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# *trans*-Dichlorobis(XPhos)palladium(II) Precatalyst for Suzuki–Miyaura Cross-Coupling Reactions of Aryl/Vinyl Sulfonates/Halides: Scope, Mechanistic Study, and Synthetic Applications

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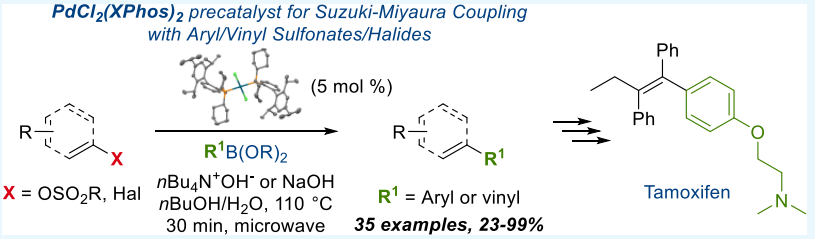


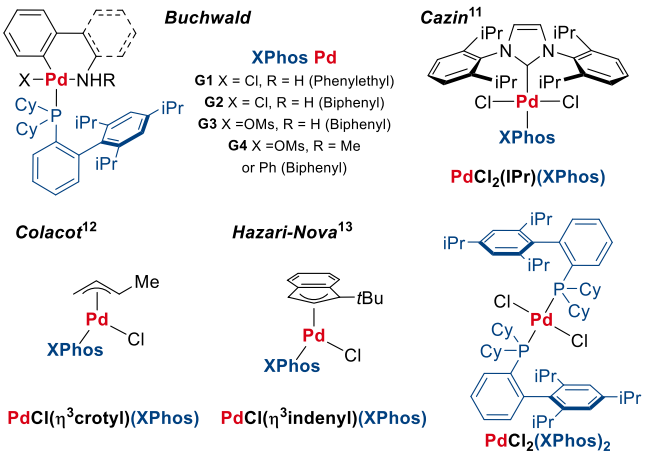

**ABSTRACT:** Suzuki–Miyaura cross-coupling reactions of aryl/vinyl sulfonates/halides with various boron species were performed using an easily available *trans*-dichlorobis(XPhos)palladium(II) precatalyst. Under microwave assistance, more than 30 coupling products were obtained with yields ranging from 23 to 99%, including the synthesis of two bioactive compounds, dubamine and tamoxifen. A mechanistic investigation of the Suzuki–Miyaura reaction was conducted notably by nuclear magnetic resonance (NMR) and high-resolution mass spectroscopy, revealing the nature of the active $Pd^0$ species and of the reducing entity.

## INTRODUCTION

The Suzuki–Miyaura coupling (SMC) reaction has become the most important and more widely employed method for building $C_{sp2}$–C bonds.[1] To improve its efficacy and expand its scope, various bulky ligands[2] have been developed such as Buchwald's dialkylbiarylphosphines.[3] Among them, the 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl ligand, so-called XPhos, has demonstrated its efficiency several times in SMC and in related cross-coupling reactions.[4] This bulky phosphine ligand was generally used together with palladium(II) salts, such as $Pd(OAc)_2$.[5] The resulting mixture *in situ* formed XPhos-$Pd^{II}$ complex(es), which evolved into the active $Pd^0$ species upon spontaneous reduction or upon exposure to a base.[6] However, prestirring the ligand and the Pd precursor could have deleterious effects on cross-coupling reactions considering the potential formation of dinuclear[6] and polynuclear metal complexes and clusters.[7] To avoid such problems, well-defined preformed palladium complexes, i.e., precatalysts,[8] have been successfully developed.

Combining the effectiveness of dialkylbiarylphosphine ligands and the advantages of precatalysts, Buchwald et al. have thus developed XPhos-based palladacycle complexes (Scheme 1) for coupling challenging boronic acid partners in SMC and other cross-coupling reactions.[9] Despite their excellent catalytic activities, these palladacycle-based precatalysts suffer from some drawbacks, such as their high temperature of activation (**Pd G1**)[9b] and low stability (**Pd G2**)[9c] or the genotoxicity of the resultant carbazole by-product[10] (**Pd G2-G4**) and more generally their 3–4 step

**Scheme 1. Precatalysts Containing the XPhos Ligand**

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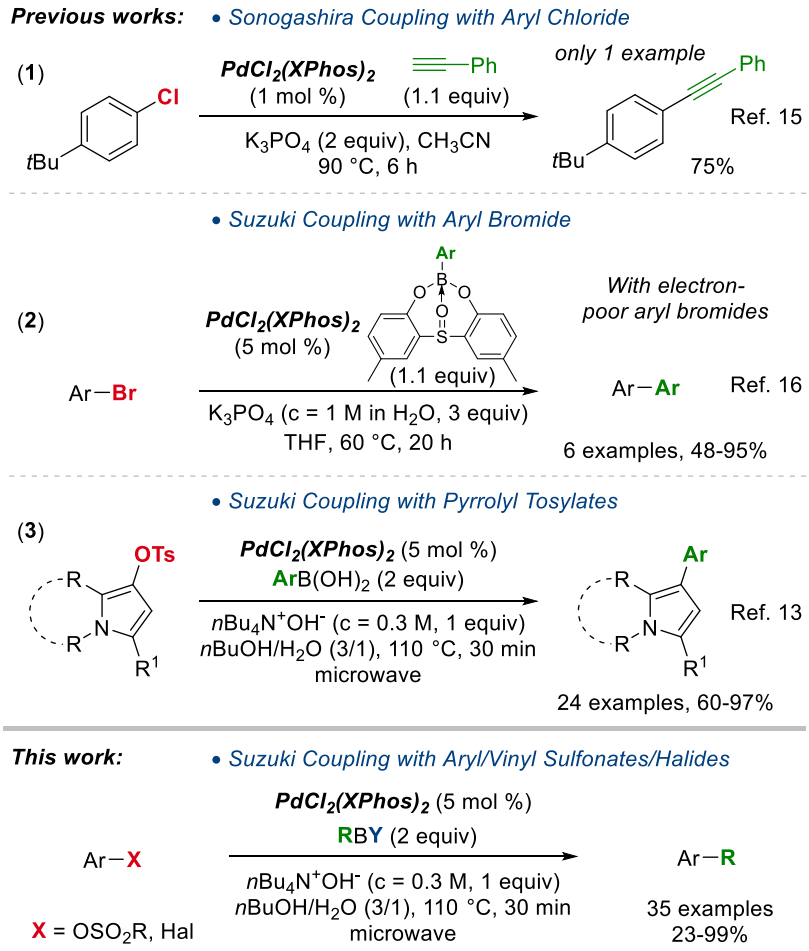
**Scheme 2. Palladium(II) Di(XPhos) Dichloride as the Precatalyst for Cross-Coupling Reactions**




synthesis even if they are now commercially available. Alternative precatalysts have thus been envisaged by combining XPhos and *N*-heterocyclic carbene or $\pi$-allyl ligands (Scheme 1). $PdCl_2$(IPr)(XPhos) developed by Cazin et al.[11] was an effective catalyst for aqueous SMC of aryl chloride at a low catalyst loading (0.03 mol %). PdCl($\eta^3$crotyl)(XPhos) introduced by Colacot et al.[12] was more active than XPhos-Pd **G3** in the same coupling with heteroaryl chlorides. A closely related PdCl($\eta^3$indenyl)(XPhos) precatalyst was developed by Hazari and Nova[13] showing comparable performance to the best-known systems on SMC with heteroaryl partners.

Surprisingly, the simplest precatalyst $PdCl_2(XPhos)_2$ (Scheme 1), easily prepared in a quantitative manner by mixing $PdCl_2(MeCN)_2$ and XPhos (2 equiv) in acetonitrile at reflux,[14] has almost never been used in palladium-catalyzed cross-coupling reactions, despite its obvious analogy to *trans*-dichlorobis(triphenylphosphine)palladium(II), one of the earliest and commonly used $L_2PdCl_2$ precatalyst.[15]

The first description of $PdCl_2(XPhos)_2$ was provided by Jong et al. in 2015 during copper-free Sonogashira cross-coupling investigations, where it was only used for comparison to more elaborated dialkylbiarylphosphine ligands (Scheme 2, eq 1).[16] In 2018, $PdCl_2(XPhos)_2$ was also used as a precatalyst in Suzuki−Miyaura coupling reactions between sulfoxide-based boronates and few electron-poor aryl bromide partners (Scheme 2, eq 2).[17] In our hand, $PdCl_2(XPhos)_2$ appeared salvaging in the development of the challenging Suzuki−Miyaura cross-coupling reaction with various 2-pyrrolyl tosylates (Scheme 2, eq 3), while mixtures of the XPhos ligand or other ligands with various $Pd^{II/0}$ sources led to unreproducible or poor yields.[14] As a result, 2-aryl pyrrole derivatives were obtained in good to excellent yields, allowing the completion of the total synthesis of the rhazinilam natural product.

The excellent results obtained from rhazinilam total synthesis inspired us to further explore the reactivity of $PdCl_2(XPhos)_2$ as a precatalyst and also to understand why this catalyst was so efficient and how it could act. We report here its application to Suzuki−Miyaura cross-coupling reactions of aryl and vinyl sulfonates or halides, and to the synthesis of relevant bioactive molecules. Moreover, a mechanistic investigation of the Suzuki−Miyaura reaction was conducted, notably by NMR and high-resolution mass spectroscopy.

## RESULTS AND DISCUSSION

As almost unknown (see Scheme 2), we started looking at the reactivity of $PdCl_2(XPhos)_2$, and especially for the best partners $PdCl_2(XPhos)_2$ was able to couple with in the Suzuki−Miyaura reaction. For that, we first engaged simple toluyl sulfonates and halides with a series of typical phenyl boron species under the conditions we set up for pyrrolyl sulfonates[14] (Scheme 3). Whatever the partners, the expected product 4-methyl-1,1′-biphenyl **2a** was obtained with yields higher than 70%. Coupled with phenylboronic acid, toluyl tosylate (Ts), *para*-methoxybenzenesulfonate (Mbs), and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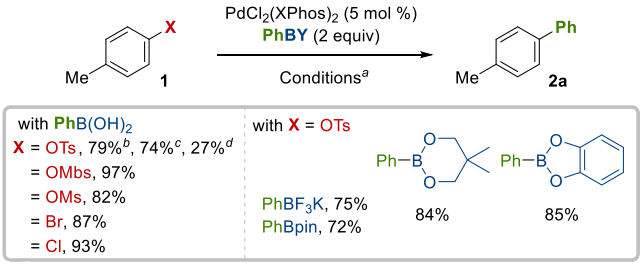
**Scheme 3. Variation of the Leaving Group and of the Boron Species in the Suzuki–Miyaura Coupling using $PdCl_2(XPhos)_2$ as the Precatalyst**

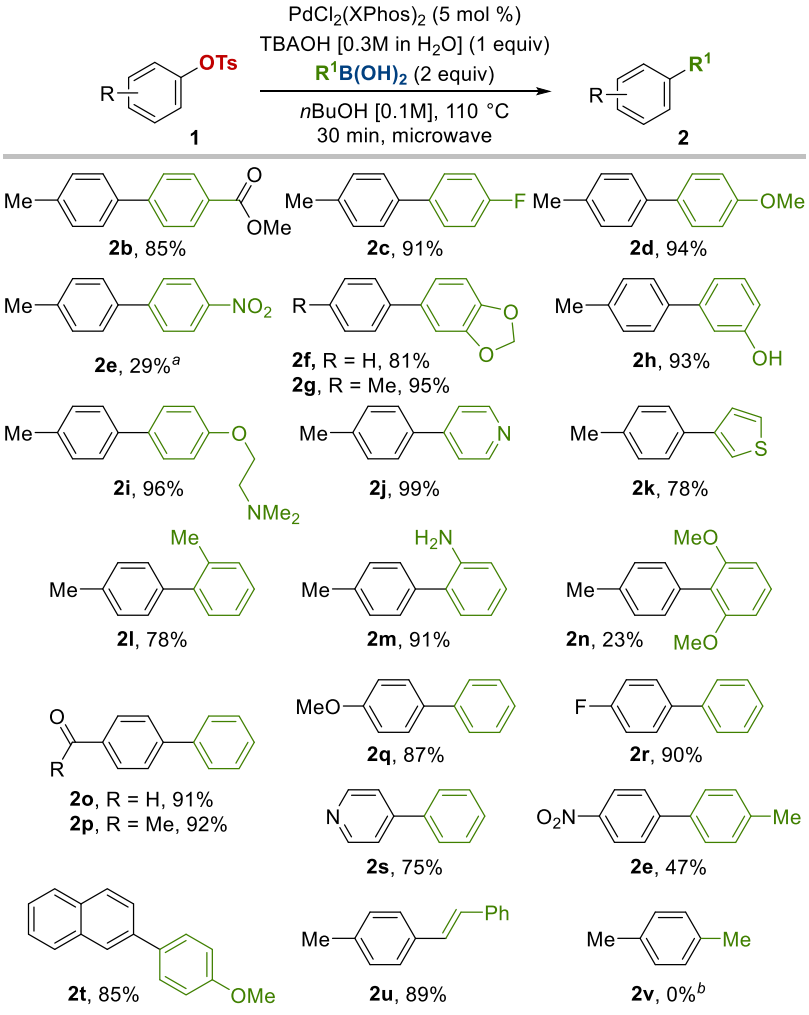



[a]TBAOH, *n*-BuOH/$H_2O$, 110 °C, 30 min, MW. [b]Yields of isolated pure products. [c]With 1 mol % of the catalyst. [d]With a mixture of $PdCl_2(MeCN)_2$/XPhos ligands.

mesylate (Ms) partners gave good to excellent results, especially for the Mbs group (97%). As expected from the use of such kind of ligand,[3] the corresponding bromide afforded the coupling product **2a** in excellent yield (87%), and even the more challenging chloride partner provided **2a** in a similar yield (93%). As the boron partner nature is known to be important in the Suzuki–Miyaura coupling,[18] we briefly surveyed this aspect. Boron reagents, more stable than boronic acids, were as effective under our reaction conditions.[18] With the less reactive toluyl tosylate, neopentylglycol, or catechol boronic esters proved to be the most efficient, yielding **2a** in 85%. Phenylboronic pinacol ester was slightly less effective (72%), probably for steric reasons, as was potassium phenyltrifluoroborate which provided similar yields (75%). It is worth noting that the SMC efficiency was weakly affected by decreasing the catalyst loading to 1 mol %, leading to **2a** with 74% of yield from the tosylate partner (79% with 5 mol %). Finally, the control experiment run with a mixture of $PdCl_2(MeCN)_2$ and XPhos afforded **2a** from toluyl tosylate in a poor 27% yield (79% with $PdCl_2(XPhos)_2$), confirming that the $PdCl_2(XPhos)_2$ precatalyst prevailed over its progenitors under our reaction conditions. Of note, without microwave activation, the SMC proceeds as well but with a long reaction time (18 h at 110 °C in an oil bath vs 30 min under microwave) but generally with lower yields (see the Supporting Information).

Despite better results achieved with arylOMbs and boronic esters, we selected aryl tosylates and boronic acids, the most challenging partners, to tackle the efficiency of $PdCl_2(XPhos)_2$

**Scheme 4. Scope of the Palladium-Catalyzed Suzuki–Miyaura Coupling of Aryl Tosylates with Various Boronic Acids**




[a]NMR yield. [b]Degradation occurred.



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as a precatalyst in the Suzuki−Miyaura reaction. Various combinations of these partners were thus subjected to the same conditions to explore the scope of this SMC variant (Scheme 4). The use of the $PdCl_2(XPhos)_2$ precatalyst demonstrated good generality and efficiency (88% in average), except for a few cases (see below). The conditions proved compatible with a wide range of functional groups such as ester, aldehyde, acetal, ether, fluoride, free hydroxy, and even free amine. Heteroaromatics, including the strongly coordinating pyridine, and alkenes also proved compatible.

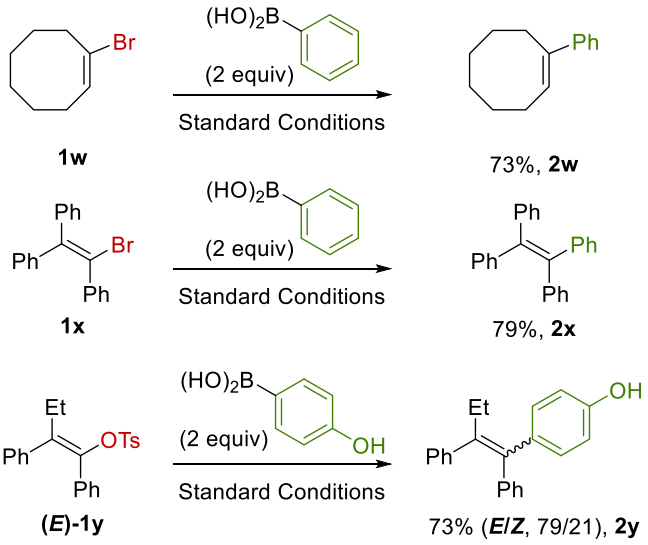
SMCs are known to be sensitive to electronic effects, which negatively impacts the reaction efficiency at the oxidative addition step for electron-rich aryl halides and related species, and at the transmetalation step for electron-poor boronic derivatives. Although the use of bulky biphenyl ligands should minimize such effects,[3b] we looked at the effects substituents may have in the presence of the $PdCl_2(XPhos)_2$ precatalyst as it is unknown. Therefore, the simple toluyl tosylate was coupled with a variety of phenylboronic acids carrying electron-withdrawing or -donating groups under the above-mentioned conditions. *para*-Alkoxylated phenylboronic acids gave slightly better yields than their *para*-deactivated counterparts (see **2d**, **2g**, **2i** vs **2b**, **2c**, **2h**), as expected from their higher nucleophilicity, which increases the transmetalation rates. No significant difference could be observed in the coupling of phenyl tosylates carrying electron-donating or -withdrawing substituents (see **2f**, **2o**−**2t**). In contrast, the nitro group either on the boronic acid or on the tosylate induced lower yields and the formation of undefined by-products (see **2e**). Despite its coordination ability, pyridine either on the boronic acid or on the tosylate led to high to quantitative yields of the coupling products (see **2j**, **2s**). The fragile thiophene boronic acid gave lower yields, as well as undefined by-products (see **2k**). The effect of steric hindrance was also briefly examined. From mono *ortho*-substituted phenylboronic acids, coupling products **2l**, **2m** were obtained in high yields. In contrast, 2,6-dimethoxyphenyl boronic acid reacted slowly and only gave low conversion and yield of the corresponding coupling product **2n**. The latter result is quite surprising as bulky biphenyl ligands are known for their efficiency in coupling hindered partners.[19] Finally, the (*E*)-2-phenylvinylboronic acid partner reacted efficiently under our reaction conditions, as demonstrated by the formation of the stilbene derivative **2u** in high yield, while methylboronic acid failed to afford coupling product **2v**.

We then briefly evaluated the compatibility of vinyl partners to our SMC reaction conditions (Scheme 5). Satisfyingly, coupling compounds **2w**-**2y** were obtained in good yields ranging from 73 to 79%, from vinyl bromide (**1w**, **1x**) or tosylate ((*E*)-**1y**) derivatives.

Overall, simple $PdCl_2(XPhos)_2$, almost quantitatively prepared in a single step, proved to be a useful and efficient catalyst for SMC of aryl and vinyl sulfonates. However, the way it acts in solution is unknown, we thus investigated its behavior in solution and in the presence of reagents under the set-up conditions.

The precise understanding of palladium-catalyzed cross-coupling reactions has greatly benefited from the detailed investigations mostly performed by Jutand et al., who combined electrochemical and NMR techniques.[20] Applying those techniques to the SMC reaction, they were able to identify each elementary step of the catalytic cycle and demonstrated the key influence of several parameters on these

**Scheme 5. $PdCl_2(XPhos)_2$ as the Precatalyst in the Suzuki−Miyaura Coupling of Vinyl Partners**




elementary steps, complicating the whole cycle.[21] In the same vein, Jutand and Grimaud have recently reported the study of *in situ* formation of XPhos-$Pd^0$ complexes and their reactivity in oxidative addition with aryl halide using cyclic voltammetry and NMR techniques.[6] This work revealed the complexity of the process starting from a mixture of XPhos ligand and $Pd^{II}(OAc)_2$ with the formation of diverse $Pd^0$ species and $Pd^I$−$Pd^I$ dimers.

As we started here from a preformed catalyst, we wondered if such complexity would still occur, and if not, what would be the key reducing step converting the $Pd^{II}$ precatalyst into which active $Pd^0$ species. To gain mechanistic insights into the SMC reaction starting from the $PdCl_2(XPhos)_2$ precatalyst, we monitored the evolution of a solution containing $PdCl_2(XPhos)_2$ in the presence of a base by combining $^{31}P$, $^1H$ NMR spectroscopies and high-resolution mass techniques (Figure 1).

The $PdCl_2(XPhos)_2$ complex was solubilized under argon in *n*-butanol at 0.1 M and this solution was diluted with $CDCl_3$ for $^1H$ NMR monitoring. $^{31}P$ NMR analysis of this mixture indicated a single signal at 45.2 ppm corresponding to the precatalyst (black spectrum, $t$ = 0 min, in Figure 1 left inset).

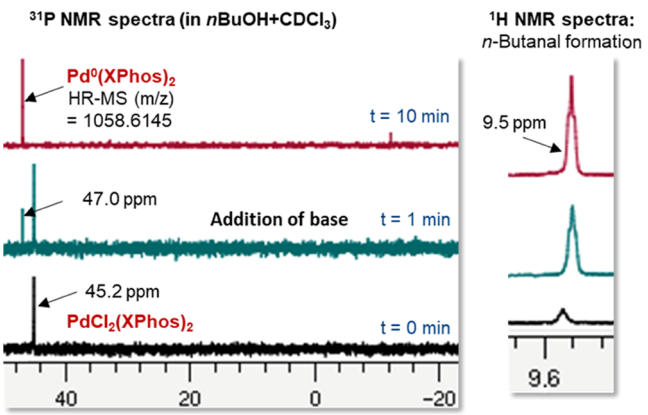



**Figure 1.** $^{31}P$ and $^1H$ NMR monitoring of the $PdCl_2(XPhos)_2$ reductive elimination.



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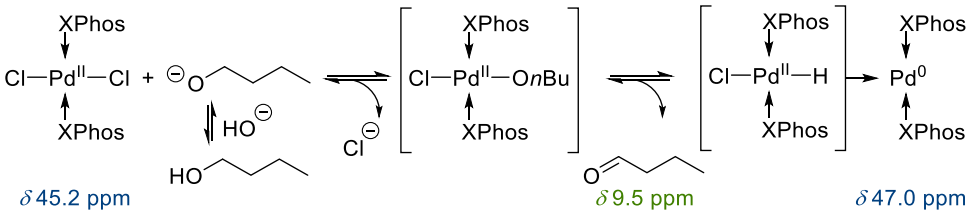
**Scheme 6. $PdCl_2(XPhos)_2$ *In Situ* Transformation as Established by $^{31}P$ and $^{1}H$ NMR Monitoring (Species in Bracket Could not be Detected)**



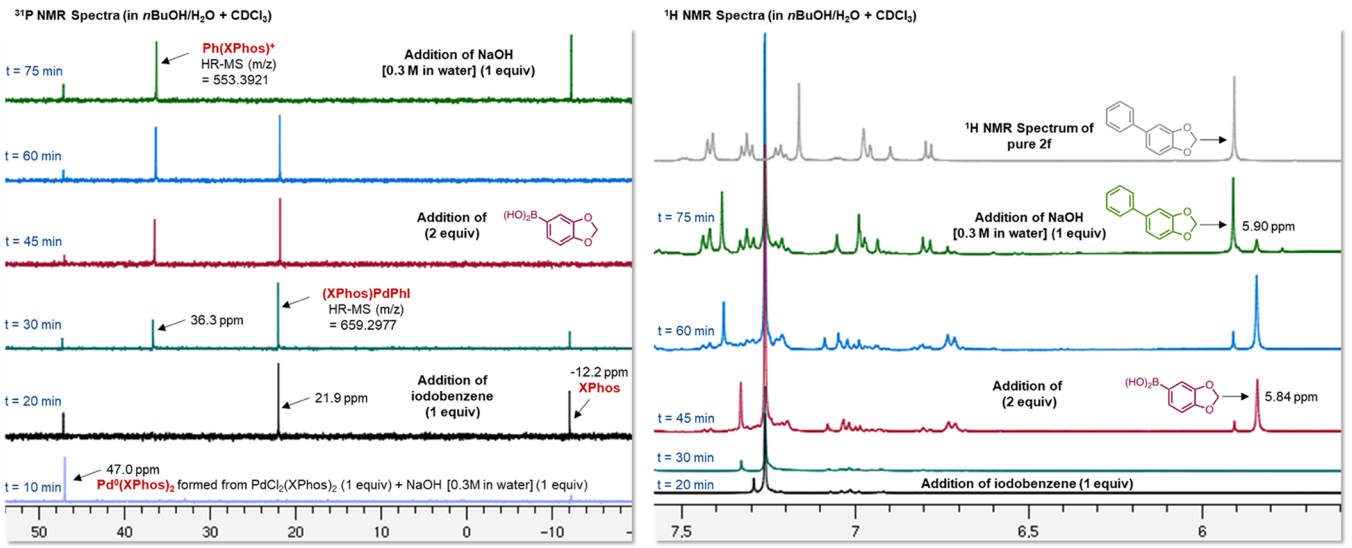




**Figure 2.** $^{31}P$ and $^{1}H$ NMR monitoring of the Suzuki−Miyaura coupling between iodobenzene and 1,3-benzodioxole-5-boronic acid using $PdCl_2(XPhos)_2$ as the precatalyst.

The addition of 1 equiv of an aqueous solution of base (TBAOH or NaOH) and heating at 110 °C induced the rapid formation of a new species at 47.0 ppm (blue-green spectrum, $t$ = 1 min). Irrespective of the nature of the base, the system evolved toward this species with complete disappearance of the initial complex within minutes (red spectrum, $t$ = 10 min). Further monitoring over 60 min showed that the system remained unchanged. Interestingly, the appearance of the 47.0 ppm signal in $^{31}P$ NMR was accompanied by the concomitant formation of a triplet signal at 9.56 ppm (Figure 1, right inset) in the $^{1}H$ NMR spectrum. The latter could be assigned to *n*-butanal. These observations strongly suggested that *n*-butanol is the reducing agent of the initial $Pd^{II}$ complex into a single $Pd^0$ species. This rapid formation and the presence of a single $Pd^0$ species is in sharp contrast with what was observed starting from $Pd(OAc)_2$ and excess XPhos.[6] To confirm that *n*-butanol is the reducing species, the same experiments in the presence of TBAOH or NaOH were performed with *tert*-butanol as the solvent. In both cases, $^{31}P$ and $^{1}H$ NMR monitoring did not show any evolution of the $PdCl_2(XPhos)_2$ signal at 45.2 ppm.

To identify the $Pd^0$ species formed in *n*-butanol, high-resolution mass spectra (ESI-TOF, HR-MS) of the solution were recorded. A set of peaks typical for the isotopic distribution of a palladium entity was observed at an m/z exact mass of 1058.6145. This value accounts for a chemical formula of $C_{66}H_{98}P_2Pd$, which corresponds to the reduced palladium complex $Pd^0(XPhos)_2$.

This data set clearly indicates that in *n*-butanol, $PdCl_2(XPhos)_2$ is rapidly converted to $Pd^0(XPhos)_2$ in the presence of the base, presumably upon chloride exchange on $Pd^{II}$ with *n*-butanoate, in situ formed upon base addition, followed by $\beta$-H-elimination (Scheme 6). It is interesting to note that the solution of the so-formed $Pd^0(XPhos)_2$ species, although stable, contains a small amount of free XPhos ($\delta$ −12.2 ppm, $^{31}P$ NMR). This observation suggests an equilibrium between the di- and mono-ligated Pd°, in line with what is known for this type of bulky ligand to ensure oxidative addition[19] and with the recent kinetic study demonstrating that the dissociation of $Pd^0(XPhos)_2$ is rate-limiting in SMC.[6]

To look at the reactivity of the so-formed $Pd^0(XPhos)_2$ species, we added toluyl sulfonate while continuously monitoring the complete cycle of the Suzuki coupling. Unfortunately, all attempts to investigate the coupling with sulfonylated partners by $^{31}P$ NMR were unsuccessful due to the formation of insoluble species making NMR monitoring impossible. Facing this situation, we decided to use iodobenzene as a coupling partner. Rewardingly, $^{31}P$ and $^{1}H$ NMR spectroscopies allowed monitoring of the coupling with this reagent and as before, intermediate species could also be analyzed by high-resolution mass spectrometry (Figure 2).

To facilitate the reading of $^{1}H$ NMR spectra, NaOH and the 5-(1,3-benzodioxolyl)boronic acid coupling partner were used. Addition of 1 equiv of iodobenzene to the $Pd^0(XPhos)_2$ solution obtained above (Figure 2, $^{31}P$ purple spectrum, $t$ = 10 min), led in 10 min to the formation of a new species at 21.9 ppm concomitantly with another signal at −12.2 ppm, typical of free XPhos (black spectrum, $t$ = 20 min). The chemical shift of the new signal was in close agreement with the one already reported by Skrydstrup[22] for the (XPhos)(I)-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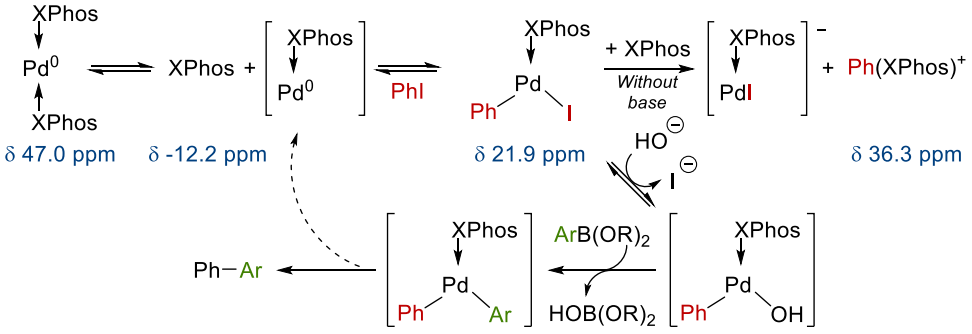
**Scheme 7. Proposed Mechanism for the Suzuki−Miyaura Coupling Starting from the $PdCl_2(XPhos)_2$ Precatalyst (Species in Bracket Could not be Detected)**




PdPh complex ($^{31}P$, $\delta$ = 21.4 ppm). HR-MS analysis confirmed its nature, with a mass of 659.2977, which corresponded to the (XPhos)Pd($C_6H_5$) complex, that is the oxidative addition product in which iodide was lost under MS conditions.[23] Without further addition, a new signal at 36.3 ppm appeared within 10 min and increased until the complete disappearance of the free XPhos signal (blue-green and red spectra, $t$ = 30 and 45 min). HR-MS analysis at that stage revealed a mass of 553.3921 corresponding to a $C_{39}H_{54}P$ formula. The latter is consistent with the phosphonium derivative $Ph(XPhos)^+$, which could be produced from reductive elimination of the oxidative addition complex in the absence of boronic acid and a base.

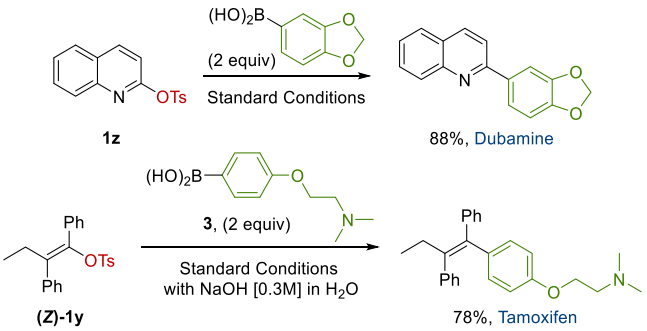
The addition of 2 equiv of 5-(1,3-benzodioxolyl)boronic acid did not induce a change in the system after another 15 min of stirring (blue spectrum, $t$ = 60 min). However, the addition of 1 equiv of a base caused the disappearance of the oxidative addition complex signal at 21.9 ppm (green spectrum, $t$ = 75 min), in agreement with transmetalation and reductive elimination processes both known to involve Pd(OH) intermediates.[21c] The XPhos signal also reappeared, due to the release of the ligand, while the already formed $Ph(XPhos)^+$ signal at 36.3 ppm remained persistent.

Parallel $^1H$ NMR monitoring allowed looking at the evolution of the boronic acid partner through its typical 1,3-benzodioxolyl methylene signal at 5.84 ppm for 5-boronic acid and at 5.90 ppm for the 5-coupled product **2f** (Figure 2, bottom, with color code identical to the $^{31}P$ spectra). As observed in $^{31}P$ NMR, the signal of boronic acid persisted for 30 min until the addition of NaOH (1 equiv; $^1H$ green spectrum, $t$ = 75 min). At this moment, this signal disappeared and concomitantly, a new signal at 5.90 ppm corresponding to **2f** appeared (see the $^1H$ gray spectrum of the pure compound for comparison).

In the $^1H$ NMR, traces of the coupling product **2f** could already be detected before NaOH addition (red and blue spectra in Figure 2). This **2f** formation was probably promoted once boronic acid was added to the slight excess of NaOH, unintentionally introduced during the first base addition necessary for the *in situ* production of the active catalytic species (see Figure 1). This combined information allowed establishing the full mechanism for the present SMC reaction catalyzed by the preformed $PdCl_2(XPhos)_2$ (Scheme 7).

To exemplify the benefit of this SMC reaction based on the $PdCl_2(XPhos)_2$ precatalyst, we applied these conditions to the synthesis of two bioactive compounds (Scheme 8). First, the natural alkaloid dubamine, exhibiting an antiviral effect against cold,[24] was readily prepared in 88% yield starting from quinolyl

**Scheme 8. Application of the Suzuki Coupling Conditions to the Synthesis of Dubamine and Tamoxifene**




tosylate **1z** by coupling with 3,4-methylene-dioxyphenylboronic acid. We then focused our attention on the challenging synthesis of tamoxifen, a drug used since the 1970s for the treatment of breast cancer and as an antiestrogenic agent.[25] The latter was readily obtained in a high yield from *Z*-vinyl tosylate (*Z*)-**1y** and boronic acid **3** as coupling partners, despite the hindrance of the former partner. Sodium hydroxide was used instead of TBAOH to minimize the formation of by-products.

## CONCLUSIONS

In conclusion, we have demonstrated here that the easily available $PdCl_2(XPhos)_2$ was an efficient precatalyst for Suzuki−Miyaura cross-coupling reactions of aryl or vinyl sulfonates/halides with various boron species (35 examples, 23−99%). The conditions proved compatible with a large palette of functional groups, including free OH, free $NH_2$, and the pyridine moiety, the latter two being strongly coordinating. The mechanism of SMC starting from $PdCl_2(XPhos)_2$ was also investigated revealing the nature of the active $Pd^0$ species and of the reducing entity. Furthermore, our SMC reaction conditions allowed the synthesis of two bioactive molecules.

## EXPERIMENTAL SECTION

**General Information.** Proton ($^1H$ NMR) and carbon ($^{13}C$ NMR) nuclear magnetic resonance spectra were recorded on 300, 400, or 500 MHz instruments. The chemical shifts are given in part per million (ppm) on the delta scale. The solvent peak was used as reference values. For $^1H$ NMR, $CDCl_3$ = 7.26 ppm. For $^{13}C$ NMR, $CDCl_3$= 77.16 ppm. Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, b = broad), coupling constants ($J$ in Hz) and integration, and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carbons with the same chemical shift as follows: chemical shift (*x* carbons). Infrared spectra were recorded neat. Wavelengths of maximum absorbance ($\nu_{max}$) are quoted in wavenumbers ($cm^{-1}$). High-resolution mass spectrum (HR-MS) data were recorded on a microTOF spectrometer equipped with an orthogonal electrospray interface (ESI). The parent ions $[M]^+$, $[M + H]^+$, $[M + K]^+$ $[M + Li]^+$, or $[M + Na]^+$ are quoted. Analytical thin-layer chromatography (TLC) was carried out on silica gel 60 $F_{254}$ plates with visualization by ultraviolet light, cerium ammonium molybdate, or potassium permanganate dip. Flash column chromatography was carried out using $SiO_2$ 60 (40−63 $\mu$m) and the procedures included the subsequent evaporation of solvents in vacuo. All commercially available reagents were used as received, all extractive procedures were performed using technical grade solvents, and all aqueous solutions were saturated unless details are given. All air- and moisture-sensitive reactions were carried out using flame-dried glassware under an argon atmosphere. A microwave monomode CEM Discover SP was used for all of the SMC (power 300 W) reactions. All aryl sulfonates **1** used were known compounds and were prepared from the commercially available phenol derivatives according to the reported procedure.[26] (*E*)-1-Bromocyclooct-1-ene **1w** and bromotriphenylethylene **1x** were synthesized following a procedure described in the literature.[27] Boronic acid **3** was prepared in two steps from 4-iodophenol using a reported procedure.[28]

**General Procedure for Suzuki−Miyaura Coupling Reactions.** A microwave reactor (10 mL) was successively loaded with the corresponding aryl/vinyl sulfonate or halide (1 equiv), $PdCl_2(XPhos)_2$ (5 mol %), and arylboronic acid (2 equiv). The tube was flushed with argon three times. Then, argon degassed *n*-BuOH (*c* = 0.1 M) was added, and the mixture was stirred at room temperature for 5 min. An argon degassed aqueous solution of TBAOH or NaOH [0.3 M] (1 equiv) was then added. The tube was placed in the microwave (300 W) and the reaction mixture was stirred at 110 °C for 30 min. The reaction was quenched with water (2 mL) and diluted with EtOAc (5 mL). The layers were separated, and the aqueous layer was extracted twice with EtOAc (5 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography (cyclohexane/EtOAc or pentane/ether) on silica gel to afford the desired product.

*4-Methyl-1,1′-biphenyl* (***2a***). Prepared following the general procedure in 79% yield (199 mg, 1.18 mmol) from *p*-tolyl 4-methylbenzenesulfonate (393.5 mg, 1.5 mmol) and phenylboronic acid. $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.55−7.52 (m, 2H), 7.47−7.43 (m, 2H), 7.40−7.35 (m, 2H), 7.30−7.25 (m, 1H), 7.22−7.18 (m, 2H), 2.35 (s, 3H); $^{13}$C NMR ($CDCl_3$, 126 MHz) $\delta$ 141.3, 138.5, 137.2, 129.6 (2C), 128.8 (2C), 127.1 (2C), 127.1 (2C), 127.1, 21.3. Consistent with the literature data.[29]

Prepared following the general procedure in 97% yield (12.6 mg, 0.075 mmol) from *p*-tolyl 4-methoxybenzenesulfonate (21.6 mg, 0.077 mmol) and phenylboronic acid.

Prepared following the general procedure in 82% yield (15.8 mg, 0.094 mmol) from *p*-tolyl methanesulfonate (21.3 mg, 0.114 mmol) and phenylboronic acid.

Prepared following the general procedure in 87% yield (23.7 mg, 0.140 mmol) from 1-bromo-4-methylbenzene (27.8 mg, 0.162 mmol) and phenylboronic acid.

Prepared following the general procedure in 93% yield (25.2 mg, 0.150 mmol) from 1-chloro-4-methylbenzene (20.4 mg, 0.161 mmol) and phenylboronic acid.

Prepared following the general procedure in 75% yield (9.0 mg, 0.053 mmol) from *p*-tolyl 4-methylbenzenesulfonate (18.7 mg, 0.071 mmol) and potassium phenyltrifluoroborate.

Prepared following the general procedure in 72% yield (10.0 mg, 0.059 mmol) from *p*-tolyl 4-methylbenzenesulfonate (21.5 mg, 0.082 mmol) and phenylboronic acid pinacol ester.

Prepared following the general procedure in 84% yield (5.7 mg, 33.9 $\mu$mol) from *p*-tolyl 4-methylbenzenesulfonate (10.5 mg, 40.0 $\mu$mol) of and 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane.

Prepared following the general procedure in 85% yield (5.8 mg, 34.5 $\mu$mol) from *p*-tolyl 4-methylbenzenesulfonate (10.6 mg, 40.4 $\mu$mol) and 2-phenyl-1,3,2-benzodioxaborole.

*Methyl 4′-Methyl-[1,1′-biphenyl]-4-carboxylate* (***2b***). Prepared following the general procedure in 85% yield (17.6 mg, 0.078 mmol) from *p*-tolyl 4-methylbenzenesulfonate (24.0 mg, 0.091 mmol) and (4-(methoxycarbonyl)phenyl)boronic acid. $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 8.12−8.06 (m, 2H), 7.65 (dq, *J* = 8.5, 2.0 Hz, 2H), 7.56−7.50 (m, 2H), 7.30−7.26 (m, 2H), 3.94 (s, 3H), 2.41 (s, 3H); $^{13}$C NMR ($CDCl_3$, 126 MHz) $\delta$ 167.2, 145.7, 138.3, 137.2, 130.2 (2C), 129.8 (2C), 128.7, 127.2 (2C), 126.9 (2C), 52.3, 21.3. Consistent with the literature data.[30]

*4-Fluoro-4′-methyl-1,1′-biphenyl* (***2c***). Prepared following the general procedure in 91% yield (12.8 mg, 0.068 mmol) from *p*-tolyl 4-methylbenzenesulfonate (19.8 mg, 0.075 mmol) and (4-fluorophenyl)boronic acid. $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.53 (ddd, *J* = 8.8, 5.4, 2.7 Hz, 2H), 7.46−7.43 (m, 2H), 7.25 (d, *J* = 7.7 Hz, 2H), 7.15−7.09 (m, 2H), 2.40 (s, 3H); $^{13}$C NMR ($CDCl_3$, 126 MHz) $\delta$ 163.4, 161.4, 137.5, 137.2, 129.7 (2C), 128.6, 128.5 127.0 (2C), 115.8, 115.6, 21.2. Consistent with the literature data.[31]

*4-Methoxy-4′-methyl-1,1′-biphenyl* (***2d***). Prepared following the general procedure in 94% yield (15.7 mg, 0.079 mmol) from *p*-tolyl 4-methylbenzenesulfonate (22.2 mg, 0.084 mmol) and (4-methoxyphenyl)boronic acid. $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.80−7.76 (m, 2H), 7.73−7.70 (m, 2H), 7.51−7.47 (m, 2H), 7.25−7.21 (m, 2H), 4.11 (s, 3H), 2.65 (s, 3H); $^{13}$C NMR ($CDCl_3$, 126 MHz) $\delta$ 159.0, 138.1, 136.5, 133.8, 129.6 (2C), 128.1 (2C), 126.7 (2C), 114.3 (2C), 55.5, 21.2. Consistent with the literature data.[32]

*4-Methyl-4′-nitro-1,1′-biphenyl* (***2e***). Prepared following the general procedure in 47% yield (34.1 mg, 0.160 mmol) from 4-nitrophenyl 4-methylbenzenesulfonate (100 mg, 0.341 mmol) and *p*-tolylboronic acid (92.7 mg, 0.682 mmol). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.28 (d, *J* = 8.9 Hz, 2H), 7.72 (d, *J* = 9.0 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.33−7.28 (d, *J* = 9.0 Hz, 2H), 2.43 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 147.7, 145.0, 139.2, 136.0, 130.0 (2C), 127.6 (2C), 127.4 (2C), 124.3 (2C), 21.4.[29]

*5-Phenylbenzo[d][1,3]dioxole* (***2f***). Prepared following the general procedure in 81% yield (30.5 mg, 0.154 mmol) from *p*-tolyl benzenesulfonate (47 mg, 0.189 mmol) and 3,4-methylenedioxyphenylboronic acid. $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 7.55−7.50 (m, 2H), 7.46−7.38 (m, 2H), 7.33 (tt, *J* = 7.3, 1.3 Hz, 1H), 7.09−7.05 (m, 2H), 6.90 (dd, *J* = 7.4, 0.8 Hz, 1H), 6.01 (s, 2H); $^{13}$C NMR ($CDCl_3$, 126 MHz) $\delta$ 147.5, 146.4, 140.3, 135.0, 128.1 (2C), 126.3 (2C), 120.0, 108.9, 107.1, 100.5. Consistent with the literature data.[33]



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*5-(p-Tolyl)benzo[d][1,3]dioxole* (**2g**). Prepared following the general procedure in 95% yield (15.3 mg, 0.072 mmol) from *p*-tolyl 4-methylbenzenesulfonate (19.8 mg, 0.076 mmol) and 3,4-methylenedioxyphenylboronic acid. $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.44−7.37 (m, 2H), 7.22 (d, $J$ = 7.8 Hz, 2H), 7.08−7.01 (m, 2H), 6.87 (d, $J$ = 8.0 Hz, 1H), 5.99 (s, 2H), 2.38 (s, 3H); $^{13}$C NMR ($CDCl_3$, 126 MHz) $\delta$ 148.2, 146.9, 138.2, 136.8, 135.7, 129.6 (2C), 126.9 (2C), 120.5, 108.7, 107.7, 101.2, 21.2. Consistent with the literature data.[34]

*4′-Methyl-[1,1′-biphenyl]-3-ol* (**2h**). Prepared following the general procedure in 93% yield (12.2 mg, 0.066 mmol) from *p*-tolyl 4-methylbenzenesulfonate (18.6 mg, 0.071 mmol) and (3-hydroxyphenyl)boronic acid. $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.50−7.43 (m, 2H), 7.30 (t, $J$ = 7.9 Hz, 1H), 7.24 (d, $J$ = 8.0 Hz, 2H), 7.16 (dt, $J$ = 7.6, 1.3 Hz, 1H), 7.05 (t, $J$ = 2.1 Hz, 1H), 6.80 (ddd, $J$ = 8.1, 2.6, 1.0 Hz, 1H), 4.73 (d, $J$ = 9.5 Hz, 1H), 2.39 (s, 3H); $^{13}$C NMR ($CDCl_3$, 126 MHz) $\delta$ 155.9, 143.1, 137.9, 137.5, 130.1, 129.6 (2C), 127.1 (2C), 119.8, 114.0, (2C) 21.3. Consistent with literature data.[35]

*N,N-Dimethyl-2-((4′-methyl-[1,1′-biphenyl]-4-yl)oxy)-ethan-1-amine* (**2i**). Prepared following the general procedure in 96% yield (15.7 mg, 61.5 mmol) from *p*-tolyl 4-methylbenzenesulfonate (16.8 mg, 63.8 mmol) and (4-(2-(dimethylamino)ethoxy)phenyl)boronic acid (see the Supporting Information). White solid. mp = 83-86°C, TLC $Rf$ = 0.24 (DCM/EtOH 10%); IR (neat) $\nu_{max}$ 498, 576, 630, 678, 787, 843, 920, 1035, 1094, 1117, 1159, 1180, 1195, 1216, 1236, 1268, 1314, 1374, 1401, 1452, 1498, 1531, 1581, 1606, 2758, 2815, 2853, 2921; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.53−7.47 (m, 2H), 7.47−7.42 (m, 2H), 7.22 (d, $J$ = 7.8 Hz, 2H), 7.01−6.95 (m, 2H), 4.11 (t, $J$ = 5.8 Hz, 2H), 2.76 (t, $J$ = 5.7 Hz, 2H), 2.38 (s, 3H), 2.36 (s, 6H); $^{13}$C NMR ($CDCl_3$, 126 MHz) $\delta$ 158.2, 137.9, 136.4, 133.8, 129.4 (2C), 127.9 (2C), 126.6 (2C), 114.8 (2C), 66.0, 58.3, 45.9 (2C), 21.1; HR-MS 256.1694 ($C_{17}H_{21}NO + H^+$) calcd 256.1696.

*4-(p-Tolyl)pyridine* (**2j**). Prepared following the general procedure in 99% yield (18.1 mg, 0.107 mmol) from *p*-tolyl 4-methylbenzenesulfonate (28.0 mg, 0.107 mmol) and pyridin-4-ylboronic acid. $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 8.66−8.61 (m, 2H), 7.59−7.52 (m, 2H), 7.52−7.45 (m, 2H), 7.30 (d, $J$ = 7.8 Hz, 2H), 2.42 (s, 3H); $^{13}$C NMR ($CDCl_3$, 126 MHz) $\delta$ 150.3 (2C), 148.3, 139.3, 135.3, 130.0 (2C), 127.0 (2C), 121.5 (2C), 21.4. Consistent with the literature data.[36]

*3-(p-Tolyl)thiophene* (**2k**). Prepared following the general procedure in 78% yield (51.5 mg, 0.236 mmol) from *p*-tolyl 4-methylbenzenesulfonate (100 mg, 0.381 mmol) and thiophen-3-ylboronic acid (97.9 mg, 0.762 mmol). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.50 (d, $J$ = 8.2 Hz, 2H), 7.43−7.33 (m, 3H), 7.21 (d, $J$ = 8.0 Hz, 2H), 2.38 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 142.5, 137.0, 133.2, 129.6 (2C), 126.5 (2C), 126.4, 126.2, 119.8, 21.3.[37]

*2,4′-Dimethyl-1,1′-biphenyl* (**2l**). Prepared following the general procedure in 78% yield (54.1 mg, 0.297 mmol) from *p*-tolyl 4-methylbenzenesulfonate (100 mg, 0.381 mmol) and *o*-tolylboronic acid. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.32−7.22 (m, 7H), 2.44 (s, 3H), 2.32 (s, 3H).$^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 141.7, 138.9, 136.2, 135.3, 130.2, 129.7, 128.9 (2C), 128.7 (2C), 126.9, 125.6, 21.1, 20.4.[38]

*4′-Methyl-[1,1′-biphenyl]-2-amine* (**2m**). Prepared following the general procedure in 91% yield (12.7 mg, 0.069 mmol) from *p*-tolyl 4-methylbenzenesulfonate (20.0 mg, 0.076 mmol) and (2-aminophenyl)boronic acid. $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.38−7.33 (m, 2H), 7.31−7.20 (m, 2H), 7.18−7.10 (m, 2H), 6.82 (td, $J$ = 7.4, 1.2 Hz, 1H), 6.79−6.74 (m, 1H), 3.76 (s, 2H), 2.41 (s, 3H); $^{13}$C NMR ($CDCl_3$, 126 MHz) $\delta$ 143.6, 137.0, 136.6, 130.6, 129.6 (2C), 129.1 (2C), 128.4, 127.8, 118.8, 115.7, 21.3. Consistent with the literature data.[39]

*2,6-Dimethoxy-4′-methyl-1,1′-biphenyl* (**2n**). Prepared following the general procedure in 23% yield (20.0 mg, 0.087 mmol) from *p*-tolyl 4-methylbenzenesulfonate (100 mg, 0.381 mmol) and (2,6-dimethoxyphenyl)boronic acid. $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.34−7.23 (m, 5H), 6.68 (d, $J$ = 8.3 Hz, 2H), 3.73 (s, 6H), 2.42 (s, 3H); $^{13}$C NMR ($CDCl_3$, 126 MHz) $\delta$ 157.6, 136.2, 130.8, 130.6 (2), 128.4 (2C), 128.3, 119.3, 104.0 (2C), 55.8 (2C), 21.3. Consistent with the literature data.[40]

*[1,1′-Biphenyl]-4-carbaldehyde* (**2o**). Prepared following the general procedure in 91% yield (20.8 mg, 0.114 mmol) from 4-formylphenyl 4-methylbenzenesulfonate (34.7 mg, 0.125 mmol) and phenylboronic acid. $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 10.06 (s, 1H), 7.99−7.94 (m, 2H), 7.79−7.74 (m, 2H), 7.64 (dt, $J$ = 6.6, 1.3 Hz, 2H), 7.49 (td, $J$ = 7.2, 6.3, 1.4 Hz, 2H), 7.46−7.39 (m, 1H); $^{13}$C NMR ($CDCl_3$, 126 MHz) $\delta$ 192.1, 147.3, 139.8, 135.3, 130.4 (2C), 129.2 (2C), 128.6, 127.8 (2C), 127.5 (2C). Consistent with the literature data.[41]

*4-Acetyl-1,1′-biphenyl* (**2p**). Prepared following the general procedure in 92% yield (31.1 mg, 0.158 mmol) from 4-acetylphenyl 4-methylbenzenesulfonate (50 mg, 0.172 mmol) and phenylboronic acid. $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 8.07−8.00 (m, 2H), 7.72−7.67 (m, 2H), 7.66−7.61 (m, 2H), 7.50−7.45 (m, 2H), 7.43−7.38 (m, 1H), 2.64 (s, 3H).; $^{13}$C NMR ($CDCl_3$, 126 MHz) $\delta$ 197.8, 145.8, 139.9, 135.9, 129.0 (2C), 128.9 (2C), 128.2, 127.3 (2C), 127.2 (2C), 26.7. Consistent with the literature data.[42]

*4-Methoxy-1,1′-biphenyl* (**2q**). Prepared following the general procedure in 87% yield (29 mg, 0.157 mmol) from 4-methoxyphenyl 4-methylbenzenesulfonate (50 mg, 0.18 mmol) and phenylboronic acid. $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 7.57−7.27 (m, 7H), 6.98 (d, $J$ = 9.0 Hz, 2H), 3.86 (s, 3H); $^{13}$C NMR ($CDCl_3$, 126 MHz) $\delta$ 159.1, 140.8, 133.8, 128.7 (2C), 128.2 (2C), 126.8 (2C), 126.7, 114.2 (2C), 55.4. Consistent with the literature data.[43]

*4-Fluoro-1,1′-biphenyl* (**2r**). Prepared following the general procedure in 90% yield (29 mg, 0.168 mmol) from 4-fluorophenyl 4-methylbenzenesulfonate (50 mg, 0.187 mmol) and phenylboronic acid. $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 7.49−7.43 (m, 4H), 7.39−7.32 (m, 2H), 7.30−7.23 (m, 1H), 7.10−6.99 (m, 2H); $^{13}$C NMR ($CDCl_3$, 126 MHz) $\delta$ 162.5 (d, $J$ = 251 Hz), 140.3, 137.4 (d, $J$ = 2.5 Hz), 128.8 (2C), 128.7 (d, $J$ = 8.7 Hz, 2C), 127.3, 127.0 (2C), 115.6 (d, $J$ = 21.3, 2C). Consistent with the literature data.[43]

*4-Phenylpyridine* (**2s**). Prepared following the general procedure in 75% yield (13.6 mg, 0.087 mmol) from pyridin-4-yl 4-methylbenzenesulfonate (29.2 mg, 0.117 mmol) and phenylboronic acid. $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.70−8.65 (m, 2H), 7.65 (dd, $J$ = 7.2, 1.9 Hz, 2H), 7.54−7.50 (m, 2H), 7.49 (d, $J$ = 7.7 Hz, 2H), 7.47−7.44 (m, 1H).; $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 150.2 (2C), 148.7, 138.2, 129.3 (2C), 129.2, 127.2 (2C), 121.9 (2C). Consistent with the literature data.[41]

*2-(4-Methoxyphenyl)naphthalene* (**2t**). Prepared following the general procedure in 85% yield (71.8 mg, 0.29 mmol) from naphthalen-2-yl 4-methylbenzenesulfonate (100 mg, 0.335 mmol) and (4-methoxyphenyl)boronic acid (101.9 mg, 0.67 mmol). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.01−7.97 (m, 1H), 7.93−7.82 (m, 2H), 7.75−7.63 (m, 3H), 7.54− 742 (m, 2H),


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7.07−6.99 (m, 2H), 3.88 (s, 3H). $^{13}$C NMR (500 MHz, $CDCl_3$) δ 159.4, 138.3, 133.9, 133.7, 132.4, 128.6 (2C), 128.5, 128.2, 127.8, 126.4, 125.8, 125.6, 125.2, 114.4 (2C), 55.5.[44]

*(E)-1-Methyl-4-styrylbenzene (**2u**).* Prepared following the general procedure in 89% yield (14.8 mg, 0.076 mmol) from *p*-tolyl 4-methylbenzenesulfonate (22.4 mg, 0.085 mmol) and *trans*-2-phenylvinylboronic acid. $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.53 (d, *J* = 7.6 Hz, 2H), 7.45 (d, *J* = 7.9 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 3.8 Hz, 1H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 2.4 Hz, 2H), 2.39 (s, 3H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 137.7, 134.6, 129.6, 129.5 (2C), 128.8 (2C), 128.7 (2C), 127.8, 127.5 (2C), 126.5 (2C), 21.4. Consistent with literature data.[45]

*(E)-1-Phenylcyclooct-1-ene (**2w**).* Prepared following the general procedure in 73% yield (43.7 mg, 0.235 mmol) from (*E*)-1-bromocyclooct-1-ene **1w** (60.0 mg, 0.32 mmol) and phenylboronic acid. $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.44−7.38 (m, 2H), 7.34−7.26 (m, 2H), 7.25−7.17 (m, 1H), 6.01 (t, *J* = 8.3 Hz, 1H), 2.66−2.60 (m, 2H), 2.33−2.26 (m, 2H), 1.69−1.62 (m, 2H), 1.61−1.56 (m, 2H), 1.57−1.50 (m, 4H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 143.3, 140.4, 128.3 (2C), 128.1, 126.6, 125.9 (2C), 30.1, 29.6, 28.6, 27.6, 27.0, 26.3. Consistent with the literature data.[46]

*1,1,2,2-Tetraphenylethene (**2x**).* Prepared following the general procedure in 79% yield (26.1 mg, 0.079 mmol) from 2-bromo-1,1,2-triphenylethylene **1x** (33.6 mg, 0.1 mmol) and phenylboronic acid. $^1$H NMR ($CDCl_3$, 300 MHz) δ 7.15−7.08 (m, 12H), 7.07−6.98 (m, 8H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 143.9 (4C), 141.1 (2C), 131.5 (8C), 127.8 (8C), 126.5 (4C). Consistent with the literature data.[47]

*4-(1,2-Diphenylbut-1-en-1-yl)phenol (**2y**).* Prepared following the general procedure using NaOH as the base in 73% yield (11.1 mg, 0.037 mmol, *E*/*Z* = 79/21) from (*E*)-1,2-diphenylbut-1-en-1-yl 4-methylbenzenesulfonate[48] (***E***)-**1y** (19.1 mg, 0.050 mmol) and (4-hydroxyphenyl)boronic acid. $^1$H NMR ($CDCl_3$, 500 MHz, mixture of *E*/*Z* isomers) δ 7.35 (t, *J* = 7.6 Hz, $2H_Z$), 7.28−6.97 (m, 18H), 6.90−6.85 (m, 2H), 6.82 (d, *J* = 8.5 Hz, $2H_E$), 6.74 (d, *J* = 8.5 Hz, $2H_Z$), 6.47 (d, *J* = 8.5 Hz, $2H_Z$), 4.74 (bs, $1H_E$), 4.51 (bs, $1H_Z$), 2.50 (q, *J* = 7.5 Hz, $2H_E$), 2.45 (q, *J* = 7.5 Hz, $2H_Z$), 0.94 (t, *J* = 7.5 Hz, $3H_E$), 0.92 (t, *J* = 7.5 Hz, $3H_Z$); $^{13}$C NMR ($CDCl_3$, 126 MHz, mixture of *E*/*Z* isomers) δ 154.2, 153.3, 143.7, 143.3, 142.4, 142.3, 142.0, 141.4, 138.2, 138.1, 136.2, 135.7, 132.1, 130.8, 129.7, 129.4, 128.1, 127.9, 127.8, 127.3, 126.5, 126.0, 125.6, 114.9, 114.2, 29.0, 13.6. Consistent with the literature data.[49]

*2-(Benzo[d][1,3]dioxol-5-yl)quinoline (**Dubamine**).* Prepared following the general procedure in 88% yield (32.6 mg, 0.13 mmol) from quinolin-2-yl 4-methylbenzenesulfonate[50] **1z** (44.6 mg, 0.148 mmol) and 3,4-methylenedioxyphenylboronic acid. $^1$H NMR ($CDCl_3$, 500 MHz) δ 8.18 (dd, *J* = 8.7, 0.8 Hz, 1H), 8.13 (dq, *J* = 8.4, 0.9 Hz, 1H), 7.83−7.78 (m, 2H), 7.75 (d, *J* = 1.8 Hz, 1H), 7.71 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.66 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.51 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.05 (s, 2H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 156.8, 149.0, 148.5, 148.3, 136.8, 134.3, 129.8, 129.7, 127.6, 127.1, 126.2, 121.9, 118.8, 108.6, 108.1, 101.5; HR-MS 250.0851 ($C_{13}H_{11}NO_2$+H$^+$) calcd 250.0863. Consistent with the literature data.[51]

*(Z)-2-(4-(1,2-Diphenylbut-1-en-1-yl)phenoxy)-N,N-dimethylethan-1-amine (**Tamoxifen**).* Prepared following the general procedure using NaOH as the base in 78% yield (14.3 mg, 38.5 μmol) from (*Z*)-1,2-diphenylbut-1-en-1-yl 4-methylbenzenesulfonate[48] (***Z***)-**1y** (18.6 mg, 49.0 μmol) and (4-(2-(dimethylamino)ethoxy)phenyl)boronic acid[27] **3**. It was obtained as a white solid; TLC $R_f$ 0.28 ($CH_2Cl_2$/EtOH 5%); $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.39−7.30 (m, 2H), 7.32−7.19 (m, 2H), 7.20−7.05 (m, 6H), 6.76 (d, *J* = 9.1, 8.6 Hz, 2H), 6.55 (d, 2H), 3.95 (t, *J* = 5.7 Hz, 2H), 2.68 (t, *J* = 5.2 Hz, 2H), 2.45 (q, *J* = 7.4 Hz, 2H), 2.32 (s, 6H), 0.92 (t, *J* = 7.3 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 156.8, 143.9, 142.5, 141.5, 138.3, 135.7, 132.0 (2C), 129.8 (2C), 129.6 (2C), 128.2 (2C), 128.0 (2C), 126.6, 126.1, 113.5 (2C), 65.5, 58.3, 45.9, 29.2 (2C), 13.8; HR-MS 372.2297 ($C_{26}H_{29}ON$+H$^+$) calcd 372.2322. Consistent with the literature data.[28]

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c05770.

Copies of $^1$H and $^{13}$C spectra (PDF)

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### Notes

The authors declare no competing financial interest.

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## ■ ABBREVIATIONS

SMC, Suzuki−Miyaura Coupling; Ts, tosyl; Mbs, *para*-methoxybenzenesulfonyl; Ms, mesyl; TBAOH, *tetra*-butylammonium hydroxide; PhBpin, phenylboronic acid pinacol ester

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