.040 g (63%). M.p. 88–90 °C (ref.[8f] 87.5–88.5 °C). ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 3.82 (s, 3 H), 6.96 (d, J = 8.8 Hz, 2 H), 7.21–7.60 (m, 7 H) ppm. GC–MS: *m/z* (%) = 184 (100) $[M]^+$, 169 (94), 141 (89), 115 (88).

4-Nitrobiphenyl (8c): Pale yellow solid. Yield: 0.048 g (69%). M.p. 111–112 °C (ref.[8f] 107.5–108.0 °C). ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C): δ = 7.38–7.56 (m, 3 H), 7.56–7.66 (m, 2 H), 7.71 (d, J = 8.8 Hz, 2 H), 8.27 (d, J = 8.8 Hz, 2 H) ppm. GC–MS: m/z (%) = 199 (99) [M]$^+$, 169 (51), 152 (100).

4-Fluorobiphenyl (8d): Colourless solid. Yield: 0.021 g (35%). M.p. 72–73 °C (ref.[19] 74.5 °C). ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C): δ = 7.13 (t, J = 8.8 Hz, 2 H), 7.30–7.65 (m, 7 H) ppm. GC–MS: m/z (%) = 172 (100) [M]$^+$, 85 (51).

4-*tert*-Butylbiphenyl (8e): Colourless solid. Yield: 0.031 g (43%). M.p. 44–46 °C. ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C): δ = 1.36 (s, 9 H), 7.22–7.62 (m, 9 H) ppm. GC–MS: m/z (%) = 210 (77) [M]$^+$, 195 (100), 167 (78), 152 (52), 83 (51).

4-Methylbiphenyl (8f): Colourless solid. Yield: 0.023 g (39%). M.p. 43–44 °C. ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C): δ = 2.38 (s, 3 H), 7.20–7.60 (m, 9 H) ppm. GC–MS: m/z (%) = 168 (100) [M]$^+$, 152 (80), 82 (44).

3-Methylbiphenyl (8g): Colourless oil. Yield: 0.017 g (30%). ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C): δ = 2.44 (s, 3 H), 7.12–7.22 (m, 1 H), 7.30–7.49 (m, 6 H), 7.53–7.65 (m, 2 H) ppm. GC–MS: m/z (%) = 168 (100) [M]$^+$, 152 (65), 83 (31).

2-Methylbiphenyl (8h): Colourless oil. Yield: 0.013 g (23%). ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C): δ = 2.27 (s, 3 H), 7.20–7.46 (m, 9 H) ppm. GC–MS: m/z (%) = 168 (100) [M]$^+$, 152 (82), 83 (41).

4-Methoxy-4′-methylbiphenyl (9f): Colourless solid. Yield: 0.027 g (40%). M.p. 106–108 °C (ref.[8f] 107–108 °C). ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C): δ = 2.37 (s, 3 H), 3.83 (s, 3 H), 6.95 (d, J = 8.8 Hz, 2 H), 7.21 (d, J = 8.0 Hz, 2 H), 7.44 (d, J = 8.0 Hz, 2 H), 7.50 (d, J = 8.8 Hz, 2 H) ppm. GC–MS: m/z (%) = 198 (100) [M]$^+$, 183 (86), 155 (53).

4-Fluoro-4′-methoxybiphenyl (10b): Colourless solid. Yield: 0.029 g (42%). M.p. 84–86 °C. ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C): δ = 3.83 (s, 3 H), 6.96 (d, J = 8.8 Hz, 2 H), 7.08 (t, J = 8.8 Hz, 2 H), 7.36–7.55 (m, 4 H) ppm. GC–MS: m/z (%) = 202 (99) [M]$^+$, 187 (97), 159 (100), 133 (89).

3-Phenylthiophene (11a): Colourless solid. Yield: 0.013 g (24%). M.p. 76–78 °C. ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C): δ = 7.25–7.46 (m, 6 H), 7.53–7.64 (m, 2 H) ppm. GC–MS: m/z (%) = 160 (100) [M]$^+$, 115 (68).

4-(3-Thienyl)anisole (11b): Colourless solid. Yield: 0.016 g (24%). M.p. 127–129 °C. ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C): δ = 3.83 (s, 3 H), 6.93 (d, J = 8.8 Hz, 2 H), 7.34 (br. abs, 3 H), 7.52 (d, J = 8.8 Hz, 2 H) ppm. GC–MS: m/z (%) = 190 (100) [M]$^+$, 175 (99), 147 (73).

4-Nitrostyrene (12c): Pale yellow oil. Yield: 0.030 g (60%). ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C): δ = 5.50 (d, J = 10.8 Hz, 1 H), 5.93 (d, J = 17.4 Hz, 1 H), 6.78 (dd, J = 17.4 and 10.8 Hz, 1 H), 7.53 (d, J = 8.0 Hz, 2 H), 8.18 (d, J = 8.0 Hz, 2 H) ppm. GC–MS: m/z (%) = 149 (100) [M]$^+$, 119 (88), 103 (80), 91 (91), 77 (95).

4-*tert*-Butylstyrene (12e): Colourless oil. Yield: 0.032 g (43%). ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C): δ = 1.32 (s, 9 H), 5.19 (d, J = 10.8 Hz, 1 H), 5.70 (d, J = 17.6 Hz, 1 H), 6.70 (dd, J = 17.6 and 10.8 Hz, 1 H), 7.35 (s, 4 H) ppm. GC–MS: m/z (%) = 160 (72) [M]$^+$, 145 (98), 117 (100), 105 (69), 91 (61), 77 (53).

4-Methoxystyrene (12b): Colourless oil. Yield: 0.019 g (41%). ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C): δ = 3.81 (s, 3 H), 5.12 (d, J = 10.8 Hz, 1 H), 5.60 (d, J = 17.6 Hz, 1 H), 6.66 (dd, J = 17.6 and 10.8 Hz, 1 H), 6.86 (d, J = 8.6 Hz, 2 H), 7.34 (d, J = 8.6 Hz, 2 H) ppm. GC–MS: m/z (%) = 134 (100) [M]$^+$, 119 (89), 91 (96), 65 (63).

4-Methylstyrene (12f): Colourless oil. Yield: 0.029 g (36%). ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C): δ = 2.34 (s, 3 H), 5.17 (d, J = 10.8 Hz, 1 H), 5.69 (d, J = 17.6 Hz, 1 H), 6.69 (dd, J = 17.6 and 10.8 Hz, 1 H), 7.12 (d, J = 8.0 Hz, 2 H), 7.30 (d, J = 8.0 Hz, 2 H) ppm. GC–MS: m/z (%) = 118 (100) [M]$^+$, 91 (58).

ESI-MS: All experiments were performed with a commercially available quadrupole mass spectrometer fitted with an electrospray ion source. The mixtures specified in Table 3 were dissolved in 1,4-dioxane and the solution was directly introduced into the mass spectrometer ion source by use of a Rheodyne injector with a 20 µL sample loop. The mobile phase flow (acetonitrile/water, 70:30 v/v, 100 µL min^{-1}) was delivered to the vaporization nozzle of the electrospray ion source with the aid of a P2000 HPLC pump and nitrogen was employed as both a drying and a nebulizing gas. The instrument was operated in the positive ion mode (ESI+). The typical ESI conditions used were: probe tip voltage of 3 kV, capillary temperature of 160 °C and skimmer cone voltage of 30 eV. Typically 10–20 spectra scans were performed. Theoretical isotope patterns were calculated by use of the *Isoform* programme. All the mass acquisitions shown in Table 3 were repeated with the skimmer cone voltage set at 10 eV and 80 eV, but the best spectra were obtained at 30 eV.

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[14] Benzenediazonium tetrafluoroborate (**2a**) was coupled with benzeneboronic acid in a THF/MeOH mixture (1:1) in the presence of 5 mol-% of Pd^0 complex **1** at room temperature for one hour to afford a 97% yield of biphenyl.

[15] Mastrorilli et al. (Ref.[4p]) have postulated that the BF$_3$ formed could be responsible for unsatisfactory conversions since its reaction with PhBF$_3$K gives the inactive PhBF$_2$ in Suzuki–Miyaura cross-couplings. The detrimental effect of BF$_3$ was in that case solved by the addition of MeOH as a cosolvent. However, in our catalytic system the use of MeOH or mixtures of MeOH/1,4-dioxane resulted in decomplexation and further loss of Pd^0 complex **1**.

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