

CHAPTER 1

CROSS-COUPLING REACTIONS OF ORGANOTRIFLUOROBORATE SALTS

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Organic Reactions, Vol. 79, Edited by Scott E. Denmark et al.

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ACKNOWLEDGMENTS

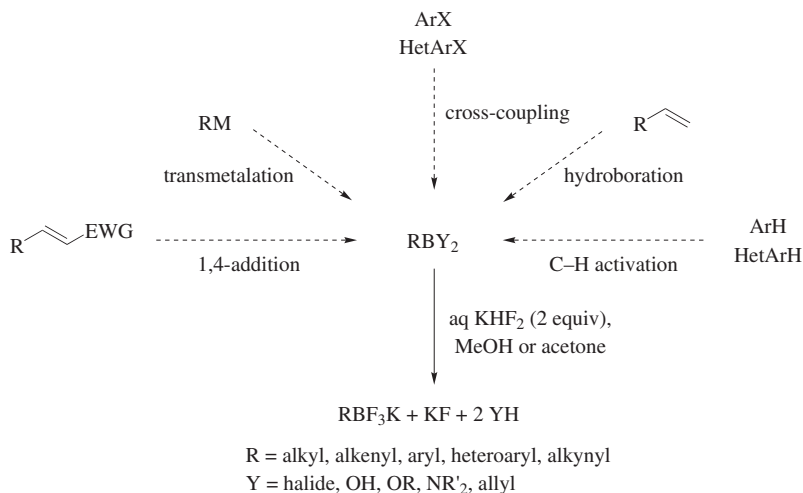
Generous financial support from the National Institutes of General Medical Sciences, the National Science Foundation, Merck, Johnson & Johnson, and Amgen is gratefully acknowledged. We also thank Aldrich, BASF, Borochem, Frontier Scientific, and Johnson Matthey for providing reagents and/or catalysts utilized during the course of our research. Finally, we thank our research colleagues, who have contributed enormously to the success of our program in organotrifluoroborate chemistry and made the discovery process so much fun.

INTRODUCTION

The Suzuki-Miyaura cross-coupling reaction is widely recognized as one of the most powerful and broadly utilized synthetic methods available for carbon-carbon bond formation.¹⁻³ The importance of this coupling process has engendered a great deal of interest from practicing synthetic chemists both in academia and, because of the commercial importance of this reaction, in industry. Largely for historical reasons, boronic acids have become the standard reagents utilized for Suzuki-Miyaura cross-coupling reactions, and hundreds of these substances are now commercially available. Thousands of papers employing the reaction have been published, and many of these have been devoted to enhancements of the original procedure. Among the latter contributions, the vast majority of these important studies have dealt with improving the transformation by optimizing critical characteristics of the reaction such as the catalyst/ligand complex, the electrophile (aryl, heteroaryl, alkenyl, alkynyl, alkyl), the nucleofuge (chlorides, sulfonates, phosphates, esters), the solvent (e.g., water, ionic liquids⁴⁻⁶), the bases required, and the conditions of the reaction (e.g., by using sonication or microwaves^{7,8}). Curiously, little effort was initially devoted to expand the scope

of the reaction by altering the essential organoboron reagent. Organotrifluoroborates are one of several classes of organoboron reagents developed to provide a complementary suite of reagents for cross-coupling, affording alternatives to the classical boronic acid derivatives.

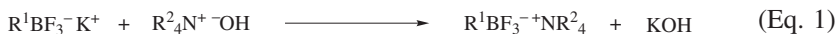
The first practical synthesis of organotrifluoroborates was reported in 1995, and involved the treatment of arylboronic acids with the inexpensive salt KHF_2 .⁹ It was subsequently determined that virtually any boronic acid could be converted to the corresponding organotrifluoroborate using the same protocol, and in fact nearly all organoboron reagents possessing an organic moiety and two labile groups (e.g., halides, $-\text{OR}$, $-\text{NR}_2$, allyl) could be transformed to the desired trifluoroborate salts. Consequently, organotrifluoroborates can be prepared by employing any of the well-known means of preparing organoboron compounds, with hydroboration, transmetalation, cross-coupling, C–H activation, and 1,4-addition being among the most important methods, followed by conversion to the salts (Scheme 1).



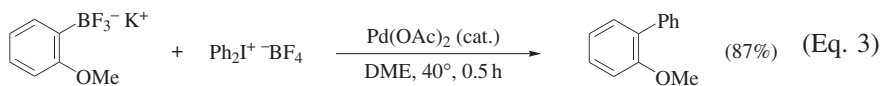
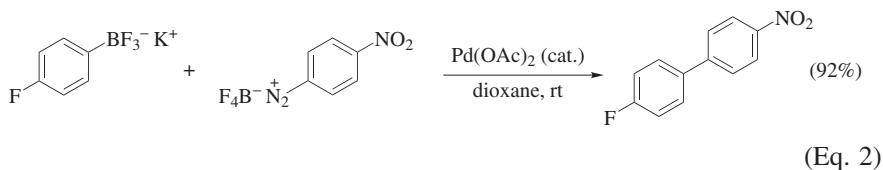
Scheme 1. Diverse approaches to organotrifluoroborates.

Owing to the commercial availability of KHF_2 , the potassium salts of the trifluoroborates are the most conveniently prepared. The potassium counterion affords materials that reliably appear as crystalline solids or free-flowing powders. The cesium salts are also stable solids,¹⁰ although the latter materials come at a greater cost both economically and in terms of their increased mass. Lithium organotrifluoroborates are somewhat unstable because of the strong thermodynamic driving force for formation of LiF , which leads to decomposition of the complex.¹¹ Alkali metal salts of the organotrifluoroborates have limited solubility in nonpolar organic solvents. For carrying out reactions in such media, the organotrifluoroborates can be readily converted to soluble tetraalkylammonium salts by treatment with tetraalkylammonium hydroxide (Eq. 1).¹² This conversion, however, incurs practical costs, including a loss of atom economy and, in

some cases (e.g., alkyltrifluoroborate derivatives), a lack of crystallinity, creating difficulties in handling.

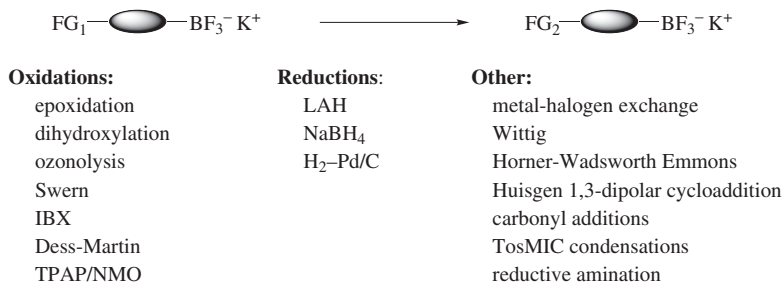


The first reported examples of organotrifluoroborates in Suzuki-type cross-coupling reactions employed highly reactive arenediazonium salts^{13,14} and diaryliodonium salts¹⁵ as electrophiles for the preparation of biaryls (Eqs. 2 and 3). Broader explorations were begun subsequently, using diverse organotrifluoroborates with a variety of electrophiles, and ongoing studies continue to expand the scope of the cross-coupling transformation.



As a result of such investigations, several defining features have emerged as hallmarks of organotrifluoroborate chemistry. For example, the tetracoordinate organotrifluoroborates generally undergo stoichiometric coupling with a variety of organic halides and pseudohalides because competing protodeboronation is often nonexistent. Aside from the boronic acids, the trifluoroborates exhibit the best atom economy of any organoboron reagents used for cross-coupling. The byproducts of the coupling of organotrifluoroborates are relatively benign fluoride salts and boric acid, minimizing environmental concerns. Perhaps most importantly, the tetracoordinate nature of these materials, anchored by exceptionally strong boron-fluorine bonds, makes them inherently inert to many of the most common reagents utilized in organic synthesis. This property has some important consequences: (1) Several classes of organotrifluoroborates have demonstrated enhanced stability on storage as compared to other organoboron reagents. This feature is particularly relevant for heteroaryl, alkenyl, alkynyl, cyclopropyl, and cyclobutyl derivatives. (2) Organoboron reagents of unprecedented structure and functional group complexity, not accessible to tricoordinate boron species, can be prepared as their trifluoroborate salts, affording new opportunities for carbon-carbon bond-forming reactions. (3) Functional groups incorporated within the organotrifluoroborates can be selectively manipulated, leaving the boron-carbon bond intact (Scheme 2). Essentially, the trifluoroborates are a protected form of boronic acids,¹⁶ with little or no penalty (and many benefits) being paid for the protection. As a result, one can initiate a synthetic sequence with a small, minimally functionalized organotrifluoroborate and build molecular complexity

from this platform while retaining the key carbon–boron bond for future processing. In this manner, the organoboron species can be carried through several synthetic steps, with performance of the key coupling reaction taking place at a point more strategically convenient. The latter two features allow practitioners to expand the role of organoborons in their synthetic planning and fundamentally change retrosynthetic analyses involving boron-based processes.



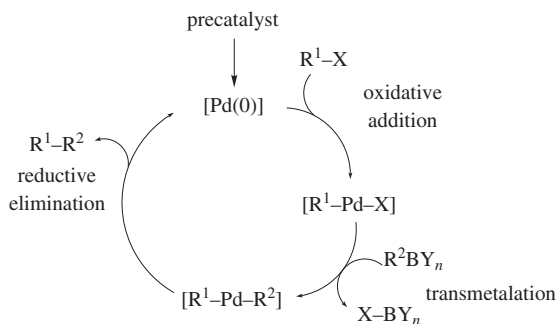
Scheme 2. Reactions tolerated by organotrifluoroborates.

This chapter outlines the scope and limitations of cross-coupling reactions employing organotrifluoroborates and comprehensively covers material published through August, 2009; the tables cover all references published through the middle of 2010. As a testament to their increasing importance, several review articles on various aspects of organotrifluoroborate chemistry have already appeared.^{11,16–23}

MECHANISTIC CONSIDERATIONS

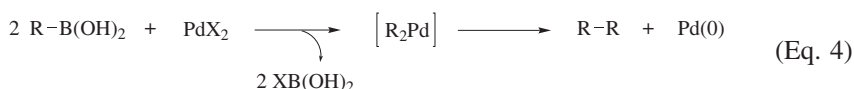
All available evidence suggests that the general mechanistic scheme for the cross-coupling of organotrifluoroborates is the same as that for cross-coupling with boronic acids and most other organometallic reagents.²⁴ Beginning with a Pd(II) precatalyst, reduction to the active Pd(0) species initiates the catalytic cycle. Oxidative addition of Pd(0) into the C–X bond of various electrophiles provides an organopalladium(II) species that subsequently undergoes transmetalation with an organoboron partner to generate a diorganopalladium intermediate. The diorganopalladium intermediate undergoes reductive elimination, completing the overall transformation with formation of the final product and regeneration of the Pd(0) species (Scheme 3).

At a more detailed level, however, important differences exist between transformations involving boronic acids, for example, and those involving the organotrifluoroborates. One such aspect is precatalyst activation. Although Pd(0) catalysts are sometimes used directly in cross-coupling reactions, their inherent instability to air oxidation makes them susceptible to decomposition if stored outside a glove box, and for this reason more stable Pd(II) precatalysts are preferred. Palladium(II) complexes are reduced in situ by any number of reductants,²⁵ including alcohols, amines, alkenes, and phosphines.²⁶ In cross-coupling reactions, the Pd(II) salts are often reduced by the organometallic reagent employed

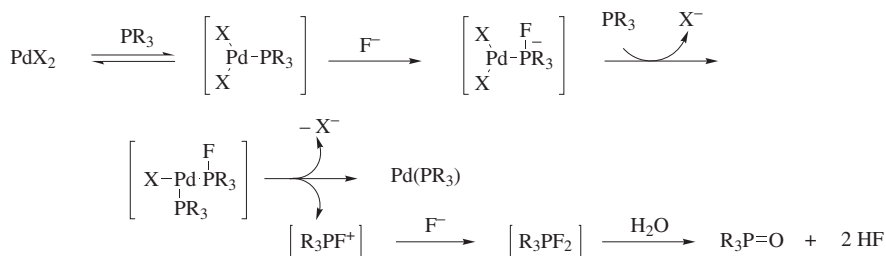


Scheme 3. General catalytic scheme for Suzuki-Miyaura cross-coupling.

in the reaction (Eq. 4). This process generates homocoupling products from the organometallic precursor.



Mechanistic studies on organotrifluoroborates have shown that <0.1% of homocoupled products are generated when these reagents are employed with Pd(II) precatalysts, even when relatively high (5 mol %) catalyst loadings are used.²⁷ This implies that $\text{PdCl}_2(\text{PPh}_3)_2$ or related Pd(II) precatalysts are completely reduced prior to transmetalation from the trifluoroborate, and that fluoride catalyzes the reduction of the Pd(II) complex via a monophosphane Pd(0) complex (Scheme 4).^{28–30}

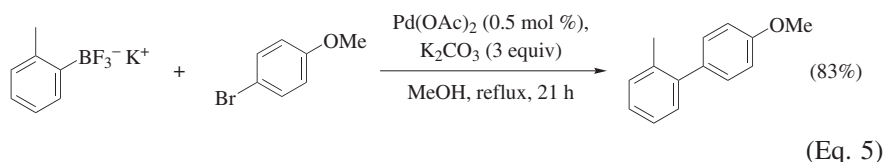


Scheme 4. Fluoride-catalyzed reduction of Pd(II) to Pd(0).

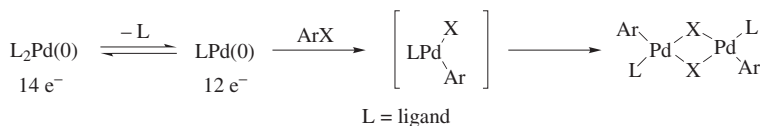
The oxidative addition step that takes place subsequent to precatalyst reduction appears to be independent of the organometallic reagent utilized, and thus to a large extent the factors that influence this step in other cross-coupling reactions will also play a significant role in organotrifluoroborate coupling reactions.^{31–34} Depending on the reaction partners involved, the oxidative addition step can be the rate-determining step in cross-coupling reactions, and thus enormous efforts have been made to understand and improve this step. In fact, understanding

the significant role that ligands play in the overall process constitutes one of the most important advances in cross-coupling protocols,^{35–38} along with the design and development of ligands that have expanded the scope of the coupling reaction.^{39–45}

The most common electrophiles for cross-coupling reactions are those containing $\text{Csp}^2\text{--X}$ bonds. For reactive aryl bromides, there is little challenge in the oxidative addition step, and thus the cross-couplings can often be carried out under ligandless conditions with very low catalyst loadings in the presence of air (Eq. 5).⁴⁶



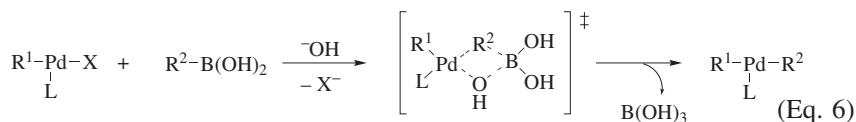
With less reactive aryl chloride electrophiles and challenging cross-coupling partners (e.g., sterically hindered systems and alkyltrifluoroborate nucleophiles), mono-ligated complexes incorporating sterically demanding, electron-rich phosphine ligands have consistently proven to be most effective catalysts.⁴³ These complexes have been engineered with design features tuned to optimal performance. Palladium(0) complexes with sterically encumbered ligands undergo oxidative addition with aryl halides by a dissociative mechanism through $[\text{LPd}(0)]$ species. Bulky ligands shift the equilibrium toward formation of these highly reactive, monocoordinated, 12-electron organopalladium intermediates (Scheme 5).^{32,47–50} The presence of large substituents on the phosphine ligand also increases the energy of the ground state in $[\text{L}_2\text{Pd}(0)]$ complexes relative to that of the $[\text{L}_2\text{Pd}(0)]$ species with smaller ligands, effectively lowering the energy of activation required to access the reactive $[\text{LPd}(0)]$ intermediate, thus further facilitating the oxidative addition process.³⁴



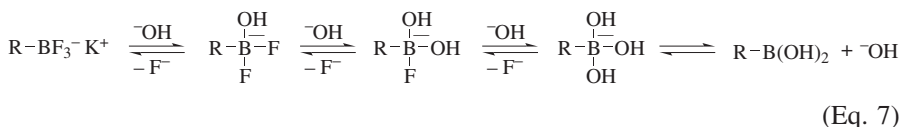
Scheme 5. Oxidative addition from $\text{L}_2\text{Pd}(0)$ complexes using sterically encumbered ligands.

Electron-rich ligands may increase catalyst performance because the higher electron density on the metal lowers the energy of activation for oxidative addition. The development of ligands such as tricyclohexylphosphine and tri(*tert*-butyl)phosphine in cross-coupling reactions reflects this concept.^{44,51} In addition to the more commonly used phosphine ligands, *N*-heterocyclic carbenes (NHCs) with similar attributes have been utilized with some success in organotrifluoroborate cross-coupling reactions.^{52,53}

One of the more interesting aspects of the organotrifluoroborate variant concerns the nature of the organoboron species undergoing transmetalation. Mechanistic^{54,55} as well as theoretical⁵⁶ studies concerning the Suzuki coupling reaction suggest that the weakly nucleophilic boronic acid derivatives undergo transmetalation via four-centered transition structures in which a bridging hydroxyl group facilitates the organic group transfer (Eq. 6).



Except for the cross-coupling reactions with the highly reactive diazonium salts and iodonium salts mentioned above, organotrifluoroborates appear to require the presence of protic solvents under basic reaction conditions.^{12,57} Early NMR and mass spectrometric studies on organotrifluoroborates under cross-coupling reaction conditions indicate that the reagents do not remain intact during the coupling, but a fluoride/hydroxy (alkoxy) exchange occurs, providing intermediates structurally similar to those generated in boronic acid couplings under basic conditions (Eq. 7).^{46,58,59} A more detailed mechanistic evaluation, combined with theoretical calculations, subsequently revealed further details of the overall process and provides explanations for the superior performance of the organotrifluoroborates in many aspects of this reaction.²⁷ The study shows that the organotrifluoroborates undergo slow hydrolysis to the intermediates as shown in (Eq. 7). Importantly, both theoretical and experimental evidence indicate that fully hydrolyzed intermediates are involved in the critical transmetalation step. The organotrifluoroborates thus serve as stable precursors of cross-coupling reagents that, unlike the organotrihydroxyborate species, are resistant to hydrolytic carbon-boron bond cleavage.

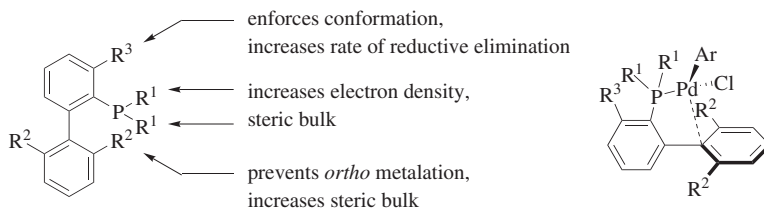


In terms of the rate of transmetalation with respect to the organic halide (R-X) employed, the order is the reverse of that observed for the oxidative addition reaction, that is, Cl > Br > I, perhaps driven by the strength of the boron-halide bond formed in the final product. This reverse order complicates the determination of the rate-limiting step for any given pair of reactants, because either of these two steps can be the slower depending on the exact nature of the substrates.

As is the case with the oxidative addition reaction, the reductive elimination step appears to be independent of the boron species utilized. Here again, the

more important component is the ligand about the metal center.⁶⁰ The two organic moieties to be bonded must be oriented *cis* about the metal for reductive elimination to occur, and bidentate ligands have the advantage of requiring the two organic substituents to be thus situated. In these systems the bite angle becomes an important factor; the observation has been made that a wider bite angle on the bidentate ligand (which necessarily brings the two organic subunits in closer proximity) leads to a faster rate of reductive elimination.^{61,62} In bidentate as well as monodentate ligand systems, both steric and electronic effects play a role in the rate of reductive elimination. A decrease of the electron density about the metal facilitates reductive elimination,⁶³ and a relief of steric strain (i.e., using sterically encumbered ligands where the “cone angle” or “buried volume” is a measure of bulk) also facilitates the overall rate of collapse to product.

All of the above considerations explain why sterically demanding, electron-rich monodentate phosphines are among the most versatile, effective, and therefore broadly useful ligands in organotrifluoroborate cross-coupling protocols (Scheme 6).^{40,43,45} Many of these ligands exhibit excellent stability in air, and their steric and electronic nature favors the [LPd(0)] form of the catalyst, providing them exceptional reactivity in the oxidative addition step of the catalytic cycle. Owing to the monodentate nature of the ligand, which frees up space about the metal center, transmetalation is also facilitated. Reductive elimination from the [LPd(II)R¹R²] species is also faster than that from [L₂Pd(II)R¹R²] species.^{64,65} Sterically hindered dialkylbiarylphosphines incorporate other design features that recommend their use, including the non-phosphine bearing aryl group that stabilizes the Pd(0) catalyst, and the installation of substituents at the *ortho* position of this ring, which prevent unproductive cyclo-metalation and also increase the steric bulk of the ligand.



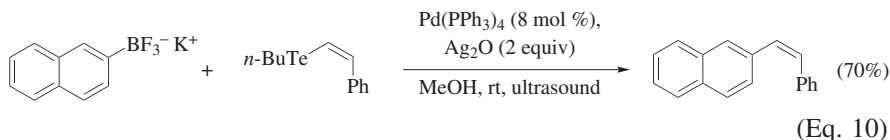
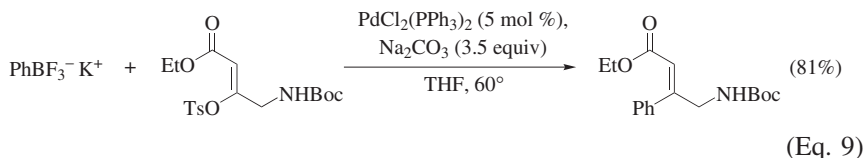
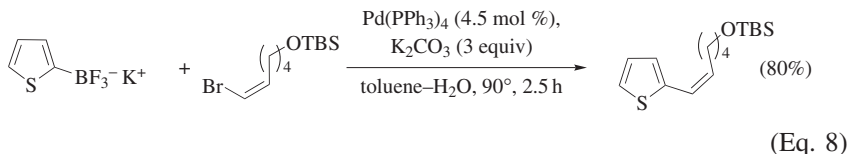
Scheme 6. Design elements in sterically hindered dialkylbiaryl phosphine ligands.

STEREOCHEMISTRY

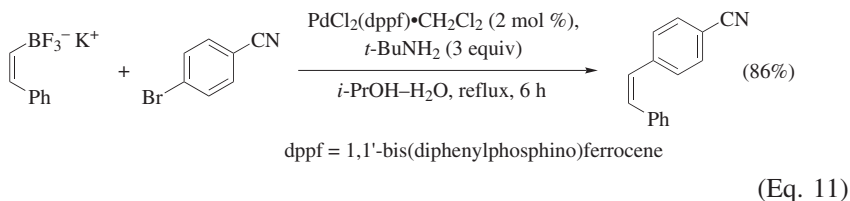
To date, the best studied and most frequently applied stereochemical aspect in organotrifluoroborate cross-coupling is the stereochemistry at the alkenyl electrophiles and alkenyltrifluoroborate nucleophiles. Strict stereochemical fidelity appears to be the norm for reported cross-couplings involving both alkenyl partners, but if conditions are not optimized, a loss of stereochemical control can occur.

Bromides are the most commonly used alkenyl electrophiles in cross-coupling of aryl- and heteroaryltrifluoroborates, and complete stereospecificity has been

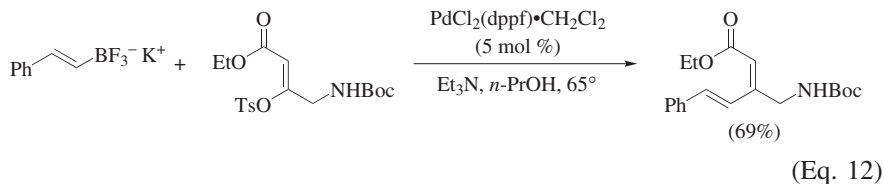
observed in the cross-coupling of (*Z*)-alkenyl bromides with diverse aryltrifluoroborates (Eq. 8).⁶⁶ Complete stereospecificity has also been observed when alkenyl iodides,⁶⁷ enol tosylates (Eq. 9),⁶⁸ and alkenyl tellurides (Eq. 10)⁶⁹ are employed as electrophiles with aryl- and heteroaryltrifluoroborates.

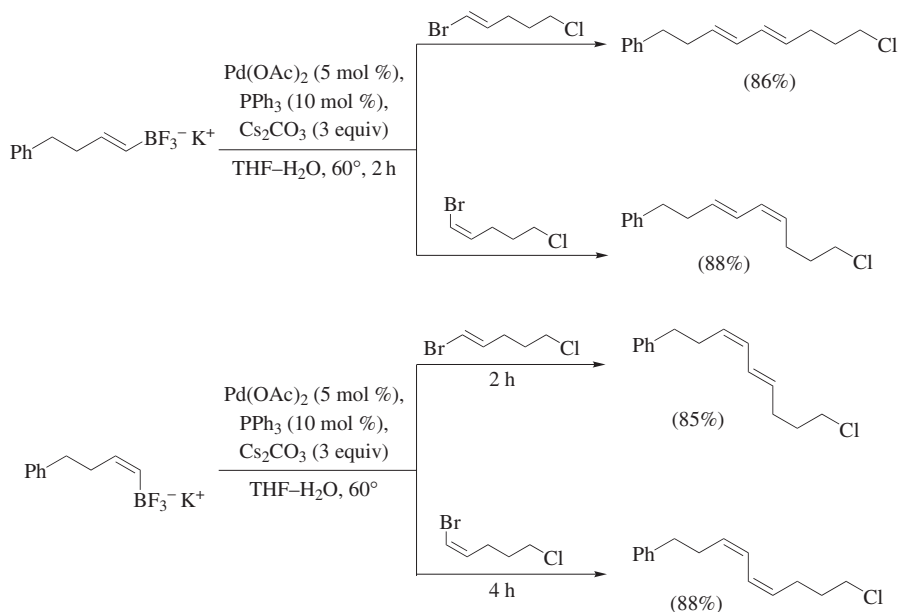


Although reaction conditions have been reported that lead to a deterioration of selectivity in coupling of stereodefined alkenyltrifluoroborates with aryl halides,⁷⁰ protocols have been developed wherein the configuration of the alkenyl component is retained (Eq. 11).⁷¹

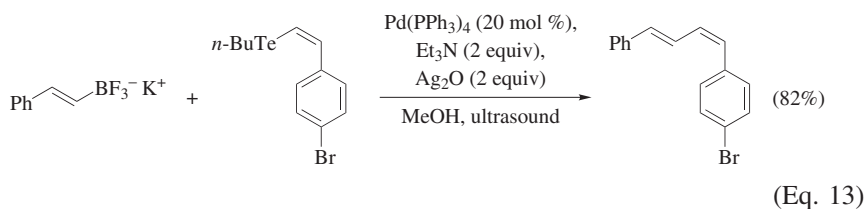


Most importantly, strict stereospecificity is maintained in both partners when conjugated dienes are prepared from alkenyltrifluoroborates and alkenyl bromides (Scheme 7).⁷² Similar stereospecificities have been observed in cross-coupling of alkenyltrifluoroborates with enol tosylates (Eq. 12)⁷³ and alkenyl tellurides (Eq. 13).⁶⁸

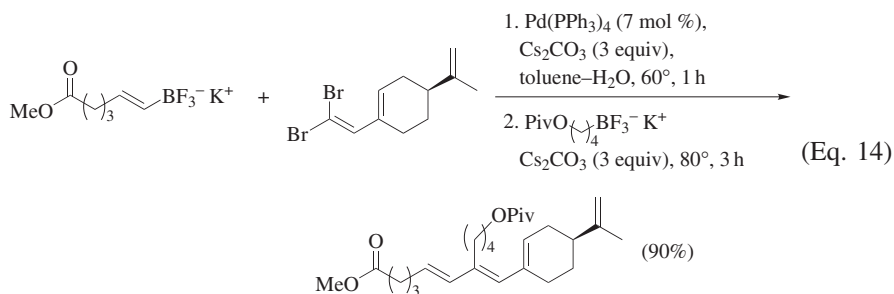




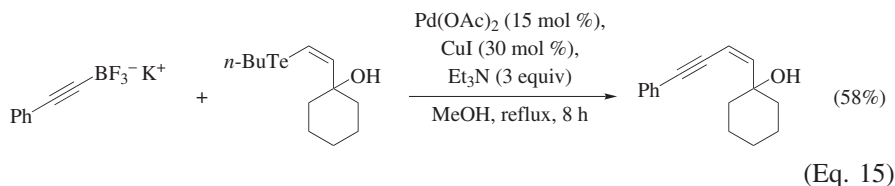
Scheme 7. Stereospecific synthesis of conjugated dienes.



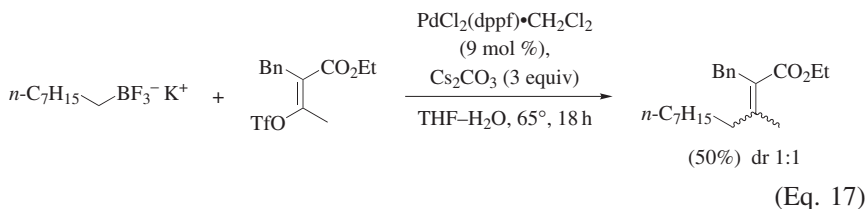
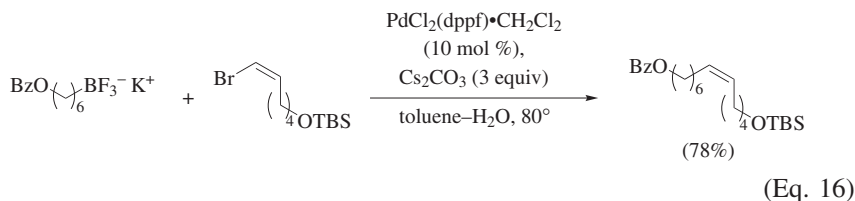
The stereospecificity of the alkenyl cross-coupling process, combined with a chemoselectivity for the less hindered bromide in 1,1-disubstituted alkenes, allows an efficient two-step, one-pot construction of conjugated dienes.⁷⁴ Alkenyl-trifluoroborates are used in the first step of the process, and alkyltrifluoroborates have been employed as the second nucleophilic partner (Eq. 14).



Far fewer studies have been carried out on the cross-coupling of alkynyltrifluoroborates with stereodefined electrophiles, but examples employing alkenyl tellurides indicate that such transformations are readily accomplished in a stereocontrolled manner (Eq. 15).⁷⁵

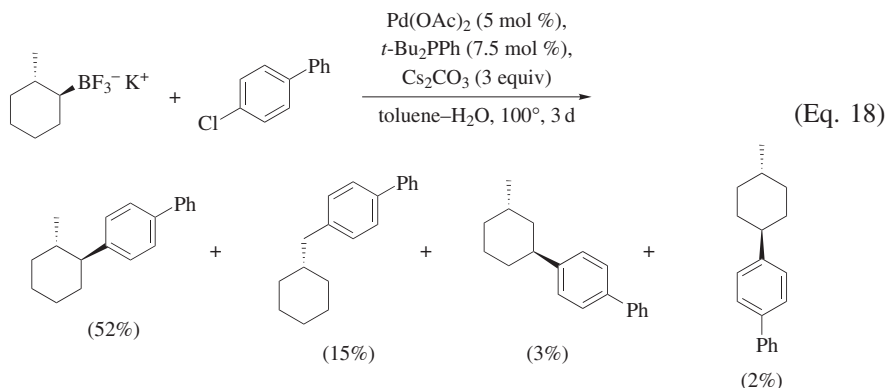


Excellent stereochemical control can be achieved in the cross-coupling of alkyltrifluoroborates with alkenyl bromides (Eq. 16).⁷⁶ However, in one reported study concerning the use of enol triflate partners, a loss of stereochemical fidelity is observed in the transformation (Eq. 17).⁵⁸

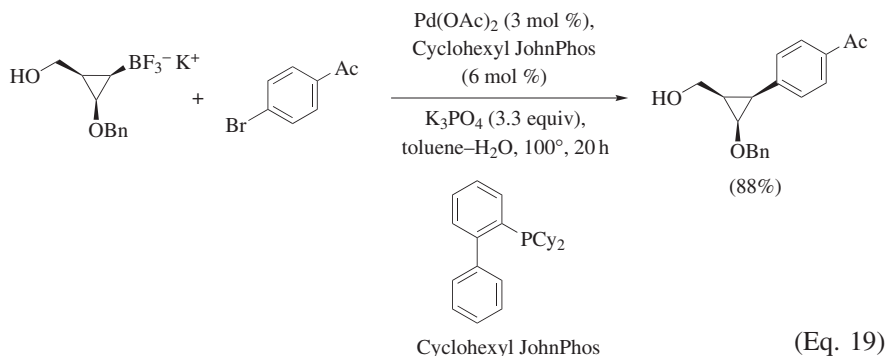


Owing to the challenges involved in the transmetalation step of the catalytic cycle and the intervention of β -hydride elimination from the diorganopalladium(II) intermediate, the efficient cross-coupling of secondary alkyl organometallic reagents is rare. An important aspect of cross-coupling of secondary alkyltrifluoroborates is the stereochemical fidelity observed in those systems where the metal constitutes one of the substituents at a stereogenic center. Few examples of this process exist in organoboron chemistry,⁷⁷ but in one study involving organotrifluoroborates, complete stereochemical fidelity is observed in the transfer of the alkyl group.⁷⁸ Unfortunately, the intervention of the β -hydride elimination/isomerization process is rather extensive, leading to a mixture of

constitutional isomers (Eq. 18).



Cyclopropanes represent a special class of secondary alkyl organometallics. The hybridization of the carbon–boron bond is between that of alkyl- and alkenyl-boron compounds, thus making transmetalation more facile than that for alkyl-boron derivatives, and β -hydride elimination is undoubtedly inhibited by the strain encountered in a transition state that would lead to a cyclopropene. In reactions that are generally high yielding, numerous examples of stereospecific cross-couplings of cyclopropyltrifluoroborates have been reported (Eq. 19).^{79–81}



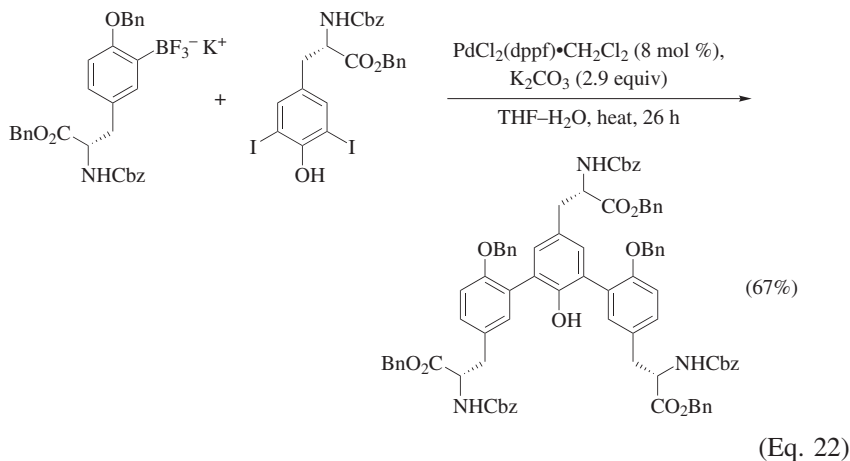
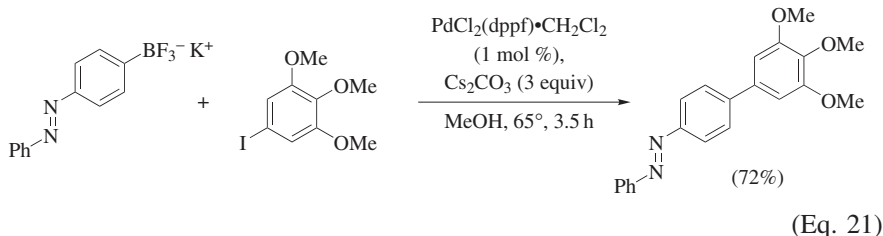
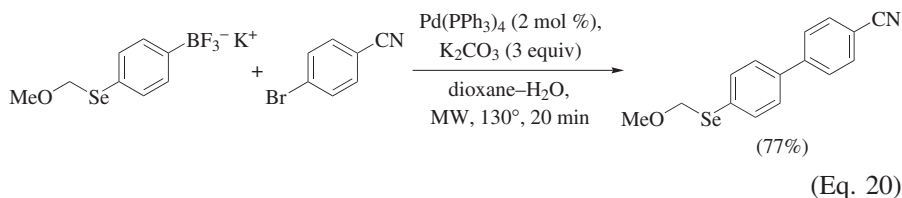
SCOPE AND LIMITATIONS

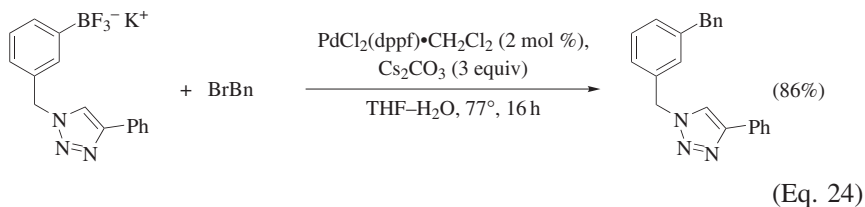
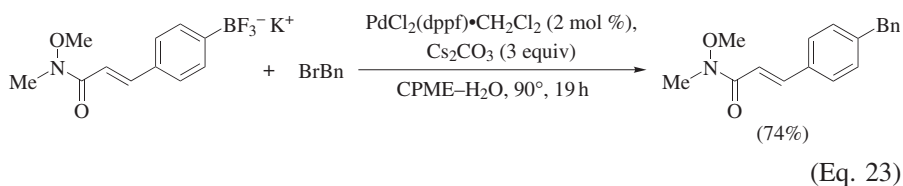
The Organotrifluoroborate

A wide range of organotrifluoroborates can be employed in cross-coupling reactions. The following section is a summary of the general reactivity pattern of the various reagents, focusing on those organotrifluoroborates that possess unique features.

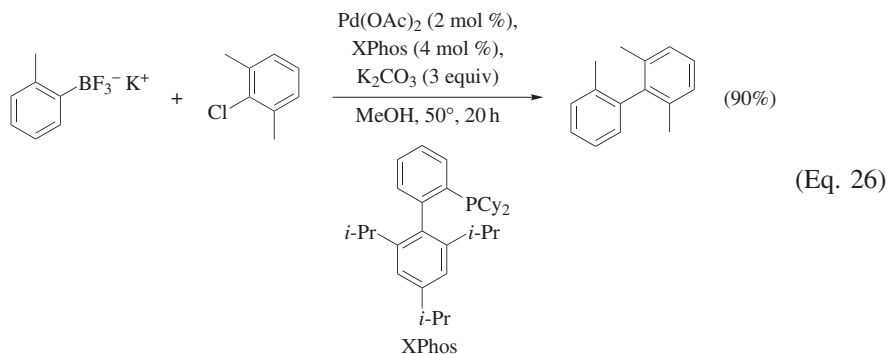
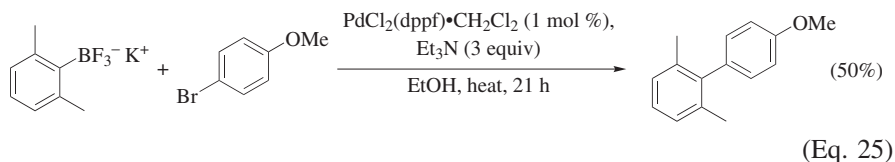
Aryltrifluoroborates. Aryltrifluoroborates represent the class of organotri-fluoroborates that is most often used in cross-coupling reactions. Virtually every substitution pattern and many functional groups have been incorporated in these systems, and for the most part acceptable cross-coupling conditions have been developed.

A variety of functional groups capable of surviving the subsequent cross-coupling step can be present within the aryltrifluoroborate substructure. In addition to the usual array of functional groups (e.g., ethers, halides, alcohols, aldehydes, ketones, esters, amines, amides, nitriles, nitro groups, and carboxylic acids), selenoethers,⁸² selenoacetals (Eq. 20),⁸² azo functional groups (Eq. 21),⁸³ protected α -amino acids (Eq. 22),⁸⁴ α,β -unsaturated Weinreb amides (Eq. 23),⁸⁵ and 1,2,3-triazoles (Eq. 24)⁸⁵ have all been incorporated as a part of the aryltrifluoroborates.



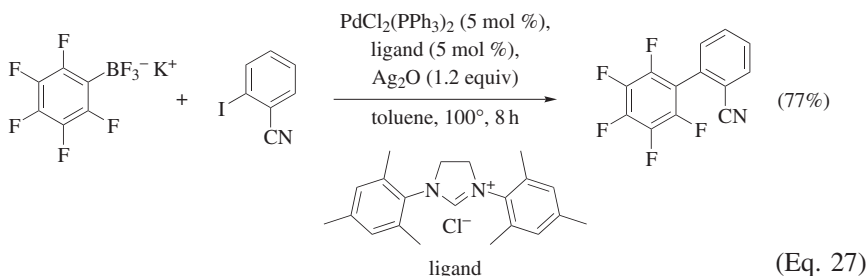


Sterically encumbered aryltrifluoroborates have traditionally been difficult to cross-couple, particularly with electron-rich aryl chloride electrophiles. Although not yet tested in the most demanding situations, aryltrifluoroborates of reasonable steric demand have been prepared and reacted with aryl bromides and aryl chlorides, permitting the construction of sterically hindered biaryl products (Eqs. 25–26).^{46,86,87}



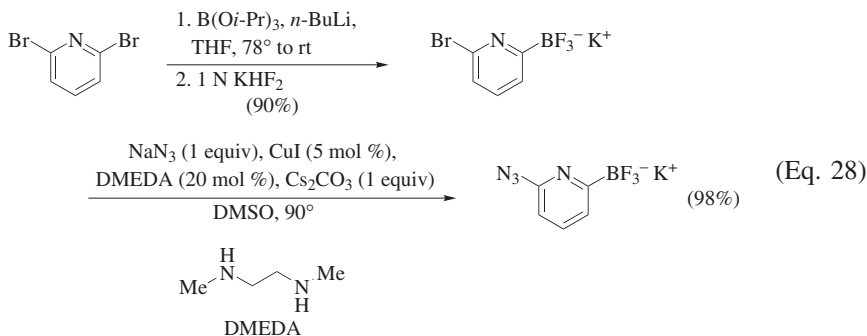
Another challenging class of arylboron compounds is that possessing an electron-deficient aromatic system. These reagents undergo facile protodeboration. One of the advantageous features of the organotrifluoroborates is their

ability to resist protodeboronation during Suzuki coupling, even in the most electron-deficient aromatic systems (Eq. 27).^{88,89}



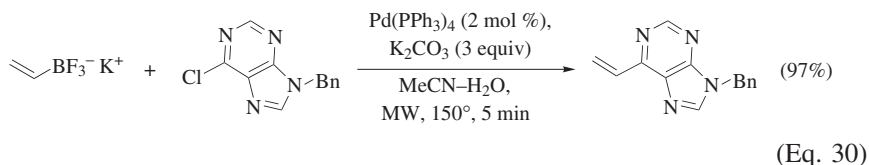
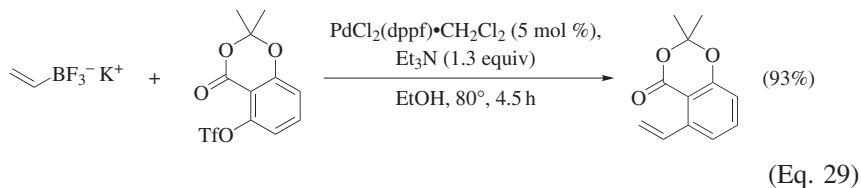
Heteroaryltrifluoroborates. Because of facile protodeboronation,⁹⁰ heteroarylboron species have proven extremely challenging to cross-couple in high yields.^{91–93} In most cases, a large excess of the heteroarylboron species is required in developing cross-coupling protocols to compensate for protodeboronation. By contrast, heteroaryltrifluoroborates are relatively resistant to protodeboronation, and diverse heteroaryltrifluoroborates have been prepared and cross-coupled effectively with a variety of electrophiles. Trifluoroborate derivatives of substituted pyrazoles, pyrroles, furans, thiophenes, indoles, isoxazoles, quinolines, isoquinolines, pyrimidines, pyridazines, and pyridines have all been employed in these studies.^{46,94,95}

Suzuki cross-couplings of 2-pyridylborons have proven to be particularly challenging,⁹⁴ but a number of protocols have been developed, providing solutions to this important problem.^{90,96–101} Of note along these lines is the synthesis and copper-promoted reaction of the substituted 2-trifluoroboratopyridine shown in (Eq. 28).¹⁰² This transformation indicates that such trifluoroborates are robust intermediates, but the development of their palladium-catalyzed cross-coupling has yet to be realized.

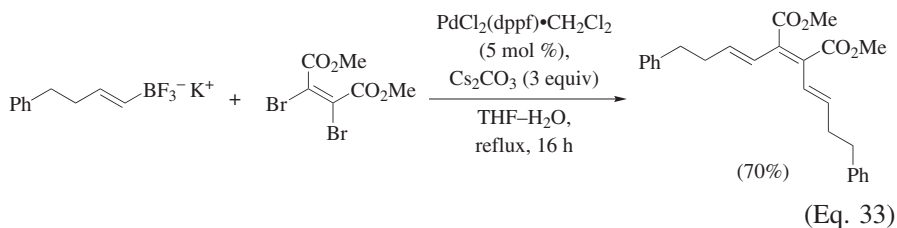
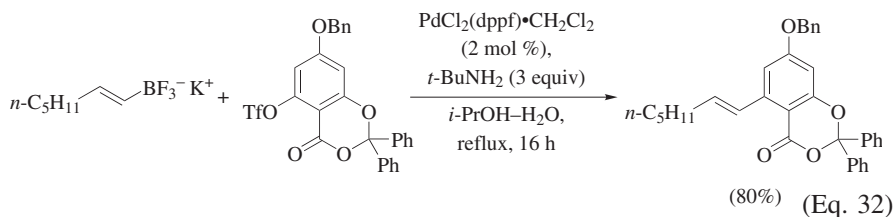
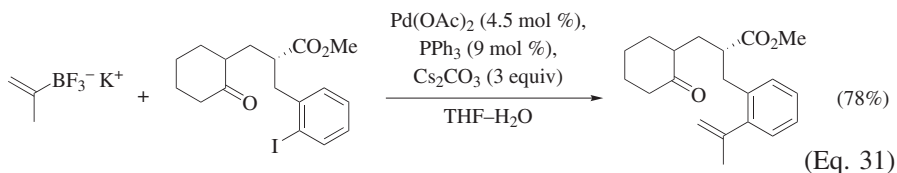


Alkenyltrifluoroborates. Although diverse alkenyltrifluoroborates have been prepared and employed in cross-coupling reactions with a variety of electrophiles, perhaps the most important and certainly the most widely used

reagent is the simplest: vinyltrifluoroborate. This vinylating agent has been used in a variety of cross-coupling reactions with a wide range of electrophiles, and it thus fills a useful niche among available vinylating agents (Eqs. 29 and 30).^{72,103–105} Although with most electrophiles the vinylated materials can be isolated in high yields, with aryl chlorides homocoupling of the halide and Heck products can diminish the yield.¹⁰⁶

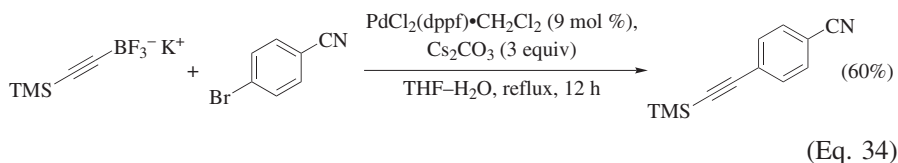


More highly elaborated alkenyltrifluoroborates, with diverse substitution patterns about the double bond, can also be effectively coupled (Eqs. 31–33).^{72,107,108} Although these reactions are usually stereospecific (Eq. 11, Scheme 7), a loss of stereochemical integrity can result when reactions have not been suitably optimized.⁷⁰

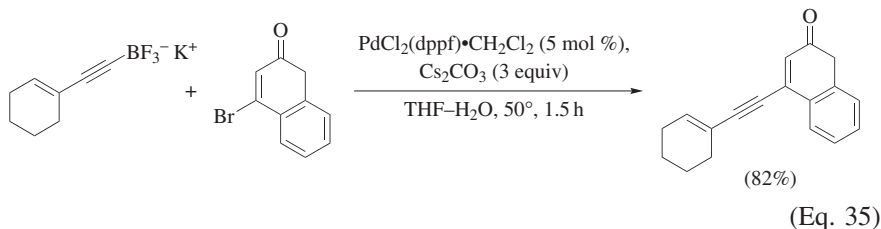


Alkynyltrifluoroborates. The cross-coupling of alkynyltrifluoroborates provides an alternative to the Sonogashira reaction for the incorporation of alkynes into organic substructures. Alkynyltrifluoroborates do not cross-couple effectively with aryldiazonium salts.¹⁴ Instead, electron transfer from the trifluoroborate to the diazonium salt occurs, resulting in products of chemical reduction. However, other aryl electrophiles can be utilized quite effectively for cross-coupling, and for aryl triflates, catalyst loading can be extraordinarily low (<0.05 mol %).¹⁰⁹

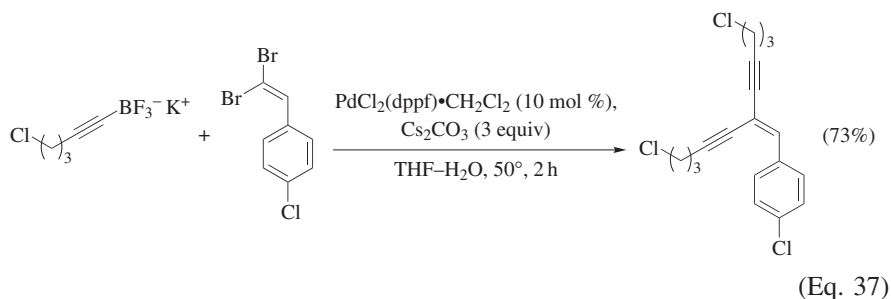
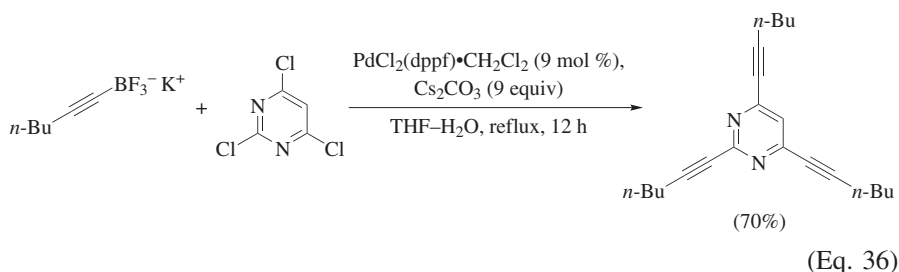
Ethynyltrifluoroborate has been prepared and is a stable, storable reagent, but attempts at utilizing it in cross-coupling procedures have resulted in coupling at both termini of the alkyne, forming symmetrical alkynes. (Trimethylsilyl)ethynyltrifluoroborate serves as a useful surrogate of ethynyltrifluoroborate (Eq. 34)¹⁰⁹ and allows the selective insertion of an ethynyl group into organic molecules upon cleavage of the trimethylsilyl protecting group.



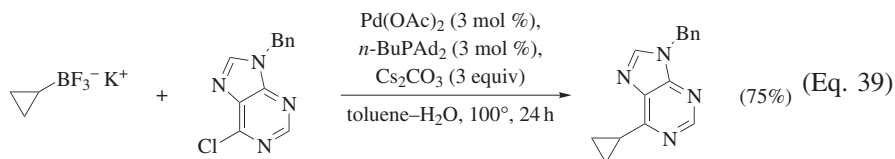
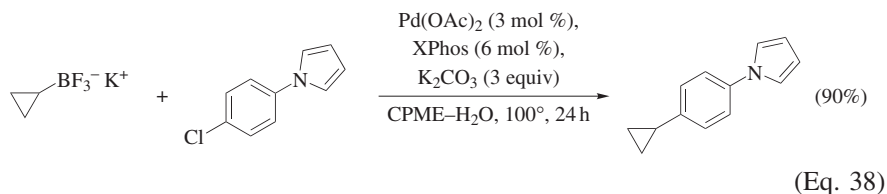
More highly elaborated alkynyltrifluoroborates can be utilized in cross-coupling reactions with a variety of electrophiles, permitting alkynes to be prepared from diverse electrophilic precursors (Eq. 35).¹¹⁰ All alkynyltrifluoroborates are more susceptible to protodeboronation than aryl- and alkenyltrifluoroborates,¹⁰⁹ and thus it is best to minimize the use of protic solvents in the cross-couplings. In some instances the palladium salts in the reaction mixture catalyze hydration of the triple bond forming ketones. This side reaction has been observed in substrates wherein neighboring groups such as aldehydes can participate in the hydration process.¹⁰⁹ Although unusual for organotrifluoroborates, anhydrous conditions are often effective for the alkynyl cross-coupling.



Multiple cross-couplings can be effected on polyhalo-substituted substrates, allowing effective syntheses of diynes and triynes from relatively simple precursors (Eqs. 36–37).^{109,111}

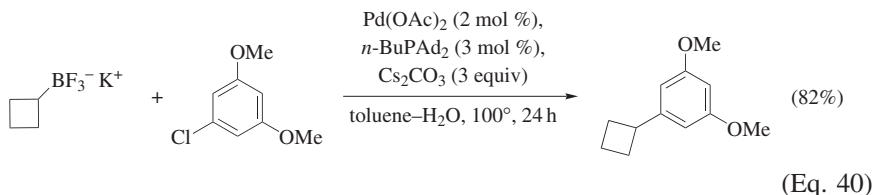


Cyclopropyltrifluoroborates and Cyclobutyltrifluoroborates. The hybridization of the C–B bond in cyclopropyl- and cyclobutylmetallic reagents render them intermediate between alkenyl and alkyl systems in terms of their reactivity in cross-coupling reactions. In contrast to the corresponding boronic acids, both cyclopropyl- and cyclobutyltrifluoroborates resist protodeboronation, and thus are indefinitely stable and storable reagents. Conditions have been developed for the cross-coupling of cyclopropyltrifluoroborates with a variety of aryl- and heteroaryl bromides and chlorides (Eqs 38–39).^{79–81,104,112} As pointed out previously (Eq. 19), these transformations are completely stereospecific.

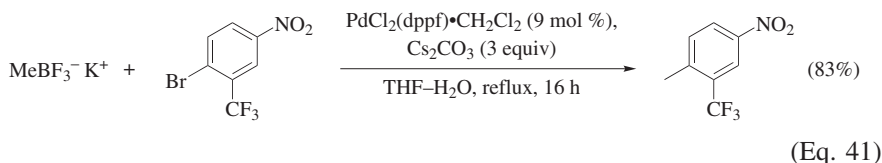


Cross-couplings of cyclobutyl derivatives have been less widely explored.¹¹² The hybridization of the carbon–boron bond is closer to that of secondary alkyl-metallic reagents, and the strain engendered in the β -hydride elimination process

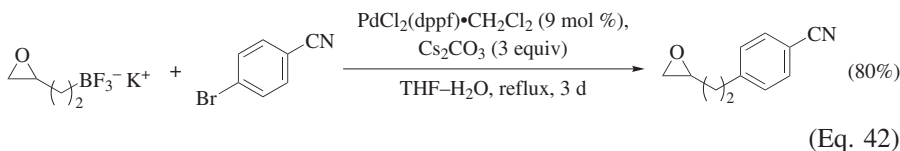
is not as high as that in the cyclopropyl system. Perhaps for these reasons, yields and reaction scope for cyclobutyltrifluoroborate cross-couplings are often lower than those of their cyclopropyl counterparts (see, however, Eq. 40).



Alkyltrifluoroborates. A diverse array of alkyltrifluoroborates has been developed for use in Suzuki-type cross-coupling reactions. Methyltrifluoroborate serves as a highly efficient and effective methylating agent. It is of value in cross-coupling with a variety of electrophiles (Eq. 41), including electron-rich aryl chlorides under appropriate conditions.^{104,113–115}

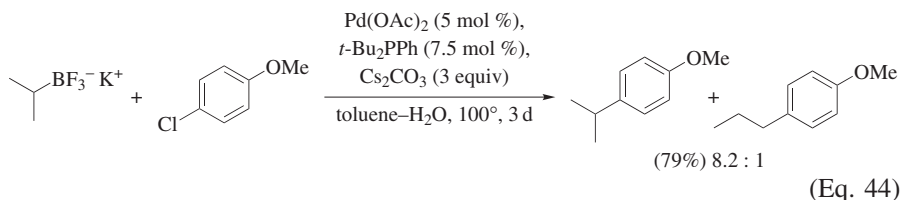
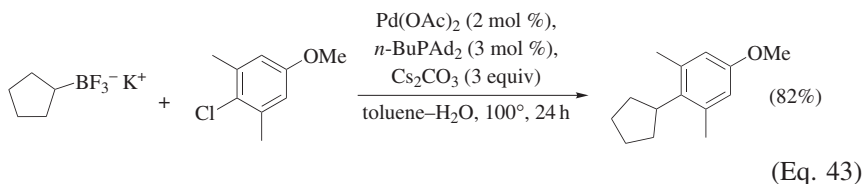


As in most Suzuki coupling reactions, primary alkyltrifluoroborates can be prepared and coupled with a diverse array of functional groups embedded within the nucleophilic partner. Alkenes, alkyl halides, alcohols, non-enolizable aldehydes, ketones, carboxylic acids, esters, amides, nitriles, thioethers, and sulfones have all demonstrated tolerance to the reaction conditions required for cross-coupling. Interestingly, epoxides can be present within the alkyltrifluoroborate, and this functional group remains intact during the cross-coupling event (Eq. 42).¹¹⁶

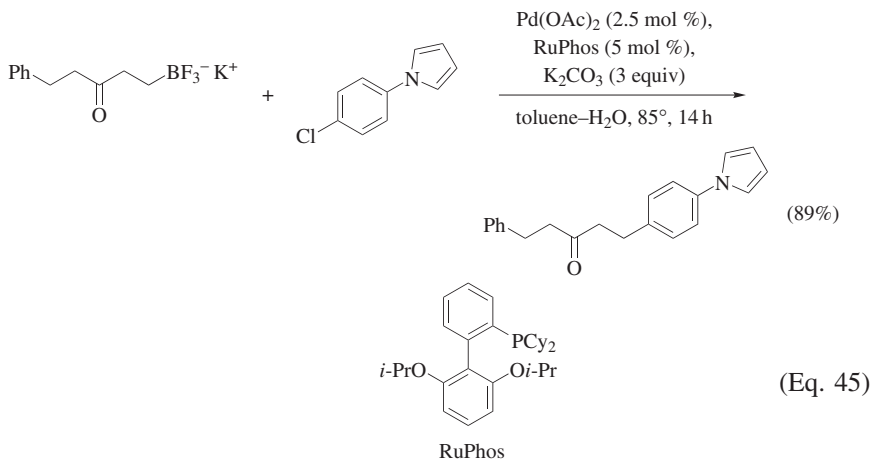


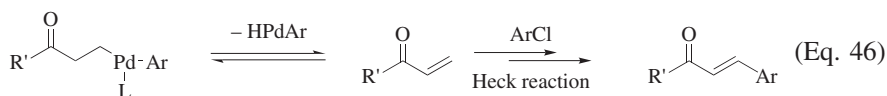
Primary alkyltrifluoroborates couple highly effectively with a variety of aryl- and heteroaryl chlorides.¹¹⁴ This protocol avoids the use of excess organoboron reagent, toxic thallium bases,¹¹⁷ and reactive organolithium compounds¹¹⁸ utilized in previously reported procedures. Because they undergo slow transmetalation and are susceptible to β -hydride elimination from the diorganopalladium intermediate, secondary organometallics pose greater challenges in cross-coupling than their primary organometallic relatives. Conditions have been developed that allow secondary alkyltrifluoroborates to undergo cross-coupling, even with highly hindered, electron-rich aryl chlorides (Eq. 43).⁷⁸ As described in the section “Side

Reactions", the coupling of secondary alkyltrifluoroborates results in the formation of isomerized products owing to processes involving competing β -hydride elimination, alkene reinsertion into the palladium–hydride bond with regiochemical reversal, and subsequent reductive elimination (Eq. 44).



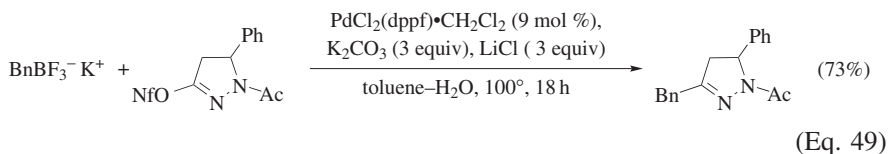
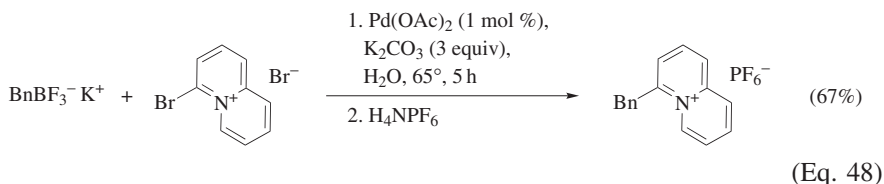
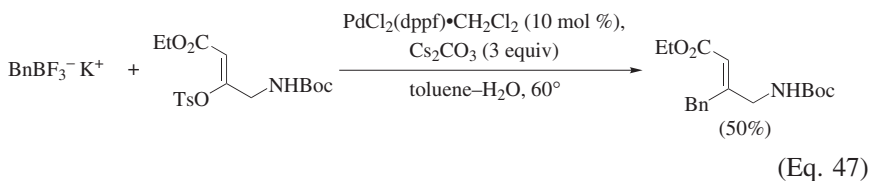
β -Trifluoroboratocarbonyls. A useful and fairly unusual subset of alkyltrifluoroborate cross-coupling reagents are the β -trifluoroboratocarbonyls.¹¹⁹ These reagents are readily prepared by conjugate addition reactions of bis(boronic) acid derivatives with α,β -unsaturated carbonyl precursors or by enolate alkylations of halomethylboron electrophiles. Ketone, hindered ester, and amide-based reagents all undergo cross-coupling with diverse aromatic and heteroaromatic halides (Eq. 45). β -Trifluoroboratoketones undergo cross-coupling quite effectively, and thus represent an unprecedented set of reagents for such transformations. Although small amounts (3–10%) of β -hydride elimination/Heck coupling products are formed with these reagents (Eq. 46),^{119,120} virtually none of these types of byproducts are observed under conditions optimized for the β -ketoamide reagents.¹²¹



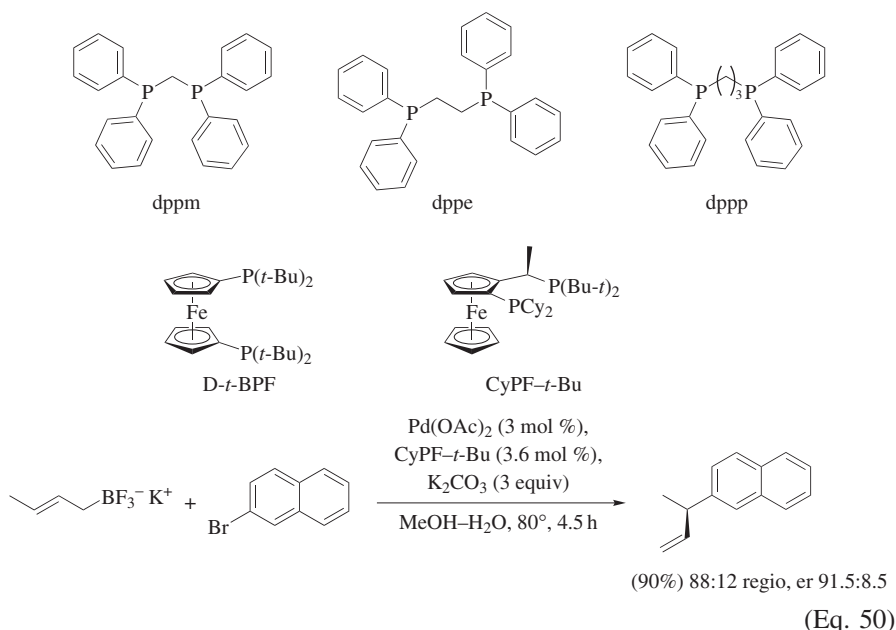


Benzyltrifluoroborates and Crotyltrifluoroborates. Benzylic and allylic metallic species represent a special subset of alkylmetallic reagents because some of these species (allyllithium and allylmagnesium derivatives) are particularly prone to homocoupling during their formation, and as a class they are generally less reactive than alkyl- or arylmetallic reagents in cross-coupling. Benzylboron compounds are less readily available than other organoboron derivatives. They are obtained principally from transmetalation reactions involving organolithium and organomagnesium precursors. In addition to these features described for benzylmetallic reagents, the related allylmetallic compounds present challenges associated with site selectivity, stereoselectivity in double bond geometry, and enantioselectivity in more highly substituted systems.

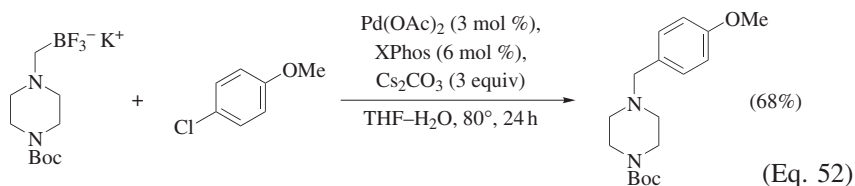
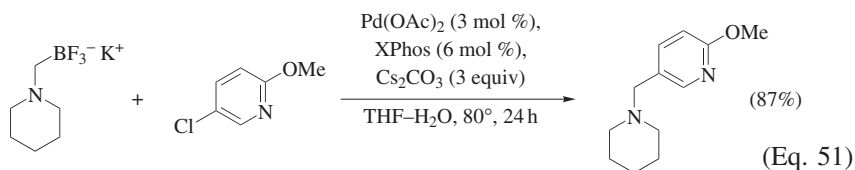
Perhaps owing to the lack of convenient synthetic approaches, few cross-couplings of benzyltrifluoroborates have been reported.^{58,68,122,123} Although the scope of these transformations has not been fully delineated, a reasonably wide range of electrophilic partners has been explored (Eqs. 47–49).

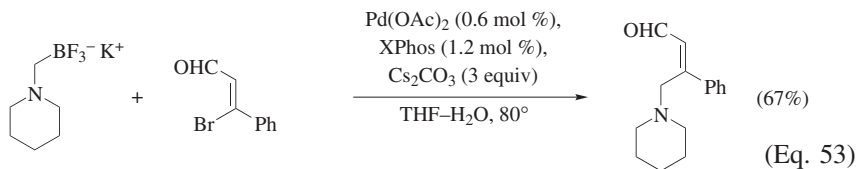


The site selectivity observed in crotyltrifluoroborate systems is greatly influenced by the ligand array used in the coupling process. Using simple phosphine ligands such as PPh₃, dpmm, dppe, and dppp, yields are low and/or carbon–carbon bond-formation is effected predominantly at the less substituted end of the allylic system.^{124,125} Employing a D-*t*-BPF or CyPF-*t*-Bu ligand, the site selectivity is nearly 100% for the internally substituted carbon, and yields are high

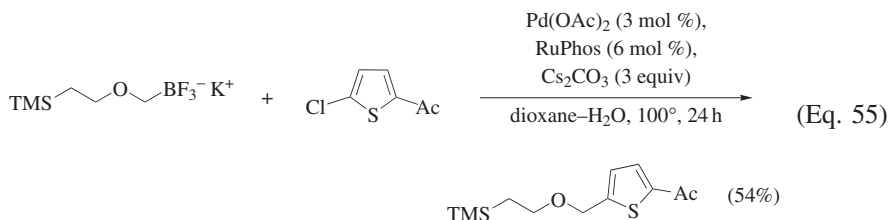
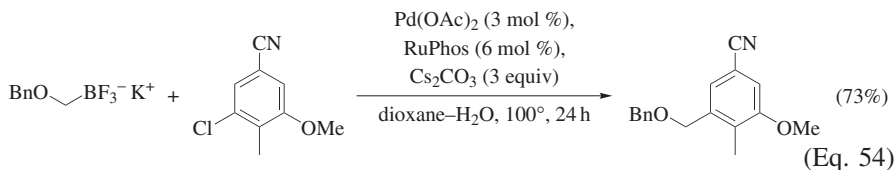
(Eq. 50).^{124–126}

Aminomethyltrifluoroborates and Alkoxyethyltrifluoroborates. Amino-methyl- and alkoxyethyltrifluoroborates represent a class of alkylating agents that provides a convenient and unique access to useful organic molecules. The aminomethylation reaction is complementary to reductive amination for the installation of this valuable functional unit into aromatic and heteroaromatic systems. To date, only the syntheses of tertiary amines have been reported using this method.^{127,128} The method appears to be quite general for a variety of aromatic and heteroaromatic bromides and chlorides (Eqs. 51–53).

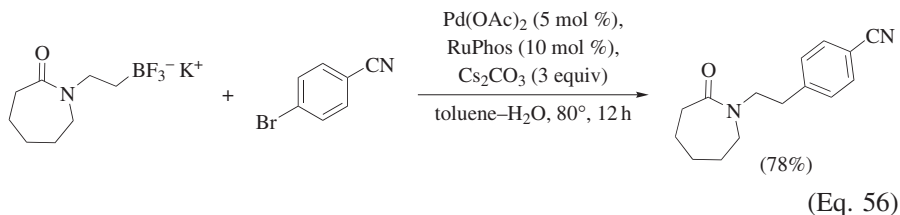


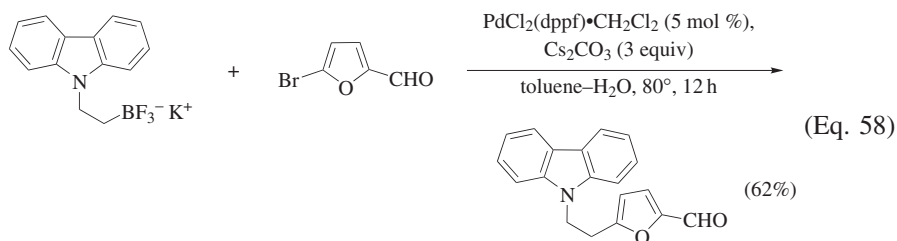
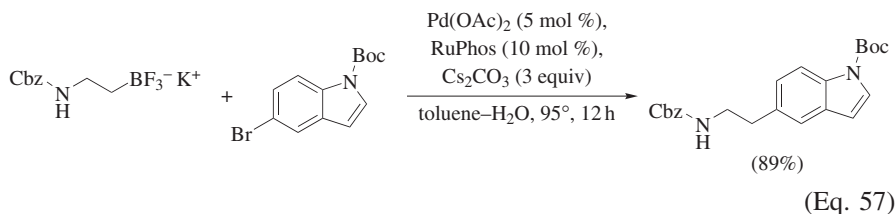


The analogous alkoxymethylation reaction also complements existing approaches to benzylic ethers and alcohols.¹²⁹ These ethers are commonly prepared by the Williamson ether synthesis, which requires access to benzylic electrophiles. A much more diverse collection of haloarenes or haloheteroarenes is available than their benzylic counterparts, and thus from a commodity chemical perspective the carbon–carbon bond-forming approach to the ethers is advantageous. By deprotection after alkoxymethylation, the cross-coupling also affords a route to benzylic alcohols. As in the aminomethylation reaction described above, diverse aryl chlorides and aryl bromides can be coupled with alkoxymethyltrifluoroborates to generate the desired target structures (Eqs. 54–55).



Aminoethyltrifluoroborates. Aminoethyltrifluoroborates comprise another relatively unique class of reagents for cross-coupling.^{130,131} Generated by the hydroboration of enamines, enamides, and enecarbamates, these reagents permit facile incorporation of an aminoethyl subunit into aryl and heteroaryl platforms through cross-coupling. Although conditions exist for the cross-coupling of aminoethyltrifluoroborates with bromide, iodide, and triflate electrophiles (Eqs. 56–58), chlorides have thus far proven recalcitrant reaction partners.





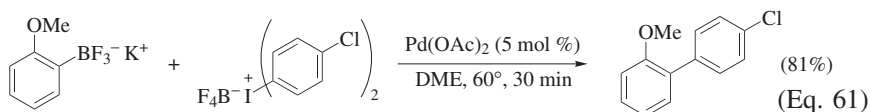
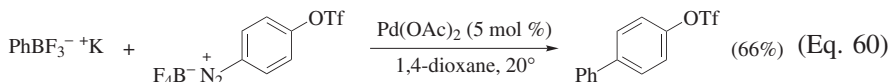
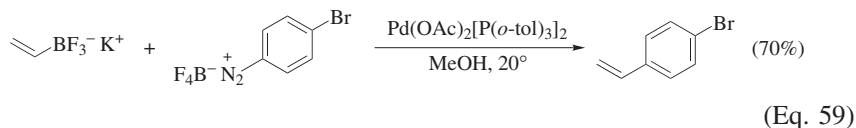
The Electrophile

Many diverse electrophiles have been used in conjunction with organotrifluoroborates in cross-coupling reactions. Despite the large number of examples, generalizations are difficult to make on the suitability of individual electrophiles for cross-coupling. An attempt is made herein to outline the known scope and limitations of various reacting partners, but this task is not without some risk. In certain instances, yields may derive from subpar optimization, wherein a thorough exploration of catalysts and reaction conditions was not undertaken. Additionally, it is important to note that most synthetic methods are developed in an attempt to apply them across a wide spectrum of reacting partners. Inevitably, one discovers individual outliers for which the general procedure does not apply. It is likely that these substrates would react satisfactorily under slightly modified conditions. Thus, the yields and scope of reactivity often depend upon how much time is invested in seeking the best possible outcome. Most importantly, the success of many transformations, and especially Suzuki coupling reactions, is highly temporal. Substrates viewed as inert a few short years ago might now be coerced to react with ease on the basis of enhanced knowledge of the mechanistic details of the reaction and the development of high-performance catalytic systems.

Aryl and Heteroaryl Electrophiles. Aryl and heteroaryl groups represent the most broadly employed class of electrophilic partners for palladium-catalyzed organotrifluoroborate cross-coupling. A good outline of reactivity has been established, and the range of suitable nucleofuges is still expanding.

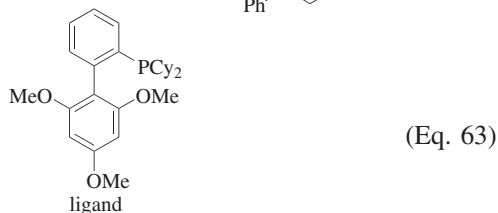
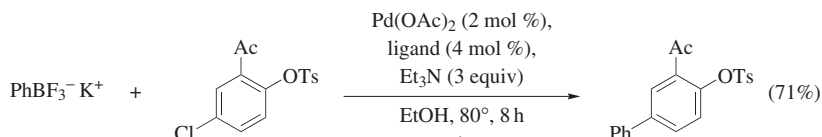
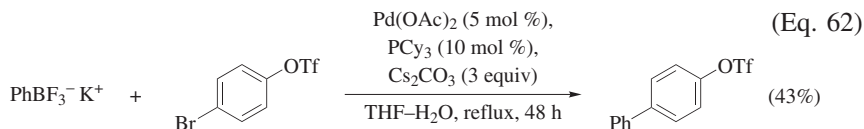
The seminal cross-coupling reactions of organotrifluoroborates focused on diazonium and iodonium salts.^{13,15} These reactions take place under extremely mild conditions and afford cross-coupling products in high yields. One of the benefits of these leaving groups is the ability to conduct selective cross-couplings in the presence of reactive halides and triflates. Although yields are sometimes

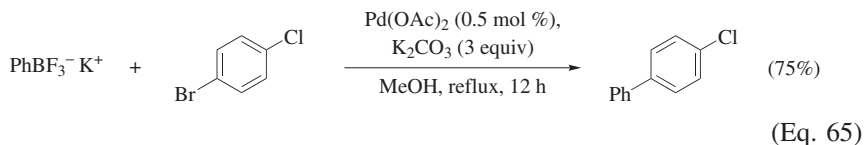
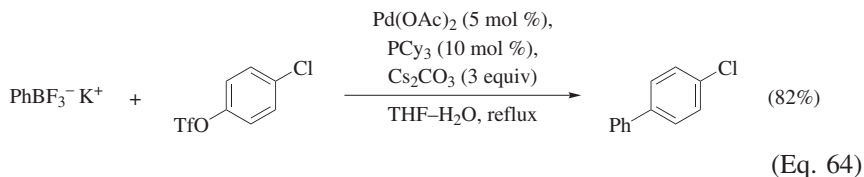
modest, diazonium salts can be selectively reacted in the presence of all halides (Eqs. 59–61).^{13, 15, 132, 133}



Halides themselves are well represented as leaving groups among aryl and heteroaryl electrophiles. In the earliest studies, bromides and, to some extent, iodides dominated the substrates utilized because they are quite reactive in the oxidative addition step of the catalytic process. However, the commercial availability of a wider array of less expensive chlorides has provided impetus to finding conditions under which these partners can be coupled effectively. This endeavor has resulted in the development of catalyst systems that work very effectively with aryl and heteroaryl chlorides,²¹ and nearly the full range of organotrifluoroborates perform effectively with these substrates.

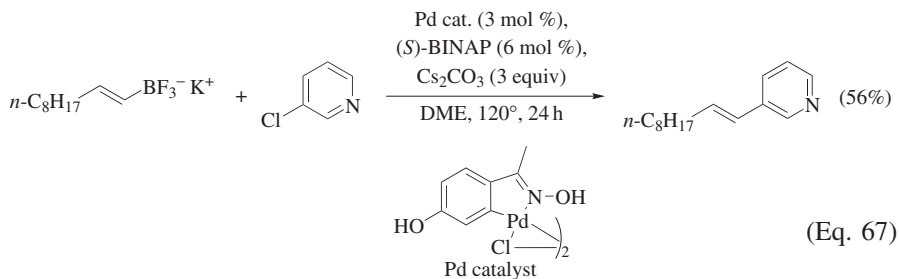
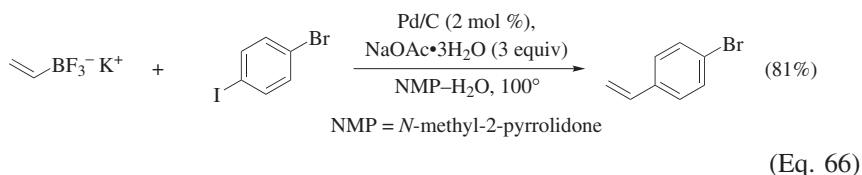
Selectivity issues can be important between and among the halides and other nucleofuges, and although some information on this subject is available,^{134–136} rigorous rate studies and even extensive qualitative observations are lacking. Nevertheless, several trends emerge. For aryl nucleophiles, the reactivity appears to be in the order $\text{I} > \text{Br} \approx \text{OTf} > \text{Cl} > \text{OTs}$ (Eqs. 62–65).



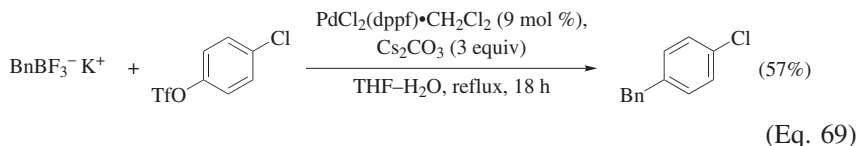
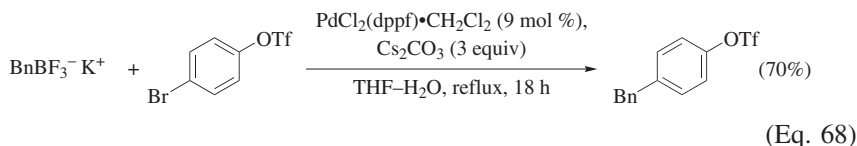


A significant caveat arises in discussing the reactivity of aryl halide electrophiles; those protocols that are successfully developed for challenging reaction partners do not necessarily translate well to electrophiles that, a priori, one might view as more reactive. For example, successful cross-coupling conditions for aryl chlorides work abysmally when applied to aryl iodide substrates, indicating that the oxidative addition is not always the key step of the catalytic cycle.

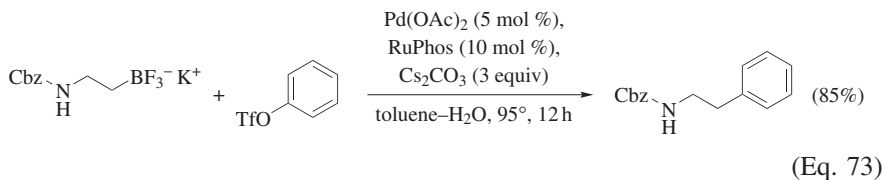
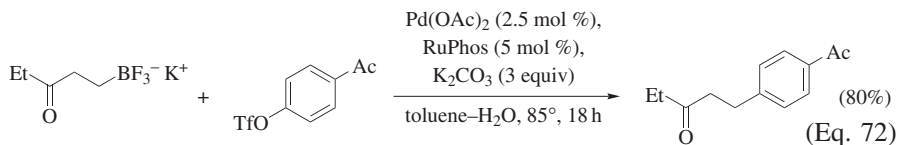
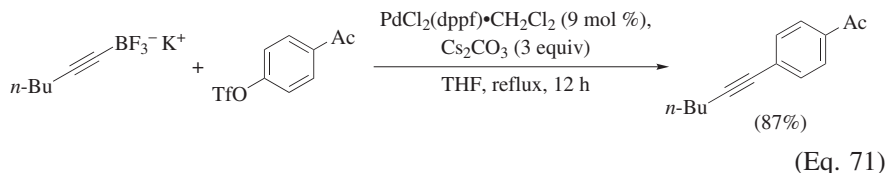
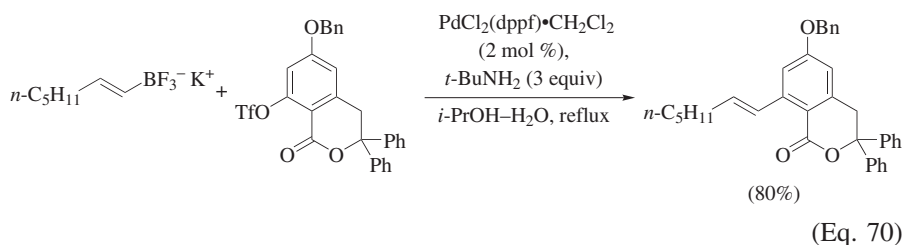
Although some rigorous reactivity studies have been performed for the coupling of aryltrifluoroborate nucleophiles with aryl electrophiles, less information is available concerning the relative coupling rates of aryl electrophiles with alkenyltrifluoroborate nucleophiles (Eq. 66).¹³⁷ Among the halide electrophiles, aryl and heteroaryl bromides and iodides are the most common. Aryl and heteroaryl chlorides require more vigorous conditions (Eq. 67).¹⁰⁵



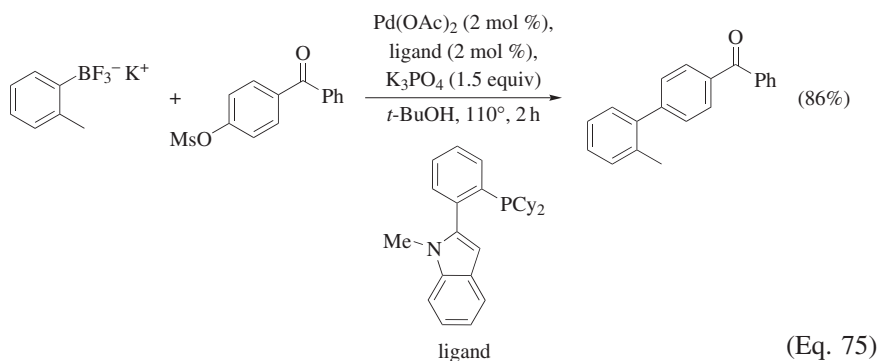
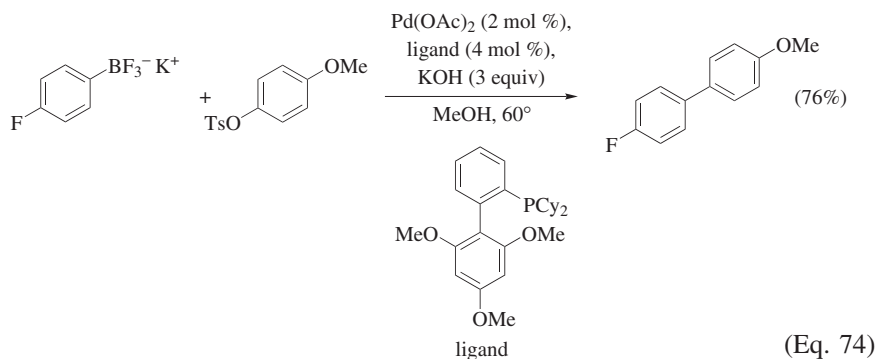
In direct competition experiments, benzyltrifluoroborates have been observed to couple selectively with aryl electrophiles. The observed order of reactivity is $\text{Br} > \text{OTf} > \text{Cl}$ (Eqs. 68–69).⁵⁸



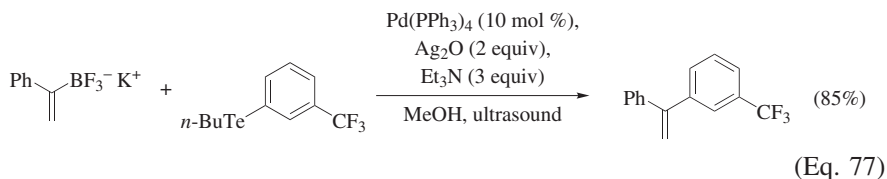
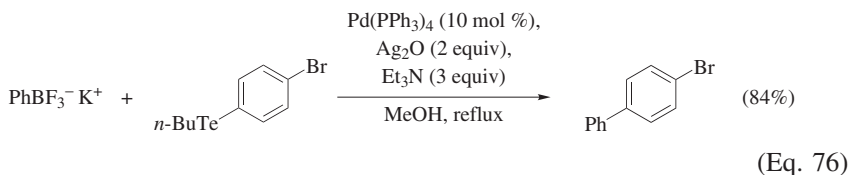
For various reasons, decidedly less effort has been devoted to an exploration of other nucleofuges in aryl electrophiles. Among these, triflates have received the most attention, providing good to excellent conversion to product with a broad range of organotrifluoroborates (Eqs. 70–73).^{58,108,109,120,131}

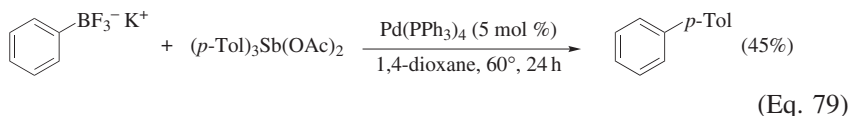
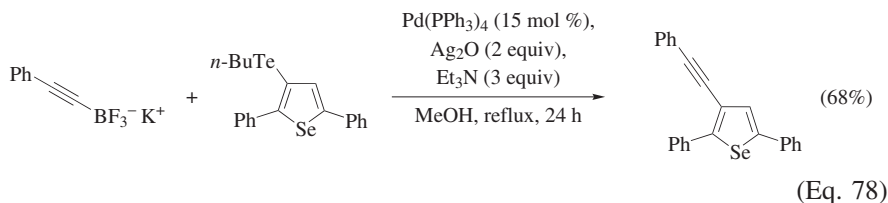


Tosylates and mesylates have been explored to a much lesser extent, with successful examples reported only for aryltrifluoroborate nucleophiles (Eqs. 74–75).^{108,135,138,139}



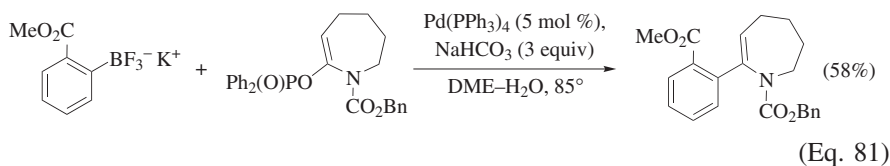
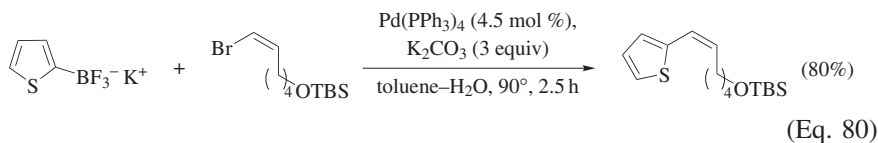
Tellurides and stiboranes¹⁴⁰ round out the classes of aryl nucleofuges that have been used in conjunction with organotrifluoroborates (Eqs. 76–79). The tellurides in particular serve as pseudohalides in numerous cross-coupling reactions, but the apparent requirement to employ two equivalents of silver salts as promoters in the reaction detracts from their appeal. Interestingly, the aryl tellurides appear to be more reactive than aryl bromides and aryl chlorides in the cross-coupling process, and tolerate a number of other functional groups as well.^{141–144}



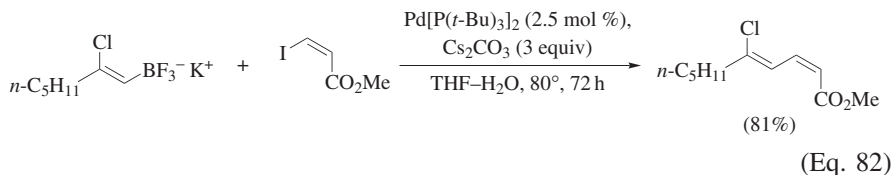


Alkenyl Electrophiles. A significantly diminished range of nucleofuges have been utilized with electrophilic alkenyl coupling partners, and a more limited subset of organotrifluoroborates have been employed in these reactions. Nevertheless, it is evident that high yields can generally be achieved, and the reactions are stereospecific and chemoselective.

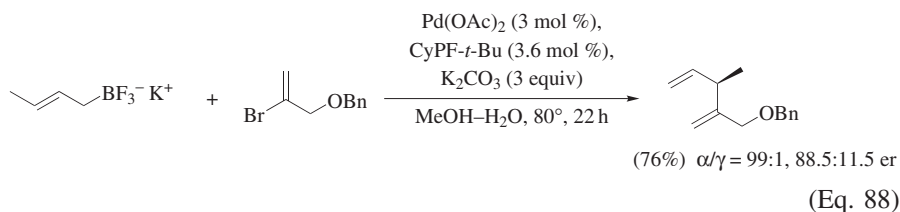
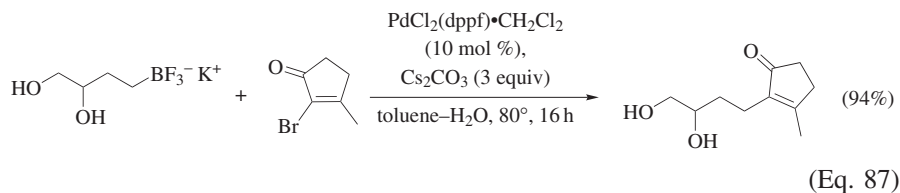
To date, alkenyl chlorides have not been employed as electrophilic alkenyl coupling partners. The most common leaving group in the alkenyl class of electrophiles is bromide. A number of functionalized aryl- and heteroaryltrifluoroborates react smoothly with alkenyl bromides, providing excellent yields of the desired products (Eq. 80).⁶⁶ The use of alkenyl iodides in reactions with aryl- and heteroaryl nucleophiles is rare.^{12,67,83,145} An enol phosphate has also been employed in coupling with an aryltrifluoroborate (Eq. 81).¹⁴⁶



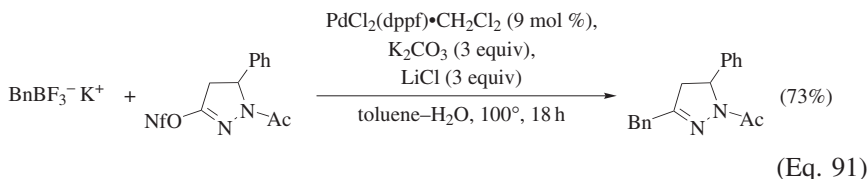
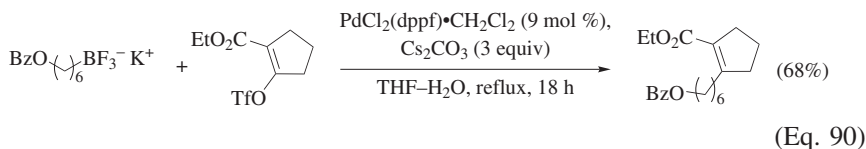
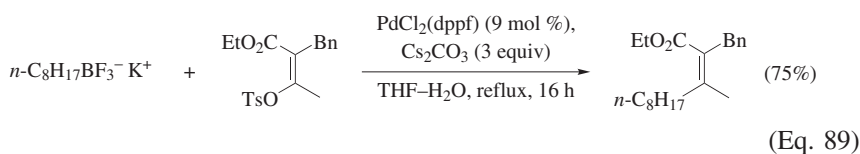
Conjugated diene syntheses can be accomplished by cross-coupling of alkenyltrifluoroborates with alkenyl halides. Although a few alkenyl iodides have been employed (Eq. 82),^{147,148} bromides dominate the scene (Eq. 83).⁷² For both, the transformations are stereospecific and tolerant of a diverse array of functional groups.



Alkenyl bromides comprise the major electrophiles for coupling with sp^3 -hybridized organotrifluoroborate nucleophiles (Eq 87).⁷⁶ Again, no alkenyl chloride or alkenyl iodide electrophiles appear to have been reported. In cross-coupling of a crotyltrifluoroborate with an alkenyl bromide in the presence of a chiral MandyPhos-type ligand, excellent site selectivity and modest enantioselectivity can be achieved (Eq. 88).¹²⁶

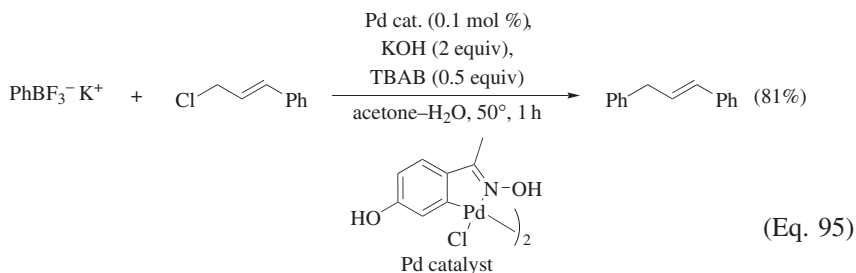
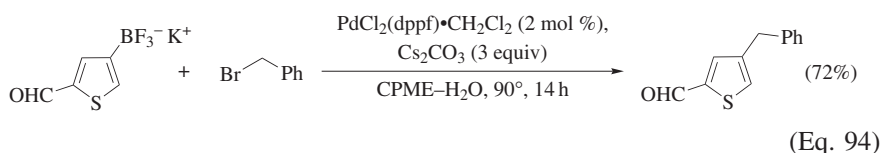
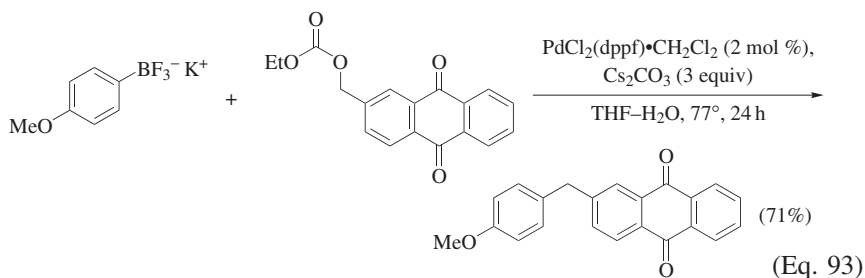
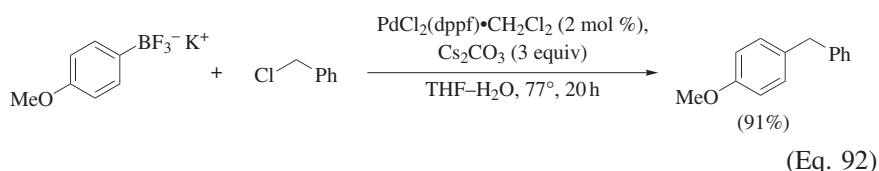


Although some sulfonates (Eqs. 89–91)^{58,123} have been employed in cross-coupling with sp^3 -hybridized organotrifluoroborate nucleophiles, this chemistry remains largely undeveloped. Yields among the few tosylates examined are modest; the triflates generally afford good yields, and the two nonaflates examined provide mixed results. More extensive studies will be required in this area to judge the practicality of the processes.



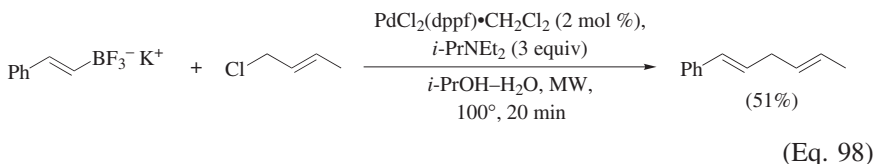
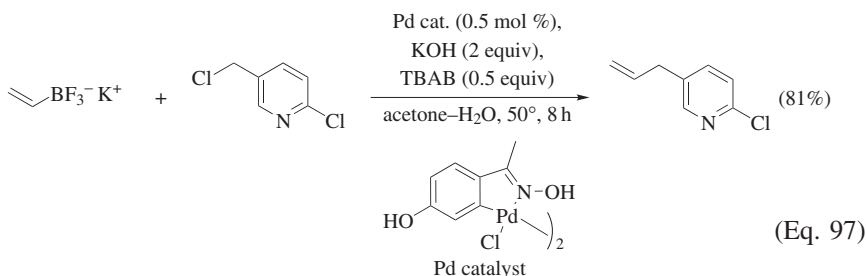
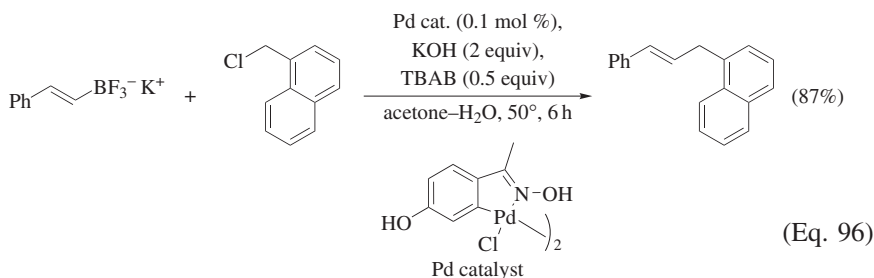
Benzyl and Allyl Electrophiles. To date the only sp^3 -type electrophiles employed with organotrifluoroborates have been the benzylic and allylic systems. The use of this class of electrophiles is further limited to aryl-, heteroaryl- and alkenyltrifluoroborates.

A variety of aryltrifluoroborates have been cross-coupled with benzylic halides (Eqs. 23, 24, and 92),⁸⁵ benzylic pseudohalides, and benzylic-type carbonates (Eq. 93). Benzyl iodides have not been explored, but benzyl chlorides and bromides couple satisfactorily. Only two heteroaryltrifluoroborates have been explored in conjunction with benzylic bromides, and both provide good yields (Eq. 94).⁸⁵ A limited number of allylic chlorides have also been partnered with phenyltrifluoroborate (Eq. 95).¹⁵⁰



In cross-coupling with alkenyltrifluoroborates, chlorides have been the exclusive coupling partners in benzylic and pseudobenzylic systems (Eqs. 96–97).⁷⁰ Skipped dienes can be prepared by the reaction of alkenyltrifluoroborates with

allylic halides (Eq. 98).^{70,151} In limited studies, allyl chlorides, bromides, and iodides all appear equally effective.



SIDE REACTIONS

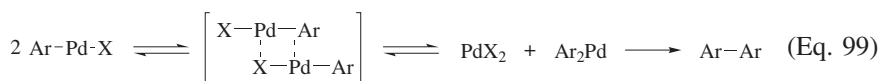
For the most part, the same unwanted byproducts encountered in Kumada, Stille, Negishi, Hiyama, and other Suzuki-type cross-coupling transformations may be observed in cross-coupling reactions performed with organotrifluoroborates. In some cases, however, there are important differences between organotrifluoroborates and other reagents that prevent the formation of these materials. Additionally, a deeper mechanistic understanding of cross-coupling processes has led to reaction designs that mitigate many of the side reactions found in earlier versions of these reactions.

It is unfortunate that minor byproducts are often ignored and/or not reported and are simply separated away from the desired products. The following discussion outlines in general terms some of the side reactions one must be aware of, and cites specific cases where more detailed information is available.

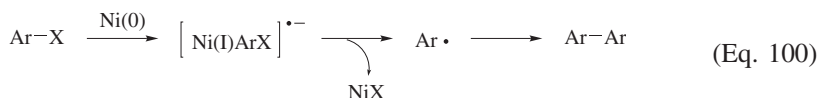
Homocoupling of the Organic Halide Electrophile

A byproduct found in many cross-coupling reactions is the dimer formed from homocoupling of the organic halide electrophile. This contaminant can

have several origins, depending on the nature of the reaction being performed. In palladium-catalyzed reactions the most common source appears to be a metathesis reaction of the originally formed oxidative addition intermediate. The organopalladium halide disproportionates, thereby generating PdX_2 salts and diorganopalladiums, the latter of which reductively eliminate forming the homocoupled product (Eq. 99).¹⁵² Because this process is kinetically second order in the palladium catalyst, and the desired cross-coupling reaction is typically first order in the catalyst, the amount of homocoupled product can often be minimized by simply lowering the catalyst loading in reactions of interest.



Nickel-catalyzed reactions are prone to providing homocoupled products through electron-transfer reactions, forming radical species that subsequently dimerize (Eq. 100).¹⁵³



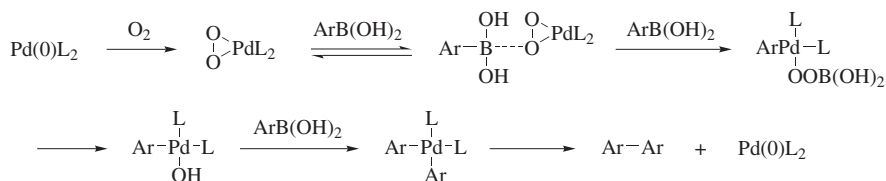
Homocoupling of the Organoboron Reagent

Byproducts from homocoupling of organoborons in cross-coupling reactions can derive from several different processes. The first mode is associated with Pd(II) precatalyst reduction to Pd(0) , which in most Suzuki reactions occurs by a double transmetalation reaction on the PdX_2 salt, followed by reductive elimination (Eq. 4).²⁷ This process generates a homocoupled product in proportion to the catalyst loading. By contrast, as outlined previously, catalyst activation in organotrifluoroborates appears to transpire through a fluoride-catalyzed hydrolytic reduction (Scheme 4) that avoids the formation of dimers when boronic acids are utilized. Cross-coupling using organotrifluoroborates thus minimizes homocoupled byproduct formation created through catalyst activation.

A related mode of organoboron homocoupling results from the metathesis reaction discussed previously (Eq. 99). This reaction generates homocoupled products derived from the electrophile, but also results in the formation of PdX_2 salts. The latter can react with organoborons, forming diorganopalladium species that reductively eliminate to yield homocoupled products derived from the nucleophilic component of the reaction. Because <0.1% of organoboron-derived homocoupling product is formed in organotrifluoroborate Suzuki-type reactions,²⁷ presumably any PdX_2 species formed by this process are reduced via the fluoride-catalyzed process described above (Scheme 4) prior to transmetalation with the organotrifluoroborate.

A third means by which organoboron reagents can lead to homocoupling products is via oxidative coupling. Mechanistic studies²⁷ suggest that the process transpires via formation of a palladium peroxo species, a process that is

either reversible or boronic acid-mediated, and is sensitive to the concentration of the boronic acid (Scheme 8).¹⁵⁴ The reaction is reportedly slow under neutral conditions, but rapid under the aqueous basic conditions typically used in Suzuki cross-coupling reactions.^{3,155} It has also been suggested that some of these homocoupled products arise upon workup of the reactions, wherein unreacted boronic acids undergo aerobic coupling in the presence of active catalyst. Organotrifluoroborates apparently do not facilitate palladium peroxo formation, and because they are only slowly (relative to catalytic turnover) hydrolyzed to boronic acids under the conditions utilized for cross-coupling, homocoupling resulting from this oxidative process is also minimized.



Scheme 8. Oxidative homocoupling of boronic acids.

Protodeboronation

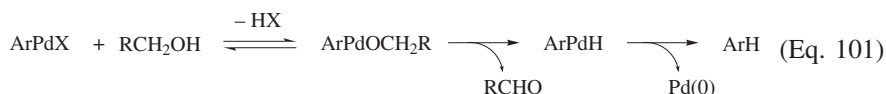
One of the banes of the Suzuki cross-coupling reaction is the formation of protodeboronated byproducts. Cross-coupling and protodeboronation occur competitively under conditions typically utilized for the Suzuki reaction with boronic acids, and consequently a significant excess of these reagents is employed in virtually every cross-coupling protocol involving these organoboron nucleophiles. The rate of protodeboronation is a function of both the reaction conditions and the structure of the organoboron reagent employed. For boronic acids, the presence of weak bases such as KHCO_3 inhibits boron–carbon bond cleavage,¹⁵⁶ and the use of anhydrous conditions with boronate ester nucleophiles is suggested to reduce the amount of protodeboronated material.¹⁵⁵ These conditions minimize the formation of trihydroxyborates $[\text{RB(OH)}_3^-]$, the intermediates believed responsible for the protodeboronated products.²⁷

Several structural classes of boronic acid are notorious for their facile protodeboronation. Some suffer boron–carbon bond cleavage during challenging cross-couplings under basic conditions (e.g., sterically hindered systems and electron-deficient aromatics).¹⁵⁵ As pointed out previously, trihydroxyborates are considered the critical intermediates responsible for protodeboronation under these conditions. However, several important classes of boronic acids are inherently unstable to protodeboronation, decomposing even upon simple benchtop storage (e.g., cyclopropyl-, cyclobutyl-, and some heteroarylboronic acids).⁹⁰ The corresponding organotrifluoroborates do not suffer protodeboronation even under strongly basic conditions at elevated temperatures for long periods of time, and nearly all can be stored on the shelf indefinitely. As discussed previously, the organotrifluoroborates serve as a stable reservoir of boronic acid derivatives, with slow fluoride–hydroxyl exchange leading to intermediates active in

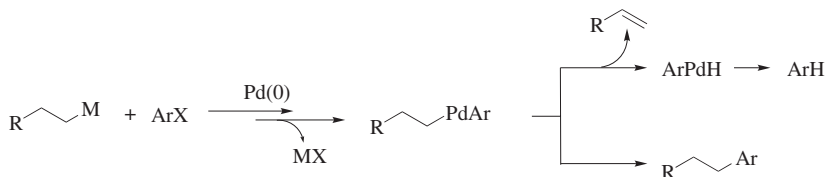
transmetalation.^{46,58,59} This phenomenon, combined with the use of low concentrations of water used in the cross-coupling (reducing the concentration of trihydroxyborate), minimizes protodeboronation in the cross-coupling transformation.

Dehalogenation of Aryl Halides

Dehalogenation of the halide electrophile is sometimes observed in organotrifluoroborate and other cross-coupling reactions, particularly when alcohol solvents are used. These products derive from an exchange of the halide on the palladium with alkoxide, with subsequent β -hydride elimination and reductive elimination (Eq. 101).¹⁵⁷ Analogous phenomena can be observed with amines present in the reaction mixture.



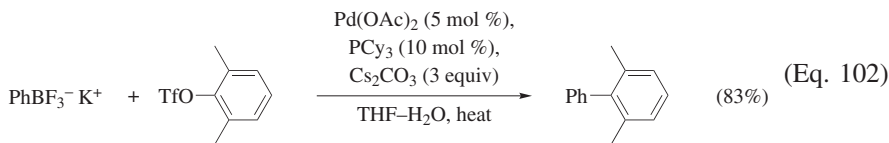
In the cross-coupling of alkylmetallic reagents the dehalogenated products may become more prevalent owing to the intervention of β -hydride elimination from the diorganopalladium intermediate (Scheme 9). This side reaction has been minimized by the development of highly effective catalyst/ligand combinations and high-throughput experimentation techniques leading to a more thorough optimization of the reaction conditions.^{78,114}



Scheme 9. β -Hydride elimination.

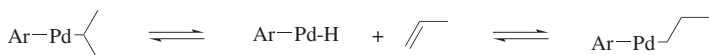
Hydrolysis of Triflates

Early studies indicated that alkyltrifluoroborates cross-couple well with electron-deficient aryl triflates, but not with electron-rich electrophiles, which are more difficult to reduce.⁵⁸ Under the conditions first investigated for cross-coupling [MeOH solvent, $\text{Pd}(\text{OAc})_2$ precatalyst, no ligand, K_2CO_3 base, reflux], competitive hydrolysis of the less reactive, electron-rich triflates occurs, leading to low yields of the final product. This phenomenon has been overcome by using catalyst systems and reaction conditions that facilitate the oxidative addition reaction [THF/ H_2O solvent, $\text{Pd}(\text{OAc})_2/\text{PCy}_3$ precatalyst, Cs_2CO_3 base, reflux], allowing efficient cross-coupling even with sterically encumbered and electron-rich reaction partners (Eq. 102).¹³⁴ With alkynyltrifluoroborate reagents, performing the cross-couplings under anhydrous conditions proves to be effective.¹⁰⁹

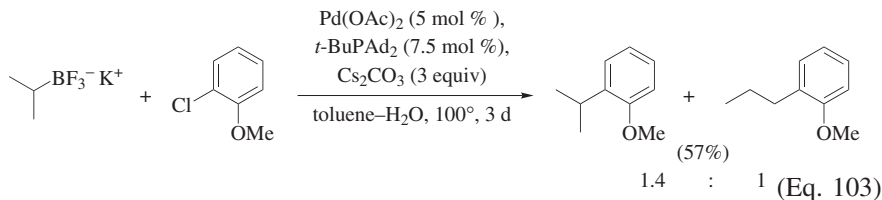


β -Hydride Elimination/Isomerization

Cross-coupling of alkylmetallic reagents has always been a challenge because of the intervention of β -hydride elimination from the diorganopalladium intermediate (Scheme 10). As pointed out above, with the advent of effective ligands and access to high-throughput experimental techniques,⁷⁸ β -hydride elimination can largely be suppressed in reactions of primary organotrifluoroborates. It remains a significant problem, however, in the cross-coupling of secondary organometallics, and particularly for those reactions that involve sterically encumbered electrophiles. In these cases, β -hydride elimination followed by hydropalladation leads to an isomeric organopalladium intermediate that can reductively eliminate, leading to isomerized products (Eqs. 18, 44, and 103).

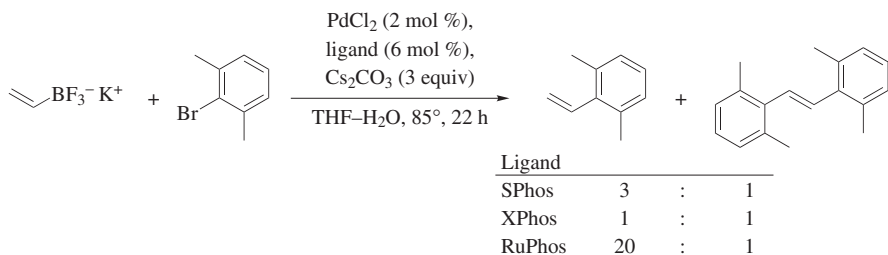


Scheme 10. Isomerization via β -hydride elimination/reinsertion.

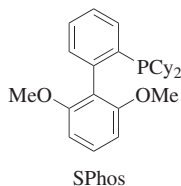


Heck-Type Coupling

Heck-type reactions can occur under conditions intended for vinyltrifluoroborate cross-coupling reactions, particularly with those substrates for which the initial cross-coupling is inherently difficult. This includes aryl chlorides and sterically encumbered aryl bromides.¹⁰⁶ To avoid unwanted Heck coupling, the ligand can be optimized so as to mitigate the formation of the alkene insertion products (Eq. 104). However, a Suzuki-Heck cascade can be used advantageously to build polymeric materials in an efficient, one-pot process.¹⁵⁸



(Eq. 104)



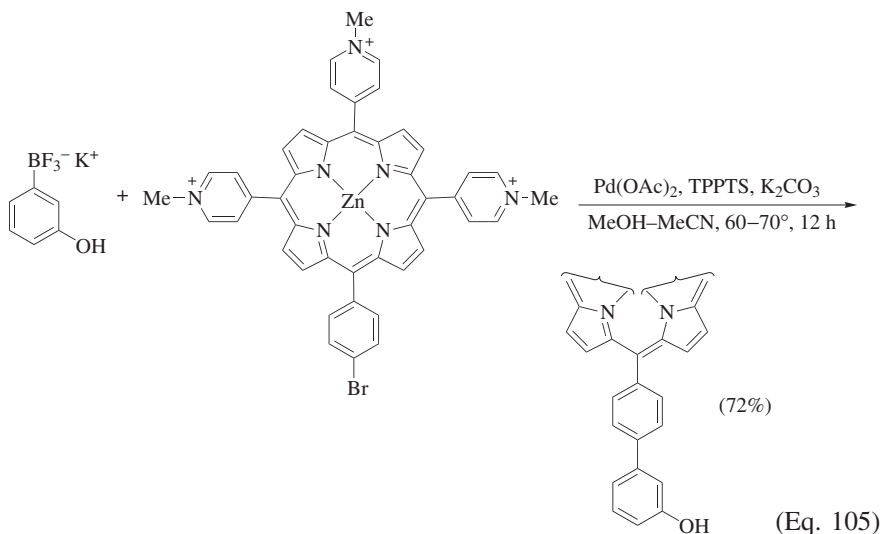
Phenol Formation

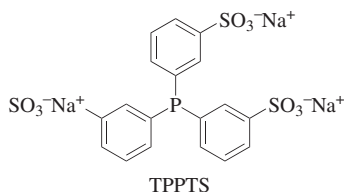
The inadvertent introduction of oxygen or the use of THF solvent containing tetrahydrofuran-2-hydroperoxide in cross-coupling reactions employing tricoordinate arylborons leads to the formation of phenol byproducts.²⁷ Oxidation of the aryltrifluoroborates to phenols is avoided under these conditions. The trifluoroborates appear to facilitate the decomposition of the tetrahydrofuran hydroperoxide by a mechanism that is not clear, but does not involve oxidation of the carbon–boron bond.

APPLICATIONS TO SYNTHESIS

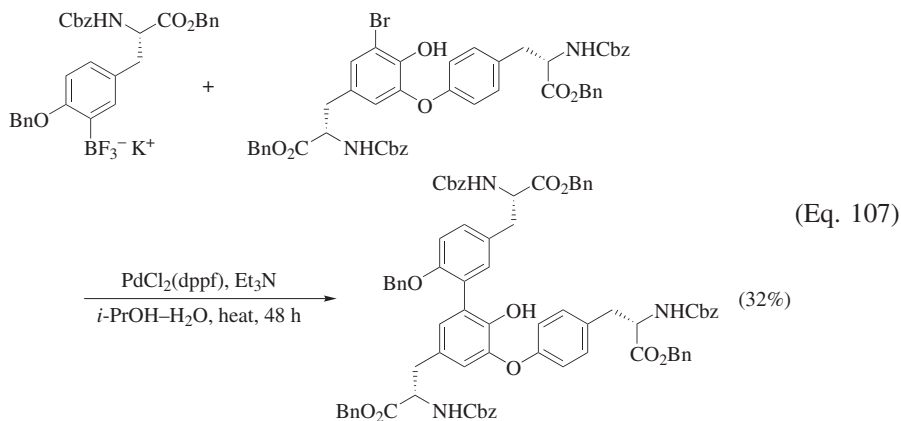
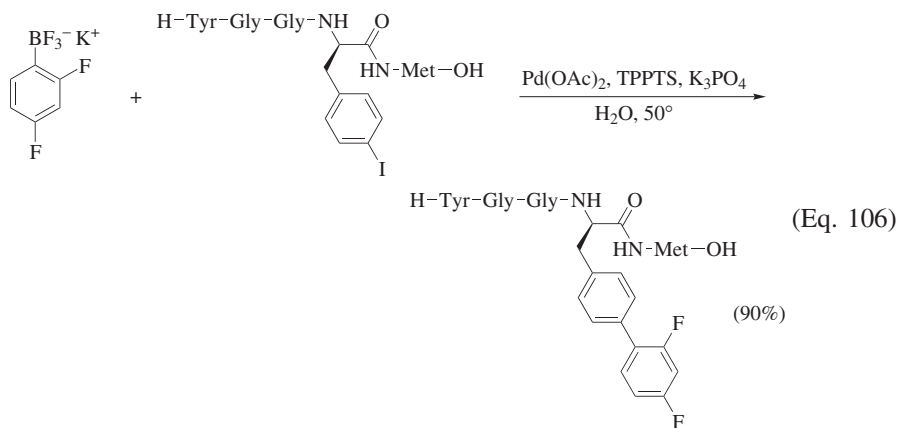
Various organotrifluoroborates have been applied to the synthesis of molecules of interest in materials science, natural products chemistry, and the construction of molecules of biological or pharmacological interest. Some examples of these are outlined below.

Porphyrins constitute an extremely valuable class of molecules that find applications as therapeutics and photosensitizers, and are used in many areas of materials science. A method was reported that allowed the elaboration of cationic zinc porphyrins via cross-coupling with aryl- and vinyltrifluoroborates under aqueous conditions, allowing libraries of these target molecules to be constructed and analyzed for their physical and chemical properties (Eq. 105).¹⁵⁹

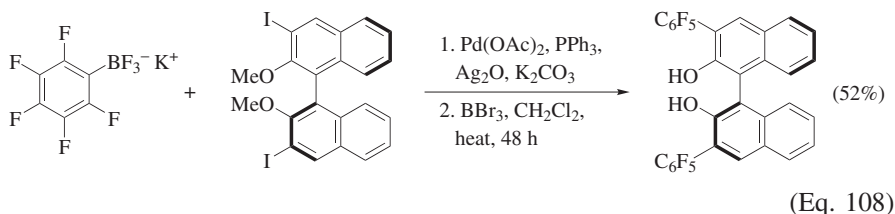




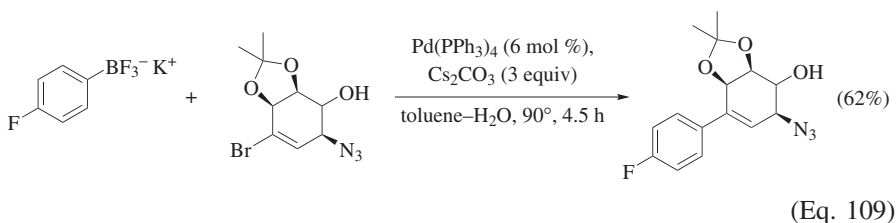
Aryltrifluoroborates have also been used to modify 4-iodophenylalanine residues of peptides through arylation (Eq. 106).¹⁶⁰ Additionally, diiodinated tyrosine derivatives have been doubly arylated under these and similar reaction conditions (Eq. 22).^{84,160} The method was employed on thermally labile, hydrophilic peptides that mimic the nature of most biologically active peptides, allowing structure-activity relationship studies to be carried out rapidly on a variety of complex, water-soluble peptides without resorting to elaborate protection/deprotection schemes. Syntheses of dityrosine and pulcherosine (Eq. 107)⁸⁴ benefited from the use of aryltrifluoroborate technologies in assembling significant components of these naturally occurring amino acid derivatives, as other cross-coupling protocols for the desired transformation proved ineffective.



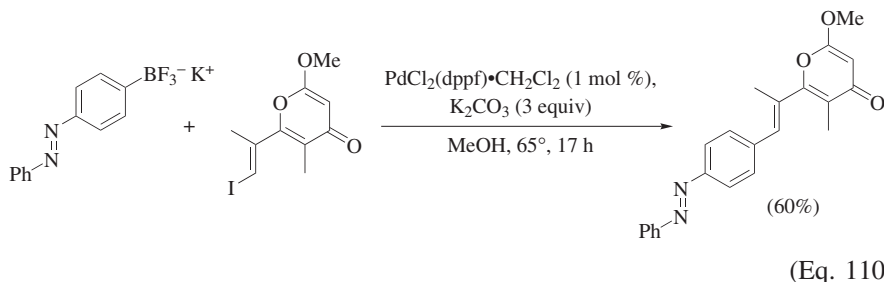
A highly electron-deficient organotrifluoroborate, pentafluorophenyltrifluoroborate, was utilized for the construction of an enantiomerically enriched binaphthol derivative that was eventually incorporated into a molybdenum imido alkylidene catalyst used for olefin metathesis reactions (Eq. 108).⁸⁹ Neither Kumada nor boronic acid Suzuki-type coupling reactions were suitable in this case.



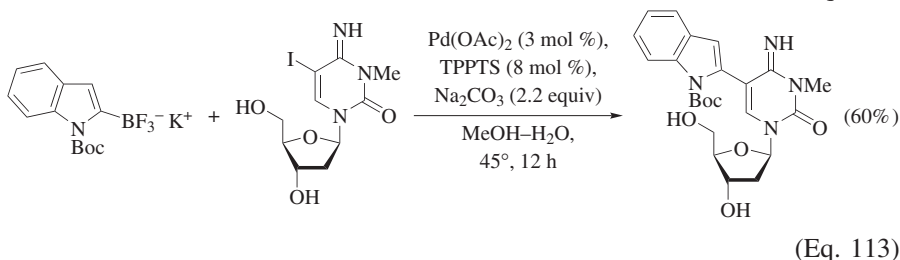
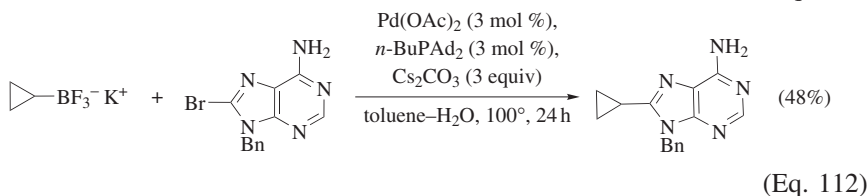
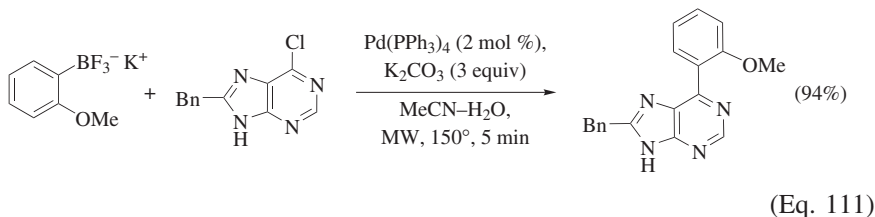
The aryltrifluoroborate version of the Suzuki coupling reaction was utilized to derivatize cyclitol substructures incorporating the azide functional group (Eq. 109).¹⁶¹ The latter could be utilized directly in Huisgen 1,3-dipolar cycloaddition reactions to generate triazoles, or reduced to amines to introduce amino acid moieties in the conduritol building block.



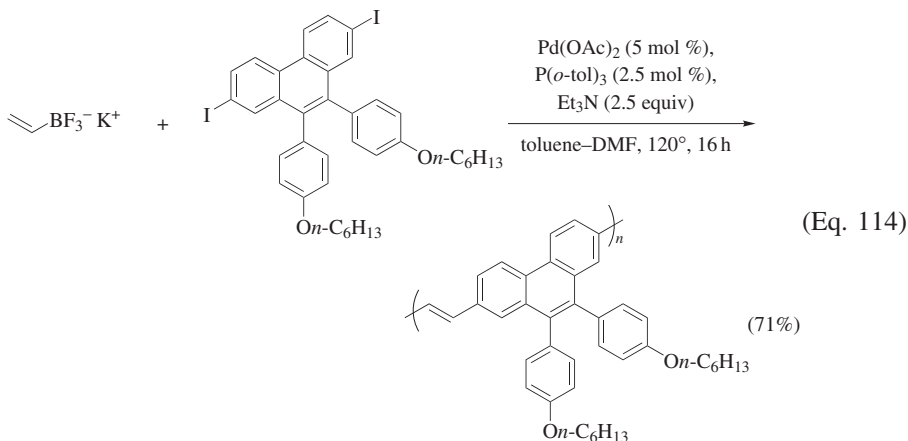
Azobenzenes are valuable as photochromic ligands for the development of photoswitches used as protein agonists and antagonists. A novel approach to these structures employs aryltrifluoroborate coupling reactions (Eq. 110).⁸³ Arylboronates and arylboronic acids proved unsuitable for the desired transformations because they were either more difficult to access and/or provided low cross-coupling yields.

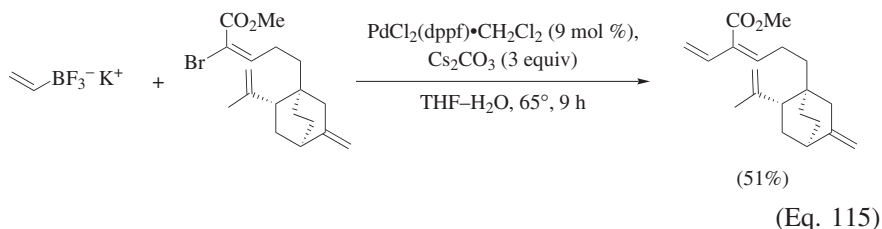


Organotrifluoroborates have been employed to generate families of modified purines. Both 6-chloropurine and 8-bromoadenine have been elaborated with aryl-, heteroaryl-, cyclopropyl-, and methyltrifluoroborates (Eqs. 111–113).^{104,145}

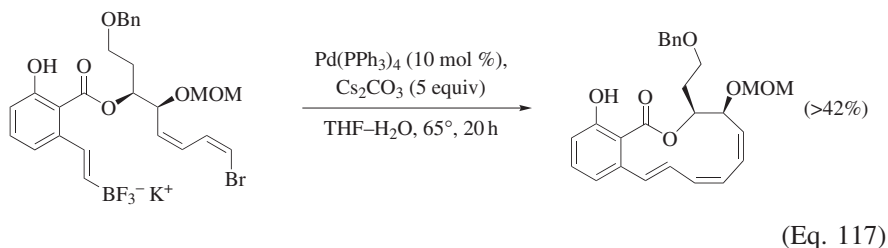
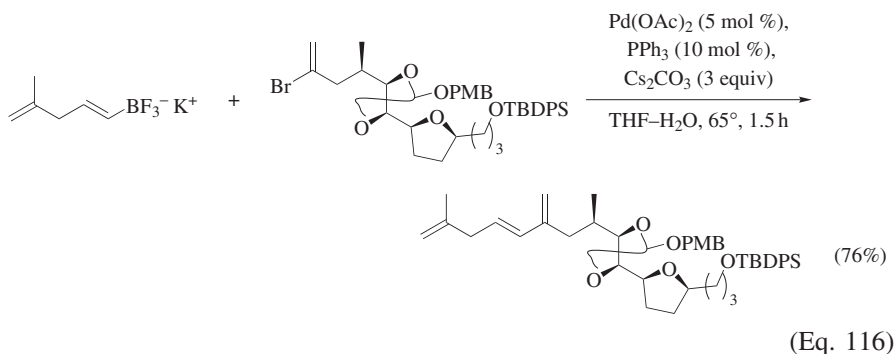


Vinyltrifluoroborate is a shelf-stable reagent that has been employed in a variety of applications, including the synthesis of poly(2,7-phenanthrylenevinylenes), which are π -conjugated polymers of potential use in constructing organic light-emitting diodes (Eq. 114).¹⁵⁸ In this application, the initial cross-coupling reaction is followed by a subsequent Heck reaction, thereby forming the observed polymeric material. Vinyltrifluoroborate has also been incorporated into small molecule synthesis schemes. For example, it was used to generate a conjugated diene used in a subsequent Diels-Alder reaction to forge a key ring in the synthesis of the serofendic acids (Eq. 115).¹⁶²



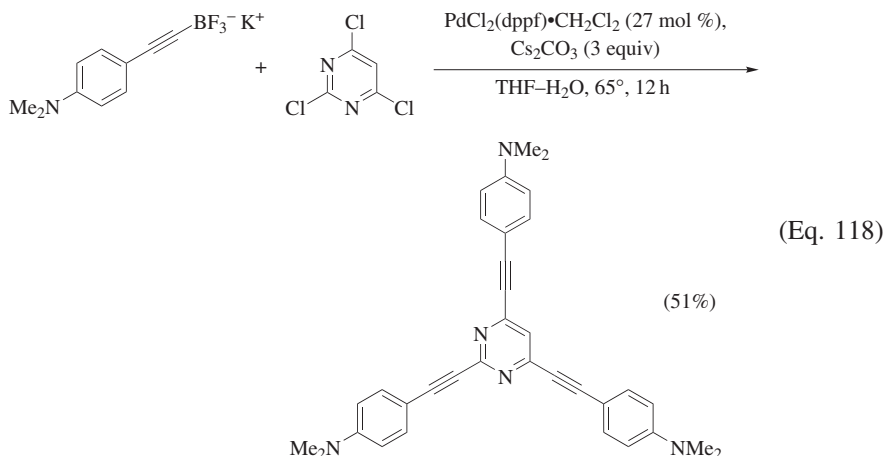


Various alkenyltrifluoroborates have found their way into total synthesis efforts. For example, an alkenyltrifluoroborate cross-coupling was employed in the construction of a fragment of amphidinolide E (Eq. 116),¹⁶³ and an intramolecular cross-coupling to form a macrocyclic lactone was utilized to form the core of oximidine II (Eq. 117).¹⁶⁴ The latter reaction overcomes a great deal of strain in the formation of the 12-membered ring, which is composed of nine contiguous sp^2 -hybridized carbon centers.

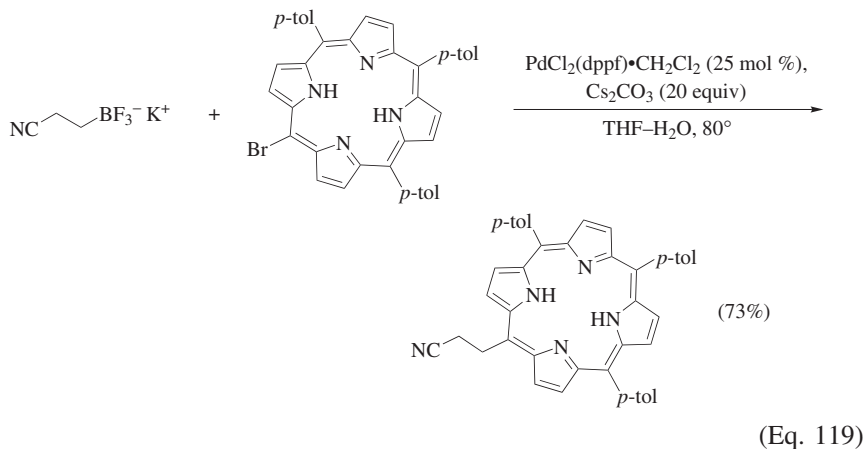


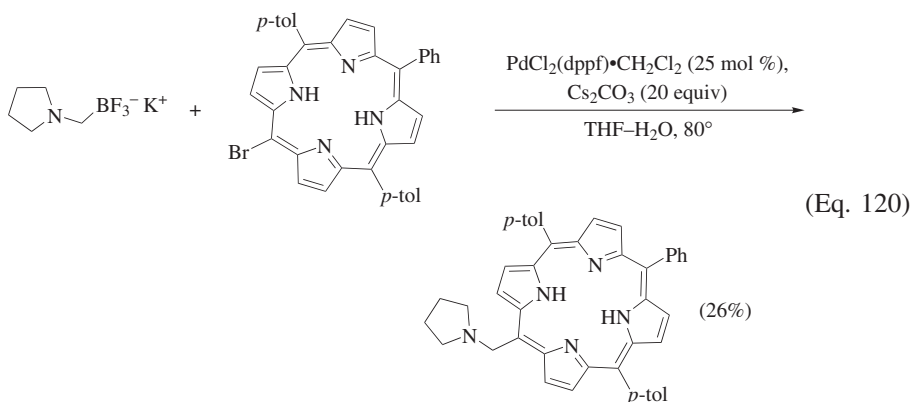
Air- and moisture-stable alkynyltrifluoroborates were utilized to generate tris(arylethynyl)pyrimidine species with potential interest as materials to be incorporated in a broad range of electronic and optoelectronic devices. The alkynyltrifluoroborates were used as a last resort when both Sonogashira and

Negishi protocols failed to produce the desired products in satisfactory yields (Eq. 118).¹⁶⁵



Alkyltrifluoroborates have not been applied extensively to the synthesis of new materials, but in one important arena (porphyrins) they have proven to be practical reagents for the elaboration of organic substructures. As described previously, porphyrins have found practical utility in areas such as photodynamic therapy, nonlinear optical materials, and solar energy conversions. A variety of alkyltrifluoroborates (including aminomethyltrifluoroborates) have been utilized for the incorporation of functionalized alkyl groups into the porphyrin substructure (Eqs. 119–120).¹¹⁵





COMPARISON WITH OTHER METHODS

Direct comparison of cross-coupling reagents is problematic because no two reagents achieve their peak performance under the same conditions—each must be separately optimized using different protocols. Thus, any report of cross-coupling where two classes of reagents are examined under identical reaction parameters undoubtedly underestimates the results for at least one of the two reactants under comparison. Nevertheless, general trends emerge concerning various reagents. The Kumada, Negishi, Stille, Suzuki, and Hiyama coupling reactions all have important roles to play in modern organic synthesis, although among all of these protocols the Suzuki-Miyaura process has become the most widely used.

Kumada couplings¹⁶⁶ are highly effective owing to the high reactivity of the organomagnesium nucleophiles, but the process suffers because the reagents are air-sensitive and thus difficult to ship and store. Additionally, although tremendous inroads have been made in forming organomagnesium reagents with functional groups incorporated within the organometallic itself, these nucleophiles still have limited functional group tolerability for both reacting partners and must be converted to less nucleophilic reagents prior to cross-coupling in more highly elaborated systems.¹⁶⁷ The value in performing Kumada coupling derives from their relative environmental soundness, their economy, and their high reactivity. Thus, they are extremely valuable for cross-coupling of minimally functionalized systems.

Most organozinc reagents are also sensitive to moisture and oxygen, and in this manner suffer from some of the same limitations as organomagnesium reagents. However, they are more tolerant of functional groups than organomagnesium reagents, and Negishi cross-couplings can be carried out in more highly elaborated systems.¹⁶⁷ Additionally, some Negishi cross-couplings can be carried out in water without the formation of a discrete organozinc reagent, providing a further benefit.¹⁶⁸

As a response to the need for air-stable, storable organometallic reagents capable of cross-coupling, organostannanes were developed and have been extensively employed. Their versatility, combined with their high reactivity and tolerance of

diverse functional groups, has made the Stille coupling one of the most widely utilized protocols yet reported.¹⁶⁹ An additional advantage of the organostannanes is the relative strength and covalent character of the carbon–tin bond, which allows chemical manipulations of functional groups within the molecule while leaving the carbon–metal bond intact. However, toxicity is a major concern in the use of organostannanes. This feature of the reagents, in addition to a lack of atom economy (due to the incorporation of organic non-transferable ligands), and the difficulty of removing tin-containing by-products, has diminished the application of Stille couplings, particularly in the industrial setting.

Hiyama and related couplings employing organosilicon reagents are receiving more and more attention.^{170–174b} These reagents are more environmentally sound than the tin reagents, particularly when fluoride-free versions of the process can be utilized. As with organostannanes, many functional groups embedded within the organosilanes can be chemically modified without cleaving the carbon–silicon bond. Other attractive features of the reagents include their relatively low cost, low toxicity, high chemical stability, and their tolerance of diverse functional groups.

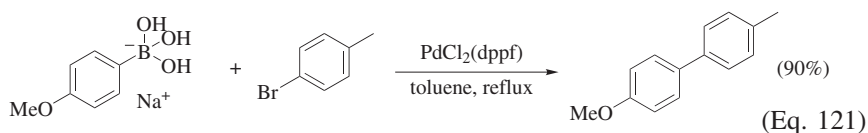
Cross-coupling reactions incorporating various organoboron reagents have come to dominate the landscape, and several different platforms have been utilized for these transformations. The availability of various trialkylboranes from diverse hydroborating reagents made them frequent partners in early Suzuki–Miyaura cross-coupling reactions. Although they have been employed extensively and effectively in this context, their scope is limited by the incompatibility of dialkylborane hydroborating reagents with a variety of functional groups. Being extremely air-sensitive reagents, the trialkylboranes must also be prepared and utilized *in situ*, making small-scale optimization onerous. They also lack the atom economy of other organoboron reagents.

Among the organoboron-based cross-coupling reagents, the boronic acids are now ubiquitous, with boronate esters playing a lesser role. Literally hundreds of boronic acids and boronate esters are currently commercially available. There is no question as to their value and importance in modern organic synthesis. However, the boronic acids are also known to possess rather significant practical limitations. The physico-chemical properties of the reagents make them less than ideal to handle. Boronic acids are often waxy solids that are difficult to purify. They exist as a mixture of the monomeric acids as well as trimeric anhydrides (boroxines), and in this sense they are inconvenient to assay and thus quantitate.¹⁷⁵ A close reading of the literature reveals that, largely because of competitive protodeboronation, boronic acids are almost always used in excess (20 to >100%), which is wasteful of precious and expensive material.

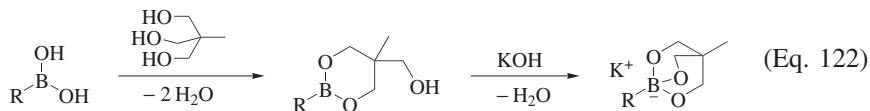
Boronate esters (in particular, the pinacolboronates) provide some advantages, but at a significant increase in cost. Thus, the monomeric pinacolboronates are more easily handled as solids and are more robust in general than the boronic acids. However, the boronates are less reactive in cross-coupling reactions, they have low atom economy, and the diols (especially pinacol) add considerable expense to the process, primarily because these reagents, like the boronic acids, are used in considerable excess in virtually all cross-coupling protocols.

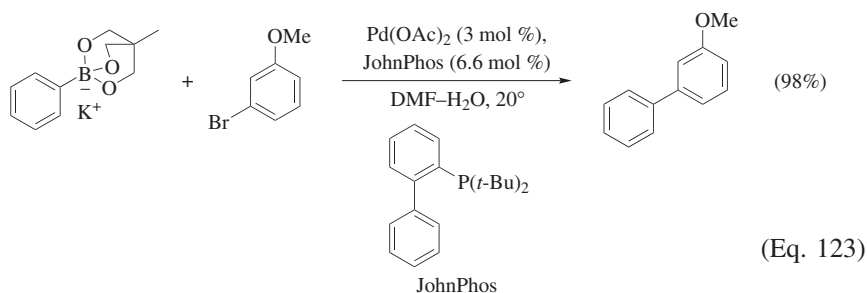
Additionally, both boronic acids and boronate esters possess the same inherent restriction: as tricoordinate boron species, their integrity can be compromised by a variety of the most useful, widely employed organic reagent classes, including acids, bases, nucleophiles, and oxidants. These reactivity patterns have the effect of limiting the manner in which these valuable reagents are employed in synthetic schemes. In the vast majority of cases, practitioners buy or make a boron substrate and immediately subject it to a cross-coupling protocol. Rarely are these reagents carried through several synthetic operations and then coupled at a point in a synthesis that might be more efficient or lead to higher convergency.

The aforementioned drawbacks have led to a surge in the development of boronic acid surrogates, or protected forms of boronic acids. As mentioned earlier, most organoboron-based cross-couplings do not readily proceed in the absence of a nucleophilic base. As a result of this observation, a number of preformed “ate” complexes have been prepared and investigated as coupling partners in the Suzuki-Miyaura reaction. In 2006, sodium trihydroxyborates were introduced as nucleophilic boronic acid surrogates.¹⁷⁶ These compounds are prepared by treatment of a toluene solution of boronic acid with sodium hydroxide. Once the “ate” complex is generated, it precipitates from solution and can be isolated easily by filtration as a free-flowing powder. However, these compounds are often difficult to obtain completely dry because they readily form hydrated complexes. When employed as a nucleophilic coupling partner, they can be used in excess to resolve the uncertain stoichiometry of the hydrated complexes. The anhydrous versions can be obtained by careful desiccation. Aryl trihydroxyborates undergo cross-coupling with aryl- and heteroaryl electrophiles to give the expected products in good yields (Eq. 121). Also, an alkyl version undergoes cross-coupling with an aryl bromide in good yield. Owing to the “ate” nature of the boron species, reactions employing trihydroxyborates can occur without the addition of a base. These are promising reagents, but to date they have not found extensive application.

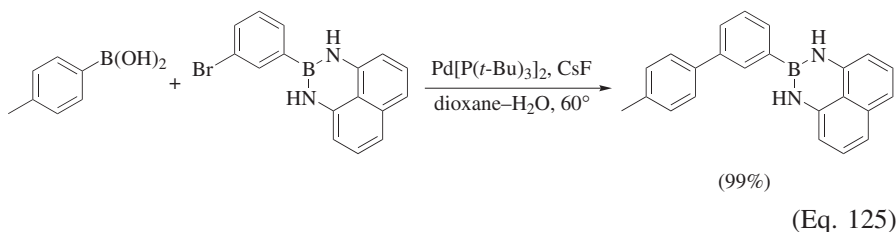
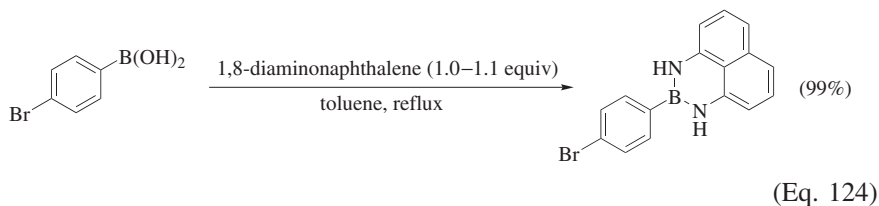


Cyclic triolborates are another class of surrogates that have been developed for use in the Suzuki-Miyaura cross-coupling reaction.¹⁷⁷ Reaction of a boronic acid with a triol generates a hydroxymethyl-bound boronate ester. Upon subsequent treatment with KOH in toluene and removal of H₂O, the triol borate precipitates and can be isolated as a white solid (Eq. 122). These compounds can react at room temperature in Pd-catalyzed cross-coupling reactions with aryl bromides, aryl chlorides, and aryl triflates, in each case without the addition of a base (Eq. 123).



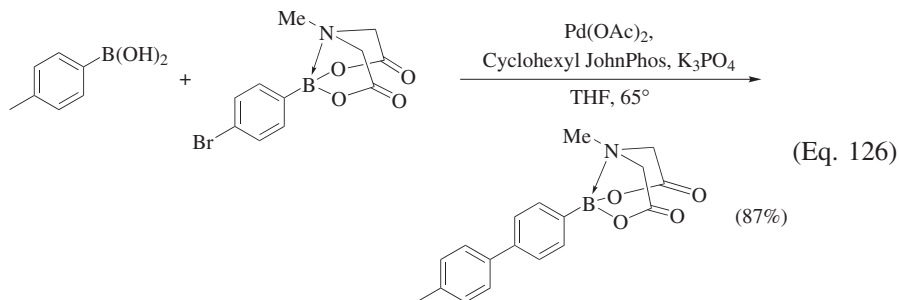


Two other classes of protected boron derivatives have been recently introduced. The first are the “B(dan)” complexes, formed by the treatment of boronic acids with 1,8-diaminonaphthalene (Eq. 124).^{178–180} This protecting group effectively lowers the Lewis acidity of the boron atom through donation of the lone pair from the nitrogen atoms into the vacant p-orbital of the boron, ultimately decreasing the overall reactivity of the boron center. Consequently, these diaminonaphthalene complexes are able to survive cross-coupling conditions used for boronic acids (Eq. 125), and they can be converted back to boronic acids in high yields by treatment with aqueous acids.



Treatment of boronic acids with *N*-methyliminodiacetic acid (MIDA) provides the second useful class of protected boronic acids. The MIDA rehybridizes the boron center from sp^2 to sp^3 , generating a tetracoordinate boron species.^{181–187} This rehybridization effectively renders the boron moiety inert to a variety of conditions that would affect tricoordinate organoborons, including oxidation and nucleophilic addition reactions. As in the case of the B(dan) compounds, anhydrous Pd-catalyzed cross-coupling reactions can be carried out in the presence of a MIDA boronate (Eq. 126). Another practical advantage of the MIDA boronates is that, unlike organotrifluoroborates, they may be isolated and purified by chromatography. They are also reported to be reliably solid materials and thus should

be subject to purification by crystallization. When required, the MIDA protecting group can be readily removed to reveal the boronic acids by treatment under mild, aqueous basic reaction conditions.



Although many of these boronic acid surrogates have been employed effectively to mask the boron atom in synthetic steps, as with any protecting group, there may be limitations associated with their use. The atom economy of the protecting groups is low, and sometimes (with B(dan) and MIDA complexes) two steps (a protection and deprotection) are required because the protected organoborons must be transformed back to the boronic acid before being employed in cross-coupling reactions. This essential unveiling of the boronic acid prior to the cross-coupling event leaves the boron moiety susceptible to the same protodeboronation issues associated with boronic acids, and an excess of these reagents is often used.

The organotrifluoroborates represent an alternative tetracoordinate boron species for cross-coupling, possessing their own strengths and limitations. As a class of reagents, the organotrifluoroborates are readily accessed from a variety of organoboron precursors by treatment with inexpensive KHF_2 , which is 20 times less expensive than pinacol and more than 100 times less expensive than MIDA on a molar basis. As alluded to previously, this procedure¹⁸⁸ leads to isolable, tractable solids that are stable to air and moisture. As of this writing, nearly 1000 structurally diverse potassium organotrifluoroborates have been prepared, and virtually all of these are easily purified as monomeric, crystalline solids or well-defined powders. Aside from the boronic acids themselves, the organotrifluoroborates are the most atom-efficient organoboron reagents currently available. Perhaps most important is the behavior of the trifluoroborates in cross-coupling. In contrast to virtually all other organoborons, the relative resistance of organotrifluoroborates to protodeboronation under cross-coupling conditions allows them to be used frequently in stoichiometric quantities relative to their electrophilic partners.

These advantages are to be weighed against some of the weaknesses of organotrifluoroborate chemistry. Among these should be mentioned the necessity to utilize KHF_2 (a hazardous material that etches glass) in the preparation of the materials, and the presence of fluoride in the reagents and waste streams, which necessitates specialized reaction vessels and disposal for large-scale syntheses.

For small-scale preparations, the inability to chromatograph the organotrifluoroborates can create minor inconveniences, although their extraordinarily high propensity to form free-flowing powders or crystalline solids can mitigate these concerns. Finally, the potassium salts of the organotrifluoroborates are not highly soluble in non-polar solvents that might be required for chemical transformation of functional groups embedded within the organotrifluoroborates. However, the easily derived tetraalkylammonium salts are miscible in even the most non-polar solvents at low temperatures, and can be used when needed.

In addition to the general attributes of organotrifluoroborates, specific classes of these reagents have demonstrated features that recommend their use over that of boronic acids. As described previously, both electron-deficient aromatics^{88,89} and many heteroaromatics^{46,94,95} undergo competitive protodeboronation during cross-coupling events. This side reaction can be greatly minimized using the corresponding organotrifluoroborates.²⁷

Potassium vinyltrifluoroborate is another valuable reagent that compares favorably with other available vinylating agents.¹⁸⁹ Its importance derives from the fact that vinylboronic acid readily polymerizes and cannot be isolated in pure form.¹⁹⁰ Vinyboron analogs such as the 2,4,6-trivinylcyclotriboroxane-pyridine complex can be employed,¹⁹¹ but a 1:1 ratio of this trimer to the electrophilic coupling partner must be used, equating to three equivalents of the vinylating agent. Although vinylboronate esters have also been employed in cross-coupling reactions,¹⁹² the diols used to prepare these reagents lead to low atom economy and add considerable expense to the overall procedure. Potassium vinyltrifluoroborate can be stored indefinitely at room temperature.¹⁰⁶

The cross-coupling of more highly substituted alkenylboronic acids often requires superstoichiometric amounts of toxic thallium bases.^{72,193–197} The use of alkenyltrifluoroborates alleviates the need for such bases, and affords cross-coupled products efficiently in high yield and with excellent stereospecificity.^{71,72}

Although the Sonogashira reaction often provides a highly effective means for alkynylation, there are instances where this protocol fails to deliver the final product. In such instances, cross-coupling reactions with discrete alkynylmetallic reagents can provide an alternative entry to the desired products. Several alkynylborons have proven effective in this regard, but virtually all of these reagents are “ate” complexes generated and employed *in situ*.^{198,199} Alkynyltrifluoroborates represent a family of stable, storable reagents that are also highly effective in cross-coupling with a variety of aryl bromides and triflates.¹⁰⁹

As is observed with many other boronic acids, cyclopropylboronic acid and cyclobutylboronic acid tend to undergo protodeboronation. This instability creates a significant safety hazard, because cyclopropane and cyclobutane can be generated in sealed bottles where these materials are stored. Cyclopropyltrifluoroborate and the cyclobutyl congener are indefinitely stable, providing storable reagents that are also highly effective in cross-coupling.¹¹²

Owing to the intervention of competitive β -hydride elimination, cross-coupling of alkylboronic acids with aryl and heteroaryl halides has always been problematic. One successful protocol employs excess silver oxide,²⁰⁰ whereas other

approaches require the use of toxic thallium bases or highly reactive organolithiums. The organotrifluoroborates provide a general solution to this challenge,¹¹³ not only for primary alkyl systems,¹¹⁴ but also for difficulties associated with methylation^{200–204} and some secondary alkyl cross-couplings.⁷⁸

The organotrifluoroborates provide solutions to problems encountered in a number of specialized cross-couplings as well. For example, although the cross-coupling of β -metallo esters²⁰⁵ has been applied to the generation of amino acid derivatives,²⁰⁶ there are limited examples of the corresponding ketone and amide derivatives.^{207,208} The β -trifluoroborato ketones, esters, and amides thus serve as unique reagents for the construction of β -aryl and β -heteroaryl carbonyls via cross-coupling.^{119–121}

In this same vein, alkoxymethyl-¹²⁹ and aminomethyltrifluoroborates^{127,128} have been developed that expand the scope of cross-coupling reactions incorporating these valuable subunits, allowing more reactive alternatives to the less desirable organostannane versions of these reagents.^{209–213}

EXPERIMENTAL CONDITIONS

The Organotrifluoroborate: Preparation and Handling

[Material Safety Data Sheet Potassium Bifluoride #333]

Caution! Potassium bifluoride (potassium hydrogen fluoride, KHF_2) is a hazardous material in terms of skin contact (corrosive, irritant, permeator), eye contact (irritant), ingestion, or inhalation. The amount of tissue damage depends on length of contact. Eye contact can result in corneal damage or blindness. Skin contact can produce inflammation and blistering. Inhalation of dust will produce irritation to the gastrointestinal or respiratory tract, characterized by burning, sneezing, and coughing. Severe over-exposure can produce lung damage, choking, unconsciousness, or death. Inflammation of the eye is characterized by redness, watering, and itching. Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering.

Chronic health problems can result from exposure to potassium bifluoride. The substance is toxic to lungs and mucous membranes. Repeated or prolonged exposure to the substance can result in target organ damage. Repeated exposure of the eyes to a low level of dust can produce eye irritation. Repeated skin exposure can cause local skin destruction, or dermatitis. Repeated inhalation of dust can produce varying degrees of respiratory irritation or lung damage.

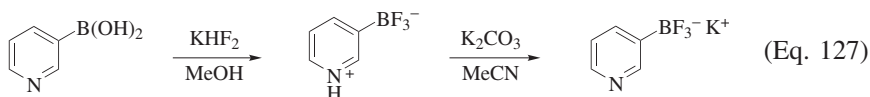
As outlined previously, potassium organotrifluoroborates can be prepared from virtually any organoboron compound with two labile groups (Scheme 1). The syntheses of organotrifluoroborates from available boronic acids or boronate esters are typically carried out in methanol or acetone,^{46,94} but other solvents can be used as well (e.g., Et_2O , MeCN).^{58,72} For multistep transformations in which the boron is initially incorporated into substrates (e.g., by hydroboration, C–H activation, transmetalation, cross-coupling, etc.), the KHF_2 can be added directly to the reaction mixture. In either case, the KHF_2 can be added in two ways: (1) as a concentrated solution in water (~ 4.5 M), or (2) as a solid, followed

by the addition of water. Yields sometimes differ depending on the mode of addition. Since potassium bifluoride etches glass, it is often convenient to carry out the trifluoroborate synthesis in Nalgene vessels. The transformation from boron precursor to trifluoroborate appears in most cases to be complete in minutes, but reaction mixtures are often allowed to stir for periods of greater than one hour with no ill effects.

Upon completion of the trifluoroborate-generating reactions, the most convenient workup involves removal of all solvents, leaving a powder consisting of the organotrifluoroborate and KF. Two isolation procedures have proven most effective. Perhaps the easiest is to perform a continuous extraction of the powder using a Soxhlet extraction apparatus. Depending on the nature of the organotrifluoroborate, acetone, isopropyl acetate, or acetonitrile can be used as the solvent. The organotrifluoroborate will dissolve in these solvents, leaving the KF in the thimble of the extraction glassware. Upon cooling, the organotrifluoroborate may precipitate or crystallize out of solution. If not, a non-polar antisolvent such as hexane or Et₂O can be used to precipitate the desired product. The second isolation method involves simple trituration of the powder with hot acetone or acetonitrile, followed by crystallization or precipitation of the organotrifluoroborate.

Some assessment of the purity of the materials can be carried out by ¹H-NMR, ¹³C-NMR, ¹¹B-NMR, and ¹⁹F-NMR. However, none of these techniques will capture the presence of inorganic salts carried along in some multistep approaches to the organotrifluoroborates, and thus for a complete appraisal of purity elemental analysis is recommended.

There is a caveat in the use of KHF₂ to prepare organotrifluoroborates containing basic amines. As a strong acid, KHF₂ generates ammonium salts, which may lead to the generation of internal trifluoroborate salts. In most cases, these internal salts can be treated with base (e.g., K₂CO₃ in MeCN) to regenerate the amine (Eq. 127). Alternatively, the internal salt may be used directly in subsequent cross-coupling reactions.⁹⁴



The potassium salts of organotrifluoroborates are consistently solids in pure form. Tetraalkylammonium salts are less reliably so, and thus they may exist as difficult to handle syrups or glasses, depending on the ammonium salts employed and the structure of the organotrifluoroborate. No reliable chromatographic methods have been reported for the isolation or purification of any organotrifluoroborates.

Virtually all classes of organotrifluoroborates may be stored indefinitely on the shelf. They are air-stable, non-hygroscopic solids. The most sensitive materials appear to be the alkynyl- and allenyltrifluoroborates, which are best stored cold.

The Cross-Coupling

The execution of cross-coupling reactions with organotrifluoroborates is at its foundation no different than that employing other organometallic reagents.

Certainly, distinctions are noted among the protocols, which is to be expected of different classes of nucleophilic agents. The combination of ingredients in Suzuki couplings (reacting partners, precatalysts, ligands, solvents, bases, additives), along with added variables such as reaction temperature and time, as well as microwave^{70,82,86,104,150,214–223} or ultrasound conditions,^{69,73,149,224} afford a very large number of possible experimental combinations.

The following discussion provides a broad overview of the experimental details that have been employed for the cross-coupling of organotrifluoroborates. An important feature of these transformations should be kept in mind: reaction conditions vary widely among different substrate pairs, and indeed probably even among individual investigators that set out to optimize a reaction for any class of reacting substrates. In other words, no a priori “best” procedure exists for any given reaction pair, and satisfactory conditions are derived empirically by trial and error, increasingly with the aid of high-throughput experimentation.⁷⁸

General Reaction Conditions. In general, the cross-couplings must be carried out in an inert atmosphere, but simple biaryl coupling reactions can be carried out in air.⁴⁶ With the exception of those transformations carried out with aryldiazonium ions,¹³ diaryliodonium ions,¹⁵ and cross-coupling of alkynyltrifluoroborates with activated bromides,¹¹⁰ virtually all organotrifluoroborate coupling reactions require elevated temperatures ($>65^{\circ}$), perhaps a reflection of the need for fluoride/hydroxide exchange to facilitate transmetalation (Eqs. 6 and 7).²⁷

Choice of Catalyst or Precatalyst and Ligand. (*See catalyst and ligand charts preceding the Tabular Survey.*) Catalyst selection is key to the success of cross-coupling reactions, particularly when challenging reaction partners are involved. Both Pd(0) and Pd(II) catalysts can be employed in organotrifluoroborate cross-couplings, with the Pd(II) species being reduced to Pd(0) by the fluoride present in the reaction mixture (Scheme 4).²⁷ The use of Pd(II) precatalysts is often preferred, because Pd(0) species are air sensitive, and their integrity is difficult to assess quickly and accurately. Most conveniently, a large number of ligands are commercially available, and thus in screening efforts for reaction optimization many permutations can be examined without investing an inordinate amount of time in creating libraries of organometallic catalytic complexes.

As pointed out previously, in very simple systems (aryl bromide electrophiles with unhindered, electron-neutral or electron-rich aryltrifluoroborate nucleophiles), ligandless cross-coupling can be carried out using Pd(OAc)₂ as the catalyst (Eq. 5).^{46,122,225} Supported catalysts, Pd/C and related species,^{214,216,217,221,226,227} have also been used on a limited basis. Other popular catalysts for cross-coupling include PdCl₂(dppf)•CH₂Cl₂, Pd(PPh₃)₄, and PdCl₂(PPh₃)₂, of which the former two have been used most extensively.

For more demanding cross-couplings, more sophisticated and elaborate systems must be employed. Besides dppf, dppb and XantPhos have been utilized as examples of chelating ligands. The most effective ligands, however, are sterically

encumbered, electron-rich monodentate ligands such as $P(o\text{-tol})_3$, PCy_3 , $P(t\text{-Bu})_3$, SPhos , RuPhos , XPhos , Cyclohexyl JohnPhos, $n\text{-BuPAd}_2$, and $t\text{-Bu}_2\text{PPh}$ (Scheme 6).²¹ These ligands facilitate cross-coupling with aryl chlorides, allow sterically demanding biaryl systems to be created, and permit transformations with alkyltrifluoroborates, including those at secondary carbon centers. In a similar manner, PEPPSI catalysts have proven effective for non-trivial couplings.^{52,53} For those substrates exhibiting significant water solubility, TPPTS has been used to carry out the critical carbon-carbon bond-forming transformation.^{104,159,160}

When reactions incorporating high-performance ligands are utilized, a Pd(II) precursor is employed to generate the active catalyst. The most commonly used salt is Pd(OAc)_2 , but PdCl_2 and Pd(acac)_2 have also been used with success. $\text{Pd}_2(\text{dba})_3$ is an effective source of Pd(0) . As a point of interest, dba can serve as an active ligand in palladium-catalyzed reactions, and is thus not always an innocent bystander.^{35-38,42} Sometimes dba can also control the rate of oxidative addition as well as the concentration of monocoordinated species in solution, which has an effect on transmetalation and reductive elimination rates as well. Consequently, profound differences in behavior may be seen between those processes employing Pd(OAc)_2 and cross-couplings incorporating $\text{Pd}_2(\text{dba})_3$ as precatalysts.

Choice of Solvent. As discussed above, with the exception of diazonium salt and diaryliodonium salt electrophiles, a hydroxylic solvent or cosolvent must be utilized in organotrifluoroborate cross-coupling reactions to enable transmetalation. Aside from this requirement, there is no restriction on the solvents that may be employed, and numerous solvents have proven effective. The reaction mixtures are often biphasic as a result of the need to perform the reaction in the presence of a protic species (Eqs. 6 and 7). The reactions typically initiate as heterogeneous reaction mixtures as a result of the relative insolubility of the organotrifluoroborate in both protic and aprotic solvents, but become homogeneous as the reactions progress.

Solvents used in organotrifluoroborate cross-coupling include water, methanol, ethanol, n -propanol, 2-propanol, *tert*-butyl alcohol, THF, dioxane, DME, cyclopentyl methyl ether (CPME), toluene, DMF, N -methyl-2-pyrrolidone (NMP), and acetonitrile. The use of ionic liquids as solvents has also been explored.¹³² The most common solvents are methanol, ethanol, THF, CPME, and toluene. Any of these solvents represents a good starting point for the examination of new coupling procedures.

Although it is clearly not necessary that the solvents be anhydrous, for the most part they should be oxygen-free, at least for those reactions that are more challenging. Deoxygenation ensures that the active Pd(0) catalyst remains active, and also prevents deleterious oxidation of the phosphine ligands to phosphine oxides. Additionally, adventitious air can also induce oxidative coupling of the organoboron reagent (Scheme 8), reducing the availability of this reagent for cross-coupling and leading to byproducts that may be difficult to separate from the target molecule.

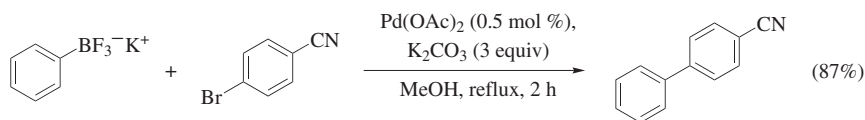
Choice of Base. Many bases have been utilized for organotrifluoroborate cross-couplings. When reactions are performed in ethereal or non-polar solvents

such as toluene, bases such as NaOAc, K_2CO_3 , Cs_2CO_3 , Na_2CO_3 , and K_3PO_4 appear to predominate, with the carbonates being the most effective. Factors such as cost and the ability to tolerate embedded functional groups play a major role in deciding which base to use. In hydroxylic solvents, amine bases seem to be most effective, with Et_3N , $i\text{-}Pr_2NEt$, and $t\text{-}BuNH_2$ all having been used. Bases used only occasionally include K_2HPO_4 , LiOH, NaOH, and KOH. The alkoxides are less appealing because as strong bases they are less tolerant of sensitive functional groups, but for cross-couplings with minimally functionalized systems they are often quite effective.

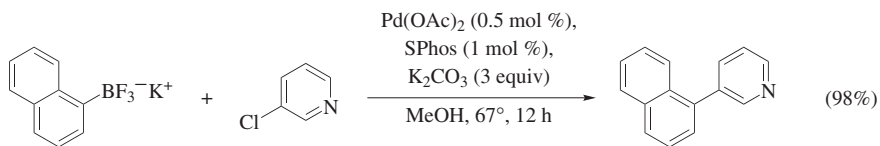
Additives. Very few additives are necessary or have been utilized in organotrifluoroborate cross-coupling reactions. Both CuI and silver salts^{69,75,88,141–144,149,224} appear to be necessary when organotellurides are employed as electrophiles. Occasionally, TBAB has been used as a phase-transfer agent for various transformations, and this salt seems to be effective in this regard.^{70,150,214,221,226,228} Both LiCl¹²³ and 18-crown-6²²⁹ have been used in isolated cases, and thus their overall effectiveness cannot be accurately assessed.

Work-Up. No special considerations are required for isolating the products of cross-coupling using organotrifluoroborate nucleophiles. The byproducts of the reaction are boric acid and fluoride salts, which are easily removed from the reaction mixture by a simple aqueous workup. When necessary, much of the residual palladium can be removed by addition of small amounts of activated charcoal.

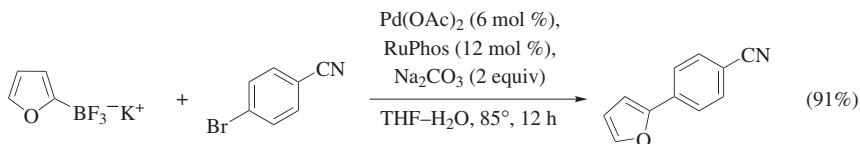
EXPERIMENTAL PROCEDURES



4-Phenylbenzonitrile [Cross-Coupling of an Aryltrifluoroborate with an Aryl Bromide Using $Pd(OAc)_2$].⁴⁶ To a suspension of potassium phenyltrifluoroborate (92.3 mg, 0.50 mmol), 4-bromobenzonitrile (91.01 mg, 0.50 mmol), and K_2CO_3 (0.2045 g, 1.50 mmol) in MeOH (0.75 mL) was added $Pd(OAc)_2$ (1.25 mL of a 2 mM solution in MeOH, 0.0025 mmol). The reaction mixture was heated at reflux for 2 h, then cooled to room temperature and diluted with H_2O (10 mL). The aqueous phase was extracted with CH_2Cl_2 (3×4 mL). The organic solution was washed with brine (10 mL) and dried ($MgSO_4$). The solution was then filtered through a short pad of silica gel, using a sequence of pentane and pentane/ CH_2Cl_2 . The solvents were removed under vacuum, and the residue was purified by chromatography on silica gel (elution with hexane) to yield 4-phenylbenzonitrile (77.9 mg, 87%): IR (neat) 2227, 1605, 1485, 768 cm^{-1} ; ^1H NMR (300 MHz, $CDCl_3$) δ 7.76–7.68 (m, 4H), 7.60–7.58 (m, 2H), 7.52–7.43 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.6, 139.1, 132.5, 129.0, 128.6, 127.6, 127.4, 118.9, 110.8. Anal. Calcd for $C_{13}H_9N$: C, 87.12; H, 5.06. Found: C, 87.04; H, 5.06.

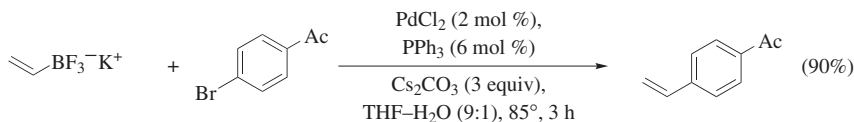


3-(Naphthalen-1-yl)pyridine [Cross-Coupling of an Aryltrifluoroborate with a Heteroaryl Chloride Using Pd(OAc)_2 and SPhos].⁸⁷ A threaded-top test tube containing a magnetic stir bar was charged with Pd(OAc)_2 (1.1 mg, 0.05 mmol), SPhos (4.1 mg, 0.01 mmol), potassium naphthyltrifluoroborate (257 mg, 1.1 mmol), and powdered anhydrous K_2CO_3 (415 mg, 3.0 mmol). The test tube was capped with a screw-top cap lined with a disposable Teflon septum, evacuated, and backfilled with argon (this process was repeated three times) through an 18-gauge needle. 3-Chloropyridine (114 mg, 1.0 mmol) was added via syringe through the septum, followed by addition of MeOH (2 mL). After the test tube was placed back under argon through the needle, the screw top cap was quickly removed and replaced with a new cap with an unpunctured septum. The reaction mixture was heated at 67° with vigorous stirring for 12 h. The reaction mixture was allowed to cool, diluted with EtOAc (10 mL), filtered through a thin pad of silica gel (eluting with 25% MeOH in EtOAc), and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (1:1 EtOAc/hexanes) to provide the title compound as a colorless oil (201 mg, 98%): ^1H NMR (300 MHz, CDCl_3) δ 8.77 (d, J = 2 Hz, 1H), 8.70 (dd, J = 2, 5 Hz, 1H), 7.96–7.90 (m, 2H), 7.85–7.79 (m, 2H), 7.59–7.41 (m, 5H).

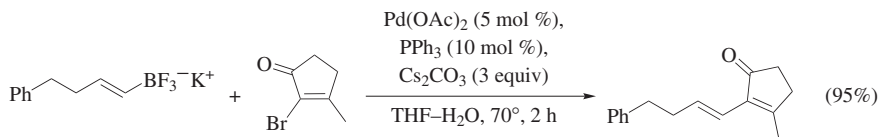


4-(Furan-2-yl)benzonitrile [Cross-Coupling of a Heteroaryltrifluoroborate with an Aryl Bromide Using Pd(OAc)_2 and RuPhos].⁹⁴ A Biotage microwave vial was charged with Pd(OAc)_2 (3.4 mg, 0.015 mmol), RuPhos (14 mg, 0.03 mmol), 4-bromobenzonitrile (46.0 mg, 0.25 mmol), potassium furan-2-yltrifluoroborate (46.0 mg, 0.26 mmol), and Na_2CO_3 (53.0 mg, 0.5 mmol). The test tube was sealed with a cap lined with a disposable Teflon septum, evacuated, and purged with nitrogen (3 x). EtOH (1.4 mL) was added via syringe, and the reaction was conventionally heated at 85° for 12 h. The reaction mixture was allowed to cool to rt and filtered through a thin pad of silica gel (elution with 25% MeOH in EtOAc). The solvent was removed under vacuum, and the crude product was purified by silica gel column chromatography (7:1 hexane/EtOAc) to yield the pure product in 91% yield (38.49 mg, 0.23 mmol) as a white solid: ^1H NMR (500 MHz, CDCl_3) δ 7.72 (d, J = 8.5 Hz, 1H), 7.63 (d, J = 8.5 Hz, 1H), 7.52 (m, 1H), 6.80 (d, J = 3.5 Hz, 1H), 6.52 (dd, J = 1.8, 3.4 Hz, 1H);

^{13}C NMR (125.8 MHz, CDCl_3) δ 152.1, 143.8, 134.8, 132.7, 124.1, 119.0, 112.3, 110.4, 108.3.

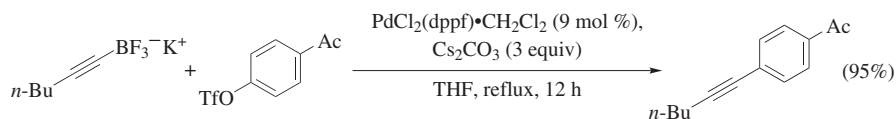


1-(4-Vinylphenyl)ethanone [Cross-Coupling of a Vinyltrifluoroborate with an Aryl Bromide Using PdCl_2 and PPh_3].¹⁰⁶ A solution of potassium vinyltrifluoroborate (134 mg, 1.00 mmol), PdCl_2 (3.5 mg, 0.02 mmol), PPh_3 (16 mg, 0.06 mmol), Cs_2CO_3 (978 mg, 3.00 mmol), and 1-(4-bromophenyl)ethanone (199 mg, 1.00 mmol) in THF/ H_2O (9:1, 2 mL) was heated at 85° under a N_2 atmosphere in a sealed tube for 3 h, then was cooled to room temperature and diluted with H_2O (3 mL), followed by extraction with CH_2Cl_2 (3×10 mL). The solvent was removed under vacuum, and the crude product was purified by silica gel chromatography (20:1 *n*-pentane/ Et_2O) to yield 1-(4-vinylphenyl)ethanone as a pale yellow solid (131.6 mg, 90%): mp 33–34°; IR 3054, 2987, 2306, 1681, 1605, 1422, 1359, 1265, 1181, 957, 922, 896, 847, 739, 705 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.92 (d, J = 8.6 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 6.76 (dd, J = 17.6, 10.9 Hz, 1H), 5.88 (dd, J = 17.6, 0.6 Hz, 1H), 5.39 (dd, J = 10.9, 0.6 Hz, 1H), 2.60 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 197.9, 142.3, 136.5, 136.2, 128.9, 126.5, 117.0, 26.8.

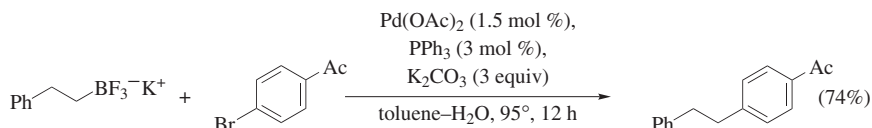


(*E*)-3-Methyl-2-(4-phenylbut-1-enyl)cyclopenten-2-one [Cross-Coupling of an Alkenyltrifluoroborate with an Alkenyl Bromide Using $\text{Pd}(\text{OAc})_2$ and PPh_3].⁷² To a mixture of potassium (*E*)-(4-phenylbut-1-enyl)-trifluoroborate (261.9 mg, 1.10 mmol), 2-bromo-3-methylcyclopent-2-en-1-one (175.02, 1.00 mmol), Cs_2CO_3 (977 mg, 3.00 mmol), $\text{Pd}(\text{OAc})_2$ (11 mg, 0.05 mmol), and PPh_3 (26 mg, 0.1 mmol) was added THF/ H_2O (10:1, 4 mL). The reaction mixture was heated at 70° with stirring under a nitrogen atmosphere for 2 h, cooled to rt, and diluted with H_2O (3 mL). The resulting mixture was extracted with Et_2O . The organic layers were combined and washed with 1 N HCl and brine, dried (MgSO_4), and filtered. The solvent was removed under vacuum, and the crude product was purified by silica gel chromatography (hexane) to afford the title compound (215.0 mg, 95%): IR (neat) 3025, 2918, 2852, 1625 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.27 (t, J = 7.5 Hz, 2H), 7.20–7.15 (m, 3H), 6.75 (dt, J = 15.8, 6.7 Hz, 1H), 6.08 (d, J = 15.8 Hz, 1H), 2.75 (t, J = 7.3 Hz, 2H), 2.49–2.44 (m, 4H), 2.39–2.38 (m, 2H), 2.08 (s, 3H); ^{13}C NMR (125.8 MHz, CDCl_3) δ 208.2, 169.6, 141.9, 135.3, 134.8, 128.4 (2C),

128.3 (2C), 125.8, 119.3, 35.9, 35.7, 34.8, 31.5, 17.5; HRMS–CI (m/z): M^+ calcd for $C_{16}H_{18}O$, 226.1357; found 226.1348.

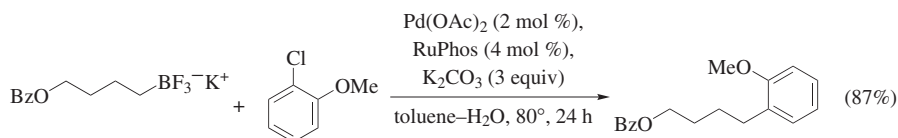


1-(4-Hex-1-ynyl)phenylethanone [Cross-Coupling of an Alkynyltrifluoroborate with an Aryl Sulfonate Using $\text{PdCl}_2(\text{dppf})\cdot\text{CH}_2\text{Cl}_2$].¹⁰⁹ Potassium (hex-1-ynyl)trifluoroborate (94 mg, 0.50 mmol), $\text{PdCl}_2(\text{dppf})\cdot\text{CH}_2\text{Cl}_2$ (36 mg, 0.045 mmol), and Cs_2CO_3 (489 mg, 1.50 mmol) were added to a flame-dried flask and dried under high vacuum for 2 h, after which time they were placed under argon. To this flask was added 4-acetylphenyl trifluoromethanesulfonate (134 mg, 0.50 mmol) and dry THF (5 mL). The solution was heated at reflux for 12 h. After this time the mixture was cooled, and 10 mL of H_2O was added to the flask. The resulting solution was then extracted with Et_2O . The combined organic extracts were washed with 1 M HCl and brine and then dried (MgSO_4). After the solid was removed by filtration, the solvent was removed under reduced pressure to leave a brown oil. The oil was purified by flash chromatography on silica gel (hexane) to afford the product as a clear oil (90.3 mg, 87%): R_f 0.50; ^1H NMR (500 MHz, CDCl_3) δ 7.88 (dd, $J = 6.7, 2.0$ Hz, 2H), 7.47 (dd, $J = 6.7, 1.9$ Hz, 2H), 2.58 (s, 3H), 2.44 (t, $J = 7.1$ Hz, 2H), 1.62–1.59 (m, 2H), 1.50–1.47 (m, 2H), 0.95 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 197.4, 135.6, 131.6, 129.2, 128.1, 94.4, 80.1, 30.6, 26.6, 22.0, 19.2, 13.6.

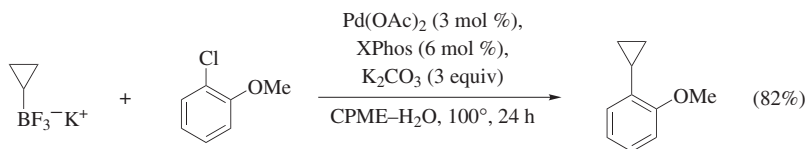


1-(4-Phenethylphenyl)ethanone [Cross-Coupling of an Alkyltrifluoroborate with an Aryl Bromide Using $\text{Pd}(\text{OAc})_2$ and PPh_3].²³⁰ A three-necked, 250-mL, round-bottomed flask, equipped with a reflux condenser, a rubber septum, a glass stopper, and a magnetic stirring bar, and connected to a vacuum-argon manifold, was charged sequentially with potassium 2-phenethyltrifluoroborate (7.77 g, 36.6 mmol), 1-(4-bromophenyl)ethanone (6.97 g, 35.0 mmol), K_2CO_3 (14.5 g, 105 mmol), PPh_3 (0.275 g, 1.05 mmol), and $\text{Pd}(\text{OAc})_2$ (0.118 g, 0.53 mmol). The flask was evacuated and filled with dry argon three times. Toluene (105 mL) and H_2O (21 mL) were added, and the resulting two-phase mixture was stirred in a 95° oil bath for 12 h or until consumption of the 1-(4-bromophenyl)ethanone was indicated by GC analysis. The mixture was cooled to rt and then was transferred to a 250-mL separatory funnel. The flask was rinsed with toluene (20 mL) and H_2O (20 mL), and the resulting layers were shaken and separated. The organic layer was washed with 10% aqueous citric acid solution (20 mL) and saturated aqueous NaCl

solution (20 mL). The organic layer was dried (Na_2SO_4 , 0.780 g) and filtered through a medium-porosity glass-fritted funnel, and the drying agent was rinsed with toluene (20 mL). The resulting solution was concentrated (50° water bath, 9 mmHg) to give a light-yellow solid, which was crystallized from MeOH to give the title compound as a light tan solid (5.79 g, 74%): mp 68–72°; IR (KBr) 1676, 1601 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.88 (d, J = 8.3 Hz, 2H), 7.30–7.15 (m, 7H), 3.01–2.92 (m, 4H), 2.58 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 197.7, 147.4, 141.0, 135.1, 128.7, 128.5, 128.4, 128.3, 126.1, 37.8, 37.3, 26.5; EIMS (70 eV) m/z : M^+ 224 (44), 209 (12), 181 (8), 133 (12), 105 (8), 91 (100), 65 (7). Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{O}$: C, 85.68; H, 7.19. Found C, 85.59; H, 7.31.

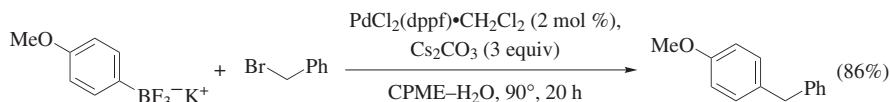


4-(2-Methoxyphenyl)butyl Benzoate [Cross-Coupling of an Alkyltrifluoroborate with an Aryl Chloride Using $\text{Pd}(\text{OAc})_2$ and RuPhos].¹¹⁴ A Biotage microwave vial was charged with $\text{Pd}(\text{OAc})_2$ (2.3 mg, 0.01 mmol), RuPhos (9.3 mg, 0.02 mmol), 2-chloroanisole (71.3 mg, 0.50 mmol), potassium 4-(benzoyloxy)butyltrifluoroborate (142 mg, 0.50 mmol), and K_2CO_3 (207 mg, 1.5 mmol). The test tube was sealed with a cap lined with a disposable Teflon septum, evacuated, and purged with N_2 (3 x). To the vial were added toluene (2.5 mL) and H_2O (0.25 mL), and then the reaction mixture was conventionally heated at 80° for 24 h. After the reaction mixture was allowed to cool to rt, GC/MS analysis showed complete conversion of the aryl chloride. The organic layer was separated, and the aqueous layer was extracted with EtOAc (3×1 mL). The resulting light yellow organic solution was concentrated and purified by silica gel column chromatography (99:1 hexane/EtOAc) to yield the product as a clear, colorless oil (124 mg, 87%): IR (neat) 3062, 2996, 2950, 2834, 1716, 1600, 1586, 1493, 1464, 1452, 1314, 1272, 1243, 1115 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.99–7.98 (d, J = 7.6 Hz, 2H), 7.50–7.48 (t, J = 7.6 Hz, 1H), 7.39–7.36 (t, J = 7.8 Hz, 2H), 7.12–7.08 (m, 2H), 6.83–6.78 (m, 2H), 4.31–4.28 (t, J = 6.4 Hz, 2H), 3.75 (s, 3H), 2.65–2.62 (t, J = 7.4 Hz, 2H), 1.78–1.68 (m, 4H); ^{13}C NMR (125.8 MHz, CDCl_3) δ 166.7, 132.7, 130.6, 130.5, 129.8, 129.5, 128.3, 127.0, 120.4, 110.3, 64.9, 55.2, 29.8, 28.5, 26.2; HRMS–ESI (m/z): $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{18}\text{H}_{20}\text{NaO}_3$, 307.1310; found, 307.1306.

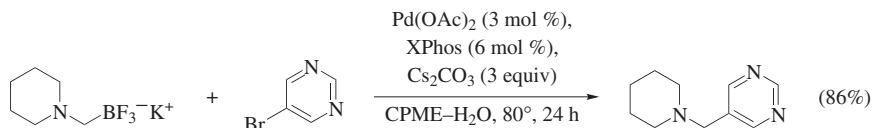


1-Cyclopropyl-2-methoxybenzene [Cross-Coupling of a Cyclopropyltrifluoroborate with an Aryl Chloride Using $\text{Pd}(\text{OAc})_2$ and XPhos].¹¹² A Biotage microwave vial was charged with $\text{Pd}(\text{OAc})_2$ (3.3 mg, 0.015 mmol),

XPhos (14.3 mg, 0.03 mmol), potassium cyclopropyltrifluoroborate (74.7 mg, 0.505 mmol), and K_2CO_3 (210 mg, 1.5 mmol). The tube was sealed with a cap lined with a disposable Teflon septum, evacuated, and purged with N_2 (3 x). 2-Chloroanisole (71.3 mg, 0.5 mmol) and CPME/ H_2O (10:1, 2 mL) were added by syringe, and the reaction mixture was stirred with conventional heating at 100° for 24 h, cooled to rt, and diluted with H_2O (1.5 mL). The reaction mixture was extracted with CH_2Cl_2 (3×5 mL). The organic layer was dried (Na_2SO_4). The solvent was removed under vacuum, and the crude product was purified by silica gel column chromatography (99:1 hexane/EtOAc), yielding the product as a light yellow oil (75.2 mg, 82%): IR (neat) 3001, 1496, 1244 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.14–7.10 (m, 1H), 6.88–6.82 (m, 3H), 3.86 (s, 3H), 2.18–2.15 (m, 1H), 0.92–0.89 (m, 2H), 0.66–0.62 (m, 2H); ^{13}C NMR (125.8 MHz, CDCl_3) δ 158.6, 132.3, 126.5, 125.1, 120.8, 110.5, 55.8, 9.6, 7.8; HRMS–CI (m/z): $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{13}\text{O}$, 148.0888; found, 148.0879.

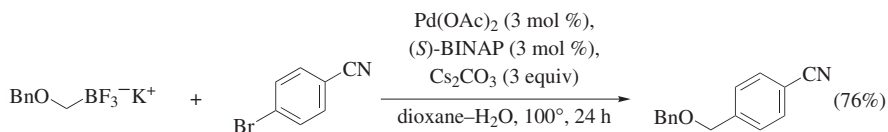


1-Benzyl-4-methoxybenzene [Cross-Coupling of an Aryltrifluoroborate with Benzyl Bromide Using $\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$].⁸⁵ A solution of potassium 4-methoxyphenyltrifluoroborate (114.4 mg, 0.50 mmol), Cs_2CO_3 (489 mg, 1.50 mmol), $\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (8 mg, 0.01 mmol), and benzyl bromide (90.6 mg, 0.50 mmol) in CPME/ H_2O (10:1, 5 mL) was heated under a N_2 atmosphere in a sealed tube. The reaction mixture was stirred at 90° for 20 h, then was cooled to rt, diluted with H_2O (2 mL), and the product was extracted with CH_2Cl_2 (3×10 mL). The solvent was removed under vacuum, and the crude product was purified by silica gel column chromatography (100:1 *n*-pentane/Et $_2\text{O}$), yielding 1-benzyl-4-methoxybenzene as a clear, colorless oil (95.4 mg, 86%): ^1H NMR (360 MHz, CDCl_3) δ 7.32 (t, $J = 7.3$ Hz, 2H), 7.29–7.24 (m, 3H), 7.18 (d, $J = 8.5$ Hz, 2H), 6.86 (d, $J = 8.5$ Hz, 2H), 3.96 (s, 2H), 3.81 (s, 3H); ^{13}C NMR (90 MHz, CDCl_3) δ 158.1, 141.4, 133.4, 130.0, 129.0, 128.6, 126.1, 114.0, 55.4, 41.2.



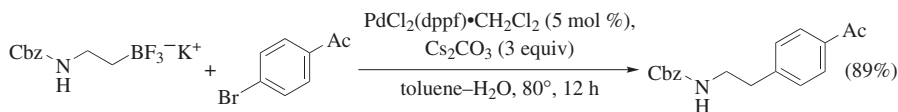
5-(Piperidin-1-ylmethyl)pyrimidine [Cross-Coupling of an Aminomethyltrifluoroborate with a Heteroaryl Bromide Using $\text{Pd}(\text{OAc})_2$ and XPhos].¹²⁸ A solution of potassium 1-trifluoroboratomethylpiperidine (111 mg, 0.55 mmol), Cs_2CO_3 (489 mg, 1.50 mmol), $\text{Pd}(\text{OAc})_2$ (3.5 mg, 0.015 mmol), XPhos (14.5 mg, 0.03 mmol), and 5-bromopyrimidine (79.5 mg, 0.50 mmol) in THF/ H_2O (10:1, 2 mL) was heated under a N_2 atmosphere in a sealed tube. The reaction mixture was stirred at 80° for 24 h, then cooled to rt and diluted with H_2O (1 mL).

The reaction mixture was extracted with CH_2Cl_2 (3×2 mL). The organic layer was dried (MgSO_4), and the solvent was removed under vacuum. The crude product was purified by silica gel chromatography (3.9:1:0.1 hexane/EtOAc/ Et_3N), yielding the product as a pale-yellow oil (75 mg, 81%): ^1H NMR (500 MHz, CDCl_3) δ 9.07 (s, 1H), 8.65 (s, 2H), 3.43 (s, 2H), 2.35 (br s, 4H), 1.56–1.52 (m, 4H), 1.41–1.40 (m, 2H); ^{13}C NMR (125.8 MHz, CDCl_3) δ 157.7, 157.5, 132.0, 58.5, 54.5, 25.9, 24.2; HRMS–CI (m/z): M^+ calcd for $\text{C}_{10}\text{H}_{15}\text{N}_3$, 177.1266; found, 177.1257.



4-[(Benzyloxy)methyl]benzonitrile [Cross-Coupling of an Alkoxyethyltrifluoroborate with an Aryl Bromide Using $\text{Pd}(\text{OAc})_2$ and (*S*)-BINAP].¹²⁹

A Biotage microwave vial was charged with potassium (benzyloxymethyl)trifluoroborate (125 mg, 0.55 mmol), $\text{Pd}(\text{OAc})_2$ (3.4 mg, 0.015 mmol), (*S*)-BINAP (9.4 mg, 0.015 mmol), and Cs_2CO_3 (448 mg, 1.50 mmol). The test tube was sealed with a cap lined with a disposable Teflon septum, evacuated, and purged with nitrogen (3 x). 4-Bromobenzonitrile (91 mg, 0.50 mmol) and dioxane/ H_2O (10:1, 2 mL) were added via syringe, and the reaction mixture was stirred with conventional heating at 100° for 24 h, then cooled to rt. The reaction mixture was extracted with EtOAc (3×3 mL), and the crude product was purified by silica gel column chromatography (15:1 hexane/EtOAc), yielding the product as a colorless oil (84.8 mg, 76%): ^1H NMR (500 MHz, CDCl_3) δ 7.65 (d, $J = 8.3$ Hz, 2H), 7.48 (d, $J = 8.4$ Hz, 2H), 7.39–7.38 (m, 3H), 7.35–7.31 (m, 2H), 4.62 (s, 4H); ^{13}C NMR (125.8 MHz, CDCl_3) δ 144.2, 137.8, 132.4, 128.7, 127.1, 119.0, 73.0, 71.3; HRMS–CI (m/z): $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{14}\text{NO}$, 224.1071; found, 224.1075.



Benzyl 4-Acetylphenethylcarbamate [Cross-Coupling of an Aminoethyltrifluoroborate with an Aryl Bromide Using $\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$].¹³¹

To a mixture of potassium β -aminoethyltrifluoroborate (69.1 mg, 0.242 mmol), 4-bromoacetophenone (47.8 mg, 0.240 mmol), Cs_2CO_3 (234.6 mg, 0.72 mmol), and $\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (9.8 mg, 0.012 mmol) under N_2 was added toluene/ H_2O (3:1, 1.5 mL). The reaction mixture was heated at 80° with stirring under a N_2 atmosphere in a sealed tube for 12 h and then cooled to rt. A saturated aqueous solution of NH_4Cl (4 mL) was added, and the resulting mixture was extracted with CH_2Cl_2 (3×5 mL). The organic layer was dried (MgSO_4) and filtered. The solvent was removed under vacuum, and the crude product was purified by silica gel chromatography (3:7 EtOAc/hexane), affording the product as a

white solid (63.5 mg, 89%): mp 84–85°; ^1H NMR (500 MHz, CDCl_3) δ 7.88 (d, $J = 8.0$ Hz, 2H), 7.36–7.26 (m, 7H), 5.09 (s, 2H), 4.82 (br s, 1H), 3.50–3.46 (m, 2H), 2.88 (app t, $J = 6.6$ Hz, 2H), 2.57 (s, 3H); ^{13}C NMR (125.8 MHz, CDCl_3) δ 197.8, 156.3, 144.6, 136.5, 135.6, 129.1, 128.7, 128.6, 128.2, 128.1, 66.7, 41.9, 36.2, 26.6.

TABULAR SURVEY

The tables cover all examples of the cross-coupling reactions of organotrifluoroborates from 1997 to the middle of 2010. The tables themselves are organized according to the nature of the organotrifluoroborate compound: aryltrifluoroborates (Table 1), heteroaryltrifluoroborates (Table 2), alkenyltrifluoroborates (Table 3), alkynyltrifluoroborates (Table 4), alkyltrifluoroborates (Table 5), cyclopropyltrifluoroborates (Table 6), benzyltrifluoroborates (Table 7), allyltrifluoroborates (Table 8), aminomethyltrifluoroborates (Table 9), alkoxymethyltrifluoroborates (Table 10), and aminoethyltrifluoroborates (Table 11). Table 12 summarizes the cross-coupling reactions of miscellaneous organotrifluoroborates, and finally, Table 13 presents carbonylative cross-coupling reactions of alkenyltrifluoroborates with aryl electrophiles.

The tables are split into sub-tables according to the nature of the electrophiles employed (aryl electrophiles, heteroaryl electrophiles, alkenyltrifluoroborates, allylic and benzylic electrophiles, etc.). Entries within sub-tables are organized according to increasing carbon count, excluding protecting groups and counterions. Unreported yields are indicated by “(—)”.

Charts 1 and 2 preceding the tables provide structures for the ligand and catalyst abbreviations and acronyms used in the tables. The following abbreviations, not including those found in the “*Journal of Organic Chemistry* Standard Abbreviations and Acronyms” list, are used in the tables:

Ad	adamantyl
CPME	cyclopentyl methyl ether
dan	1,8-diaminonaphthalene
dba	dibenzylideneacetone
$\text{Fc}(i\text{-Pr})_2$	1,1'-bis(diisopropylphosphino)ferrocene
MW	microwave irradiation
Nf	perfluoro-1-butanesulfonate
NMP	<i>N</i> -methyl-2-pyrrolidone
PMP	<i>p</i> -methoxyphenyl
PTS	<i>p</i> -toluenesulfonic acid
TBDPS	<i>tert</i> -butyldiphenylsilyl
tol	tolyl, methylphenyl

CHART 1. ABBREVIATIONS AND ACRONYMS FOR Pd CATALYSTS APPEARING IN THE TABULAR SURVEY

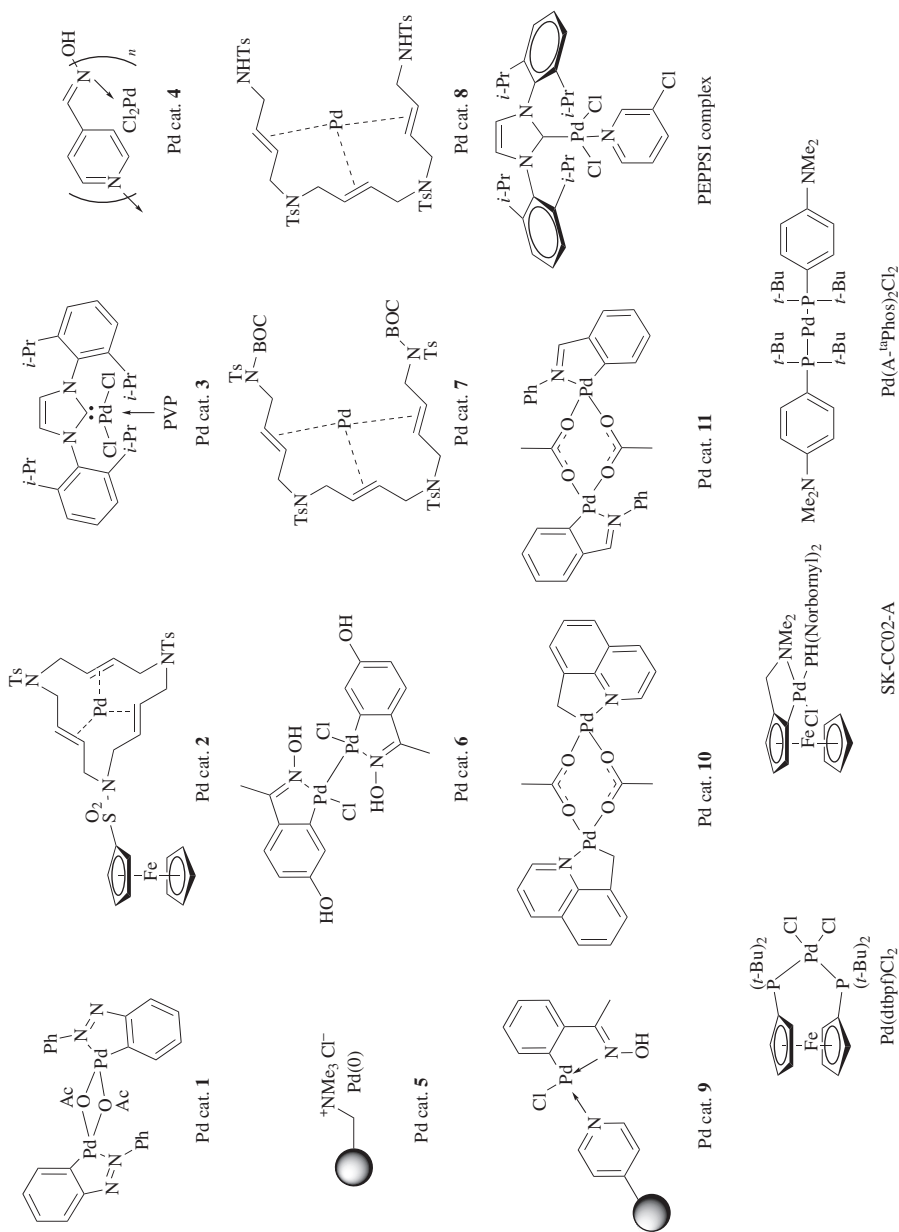
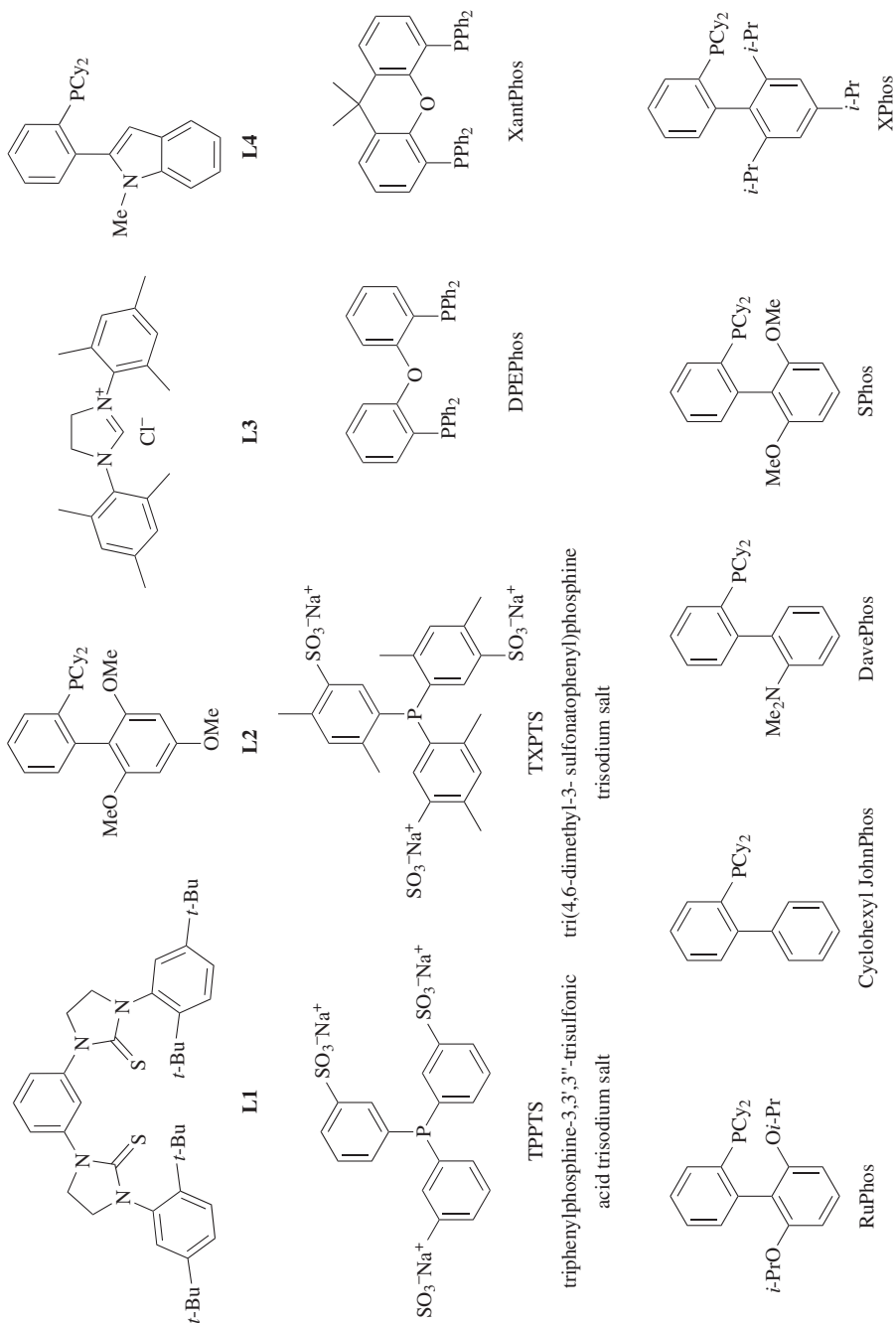


CHART 2. ABBREVIATIONS AND ACRONYMS FOR LIGANDS APPEARING IN THE TABULAR SURVEY



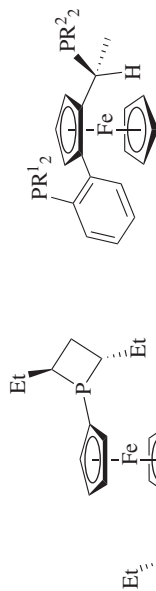
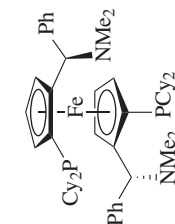
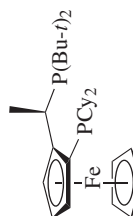
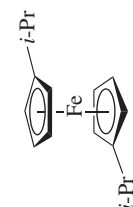
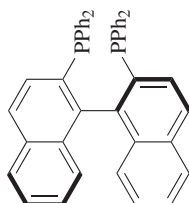
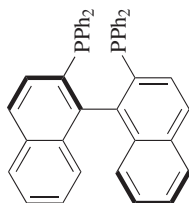
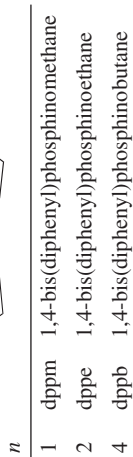
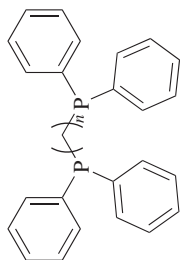
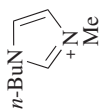
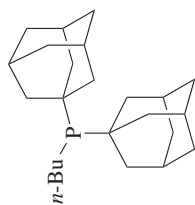


TABLE 1A. CROSS-COUPLING OF ARYL-TRIFLUOROBORATES WITH ARYL ELECTROPHILES

Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
PhBF ₃ ⁻ K ⁺		Pd(OAc) ₂ (5%), DME, 60°, 30 min	R H (99) Cl (92) Me (97)	15
		Pd cat. 1 (x%), [bmim] ⁺ -BF ₄ -MeOH, rt	R Br 4 180 (79) Cl 4 3 (95) OMe 2 180 (78) CO ₂ Et 2 5 (82)	132
		Pd cat., [bmim] ⁺ -BF ₄ -MeOH, rt	Pd cat. Time (min) 10 30 (65) 11 10 (84)	132
		Pd cat. 2 (x%), 1,4-dioxane	x Temp (°) Time (h) 5 rt 17 (63) 5 50 3 (45) 10 rt 22 (62)	231
		Catalyst (10%), additive (2 eq.), Et ₃ N, MeOH, reflux		142
		Catalyst Additive		
		Pd(acac) ₂ Cul (30)		
		Pd(acac) ₂ Ag ₂ O (55)		
		PdCl ₂ (dppf)•CH ₂ Cl ₂ Ag ₂ O (80)		
		Pd(PPh ₃) ₄ Ag ₂ O (83)		

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

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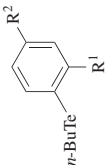
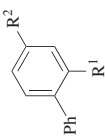
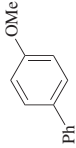
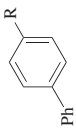
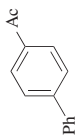
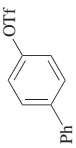
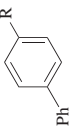
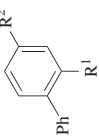
	Reaction Conditions		R ¹ R ²	
			H NO ₂	(89)
(PhBF ₃ ⁻)(<i>n</i> -Bu ₄ N ⁺)	Pd(PPh ₃) ₄ (10%), Ag ₂ O (2 eq), Et ₃ N (3 eq), MeOH, reflux		H I	(42)
			H OH	(92)
			H Cl	(83)
			H Br	(84)
			H Me	(80)
			H Ac	(80)
			H CO ₂ Me	(83)
			Me H	(74)
				142
PhBF ₃ ⁻ K ⁺	Pd(dtbpf)Cl ₂ (2%), Et ₃ N (3 eq), PTS-H ₂ O, rt, 2 h		(99)	232
	Pd(OAc) ₂ (0.5%), K ₂ CO ₃ (3 eq), H ₂ O, 2 h		R Temp (°)	
			OH 65	(82)
			CO ₂ H rt	(90)
			NHAc 65	(55)
				136
	Pd cat. 3 (0.2%), Cs ₂ CO ₃ , MeOH, 60°, 1 d		(82)	233
	Pd(OAc) ₂ (5%), PCy ₃ (10%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, reflux, 48 h		(43)	134
	Pd(OAc) ₂ (0.5%), K ₂ CO ₃ (3 eq), MeOH, reflux, 2 h		R	
			NO ₂ (98)	136
			OMe (78)	
	Pd(OAc) ₂ (1%), PPh ₃ (1%), K ₂ CO ₃ (3 eq), MeOH, reflux		R ¹ R ² Time (h)	
			H NMe ₂ 14	(65) 46
			OMe OMe 18	(75)

TABLE 1A. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.																											
PhBF ₃ ·K ⁺		Pd (2.5 ppm), Na ₂ CO ₃ (3.7 eq), TBAB (1 eq), EtOH–H ₂ O, MW, 150°, 5 min	<table><tr><th>R¹</th><th>R²</th><th></th></tr><tr><td>H</td><td>H</td><td>(87)</td></tr><tr><td>H</td><td>OH</td><td>(90)</td></tr><tr><td>H</td><td>NH₂</td><td>(97)</td></tr><tr><td>H</td><td>Me</td><td>(95)</td></tr><tr><td>H</td><td>OMe</td><td>(96)</td></tr><tr><td>H</td><td>Ac</td><td>(95)</td></tr><tr><td>Me</td><td>H</td><td>(24)</td></tr><tr><td>CN</td><td>H</td><td>(93)</td></tr></table>	R ¹	R ²		H	H	(87)	H	OH	(90)	H	NH ₂	(97)	H	Me	(95)	H	OMe	(96)	H	Ac	(95)	Me	H	(24)	CN	H	(93)	214
	R ¹	R ²																													
	H	H	(87)																												
	H	OH	(90)																												
H	NH ₂	(97)																													
H	Me	(95)																													
H	OMe	(96)																													
H	Ac	(95)																													
Me	H	(24)																													
CN	H	(93)																													
		PdCl ₂ (1.2%), K ₂ CO ₃ (3 eq), MeOH–H ₂ O, MW, 125°, 20 min	<table><tr><th>R¹</th><th>R²</th><th></th></tr><tr><td>H</td><td>NO₂</td><td>(73)</td></tr><tr><td>H</td><td>OMe</td><td>(99)</td></tr><tr><td>H</td><td>CN</td><td>(73)</td></tr><tr><td>H</td><td>Ac</td><td>(97)</td></tr><tr><td>Me</td><td>H</td><td>(71)</td></tr></table>	R ¹	R ²		H	NO ₂	(73)	H	OMe	(99)	H	CN	(73)	H	Ac	(97)	Me	H	(71)	215									
R ¹	R ²																														
H	NO ₂	(73)																													
H	OMe	(99)																													
H	CN	(73)																													
H	Ac	(97)																													
Me	H	(71)																													
		PdCl ₂ (1.2%), K ₂ CO ₃ (3 eq), MeOH, MW, 125°, 20 min	<table><tr><th>R¹</th><th>R²</th><th></th></tr><tr><td>H</td><td>NO₂</td><td>(69)</td></tr><tr><td>H</td><td>OMe</td><td>(79)</td></tr><tr><td>H</td><td>CN</td><td>(55)</td></tr><tr><td>H</td><td>Ac</td><td>(86)</td></tr><tr><td>Me</td><td>H</td><td>(43)</td></tr></table>	R ¹	R ²		H	NO ₂	(69)	H	OMe	(79)	H	CN	(55)	H	Ac	(86)	Me	H	(43)	215									
R ¹	R ²																														
H	NO ₂	(69)																													
H	OMe	(79)																													
H	CN	(55)																													
H	Ac	(86)																													
Me	H	(43)																													
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (1%), Et ₃ N (3 eq), MeOH–THF, reflux, 15 h	 (70)	46																											

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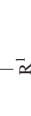
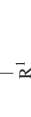
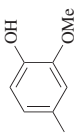
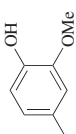
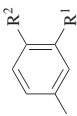
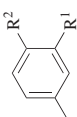
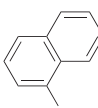
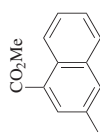
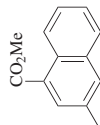
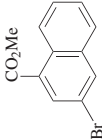
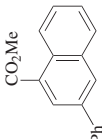
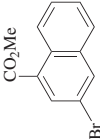
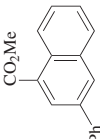
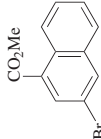
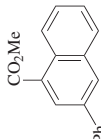
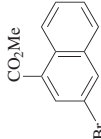
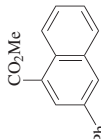
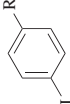
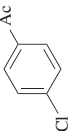
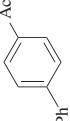
		Pd/porous glass (0.45%), Na₂CO₃ (4 eq), additive, H₂O, MW, 150°, 10 min	216																								
		<table> <tr> <th>R¹</th><th>R²</th><th>Additive</th><th>Cycle:</th><th>1</th><th>2</th><th>3</th><th>4</th></tr> <tr> <td>H</td><td>OH</td><td>—</td><td>(96)</td><td>(95)</td><td>(98)</td><td>(95)</td><td></td></tr> <tr> <td>Me</td><td>Me</td><td>TBAB (1 eq)</td><td>(78)</td><td>(72)</td><td>(46)</td><td>(40)</td><td></td></tr> </table>	R ¹	R ²	Additive	Cycle:	1	2	3	4	H	OH	—	(96)	(95)	(98)	(95)		Me	Me	TBAB (1 eq)	(78)	(72)	(46)	(40)		
R ¹	R ²	Additive	Cycle:	1	2	3	4																				
H	OH	—	(96)	(95)	(98)	(95)																					
Me	Me	TBAB (1 eq)	(78)	(72)	(46)	(40)																					
		Pd/C (1%), aq. KOH (2 eq), H₂O, MW, 120°	217																								
			<table> <tr> <th></th><th>Time (min)</th></tr> <tr> <td></td><td>15 (64)</td></tr> <tr> <td></td><td>30 (72)</td></tr> <tr> <td></td><td>60 (68)</td></tr> </table>		Time (min)		15 (64)		30 (72)		60 (68)																
	Time (min)																										
	15 (64)																										
	30 (72)																										
	60 (68)																										
		Pd(dba)₂ (0.1%), L1 (0.1%) K₂CO₃ (2 eq), NMP–H₂O, 100°	234																								
		<table> <tr> <th>R¹</th><th>R²</th></tr> <tr> <td>NO₂</td><td>H (99)</td></tr> <tr> <td>H</td><td>CHO (87)</td></tr> </table>	R ¹	R ²	NO ₂	H (99)	H	CHO (87)																			
R ¹	R ²																										
NO ₂	H (99)																										
H	CHO (87)																										
		Pd(OAc)₂ (x%), K₂CO₃ (3 eq), MeOH, reflux	136																								
		<table> <tr> <th>x</th><th>Time (h)</th></tr> <tr> <td>0.5</td><td>2 (75)</td></tr> <tr> <td>2</td><td>2 (88)</td></tr> <tr> <td>0.2</td><td>9 (80)</td></tr> </table>	x	Time (h)	0.5	2 (75)	2	2 (88)	0.2	9 (80)																	
x	Time (h)																										
0.5	2 (75)																										
2	2 (88)																										
0.2	9 (80)																										
		PdCl₂ (1.2%), K₂CO₃ (3 eq), MW, 125°, 20 min	215																								
		<table> <tr> <th>Solvent</th><th>(76)</th><th>(96)</th></tr> <tr> <td>MeOH</td><td></td><td></td></tr> <tr> <td>MeOH–H₂O</td><td></td><td></td></tr> </table>	Solvent	(76)	(96)	MeOH			MeOH–H ₂ O																		
Solvent	(76)	(96)																									
MeOH																											
MeOH–H ₂ O																											
		Pd(OAc)₂ (10%), K₂CO₃ (3 eq), DME–H₂O–EtOH, MW, 110°, 7 min	216																								
		<table> <tr> <th></th><th>(99)</th></tr> <tr> <td></td><td></td></tr> </table>		(99)																							
	(99)																										

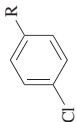
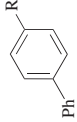
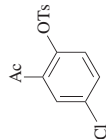
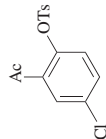
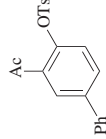
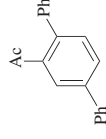
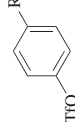
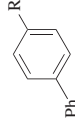
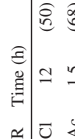
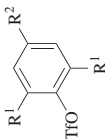
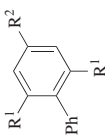
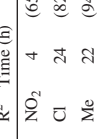
TABLE 1A. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
PhBF ₃ ⁻ K ⁺		Pd(II)EnCat TM (10%), K ₂ CO ₃ (3 eq), DME-H ₂ O-EtOH, MW, 110°, 7 min	 (40)	218
		Pd cat. 4 (10%), K ₂ CO ₃ (3 eq), DME-H ₂ O-EtOH, MW, 110°, 7 min	 (99)	218
		Pd cat. 5 (10%), K ₂ CO ₃ (3 eq), DME-H ₂ O-EtOH, MW, 110°, 7 min	 (10)	218
		Pd cat. 9 (10%), K ₂ CO ₃ (3 eq), DME-H ₂ O-EtOH, MW, 110°, 7 min	 (0)	218
		Pd (2.5 ppm), Na ₂ CO ₃ (3.7 eq), TBAB (1 eq), EtOH-H ₂ O, MW, 150°, 5 min	R Me (86) OMe (93) Ac (98)	214
		Pd (2.5 ppm), Na ₂ CO ₃ (3.7 eq), TBAB (1 eq), EtOH-H ₂ O, MW, 150°, 5 min	 (4)	214

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	PEPFSI complex (2%), base (3 eq), MeOH		Base	Temp (°)	235
			K ₂ CO ₃	60	(90)
			K ₂ CO ₃	rt	(86)
			KOH	60	(91)
			K ₃ PO ₄	60	(84)
	Pd(OAc) ₂ (2%), L2 (4%), Et ₃ N (3 eq), EtOH, 80°, 6 h		(84)		135
	Pd source (0.01%), K ₂ CO ₃ (2 eq), TBAB (0.5 eq), H ₂ O, 100°				150
	Pd Source	Time			
	Pd(OAc) ₂	—	20 h	(28) ^a	
	Pd(OAc) ₂	MW	15 min	(19) ^a	
	PdCl ₂	MW	15 min	(16) ^a	
	Pd cat. 6 (5%), K ₂ CO ₃ (2 eq), TBAB (γ eq), H ₂ O, 100°				150
	R	x	y	Time (h)	
	NH ₂	1	1	10	(53)
	OMe	1	1	6	(83)
	Ac	0.01	0.5	20	(82)
	Ac	0.05	0.5	7	(91)
	CH ₃ CO ₂ H	1	0.5	4	(55)

TABLE 1A. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
PhBF ₃ ·K ⁺		Pd cat. 6 (x%), K ₂ CO ₃ (2 eq), TBAB (y eq), H ₂ O, MW, 100°		150
		R x y Time (min)		
		NH ₂ 1 1 20 (71)		
		OMe 1 1 20 (90)		
		Ac 0.01 0.5 15 (87)		
		CH ₂ CO ₂ H 1 0.5 15 (86)		
		Pd(OAc) ₂ (2%), L2 (4%), Et ₃ N (3 eq), EtOH, 80°		135
		Time (h)		
		8 I (71) 18 I (38) + II (36)		
		Pd(OAc) ₂ (0.5%), K ₂ CO ₃ (3 eq), MeOH, reflux		136
		R Time (h)		
		Cl 12 (50) Ac 1.5 (68)		
		Pd(OAc) ₂ (5%), PCy ₃ (10%), C ₅ F ₅ CO ₃ (3 eq), THF–H ₂ O, reflux		134
		R ¹ R ² Time (h)		
		H NO ₂ 4 (65) H Cl 24 (82) H Me 22 (94) H OMe 20 (92) Me H 72 (83)		

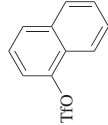
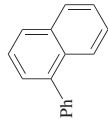
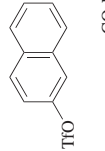
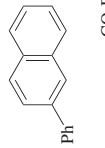
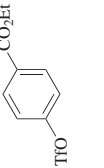
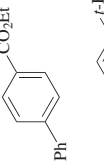
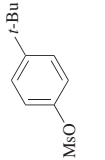
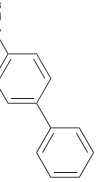
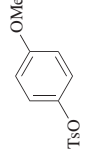
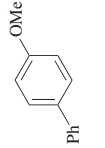
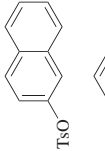
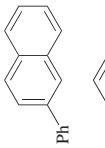
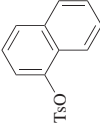
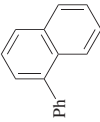
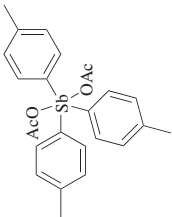
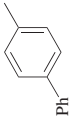
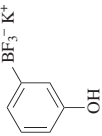
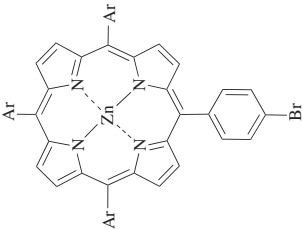
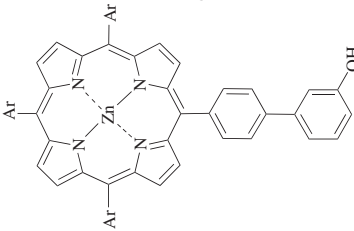
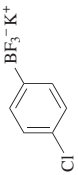
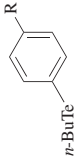
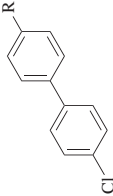
		Pd(OAc) ₂ (5%), PCy ₃ (10%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, reflux, 22 h	134
		Pd(OAc) ₂ (5%), PCy ₃ (10%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, reflux, 20 h	134
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (2%), CsOAc (2 eq), THF-H ₂ O, reflux	236
		Pd(OAc) ₂ (2%), L4 (2%), K ₃ PO ₄ (1.5 eq), <i>t</i> -BuOH, 110°, 15 h	138
		Pd(OAc) ₂ (2%), L2 (4%), base (3 eq), MeOH, 60°, 24 h	135
		Pd(OAc) ₂ (2%), L2 (4%), KOH (3 eq), MeOH, 60°	135
		Pd(OAc) ₂ (2%), L2 (4%), KOH (3 eq), MeOH, 60°	135

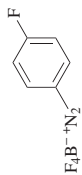
TABLE 1A. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
$\text{PhBF}_3^- \text{K}^+$		$\text{Pd(PPh}_3)_4$ (5%), 1,4-dioxane, 60°, 24 h	 (45)	140
		Pd(OAc)_2 , TPPTS, K_2CO_3 , $\text{MeCN-H}_2\text{O}$, 60–70°, 12 h	 (72)	159
		$\text{Pd(PPh}_3)_4$ (10%), Ag_2O (2 eq), Et_3N (3 eq), MeOH , reflux	$\text{Ar} = \text{---} \text{N}^+\text{---Me}$ 	142

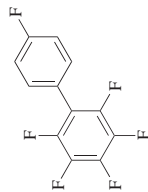
C₆

TABLE 1A. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc)2 (5%), TPPTS (15%), K3PO4 (7.5 eq), H2O, 50°		160
C ₆				
	Peptide	Time (h)		
	H-Tyr-Gly-Gly-4-iodo-Phe-Leu-OH	24	(98)	
	H-Gly-Gly-4-iodo-Phe-Leu-OH	3	(84)	
	For-Met-Leu-4-iodo-Phe-OH	3	(100)	
	H-Tyr-Gly-Gly-4-iodo-Phe-Met-OH	3	(90)	
	H-Tyr-D-Ala-4-iodo-Phe-Gly-Tyr-Pro-Ser-NH ₂	3	(76)	
	H-Met-Glu-His-4-iodo-Phe-Arg-Trp-Gly-OH	24	(24)	
		Pd(PPh ₃) ₄ (5%), DME, 20°	Ar 2,3,4,5-C ₆ H ₄ F ₄ (45) ^b 2,3,5,6-C ₆ H ₃ F ₄ (23) ^b 2,3,4,6-C ₆ H ₃ F ₄ (20) ^b 3,4,5-C ₆ H ₂ F ₃ (27) ^b	237
		Pd(OAc) ₂ , dioxane, 20°		237

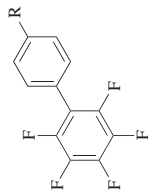


Pd source, solvent, 20°



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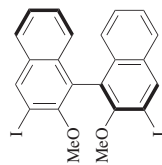
Pd cat.	Solvent	
Pd black	dioxane	(8) ^b
Pd(PPh ₃) ₄	dioxane	(14)
Pd ₂ (μ-OAc) ₂ (P(<i>o</i> -tol) ₂ C ₆ H ₄ CH ₂) ₂	dioxane	(4) ^b
Pd ₂ (μ-OAc) ₂ (P(<i>o</i> -tol) ₂ C ₆ H ₄ CH ₂) ₂	MeOH	(0) ^b
Pd(PPh ₃) ₄	DMF	(3) ^b
Pd(PPh ₃) ₄	DME	(32)



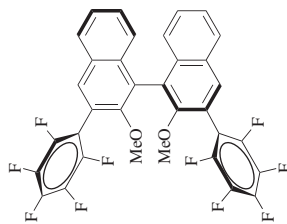
Pd(PPh₃)₄ (5%), DME, 20°

237

R	(30) ^b
H	(13)
NO ₂	(10)
Me	(27) ^b
OMe	(46)
CO ₂ Et	



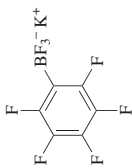
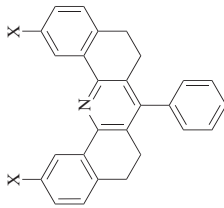
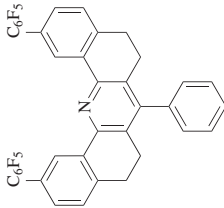
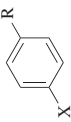
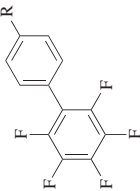
Pd(OAc)₂ (17%), PPh₃ (34%),
Ag₂O (4 eq), K₂CO₃ (6.7 eq),
toluene, 110°, 48 h



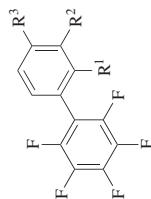
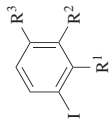
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89

TABLE 1A. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc) ₂ (0.1%), PPh ₃ (0.2%), K ₂ CO ₃ , toluene, 100°	 X Br (0) 238 I (20)	
		Pd(OAc) ₂ (10%), PPh ₃ (20%), K ₂ CO ₃ (2 eq), Ag ₂ O (1.2 eq), toluene, 100°	 X R Time (h) Br F 3 (28) ^b Br NO ₂ 5 (36) ^b Br NO ₂ 24 (62) ^b Br OMe 24 (25) ^b I H 3 (90) I NO ₂ 3 (81) I Me 3 (93) I CO ₂ Et 3 (82)	239

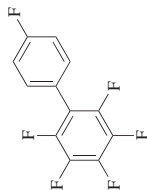
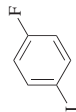
C₆



$\text{PdCl}_2(\text{PPh}_3)$ (5%), **L3** (5%),
 Ag_2O (1.2 eq),
 toluene, 100° , 8 h

88

R^1	R^2	R^3	
H	H	H	(99)
H	H	F	(96)
H	H	NH_2	(3)
H	H	NO_2	(99)
H	H	Me	(91)
H	H	CN	(80)
H	H	CF_3	(80)
H	H	Ph	(86)
H	H	$4\text{-O}_2\text{NC}_6\text{H}_4$	(80)
H	CN	H	(96)
NO_2	H	H	(27)
Me	H	H	(49)
CN	H	H	(77)

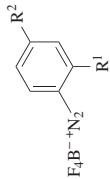
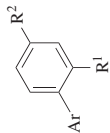
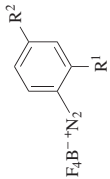
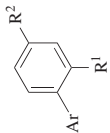


Pd source (10%),
 ligand (20%),
 K_2CO_3 (2 eq),
 Ag_2O (1.2 eq), toluene,
 100° , 3 h

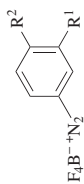
239

Pd Source	Ligand	
$\text{Pd}(\text{OAc})_2$	none	(0)
$\text{Pd}(\text{OAc})_2$	$\text{P}(o\text{-tol})_3$	(67)
$\text{Pd}(\text{OAc})_2$	PPh_3	(92)
$\text{Pd}(\text{PPh}_3)_4$	none	(71)

TABLE 1A. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (*Continued*)

Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.																								
ArBF ₃ ⁻ K ⁺		Pd(OAc) ₂ (5%), 1,4-dioxane, 20°	 <table> <tr> <th>Ar</th><th>R¹</th><th>R²</th><th>Time (h)</th></tr> <tr> <td>Ph</td><td>H</td><td>Me</td><td>3.7 (88)^c</td></tr> <tr> <td>Ph</td><td>H</td><td>OTf</td><td>1 (66)</td></tr> <tr> <td>Ph</td><td>OMe</td><td>OMe</td><td>6.5 (69)</td></tr> <tr> <td>4-FC₆H₄</td><td>H</td><td>NO₂</td><td>2.5 (92)</td></tr> <tr> <td>2,4-Cl₂-C₆H₃</td><td>H</td><td>CO₂Et</td><td>72 (26)^c</td></tr> </table>	Ar	R ¹	R ²	Time (h)	Ph	H	Me	3.7 (88) ^c	Ph	H	OTf	1 (66)	Ph	OMe	OMe	6.5 (69)	4-FC ₆ H ₄	H	NO ₂	2.5 (92)	2,4-Cl ₂ -C ₆ H ₃	H	CO ₂ Et	72 (26) ^c	13
Ar	R ¹	R ²	Time (h)																									
Ph	H	Me	3.7 (88) ^c																									
Ph	H	OTf	1 (66)																									
Ph	OMe	OMe	6.5 (69)																									
4-FC ₆ H ₄	H	NO ₂	2.5 (92)																									
2,4-Cl ₂ -C ₆ H ₃	H	CO ₂ Et	72 (26) ^c																									
		Pd ₂ (μ-OAc) ₂ , (P(<i>o</i> -tol) ₃) ₂ (5%), MeOH, 20°	 <table> <tr> <th>Ar</th><th>R¹</th><th>R²</th><th>Time (h)</th></tr> <tr> <td>Ph</td><td>H</td><td>I</td><td>22 (41)</td></tr> <tr> <td>2,4-Cl₂-C₆H₃</td><td>H</td><td>CO₂Et</td><td>1.5 (73)</td></tr> <tr> <td>2,4-Cl₂-C₆H₃</td><td>OMe</td><td>OMe</td><td>20 (trace)</td></tr> <tr> <td>3-O₂NC₆H₄</td><td>H</td><td>Br</td><td>8 (60)</td></tr> </table>	Ar	R ¹	R ²	Time (h)	Ph	H	I	22 (41)	2,4-Cl ₂ -C ₆ H ₃	H	CO ₂ Et	1.5 (73)	2,4-Cl ₂ -C ₆ H ₃	OMe	OMe	20 (trace)	3-O ₂ NC ₆ H ₄	H	Br	8 (60)	13				
Ar	R ¹	R ²	Time (h)																									
Ph	H	I	22 (41)																									
2,4-Cl ₂ -C ₆ H ₃	H	CO ₂ Et	1.5 (73)																									
2,4-Cl ₂ -C ₆ H ₃	OMe	OMe	20 (trace)																									
3-O ₂ NC ₆ H ₄	H	Br	8 (60)																									

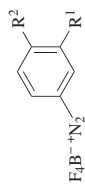
C₆



Pd cat. **7** (5%),
base (1.1 eq),
1,4-dioxane, rt

240

Ar	R ¹	R ²	Base	Time (h)
Ph	H	H	—	24 (0)
Ph	H	H	K ₂ CO ₃	2.25 (64)
Ph	H	Me	K ₂ CO ₃	24 (24)
Ph	H	Me	CaCO ₃	25 (44)
Ph	H	OMe	K ₂ CO ₃	16 (28)
Ph	Me	H	K ₂ CO ₃	28 (53)
Ph	Me	H	CaCO ₃	24 (38)
4-FC ₆ H ₄	H	H	—	24 (0)
4-FC ₆ H ₄	H	H	K ₂ CO ₃	28 (55)
4-FC ₆ H ₄	H	OMe	K ₂ CO ₃	26 (91)



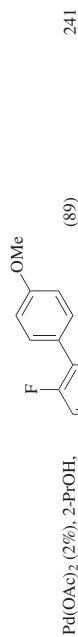
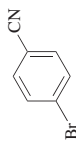
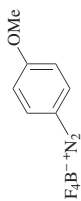
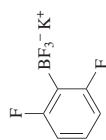
Pd cat. **8** (5%),
K₂CO₃ (1.1 eq),
1,4-dioxane, rt

240

Ar	R ¹	R ²	Time (h)
Ph	H	H	22 (65)
Ph	H	Me	24 (53)
Ph	H	OMe	23 (54)
Ph	Me	H	24 (55)
4-FC ₆ H ₄	H	H	24 (0)

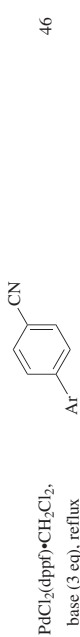
TABLE 1A. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)		Refs.
C ₆ ArBF ₃ ⁻ K ⁺		Pd cat. 2 (5%), 1,4-dioxane			231
C ₆ 		Pd(OAc) ₂ (2%), <i>n</i> -PrOH, MW, 40°, 5 min			241



$\text{Pd}(\text{OAc})_2$ (2%), 2-PrOH,
MW, 75°, 10 min

241



$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$,
base (3 eq), reflux

46

Ar	% Pd	Base	Time (h)	Solvent
3-O ₂ NC ₆ H ₄	0.5	Et ₃ N	12	EtOH (89)
2,6-F ₂ C ₆ H ₃	1	Et ₃ N	6	EtOH (86)
2,3,4,5,6-F ₅ C ₆	5	<i>i</i> -Pr ₂ NEt	36	MeOH–THF (10)
2,3,4,5,6-F ₅ C ₆	5	<i>i</i> -Pr ₂ NEt	36	THF (38)

TABLE 1A. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (*Continued*)

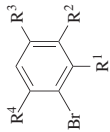
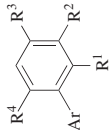
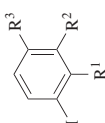
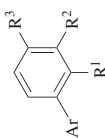
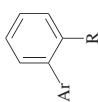
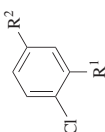
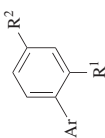
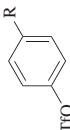
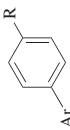
Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.						
$\text{ArBF}_3^- \text{K}^+$		$\text{Pd}(\text{OAc})_2$ (x%), K_2CO_3 (3 eq), MeOH, reflux								
	Ar	R ¹	R ²	R ³	R ⁴	x	Time			
	Ph	H	H	H	Cl	H	0.5	12 h	(75)	136
	Ph	H	H	H	OH	H	0.5	36 h	(40)	136
	Ph	H	H	H	NO ₂	H	0.5	45 min	(>99)	136
	Ph	H	H	H	CN	H	0.5	1 h	(87)	46
	Ph	H	H	H	CO ₂ H	H	0.5	2 h	(96)	46
	Ph	H	H	H	CF ₃	H	0.5	1 h	(79)	136
	Ph	H	H	H	OMe	H	0.5	2 h	(95)	136
	Ph	H	H	H	CO ₂ H	H	0.5	2 h	(96)	46
	Ph	H	H	H	NMe ₂	H	0.5	24 h	(trace)	136
	Ph	H	H	H	NHAc	H	0.5	18 h	(62)	136
	Ph	H	H	H	COPh	H	0.5	45 min	(92)	136
	Ph	H	H	CO ₂ Me	H	H	0.5	1 h	(87)	136
	Ph	CHO	H	H	H	H	0.5	1 h	(89)	46
	Ph	OMe	H	H	OMe	H	1	24 h	(50)	136
	Ph	Me	H	H	Me	Me	2	12 h	(38)	136
	Ph	Me	H	H	Me	Me	5	36 h	(52)	136
	4-FC ₆ H ₄	H	H	H	NO ₂	H	1	2 h	(96)	136
	4-FC ₆ H ₄	H	H	H	CN	H	0.5	2 h	(96)	46

TABLE 1A. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.																																																		
$\text{ArBF}_3^- \text{K}^+$		$\text{PdCl}_2(\text{dppf}) \bullet \text{CH}_2\text{Cl}_2$ (2%), <i>i</i> -Pr ₂ NEt (3 eq), <i>i</i> -PrOH–H ₂ O, MW, 100°, 10 min	 <table><tr><th>Ar</th><th>R¹</th><th>R²</th><th>R³</th><th></th></tr><tr><td>Ph</td><td>H</td><td>H</td><td>Cl</td><td>(98)</td></tr><tr><td>Ph</td><td>H</td><td>H</td><td>F</td><td>(84)</td></tr><tr><td>Ph</td><td>H</td><td>H</td><td>OMe</td><td>(100)</td></tr><tr><td>Ph</td><td>H</td><td>H</td><td>Ac</td><td>(93)</td></tr><tr><td>Ph</td><td>H</td><td>NO₂</td><td>H</td><td>(98)</td></tr><tr><td>Ph</td><td>OMe</td><td>H</td><td>H</td><td>(100)</td></tr><tr><td>Ph</td><td>Me</td><td>H</td><td>Me</td><td>(77)</td></tr><tr><td>4-FC₆H₄</td><td>H</td><td>H</td><td>Ac</td><td>(96)</td></tr><tr><td>2,4,6-F₃C₆H₂</td><td>H</td><td>H</td><td>F</td><td>(50)</td></tr></table>	Ar	R ¹	R ²	R ³		Ph	H	H	Cl	(98)	Ph	H	H	F	(84)	Ph	H	H	OMe	(100)	Ph	H	H	Ac	(93)	Ph	H	NO ₂	H	(98)	Ph	OMe	H	H	(100)	Ph	Me	H	Me	(77)	4-FC ₆ H ₄	H	H	Ac	(96)	2,4,6-F ₃ C ₆ H ₂	H	H	F	(50)	219
	Ar	R ¹	R ²	R ³																																																		
Ph	H	H	Cl	(98)																																																		
Ph	H	H	F	(84)																																																		
Ph	H	H	OMe	(100)																																																		
Ph	H	H	Ac	(93)																																																		
Ph	H	NO ₂	H	(98)																																																		
Ph	OMe	H	H	(100)																																																		
Ph	Me	H	Me	(77)																																																		
4-FC ₆ H ₄	H	H	Ac	(96)																																																		
2,4,6-F ₃ C ₆ H ₂	H	H	F	(50)																																																		
		Pd/PVP (1%), K ₂ CO ₃ (2 eq), H ₂ O, reflux, 4 h	 <table><tr><th>Ar</th><th>R</th><th></th></tr><tr><td>Ph</td><td>H</td><td>(91)</td></tr><tr><td>Ph</td><td>Me</td><td>(92)</td></tr><tr><td>4-BrC₆H₄</td><td>H</td><td>(93)</td></tr><tr><td>4-ClC₆H₄</td><td>H</td><td>(95)</td></tr><tr><td>4-FC₆H₄</td><td>H</td><td>(94)</td></tr></table>	Ar	R		Ph	H	(91)	Ph	Me	(92)	4-BrC ₆ H ₄	H	(93)	4-ClC ₆ H ₄	H	(95)	4-FC ₆ H ₄	H	(94)	221																																
Ar	R																																																					
Ph	H	(91)																																																				
Ph	Me	(92)																																																				
4-BrC ₆ H ₄	H	(93)																																																				
4-ClC ₆ H ₄	H	(95)																																																				
4-FC ₆ H ₄	H	(94)																																																				
		Pd/C , TBAB (0.5 eq), NaOH (2.5 eq), H ₂ O, 100°, 2 h	 <table><tr><th>Ar</th><th>R¹</th><th>R²</th><th></th></tr><tr><td>Ph</td><td>NO₂</td><td>H</td><td>(89)</td></tr><tr><td>4-FC₆H₄</td><td>H</td><td>NO₂</td><td>(98)</td></tr></table>	Ar	R ¹	R ²		Ph	NO ₂	H	(89)	4-FC ₆ H ₄	H	NO ₂	(98)	226																																						
Ar	R ¹	R ²																																																				
Ph	NO ₂	H	(89)																																																			
4-FC ₆ H ₄	H	NO ₂	(98)																																																			

C₆

		Pd(OAc) ₂ (1.2%), MW, 95°, 15 min	Ar	R			
			Ph	Ac	(90)		
			3-O ₂ NC ₆ H ₄	H	(50)		
			4-ClC ₆ H ₄	H	(98)		
			4-ClC ₆ H ₄	Ac	(89)		
			4-ClC ₆ H ₄	NO ₂	(86)		
			4-ClC ₆ H ₄	CN	(51)		
			4-FC ₆ H ₄	CN	(99)		
			2,6-F ₂ C ₆ H ₃	CN	(51)		
			Ar	R			
			Ph	NO ₂	(55)		
			Ph	CN	(93)		
			Ph	CHO	(86)		
			Ph	CF ₃	(81)		
			Ph	OMe	(42)		
			Ph	Ac	(77)		
			Ph	CO ₂ Et	(99)		
			4-FC ₆ H ₄	CN	(89)		
					135		
			Ar	R ¹	R ²	R ³	
			Ph	H	H	H	(94)
			Ph	H	H	Me	(90)
			Ph	H	H	CHO	(trace)
			Ph	H	H	CMe ₂ Et	(75)
			Ph	Me	H	H	(82)
			Ph	Me	Me	H	(80)
			4-FC ₆ H ₄	H	H	OMe	(76)

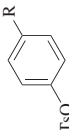
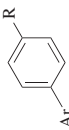
		Pd(OAc) ₂ (2%), L2 (4%), Et ₃ N (3 eq), EtOH, 80°, 0.5–6h	Ar	R			
			Ph	NO ₂	(55)		
			Ph	CN	(93)		
			Ph	CHO	(86)		
			Ph	CF ₃	(81)		
			Ph	OMe	(42)		
			Ph	Ac	(77)		
			Ph	CO ₂ Et	(99)		
			4-FC ₆ H ₄	CN	(89)		
					135		
			Ar	R ¹	R ²	R ³	
			Ph	H	H	H	(94)
			Ph	H	H	Me	(90)
			Ph	H	H	CHO	(trace)
			Ph	H	H	CMe ₂ Et	(75)
			Ph	Me	H	H	(82)
			Ph	Me	Me	H	(80)
			4-FC ₆ H ₄	H	H	OMe	(76)

TABLE 1A. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.																																
		$\text{Pd}_2(\text{dba})_3$ (0.5%), $\text{P}(t\text{-Bu})_3$ (1.2%), THF, rt, 12 h		57																																
		$\text{Pd}(\text{OAc})_2$ (x%), SPhos (y%), K_2CO_3 (3 eq), MeOH		87																																
	<table> <tr> <th>R¹</th><th>R²</th><th>R³</th><th>R⁴</th><th>x</th><th>y</th><th>Temp (°)</th><th>Time (h)</th></tr> <tr> <td>H</td><td>H</td><td>OMe</td><td>H</td><td>0.5</td><td>1</td><td>reflux</td><td>12 (89)</td></tr> <tr> <td>Me</td><td>H</td><td>H</td><td>Me</td><td>2</td><td>4</td><td>50</td><td>20 (92)</td></tr> <tr> <td>Me</td><td>Ph</td><td>H</td><td>H</td><td>0.5</td><td>1</td><td>reflux</td><td>12 (84)</td></tr> </table>	R ¹	R ²	R ³	R ⁴	x	y	Temp (°)	Time (h)	H	H	OMe	H	0.5	1	reflux	12 (89)	Me	H	H	Me	2	4	50	20 (92)	Me	Ph	H	H	0.5	1	reflux	12 (84)			
R ¹	R ²	R ³	R ⁴	x	y	Temp (°)	Time (h)																													
H	H	OMe	H	0.5	1	reflux	12 (89)																													
Me	H	H	Me	2	4	50	20 (92)																													
Me	Ph	H	H	0.5	1	reflux	12 (84)																													
		$\text{Pd}(\text{OAc})_2$ (0.5%), SPhos (1%), K_2CO_3 (3 eq), MeOH, reflux, 12 h		87																																
		$\text{Pd}(\text{OAc})_2$ (2%), L4 (2%), K_3PO_4 (1.5 eq), <i>t</i> -BuOH, 110°, 2 h		138																																
		$\text{Pd}(\text{OAc})_2$ (1%), L4 (1%), $\text{K}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ (3 eq), <i>t</i> -BuOH, 110°, 3 h		284																																

C₇

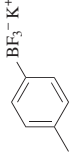
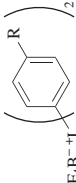
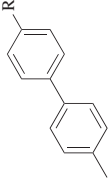
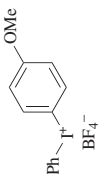
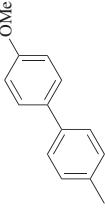
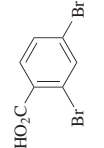
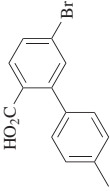
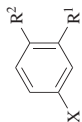
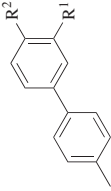
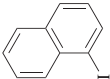
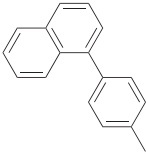
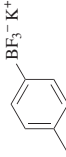
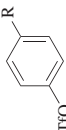
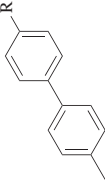
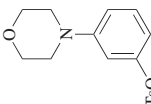
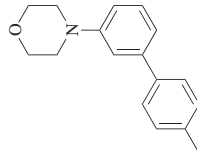
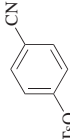
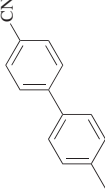
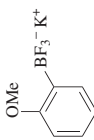
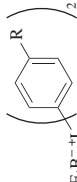
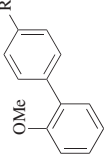
		$\text{Pd}(\text{OAc})_2$ (5%), DME, 60°, 30 min		R H (93) Cl (89) Me (95)	15
		$\text{Pd}(\text{OAc})_2$ (5%), DME, 60°, 30 min	(97)		15
		$\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (1.5%), LiOH (2.2 eq), NMP-H ₂ O, 65°, 36 h	(72)		242
		Pd/C (10%), K ₂ CO ₃ (2 eq), EtOH-H ₂ O, 50°, 24 h	X R ¹ R ² Br H H (65) Br H NO ₂ (85) Br H CN (65) Br Me H (63) I H Me (42)		227
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (2%), <i>i</i> -Pr ₂ NEt (3 eq), <i>i</i> -PrOH-H ₂ O, MW, 100°, 10 min	(85)		219

TABLE 1A. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (*Continued*)

Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.														
		Pd(OAc)₂ (1.2%), MW, 95°, 15 min	 <table><tr><td>R</td><td>(92)</td></tr><tr><td>H</td><td>(88)</td></tr><tr><td>NO₂</td><td>(88)</td></tr><tr><td>Me</td><td>(63)</td></tr><tr><td>CN</td><td>(85)</td></tr><tr><td>OMe</td><td>(61)</td></tr><tr><td>Ac</td><td>(94)</td></tr></table>	R	(92)	H	(88)	NO ₂	(88)	Me	(63)	CN	(85)	OMe	(61)	Ac	(94)	86
R	(92)																	
H	(88)																	
NO ₂	(88)																	
Me	(63)																	
CN	(85)																	
OMe	(61)																	
Ac	(94)																	
		Pd(OAc)₂ (2%), L2 (4%), KOH (3 eq), MeOH, 60°, 24 h	 (88)	135														
		Pd(OAc)₂ (2%), L2 (4%), Et₃N (3 eq), EtOH, 80°	 (98)	135														
		Pd(OAc)₂ (5%), DME, 60°, 30 min	 <table><tr><td>R</td><td>(87)</td></tr><tr><td>H</td><td>(87)</td></tr><tr><td>Cl</td><td>(81)</td></tr><tr><td>Me</td><td>(84)</td></tr></table>	R	(87)	H	(87)	Cl	(81)	Me	(84)	15						
R	(87)																	
H	(87)																	
Cl	(81)																	
Me	(84)																	

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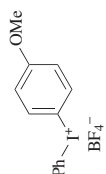
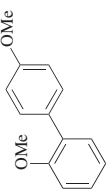
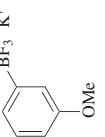
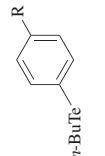
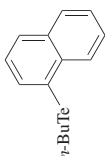
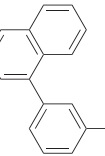
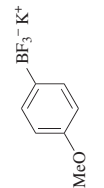
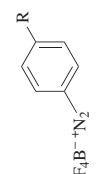
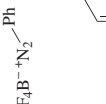
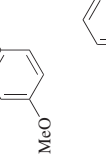
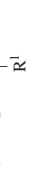
		Pd(OAc)₂ (5%), DME, 60°, 30 min	(87)	15									
		Pd(PPh₃)₄ (10%), Ag₂O (2 eq), Et₃N (3 eq), MeOH, reflux	<table><tr><th>R</th><th>(78)</th><th>(80)</th></tr><tr><td>H</td><td></td><td></td></tr><tr><td>Cl</td><td></td><td></td></tr></table>	R	(78)	(80)	H			Cl			142
R	(78)	(80)											
H													
Cl													
		Pd(PPh₃)₄ (10%), Ag₂O (2 eq), Et₃N (3 eq), MeOH, reflux	(79)	142									
		Pd cat. 2 (5%), 1,4-dioxane	<table><tr><th>R</th><th>Time (h)</th></tr><tr><td>H</td><td>19 (43)</td></tr><tr><td>OMe</td><td>18 (40)</td></tr></table>	R	Time (h)	H	19 (43)	OMe	18 (40)	231			
R	Time (h)												
H	19 (43)												
OMe	18 (40)												
		Pd cat. 7 (5%), K₂CO₃ (1.1 eq), 1,4-dioxane, rt, 24 h	(85)	240									
		Pd(OAc)₂ (5%), 1,4-dioxane, 20°	<table><tr><th>R¹</th><th>R²</th><th>Time (h)</th></tr><tr><td>H</td><td>Me</td><td>4 (86)</td></tr><tr><td>Ac</td><td>H</td><td>1.7 (96)</td></tr></table>	R ¹	R ²	Time (h)	H	Me	4 (86)	Ac	H	1.7 (96)	13
R ¹	R ²	Time (h)											
H	Me	4 (86)											
Ac	H	1.7 (96)											

TABLE 1A. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.	
		Pd(PPh ₃) ₄ (10%), Ag ₂ O (2 eq), Et ₃ N (3 eq), MeOH, reflux	 R H (81) Cl (75)	142	
		Pd(PPh ₃) ₄ (10%), Ag ₂ O (2 eq), Et ₃ N (3 eq), MeOH, reflux	 (87)	142	
		Pd(OAc) ₂ (2%), PPh ₃ (2%), K ₂ CO ₃ (3 eq), MeOH, reflux, 24 h	 (52)	46	
		Pd(OAc) ₂ (10%), TPPTS (30%), K ₃ PO ₄ (15 eq), H ₂ O, 50°, 24 h	 I + 160	160	
				II	
Peptide (X)					
Ac-Phe-3,5-diiodo-Tyr-OH	I	(0)	(92)		
H-3,5-diiodo-Tyr-Gly-Gly-Phe-Leu-OH	II	(0)	(92)		
H-3,5-dibromo-Tyr-Gly-Gly-Phe-Leu-OH	I	(0)	(0)		
H-3,5-diiodo-Tyr-Gly-Gly-Phe-Met-OH	II	(17)	(83)		
H-3,5-diiodo-Tyr-D-Ala-Phe-Gly-Tyr-Pro-Ser-NH ₂	I	(8)	(40)		

C₇

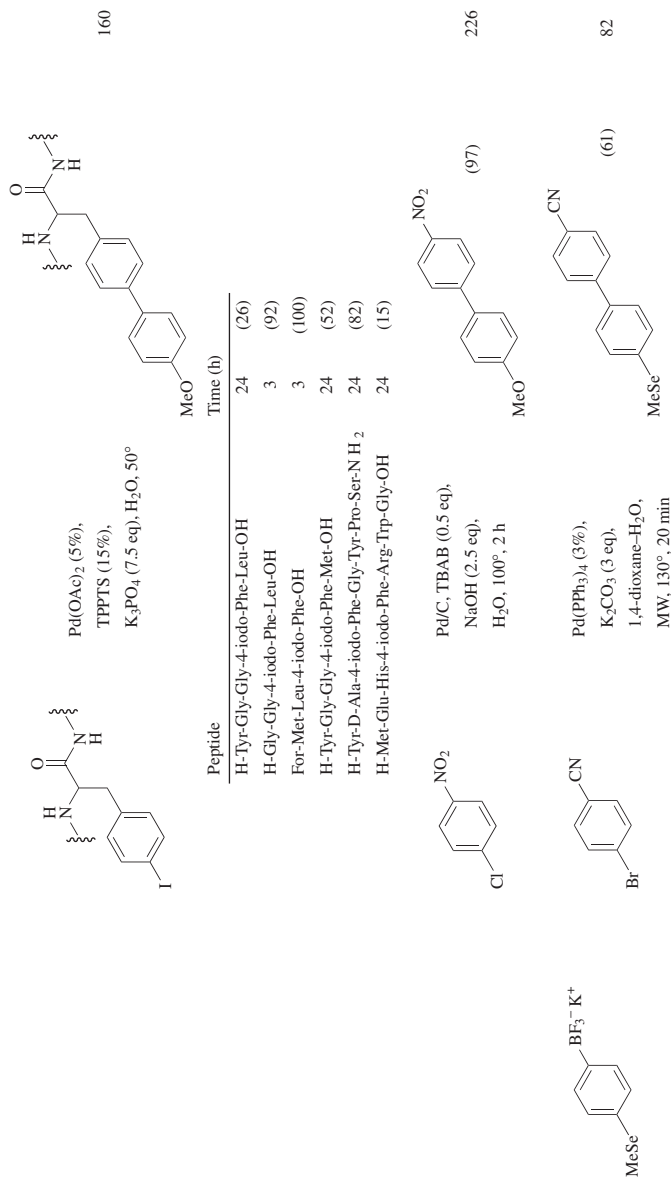
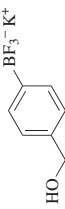
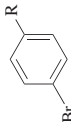
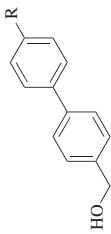
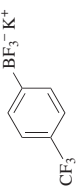
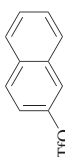
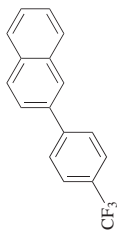
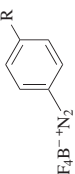
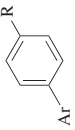


TABLE 1A. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (*Continued*)

Aryltrifluoroborate		Electrophile	Conditions	Product(s) and Yield(s) (%)		Refs.
		Pd(OAc)₂ (5%), K₂CO₃ (3 eq), MeOH		Me reflux 1 h (77) CN reflux 1 h (75) Me MW 5 min (92) CN MW 5 min (94)	222	
		Pd(OAc)₂ (5%), PCy₃ (10%), Cs₂CO₃ (3 eq), THF-H₂O, reflux, 20 h		(92)	134	
		Pd₂(μ-OAc)₂, (P(<i>o</i>-tol)₃)₂ (5%), MeOH, 20°		Ar	13	

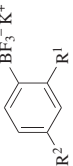
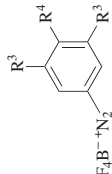
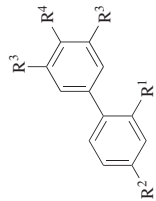
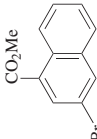
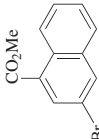
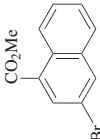
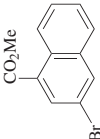
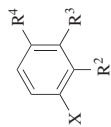
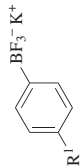
		Pd(OAc)₂ (2%), <i>n</i>-PrOH, MW, 40°, 5 min		241																				
ArBF ₃ ⁻ K ⁺			<table><tr><th>R¹</th><th>R²</th><th>R³</th><th>R⁴</th></tr><tr><td>H</td><td>Me</td><td>H</td><td>Me</td></tr><tr><td>H</td><td>Me</td><td>H</td><td>OMe</td></tr><tr><td>H</td><td>Me</td><td>Cl</td><td>H</td></tr><tr><td>Me</td><td>H</td><td>H</td><td>OMe</td></tr></table>	R ¹	R ²	R ³	R ⁴	H	Me	H	Me	H	Me	H	OMe	H	Me	Cl	H	Me	H	H	OMe	218
R ¹	R ²	R ³	R ⁴																					
H	Me	H	Me																					
H	Me	H	OMe																					
H	Me	Cl	H																					
Me	H	H	OMe																					
		Pd(OAc)₂ (10%), K₂CO₃ (3 eq), DME-H₂O-EtOH, MW, 110°, 7 min	<table><tr><th>Ar</th></tr><tr><td>4-MeOC₆H₄</td></tr><tr><td>4-NCC₆H₄</td></tr></table>	Ar	4-MeOC ₆ H ₄	4-NCC ₆ H ₄	218																	
Ar																								
4-MeOC ₆ H ₄																								
4-NCC ₆ H ₄																								
		Pd cat. 4 (10%), K₂CO₃ (3 eq), DME-H₂O-EtOH, MW, 110°, 7 min	<table><tr><th>Ar</th></tr><tr><td>4-MeOC₆H₄</td></tr><tr><td>4-NCC₆H₄</td></tr></table>	Ar	4-MeOC ₆ H ₄	4-NCC ₆ H ₄	218																	
Ar																								
4-MeOC ₆ H ₄																								
4-NCC ₆ H ₄																								
		Pd(II)EnCatTM (10%), K₂CO₃ (3 eq), DME-H₂O-EtOH, MW, 110°, 7 min	<table><tr><th>Ar</th></tr><tr><td>4-MeOC₆H₄</td></tr><tr><td>4-NCC₆H₄</td></tr></table>	Ar	4-MeOC ₆ H ₄	4-NCC ₆ H ₄	218																	
Ar																								
4-MeOC ₆ H ₄																								
4-NCC ₆ H ₄																								
		Pd cat. 5 (10%), K₂CO₃ (3 eq), DME-H₂O-EtOH, MW, 110°, 7 min	<table><tr><th>Ar</th></tr><tr><td>4-MeOC₆H₄</td></tr><tr><td>4-NCC₆H₄</td></tr></table>	Ar	4-MeOC ₆ H ₄	4-NCC ₆ H ₄	218																	
Ar																								
4-MeOC ₆ H ₄																								
4-NCC ₆ H ₄																								

TABLE 1A. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

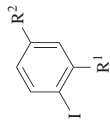
</



Pd (2.5 ppm),
 Na_2CO_3 (3.7 eq),
 TBAB (1 eq), EtOH-H₂O,
 MW, 150°, 5 min

221

R ¹	X	R ²	R ³	R ⁴
Me	Br	H	H	H (78)
Me	Br	H	H	Me (67)
Me	Br	H	H	Ac (82)
Me	I	H	H	H (96)
Me	I	H	H	Me (94)
Me	I	H	H	Ac (95)
Me	I	H	F	H (90)
Me	I	F	H	H (93)
OMe	I	H	H	H (90)

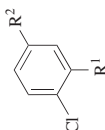
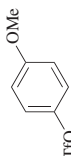
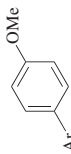
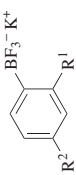
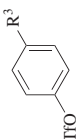
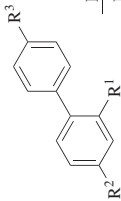


$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (2%),
i-Pr₂NEt (3 eq),
i-PrOH-H₂O,
 MW, 100°, 10 min

219

Ar	R ¹	R ²
4-MeC ₆ H ₄	H	F (92)
4-CF ₃ C ₆ H ₄	H	F (98)
4-CF ₃ C ₆ H ₄	H	Cl (98)
4-CF ₃ C ₆ H ₄	Me	H (86)
4-CF ₃ C ₆ H ₄	OMe	H (94)

TABLE 1A. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)					Refs.		
ArBF ₃ ⁻ K ⁺		Pd cat. 6 (5%), K ₂ CO ₃ (2 eq), TBAB (y eq), H ₂ O, 100°	x	y	Time	Ar	R ¹	R ²		
			0.05	0.5	—	8 h	4-CF ₃ C ₆ H ₄	H	Ac	(78)
			1	1	—	5 h	4-MeC ₆ H ₄	CN	H	(85)
			1	1	MW	20 min	4-MeC ₆ H ₄	CN	H	(88) ^a
			1	1	—	16 h	2-MeC ₆ H ₄	CN	H	(73)
			1	1	MW	20 min	2-MeC ₆ H ₄	CN	H	(84) ^a
		Pd(OAc) ₂ (5%), PCy ₃ (10%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, reflux, 20 h					Ar			
										
							4-MeC ₆ H ₄	(66)		134
							4-CF ₃ C ₆ H ₄	(59)		
					4-MeOC ₆ H ₄	(76)				
		Pd(OAc) ₂ (1.2%), MW, 95°, 15 min								
			R ¹	R ²	R ³					
			Me	H	Ac	(85)				
			H	OMe	H	(95)				

C₇

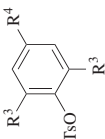
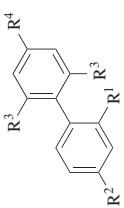
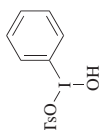
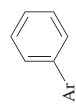
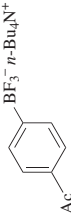
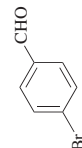
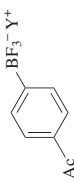
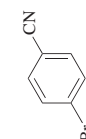
		Pd(OAc)₂ (2%), L2 (4%), KOH (3 eq), MeOH, 60°, 0.5–6 h	135																								
		<table><tr><th>R¹</th><th>R²</th><th>R³</th><th>R⁴</th></tr><tr><td>H</td><td>Me</td><td>H</td><td>OMe</td></tr><tr><td>H</td><td>Me</td><td>H</td><td>Ph</td></tr><tr><td>H</td><td>Me</td><td>Me</td><td>H</td></tr><tr><td>H</td><td>CF₃</td><td>H</td><td>OMe</td></tr><tr><td>OMe</td><td>H</td><td>H</td><td>OMe</td></tr></table>	R ¹	R ²	R ³	R ⁴	H	Me	H	OMe	H	Me	H	Ph	H	Me	Me	H	H	CF ₃	H	OMe	OMe	H	H	OMe	(97) (64) (32) (37) (53)
R ¹	R ²	R ³	R ⁴																								
H	Me	H	OMe																								
H	Me	H	Ph																								
H	Me	Me	H																								
H	CF ₃	H	OMe																								
OMe	H	H	OMe																								
		Pd(OAc)₂ (5%), DME, 60°, 30 min	15																								
ArBF ₃ [−] K ⁺		<table><tr><th>Ar</th></tr><tr><td>2-MeOC₆H₄</td></tr><tr><td>4-MeC₆H₄</td></tr></table>	Ar	2-MeOC ₆ H ₄	4-MeC ₆ H ₄	(87) (94)																					
Ar																											
2-MeOC ₆ H ₄																											
4-MeC ₆ H ₄																											
C ₈																											
		Pd(OAc)₂ (5%), dppb (5%), Cs₂CO₃ (1.25 eq), DME–H₂O, 50°, 24 h	12																								
		Pd(OAc)₂ (x%), PPh₃ (y%), K₂CO₃ (3 eq), MeOH, reflux, 16 h	(75)																								
	<table><tr><th>Y</th><th>x</th><th>y</th></tr><tr><td>n-Bu₄N</td><td>5</td><td>10</td></tr><tr><td>K</td><td>0.5</td><td>0.5</td></tr></table>	Y	x	y	n-Bu ₄ N	5	10	K	0.5	0.5	<table><tr><th></th><th>(87)</th><th>(70)</th></tr><tr><td>243</td><td></td><td></td></tr><tr><td>46</td><td></td><td></td></tr></table>		(87)	(70)	243			46									
Y	x	y																									
n-Bu ₄ N	5	10																									
K	0.5	0.5																									
	(87)	(70)																									
243																											
46																											

TABLE 1A. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(PPh3)4 (3%), K2CO3 (3 eq), 1,4-dioxane-H2O, MW, 130°, 20 min		82
		Pd(OAc)2 (5%), K2CO3 (3 eq), MeOH		222
		Pd(OAc)2 (0.6%), K2CO3 (3 eq), MeOH, reflux, 2 h		244
		Pd (2.5 ppm), Na2CO3 (3.7 eq), TBAB (1 eq), EtOH-H2O, MW, 150°, 5 min		214

C₈

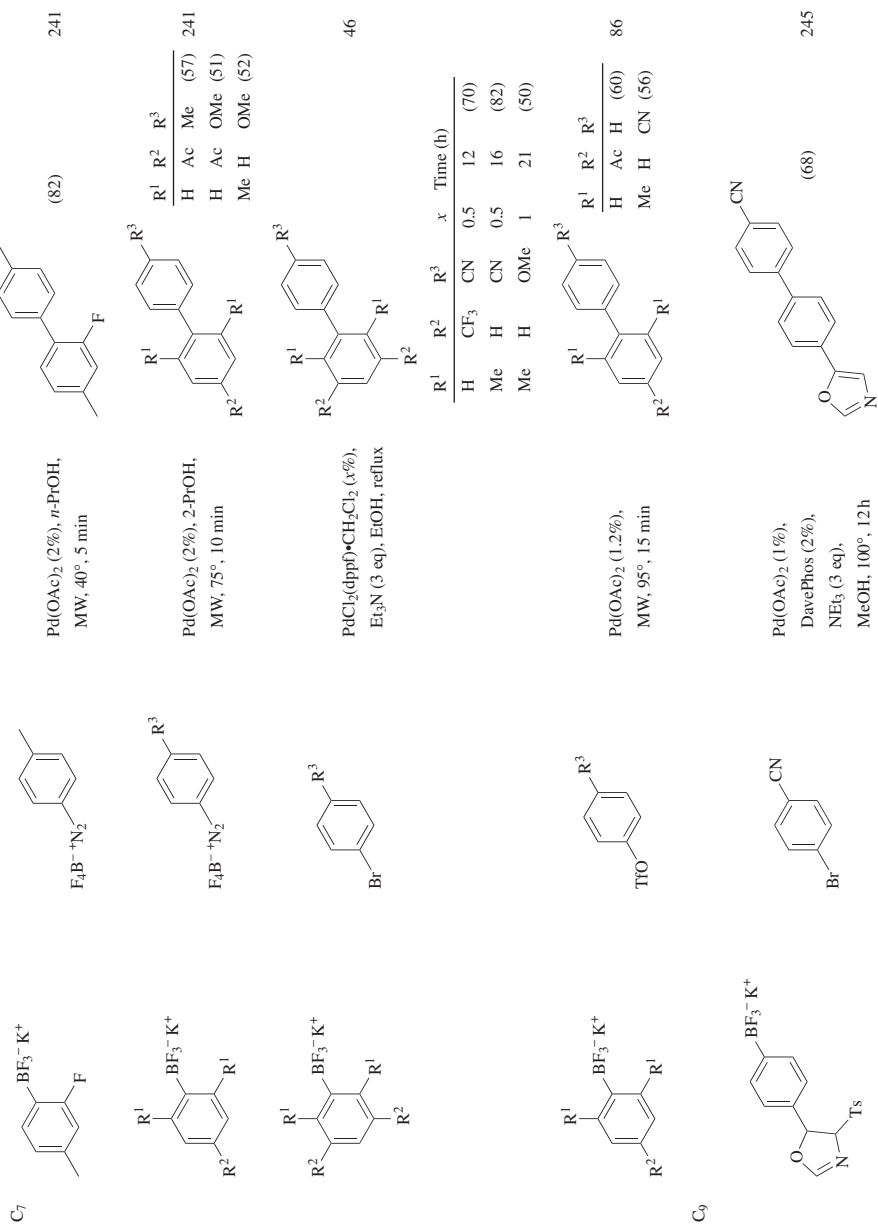


TABLE 1A. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

	Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.						
C ₉			Pd(OAc)₂ (1%), DavePhos (2%), NEt₃ (3 eq), MeOH, 100°, 12 h	<table><tr><th colspan="2">R</th></tr><tr><td>H</td><td>(73)</td></tr><tr><td>F</td><td>(55)</td></tr></table> 245	R		H	(73)	F	(55)	
R											
H	(73)										
F	(55)										
C ₁₀			Pd(OAc)₂, TPPTS, K₂CO₃, MeCN-H₂O, 60–70°, 12 h	(67) Ar = 159							

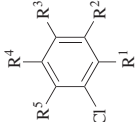
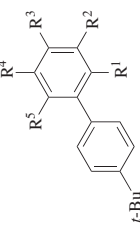
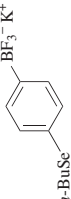
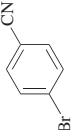
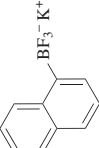
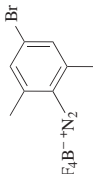
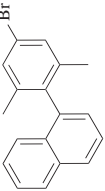
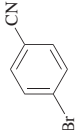
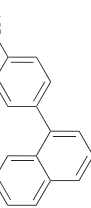
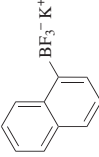
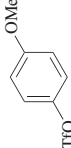
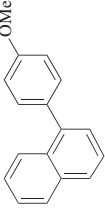
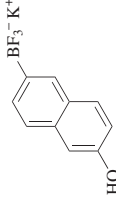
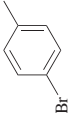
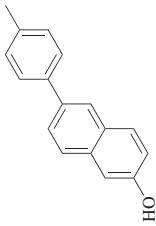
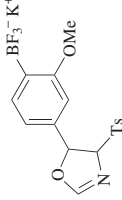
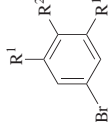
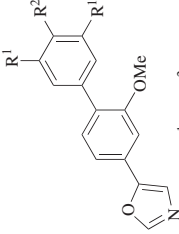
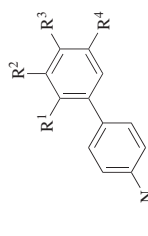
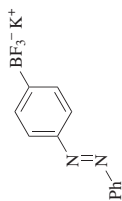
								$\text{Pd}(\text{OAc})_2$ ($x\%$), SPhos ($y\%$), K_2CO_3 (3 eq), MeOH	87									
R^1	R^2	R^3	R^4	R^5	x	y	Temp ($^\circ$)	Time (h)										
H	H	<i>n</i> -Bu	H	H	0.5	1	reflux	16	(90)									
H	OMe	H	OMe	H	0.5	1	50	12	(93)									
H	CO ₂ Me	H	H	H	0.5	1	50	12	(96)									
Me	H	H	H	Me	1	2	50	12	(91)									
				$\text{Pd}(\text{PPh}_3)_4$ (3%), K_2CO_3 (3 eq), 1,4-dioxane-H ₂ O, MW, 130°, 20 min						 (64)	82							
				Pd catalyst (5%), solvent, 20°							13							
				Pd cat. $\text{Pd}(\text{OAc})_2$ $\text{Pd}_2(\mu\text{-OAc})_2(\text{P}(o\text{-tol})_3)_2$						<table><tr><th>Solvent</th><th>Time (h)</th></tr><tr><td>1,4-dioxane</td><td>24 (21)</td></tr><tr><td>MeOH</td><td>120 (10)^c</td></tr></table>	Solvent	Time (h)	1,4-dioxane	24 (21)	MeOH	120 (10) ^c	 (60)	46
Solvent	Time (h)																	
1,4-dioxane	24 (21)																	
MeOH	120 (10) ^c																	

TABLE 1A. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

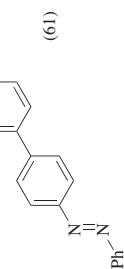
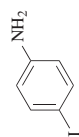
Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc) ₂ (5%), PCy ₃ (10%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, reflux, 20 h	 (71)	134
		Pd(OAc) ₂ (5%), K ₂ CO ₃ (3 eq), MeOH		222
		Pd(OAc) ₂ (1%), DavePhos (2%), NEt ₃ (3 eq), MeOH, 100°, 12 h		245

C₁₂

$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (1%),
base (3 eq), MeOH, 65°

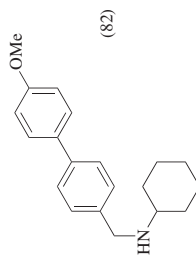
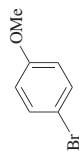
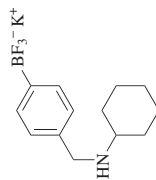
83

R ¹	R ²	R ³	R ⁴	Base	Time (h)	
H	OMe	OMe	OMe	C ₅ -CO ₃	3.5	(72)
OH	OMe	H	CHO	C ₅ -CO ₃	4.7	(49)
H	H	Ac	H	K ₂ CO ₃	2	(65)
H	H	NO ₂	H	C ₅ -CO ₃	3.5	(66)
H	H	F	H	C ₅ -CO ₃	2	(47)
H	H	CH ₂ OH	H	<i>i</i> -Pr ₂ NEt	2	(61)



$\text{Pd}(\text{OAc})_2$, PPh₃,
K₂CO₃ (3 eq), MeOH,
65°, 14 h

83

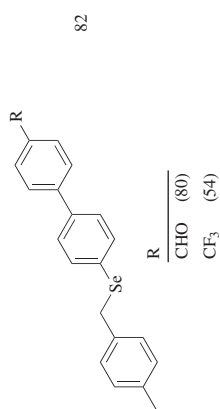
C₁₃

$\text{Pd}(\text{OAc})_2$ (3%),
K₂CO₃ (3 eq),
MeOH, 75°, 3 h

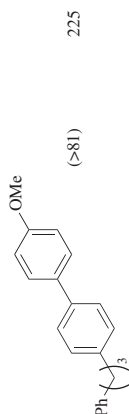
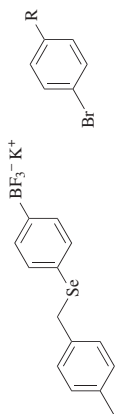
246

TABLE 1A. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

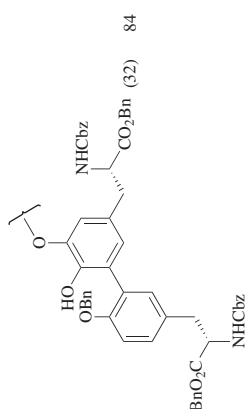
Aryltrifluoroborate		Electrophile	Conditions	Product(s) and Yield(s) (%)		Refs.
C ₁₃			Pd source (3%), base (3 eq), 1,4-dioxane-H ₂ O, MW			82
				Pd Source	Base	Time
				Pd(PPh ₃) ₄	K ₂ CO ₃	100 1 h (42)
				Pd(PPh ₃) ₄	K ₂ CO ₃	130 20 min (87)
				Pd(OAc) ₂	Cs ₂ CO ₃	130 30 min (76)
C ₁₄			Pd(PPh ₃) ₄ (3%), K ₂ CO ₃ (3 eq), 1,4-dioxane-H ₂ O, MW, 130°, 20 min			82
				Pd Source	Base	Time
				Pd(PPh ₃) ₄	K ₂ CO ₃	100 1 h (42)
				Pd(PPh ₃) ₄	K ₂ CO ₃	130 20 min (87)
				Pd(OAc) ₂	Cs ₂ CO ₃	130 30 min (76)
C ₁₄			Pd(PPh ₃) ₄ (3%), K ₂ CO ₃ (3 eq), 1,4-dioxane-H ₂ O, MW, 130°, 20 min			82
				Pd Source	Base	Time
				Pd(PPh ₃) ₄	K ₂ CO ₃	100 1 h (42)
				Pd(PPh ₃) ₄	K ₂ CO ₃	130 20 min (87)
				Pd(OAc) ₂	Cs ₂ CO ₃	130 30 min (76)



Pd(PPh₃)₄ (3%),
K₂CO₃ (3 eq),
1,4-dioxane-H₂O,
MW, 130°, 20 min



Pd(OAc)₂ (0.5%),
K₂CO₃ (3 eq), MeOH



PdCl₂(dppf)•CH₂Cl₂ (10%),
Et₃N (6 eq),
i-PrOH-H₂O, reflux, 48 h

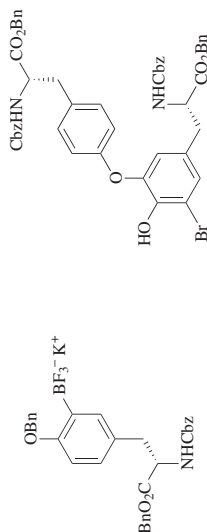
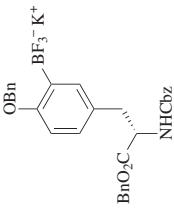
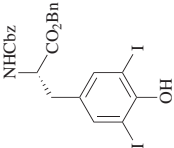
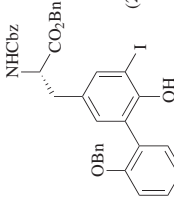
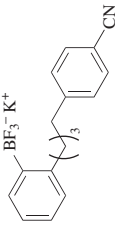
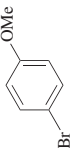
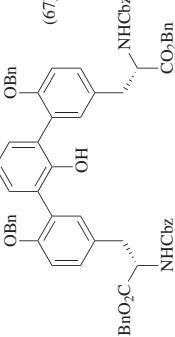
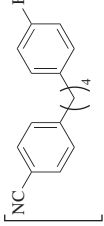
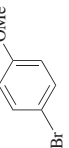
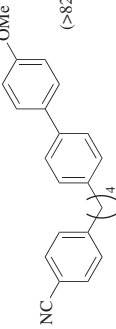
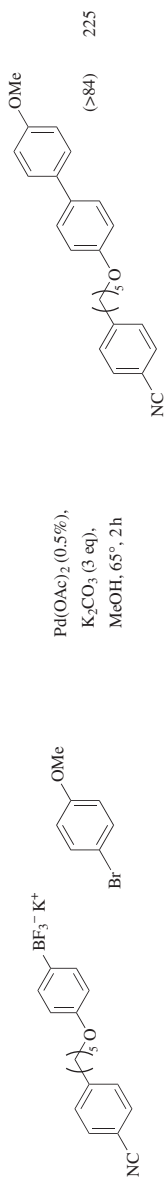


TABLE 1A. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₆			 (22) + 84 PdCl₂(dppf)•CH₂Cl₂ (8%), K₂CO₃ (2.9 eq), THF–H₂O, reflux, 26 h	
C ₁₇			 (67) Pd(OAc)₂ (0.5%), K₂CO₃ (3 eq), MeOH, 65°, 2 h	225
			 (>82) Pd(OAc)₂ (0.5%), K₂CO₃ (3 eq), MeOH, 65°, 2 h	225



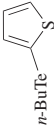
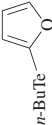
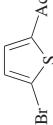
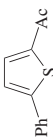
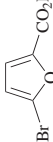
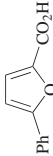
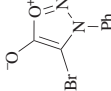
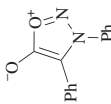
^a The yield of the crude product was determined by ^1H NMR.

^b The yield of the crude product was determined by ^{19}F NMR.

^c The yield of the product was determined by GC analysis.

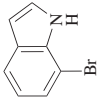
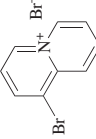
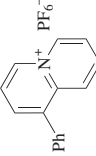
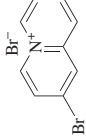
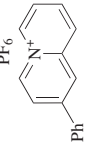
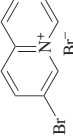
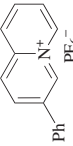
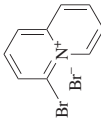
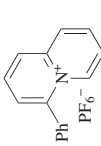
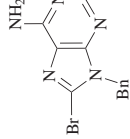
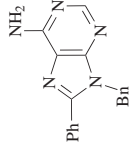
^d The trifluoroborate derivative comes from the hydroboration/cross-coupling reaction of the corresponding 1,2-dibora species.

TABLE 1B. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH HETEROARYL ELECTROPHILES

Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
PhBF ₃ ·K ⁺ C ₆		Pd(PPh ₃) ₄ (10%), Ag ₂ O (2 eq), Et ₃ N (3 eq), MeOH, reflux, 90 min	 (46)	142
		Pd(PPh ₃) ₄ (10%), Ag ₂ O (2 eq), Et ₃ N (3 eq), MeOH, reflux, 90 min	 (63)	142
		Pd (2.5 ppm), Na ₂ CO ₃ (3.7 eq), TBAB (1 eq), EtOH-H ₂ O, MW, 150°, 5 min	 (78)	214
		Pd(OAc) ₂ (0.5%), K ₂ CO ₃ (3 eq), MeOH, reflux, 50 min	 (93)	46
		Pd(OAc) ₂ (0.5%), K ₂ CO ₃ (3 eq)	 (46)	46
		Solvent Temp Time (h) MeOH reflux 8 (49) H ₂ O 65° 6 (67)		
		PdCl ₂ (PPh ₃) ₂ (5%), K ₃ PO ₄ (3 eq), DME-H ₂ O, MW, 130°, 0.5 h	 (81)	247

				X	Time (h)		
					Br	Cl	
(PhBF ₃) ⁻ (n-Bu ₄ N ⁺)			Pd(OAc) ₂ (5%), K ₂ CO ₃ (1 eq), 18-crown-6 (0.5 eq), toluene, 110°				229
			Pd(PPh ₃) ₄ (10%), Ag ₂ O (2 eq), Et ₃ N (3 eq), MeOH, reflux		(65)		142
			Pd (2.5 ppm), Na ₂ CO ₃ (3.7 eq), TBAB (1 eq), EtOH-H ₂ O, MW, 150°, 5 min		(11)		214
			Pd(OAc) ₂ (1%), K ₂ CO ₃ (3 eq), MeOH, reflux, 5 h		(70)		46
			Pd(OAc) ₂ (1%), K ₂ CO ₃ (3 eq), MeOH, reflux, 2 h		(90)		46
			Pd(OAc) ₂ (5%), dppb (5%), Cs ₂ CO ₃ (1.25 eq), DME-H ₂ O, 50°, 24 h		(93)		12
			PdCl ₂ (dppf)•CH ₂ Cl ₂ (5%), K ₃ PO ₄ (4 eq), DMF-THF, 70°, 6 h		(85)		248
			Pd(OAc) ₂ (1%), K ₂ CO ₃ (3 eq), MeOH, reflux, 5 h		(92)		46

TABLE 1B. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH HETEROARYL ELECTROPHILES (*Continued*)

Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
PhBF ₃ ⁻ K ⁺		Pd(OAc) ₂ (0.5%), K ₂ CO ₃ (3 eq), MeOH, reflux, 12 h	 (44)	46
		1. Pd(OAc) ₂ (1%), K ₂ CO ₃ (3 eq), H ₂ O, 65°, 5 h 2. H ₄ NPF ₆	 (93)	122
		1. Pd(OAc) ₂ (1%), K ₂ CO ₃ (3 eq), H ₂ O, 65°, 5 h 2. H ₄ NPF ₆	 (76)	122
		1. Pd(OAc) ₂ (1%), K ₂ CO ₃ (3 eq), H ₂ O, 65°, 5 h 2. H ₄ NPF ₆	 (74)	122
		1. Pd(OAc) ₂ (1%), K ₂ CO ₃ (3 eq), H ₂ O, 65°, 5 h 2. H ₄ NPF ₆	 (24)	122
		Pd(PPh ₃) ₄ (2%), K ₂ CO ₃ (3 eq), MeCN-H ₂ O, MW, 150°, 5 min	 (96)	104

C₆

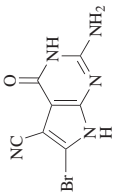
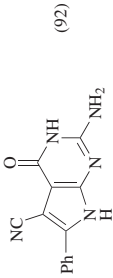
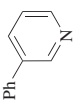
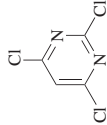
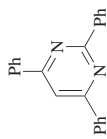
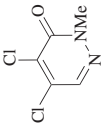
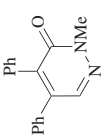
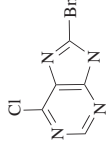
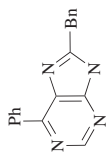
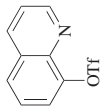
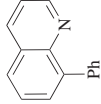
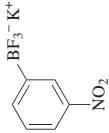
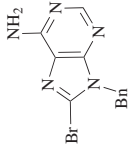
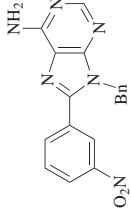
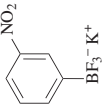
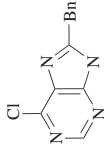
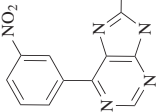
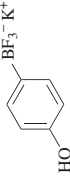
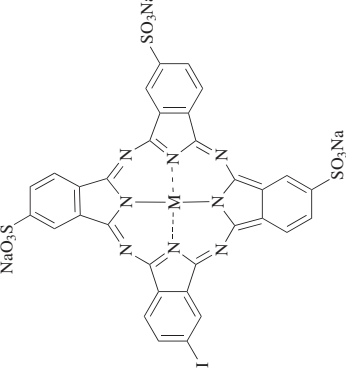
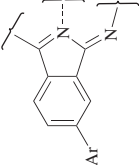
	$\text{PdCl}_2(\text{PPh}_3)_2$ (5%), <i>t</i>-BuNH₂ (3 eq), 2-propanol-H₂O, 85°, 4 d		249
	Pd cat. 6 (1%), K₂CO₃ (2 eq), TBAB (1 eq), H₂O, 100°		150
	Pd cat. 6 (1%), K₂CO₃ (2 eq), TBAB (1 eq), H₂O, 100°		150
	Pd cat. 6 (1%), K₂CO₃ (2 eq), TBAB (1 eq), H₂O, 100°		150
	Pd(PPh₃)₄ (2%), base (3 eq)		104
	Pd(OAc)₂ (5%), PCy₃ (10%), Cs₂CO₃ (3 eq), THF-H₂O, reflux, 24 h		134

TABLE 1B. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH HETEROARYL ELECTROPHILES (Continued)

Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$\text{Pd}(\text{PPh}_3)_4$ (4%), K_2CO_3 (3 eq), $\text{MeCN-H}_2\text{O}$, MW, 150° , 5 min	 $\frac{x}{2 \text{ (53)}}$ $\frac{4 \text{ (90)}}$	104
		$\text{Pd}(\text{PPh}_3)_4$ (2%), K_2CO_3 (3 eq), $\text{MeCN-H}_2\text{O}$, MW, 150° , 5 min	 (79)	104
		$\text{Pd}(\text{OAc})_2$, TXPTS, Na_2CO_3 , $\text{MeCN-H}_2\text{O}$	 (—) 250 Ar = 4-HOC ₆ H ₄ M = GaOH	

C₆

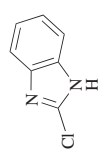
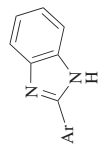
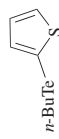
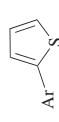
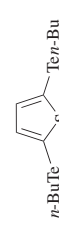
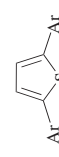
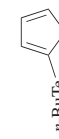
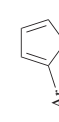
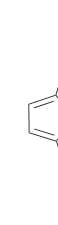
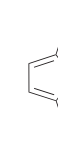
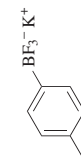
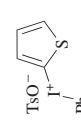
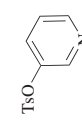
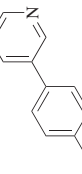
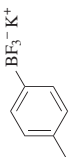
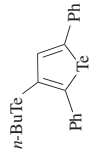
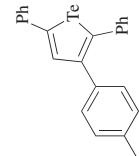
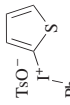
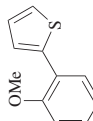
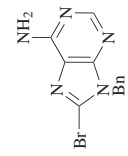
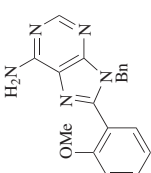
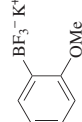
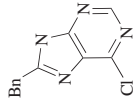
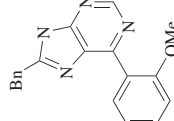
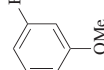
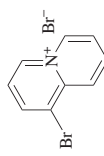
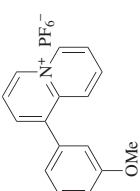
ArBF ₃ ⁻ K ⁺			PdCl ₂ (PPh ₃) ₂ (10%), K ₂ CO ₃ , MeCN, MW, 150°, 30 min	Ar	(79)	223
			Pd(OAc) ₂ (10%), dppf (20%), Ag ₂ O (2 eq), MeOH, rt, 1.5 h	Ph 3-H ₂ NC ₆ H ₄ 4-FC ₆ H ₄	(55) (71) (56)	143
			Pd(OAc) ₂ (10%), dppf (20%), Ag ₂ O (2 eq), MeOH, rt, 2 h	Ar	(45)	143
			Pd(OAc) ₂ (10%), dppf (20%), Ag ₂ O (2 eq), MeOH, rt, 1.5 h	Ph 3-H ₂ NC ₆ H ₄ 4-FC ₆ H ₄	(50) (32)	143
			Pd(OAc) ₂ (10%), dppf (20%), Ag ₂ O (2 eq), MeOH, rt, 1.5 h	Ar	(68)	143
			Pd(OAc) ₂ (10%), dppf (20%), Ag ₂ O (2 eq), MeOH, rt, 1.5 h	Ph 3-H ₂ NC ₆ H ₄ 4-FC ₆ H ₄	(73) (35) (55)	143
C ₇			Pd(OAc) ₂ (5%), DME, 60°, 30 min	(91)		15
			Pd(OAc) ₂ (2%), L2 (4%), Et ₃ N (3 eq), EtOH, 80°, 5 h	(37)		135

TABLE IB. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH HETEROARYL ELECTROPHILES (Continued)

Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$\text{Pd}(\text{PPh}_3)_4$, Et_3N (3 eq), Ag_2O , MeOH , reflux	 (86)	139
		$\text{Pd}(\text{OAc})_2$ (5%), DME , 60° , 30 min	 (83)	15
		$\text{Pd}(\text{PPh}_3)_4$ (2%), K_2CO_3 (3 eq), $\text{MeCN-H}_2\text{O}$, MW, 150° , 5 min	 (96)	104
		$\text{Pd}(\text{PPh}_3)_4$ (2%), K_2CO_3 (3 eq), $\text{MeCN-H}_2\text{O}$, MW, 150° , 5 min	 (94)	104
		1. $\text{Pd}(\text{OAc})_2$ (1%), K_2CO_3 (3 eq), H_2O , 65° , 5 h 2. H_4NPF_6	 (93)	122

C₇

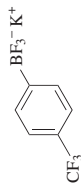
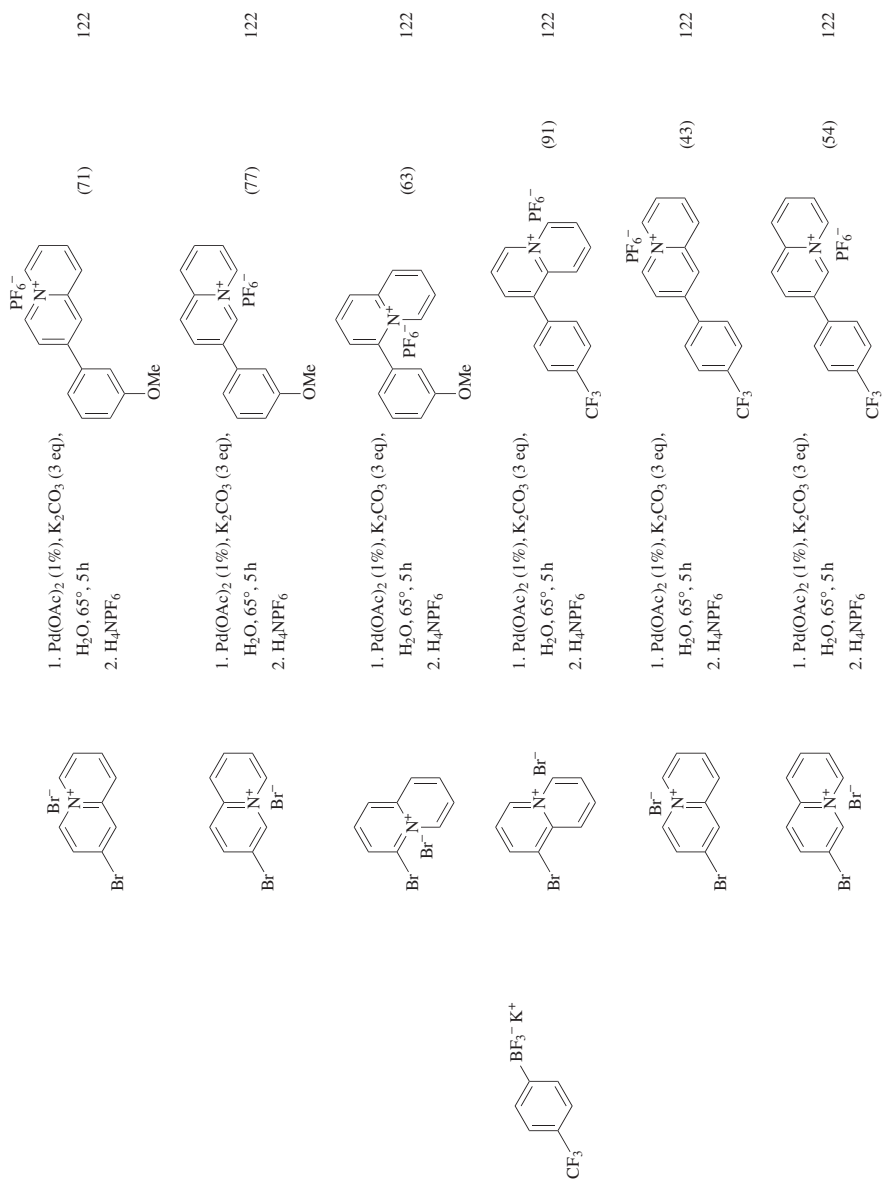


TABLE 1B. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH HETEROARYL ELECTROPHILES (Continued)

Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. Pd(OAc) ₂ (1%), K ₂ CO ₃ (3 eq), H ₂ O, 65°, 5 h 2. H ₄ NPF ₆		122
		Pd(PPh ₃) ₄ (2%), K ₂ CO ₃ (3 eq), MeCN-H ₂ O, MW, 150°, 5 min		104
		Pd(PPh ₃) ₄ (2%), K ₂ CO ₃ (3 eq), MeCN-H ₂ O, MW, 150°, 5 min		104
		Pd(PPh ₃) ₄ (2%), K ₂ CO ₃ (3 eq), MeCN-H ₂ O, MW, 150°, 5 min		104

C₇

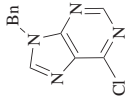
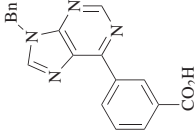
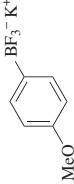
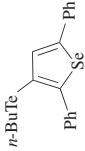
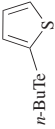
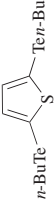
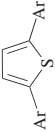
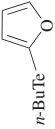
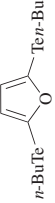
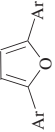
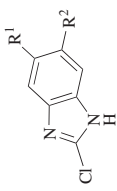
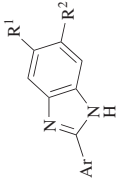
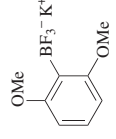
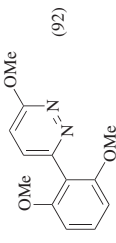
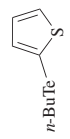
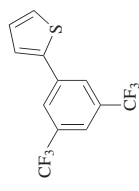
	 (71)	$\text{Pd}(\text{PPh}_3)_4$ (2%), K_2CO_3 (3 eq), $\text{MeCN-H}_2\text{O}$, MW, 150°, 5 min	104
 $\text{ArBF}_3^- \text{K}^+$	 $n\text{-BuTe}$	$\text{Pd}(\text{OAc})_2$ (10%), Et_3N, CuI (20%), MeOH, reflux, 4 h	141
 $n\text{-BuTe}$	 Ar	$\text{Pd}(\text{OAc})_2$ (10%), dppf (20%), Ag_2O (2 eq), MeOH, rt, 1.5 h	143
 $n\text{-BuTe}$	 Ar	$\text{Pd}(\text{OAc})_2$ (10%), dppf (20%), Ag_2O (2 eq), MeOH, rt, 1.5 h	143
 $n\text{-BuTe}$	 Ar	$\text{Pd}(\text{OAc})_2$ (10%), dppf (20%), Ag_2O (2 eq), MeOH, rt, 1.5 h	143
 $n\text{-BuTe}$	 Ar	$\text{Pd}(\text{OAc})_2$ (10%), dppf (20%), Ag_2O (2 eq), MeOH, rt, 2 h	143

TABLE IB. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH HETEROARYL ELECTROPHILES (Continued)

Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇	 $\text{ArBF}_3^- \text{K}^+$	$\text{PdCl}_2(\text{PPh}_3)_2$ (10%), K_2CO_3 , MeCN , MW, 150° , 30 min		223
C ₈	 $\text{ArBF}_3^- \text{K}^+$	PEPFSI complex (2%), K_2CO_3 (3 eq), MeOH , 6 h	 (92)	235
C ₈	 $n\text{-BuTe}$	$\text{Pd}(\text{OAc})_2$ (10%), dppf (20%), Ag_2O (2 eq), MeOH , rt, 1.5 h	 (0)	143

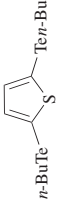
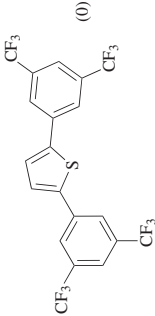
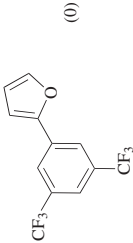
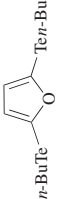
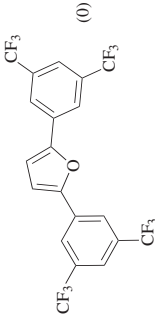
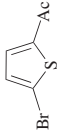
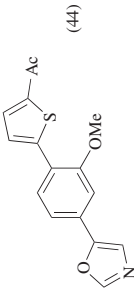
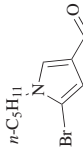
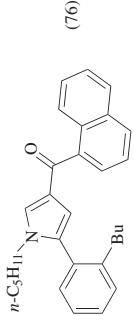
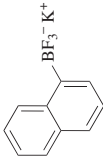
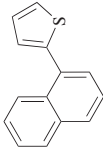
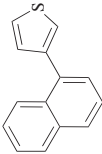
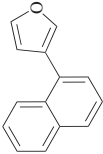
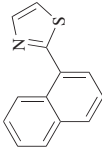
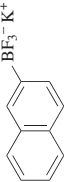
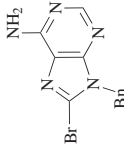
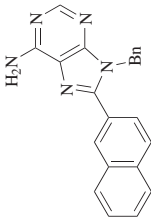
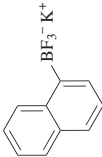
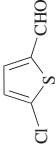
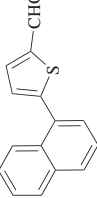
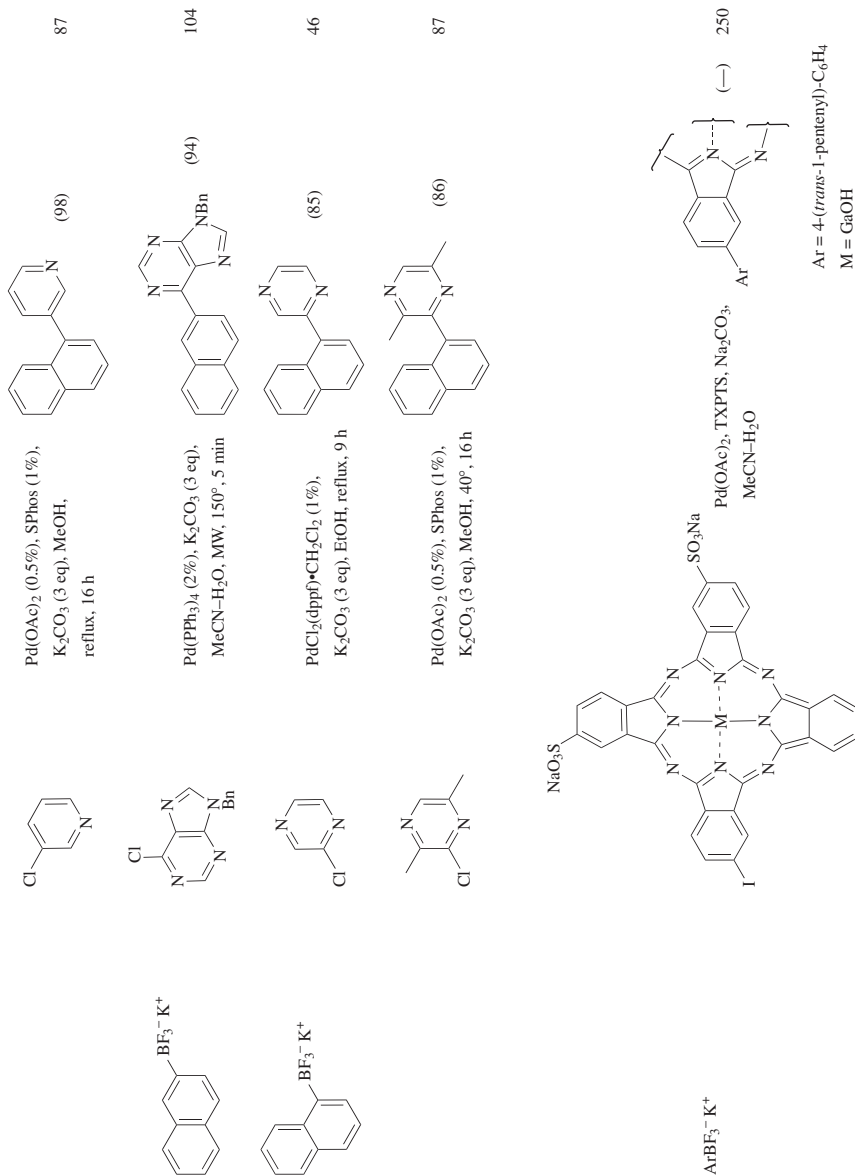
		Pd(OAc) ₂ (10%), dppf (20%), Ag ₂ O (2 eq), MeOH, rt, 1.5 h	143
		Pd(OAc) ₂ (10%), dppf (20%), Ag ₂ O (2 eq), MeOH, rt, 1.5 h	143
		Pd(OAc) ₂ (10%), dppf (20%), Ag ₂ O (2 eq), MeOH, rt, 1.5 h	143
		Pd(OAc) ₂ (1%), DavePhos (2%), NEt ₃ (3 eq), MeOH, 100°, 12 h	245
		Pd(PPh ₃) ₄ , K ₂ CO ₃ , <i>n</i> -Bu ₄ NBr, toluene-H ₂ O, reflux, 24 h	228

TABLE IB. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH HETEROARYL ELECTROPHILES (Continued)

Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (2%), K_2CO_3 (3 eq), EtOH, reflux, 13 h	 (83)	46
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (2%), K_2CO_3 (3 eq), EtOH, reflux, 13 h	 (72)	46
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (2%), K_2CO_3 (3 eq), EtOH, reflux, 9 h	 (68)	46
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (2%), K_2CO_3 (3 eq), EtOH, reflux, 13 h	 (80)	46
		$\text{Pd}(\text{PPh}_3)_4$ (2%), K_2CO_3 (3 eq), $\text{MeCN-H}_2\text{O}$, MW, 150° , 5 min	 (97)	104
		$\text{Pd}(\text{OAc})_2$ (1%), SPhos (2%), K_2CO_3 (3 eq), MeOH, reflux, 16 h	 (85)	87

C₁₀



C₁₁

TABLE 1B. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH HETEROARYL ELECTROPHILES (Continued)

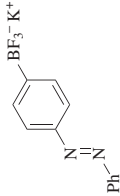
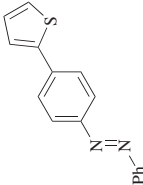
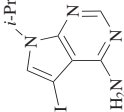
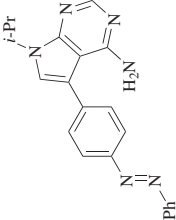
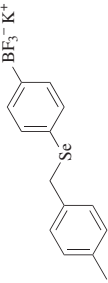
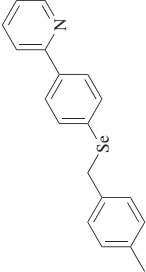
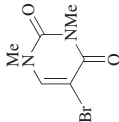
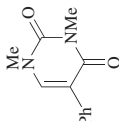
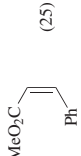
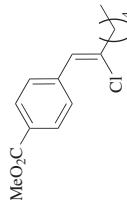
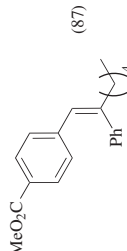
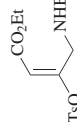
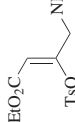
Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₂ 		PdCl ₂ (dppf)•CH ₂ Cl ₂ (1%), K ₂ CO ₃ (3 eq), MeOH, 65°, 2 h	 (61)	83
		PdCl ₂ (dppf)•CH ₂ Cl ₂ , <i>i</i> -Pr ₂ NEt, EtOH, reflux	 (59)	83
C ₁₄ 		Pd(PPh ₃) ₄ (3%), K ₂ CO ₃ (3 eq), 1,4-dioxane-H ₂ O, MW, 130°, 20 min	 (91)	82

TABLE 1C. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH ALKENYL ELECTROPHILES

Aryltrifluoroborate		Electrophile	Conditions	Product(s) and Yield(s) (%)			Refs.
C ₆ PhBF ₃ ⁻ K ⁺			Pd source (x%), additive (2 eq), MeOH, rt, ultrasound, 40 min	Pd Source	x	Additive	69
					Pd(acac) ₂	10 Ag ₂ O (10)	
					Pd(PPh ₃) ₄	10 Ag ₂ O (79)	
					Pd(PPh ₃) ₄	10 CuI (0)	
					Pd(PPh ₃) ₄	8 Ag ₂ O (82)	
			Pd(PPh ₃) ₄ (x%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 90°		x	Time	66
					1.2	5 h (92)	
			Pd(OAc) ₂ (0.5%), K ₂ CO ₃ (3 eq), MeOH, reflux, 3 h		(70)		136
			Pd (2.5 ppm), Na ₂ CO ₃ (3.7 eq), TBAB (1 eq), EtOH-H ₂ O, MW, 150°, 5 min		(75) (Z)/(E) = 10:90		214
			Pd(PPh ₃) ₄ (2%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 90°, 30 min		(94)		66
			Pd(PPh ₃) ₄ (2%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 90°, 1.8 h		(87)		66
			Pd(PPh ₃) ₄ (2%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 90°, 1 h		(87)		66

TABLE IC. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH ALKENYL ELECTROPHILES (Continued)

Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
$\text{PhBF}_3^- \text{K}^+$		$\text{Pd}(\text{PPh}_3)_4$ (2%), K_2CO_3 (3 eq), toluene- H_2O , 90°, 3 h	 (88)	66
$(\text{PhBF}_3^-) (n\text{-Bu}_4\text{N}^+)$		$\text{Pd}(\text{OAc})_2$ (5%), dppb (5%), Cs_2CO_3 (1.25 eq), DME- H_2O		12
		X R ¹ R ² R ³ Temp (°) Time (h)		
		Br Me Me Me rt 12 (91)		
		I H H CO ₂ Et 50 24 (55)		
$\text{PhBF}_3^- \text{K}^+$		$\text{Pd}(\text{OAc})_2$ (4%), PPh_3 (9%), NaOH (4.7 eq), THF, 60°, 4 h	 (25)	67
		$\text{Pd}_2(\text{dba})_3$ (2.5%), RuPhos (10%), Cs_2CO_3 (3 eq), THF- H_2O , 80°, 36 h	 (87)	148
		$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (5%), aq Na ₂ CO ₃ (3.5 eq), THF, 60°	 (78)	68
		$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (5%), aq Na ₂ CO ₃ (3.5 eq), THF, 60°	 (81)	68

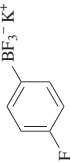
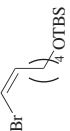
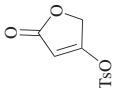
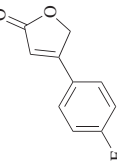
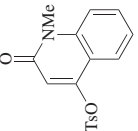
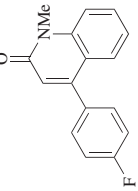
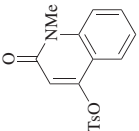
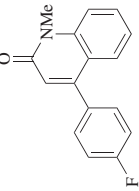
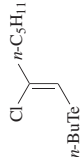
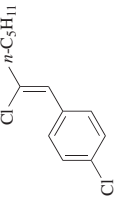
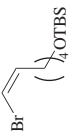
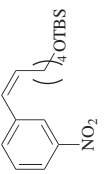
		$\text{Pd}(\text{PPh}_3)_4$ (2%), K_2CO_3 (3 eq), toluene– H_2O , 90°, 55 min		(95)	66
		$\text{RhCl}(\text{PPh}_3)_3$ (2%), dppf (2%), K_2HPO_4 (4 eq), toluene, 80°, 12 h		(64)	251
		$\text{Pd}(\text{PPh}_3)_4$ (5%), Cs_2CO_3 (8 eq), toluene, 80°, 12 h		(48)	252
		$\text{RhCl}(\text{PPh}_3)_3$ (2%), dppf (2%), K_2HPO_4 (4 eq), toluene, 80°, 12 h		(46)	251
		$\text{Pd}(\text{PPh}_3)_4$ (10%), Et_3N (2 eq), Ag_2O (1 eq), MeOH, ultrasound, 60 min		(69)	224
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (4.5%), K_2CO_3 (3 eq), toluene– H_2O , 90°, 55 min		(90)	66

TABLE IC. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH ALKENYL ELECTROPHILES (Continued)

Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
$\text{ArBF}_3^- \text{K}^+$		$\text{Pd}(\text{PPh}_3)_4$ (8%), Ag_2O (2 eq), MeOH, rt, ultrasound	 Ar R	69
		$\text{Pd}(\text{PPh}_3)_4$ (6%), C_5CO_3 (3 eq), toluene-H ₂ O, 90°	 Ar Time (h)	161
		$\text{RhCl}(\text{PPh}_3)_3$ (2%), dppf (2%), K_2HPO_4 (4 eq), toluene, 80°, 12 h	 Ar (89) (89)	251
		$\text{RhCl}(\text{PPh}_3)_3$ (2%), dppf (2%), K_2HPO_4 (4 eq), toluene, 80°, 12 h	 Ar R ¹ R ²	251

	$\text{Pd}(\text{PPh}_3)_4$ (5%), Cs_2CO_3 (8 eq), toluene, 80°, 12 h		Ar <table><tr><th>Ar</th><th>R</th><th></th></tr><tr><td>Ph</td><td>H</td><td>(86)</td></tr><tr><td>Ph</td><td>Cl</td><td>(46)</td></tr><tr><td>Ph</td><td>F</td><td>(61)</td></tr><tr><td>Ph</td><td>Me</td><td>(58)</td></tr><tr><td>4-FC₆H₄</td><td>H</td><td>(80)</td></tr><tr><td>4-FC₆H₄</td><td>Cl</td><td>(92)</td></tr><tr><td>4-FC₆H₄</td><td>F</td><td>(86)</td></tr><tr><td>4-FC₆H₄</td><td>Me</td><td>(89)</td></tr></table>	Ar	R		Ph	H	(86)	Ph	Cl	(46)	Ph	F	(61)	Ph	Me	(58)	4-FC ₆ H ₄	H	(80)	4-FC ₆ H ₄	Cl	(92)	4-FC ₆ H ₄	F	(86)	4-FC ₆ H ₄	Me	(89)	252
Ar	R																														
Ph	H	(86)																													
Ph	Cl	(46)																													
Ph	F	(61)																													
Ph	Me	(58)																													
4-FC ₆ H ₄	H	(80)																													
4-FC ₆ H ₄	Cl	(92)																													
4-FC ₆ H ₄	F	(86)																													
4-FC ₆ H ₄	Me	(89)																													
	$\text{RhCl}(\text{PPh}_3)_3$ (2%), dppf (2%), K_2HPO_4 (4 eq), toluene, 80°, 12 h		(66)	251																											
	$\text{RhCl}(\text{PPh}_3)_3$ (2%), dppf (2%), K_2HPO_4 (4 eq), toluene, 80°, 12 h		(99)	251																											
	$\text{Pd}(\text{PPh}_3)_4$ (5%), Cs_2CO_3 (8 eq), toluene, 80°, 12 h		(68)	252																											

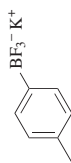


TABLE IC. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH ALKENYL ELECTROPHILES (Continued)

Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		RhCl(PPh ₃) ₃ (2%), dppf (2%), K ₂ HPO ₄ (4 eq), toluene, 80°, 12 h	 (42)	251
		Pd(PPh ₃) ₄ (5%), Cs ₂ CO ₃ (8 eq), toluene, 80°, 12 h	 R ¹ R ² H H (89) Cl H (87) F H (77) Me H (85) Me Me (86)	252
		RhCl(PPh ₃) ₃ (2%), dppf (2%), K ₂ HPO ₄ (4 eq), toluene, 80°, 12 h	 R ¹ R ² H H (75) Cl H (69) F H (92) Me H (67) Me Me (54)	251
		Pd(PPh ₃) ₄ (10%), Et ₃ N, Ag ₂ O, MeOH, ultrasound, 20 min	 R n-Bu (85) Ph (72) 4-MeC ₆ H ₄ (65)	224

C₇

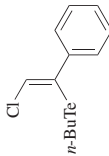
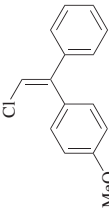
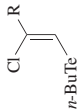
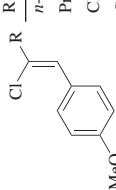
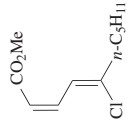
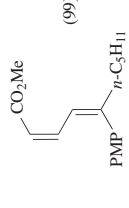
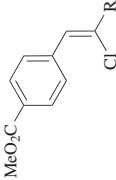
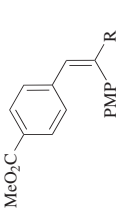
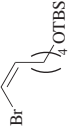
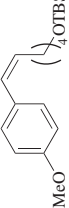
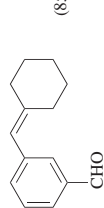
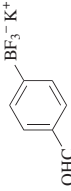
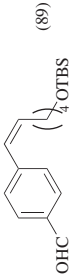
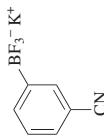
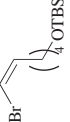
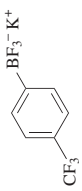
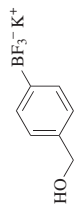
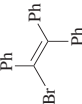
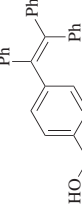
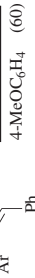
		Pd source (10%), Et ₃ N, Ag ₂ O, MeOH, ultrasound, 20 min	Pd Source Pd ₂ (dba) ₃ (40) Pd(OAc) ₂ (44) Pd(PPh ₃) ₄ (60)	224 (40) (44) (60)
		Pd(PPh ₃) ₄ (10%), Et ₃ N (2 eq), Ag ₂ O (1 eq), MeOH, ultrasound	R Time (min) <i>n</i> -C ₃ H ₁₁ 30 (82) Pr 60 (58) 224 CH ₂ OMe 40 (73) C(Me)=CH ₂ 40 (82) <i>t</i> -Bu 60 (74) Ph 20 (80)	
		Pd ₂ (dba) ₃ (2.5%), RuPhos (10%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, 80°, 12–36 h	(99)	148
		Pd ₂ (dba) ₃ (2.5%), RuPhos (10%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, 80°	R <i>n</i> -C ₃ H ₁₁ (89) Ph (84)	148 (89) (84)
		Pd(PPh ₃) ₄ (2%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 90°, 40 min	(97)	66
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (2%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 90°, 1 h	(85)	66

TABLE IC. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH ALKENYL ELECTROPHILES (Continued)

Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (4.5%), K_2CO_3 (3 eq), toluene- H_2O , 90°, 3.5 h	 (89)	66
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (4.5%), K_2CO_3 (3 eq), toluene- H_2O , 55°, 7.5 h	 (86)	66
		$\text{Pd}(\text{PPh}_3)_4$ (4.5%), $\text{P}(t\text{-Bu})_3$ (9%), K_2CO_3 (3 eq), toluene- H_2O , 90°, 3 h	 (89)	66
		$\text{Pd}(\text{OAc})_2$ (0.5%), K_2CO_3 (3 eq), MeOH		222
		Temp Time — reflux 1 h (75) MW — 5 min (94)		69

$\text{Pd}(\text{PPh}_3)_4$ (6%),
 Cs_2CO_3 (3 eq),
 toluene- H_2O , 90°

R ¹	R ²	Time (h)
H	Me	1.7 (70)
H	OMe	2 (71)
H	CF ₃	6.5 (57)
H	CHO	3 (45)
H	CO ₂ H	9 (0)
Me	H	8 (60)

$\text{Pd}(\text{PPh}_3)_4$ (2%),
 Cs_2CO_3 (3 eq),
 toluene- H_2O , 90°

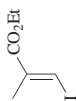
R ¹	R ²	Time
H	Me	25 min (93)
Me	H	1.5 h (91)

$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (2%),
 K_2CO_3 (3 eq),
 toluene- H_2O , 90°

R ¹	R ²	R ³	R ⁴	R ⁵	Time (h)
H	CHO	H	Me	Me	1.5 (96)
CHO	H	Me	Me	Me	2 (94)
CHO	H	Ph	H	H	3 (89)

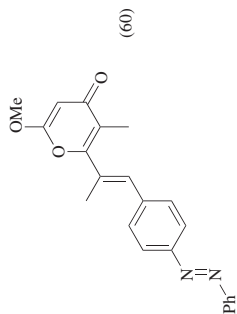
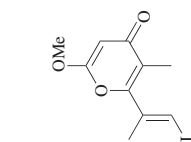
TABLE IC. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH ALKENYL ELECTROPHILES (Continued)

Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈				66
				146
C ₁₀				69
				66
				66
				253

[K+].[B-](F)(F)Fc1ccc(cc1)/N=N/c2ccccc2

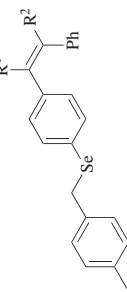
$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (1%),
 Cs_2CO_3 (3 eq),
 MeOH, 65°, 4.7 h

(41)



$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (1%),
 K_2CO_3 (3 eq),
 MeOH, 65°, 17 h

(69)

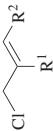
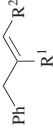
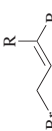
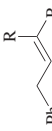
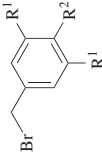
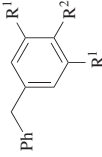


$\text{Pd}(\text{PPh}_3)_4$ (3%), K_2CO_3 (3 eq),
1,4-dioxane- H_2O , MW, 130°,
20 min

82

R ¹	R ²	
CHO	H	(74)
Ph	Ph	(66)

TABLE 1D. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH ALLYLIC AND BENZYLIC ELECTROPHILES

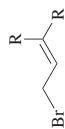
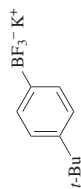
Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆ PhBF ₃ ⁻ K ⁺		Pd cat. 6 (0.1%), KOH (2 eq), TBAB (0.5 eq), acetone-H ₂ O		150
		Pd(OAc) ₂ (5%), 1,4-dioxane, 100°		254
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (2%), C ₅ CO ₃ (3 eq), THF-H ₂ O, 77°		85

	Pd cat. 6 (0.1%), KOH (2 eq), TBAB (0.5 eq), acetone-H ₂ O		150																				
	<table> <tr> <th>R¹</th><th>R²</th><th>Temp (°)</th><th>Time (h)</th></tr> <tr> <td>H</td><td>H</td><td>50</td><td>4 (81)</td></tr> <tr> <td>OMe</td><td>H</td><td>25</td><td>48 (71)^a</td></tr> <tr> <td>OMe</td><td>H</td><td>50</td><td>2.5 (86)</td></tr> <tr> <td>H</td><td>Cl</td><td>50</td><td>2 (82)</td></tr> </table>	R ¹	R ²	Temp (°)	Time (h)	H	H	50	4 (81)	OMe	H	25	48 (71) ^a	OMe	H	50	2.5 (86)	H	Cl	50	2 (82)		
R ¹	R ²	Temp (°)	Time (h)																				
H	H	50	4 (81)																				
OMe	H	25	48 (71) ^a																				
OMe	H	50	2.5 (86)																				
H	Cl	50	2 (82)																				
	Pd(OAc) ₂ (0.1%), KOH (2 eq), TBAB (0.5 eq), acetone-H ₂ O, 50°, 4 h		150																				
ArBF ₃ ⁻ K ⁺	PdCl ₂ (dppf)•CH ₂ Cl ₂ (2%), Cs ₂ CO ₃ (3 eq), CPME-H ₂ O, 90°		85																				
		<table> <tr> <th>Ar</th><th>X</th><th>R</th><th>Time (h)</th></tr> <tr> <td>Ph</td><td>Br</td><td>H</td><td>16 (85)</td></tr> <tr> <td>3-O₂NC₆H₄</td><td>Br</td><td>H</td><td>15 (69)</td></tr> <tr> <td>Ph</td><td>Cl</td><td>OMe</td><td>14 (78)</td></tr> </table>	Ar	X	R	Time (h)	Ph	Br	H	16 (85)	3-O ₂ NC ₆ H ₄	Br	H	15 (69)	Ph	Cl	OMe	14 (78)					
Ar	X	R	Time (h)																				
Ph	Br	H	16 (85)																				
3-O ₂ NC ₆ H ₄	Br	H	15 (69)																				
Ph	Cl	OMe	14 (78)																				
	Pd(OAc) ₂ (5%), 1,4-dioxane, 100°		254																				
		<table> <tr> <th>R</th><th>Time (h)</th></tr> <tr> <td>H</td><td>6 (85)</td></tr> <tr> <td>Me</td><td>12 (87)</td></tr> </table>	R	Time (h)	H	6 (85)	Me	12 (87)															
R	Time (h)																						
H	6 (85)																						
Me	12 (87)																						
	PdCl ₂ (dppf)•CH ₂ Cl ₂ (2%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, 77°, 18 h		85																				

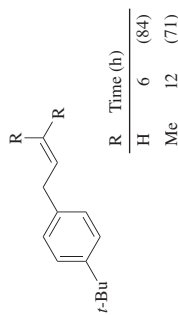
C₇

TABLE 1D. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH ALLYLIC AND BENZYLIC ELECTROPHILES (Continued)

Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.													
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (2%), $\text{C}_5\text{H}_5\text{CO}_3$ (3 eq), $\text{THF}-\text{H}_2\text{O}$, 77°, 24 h		(71) 85													
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (2%), $\text{C}_5\text{H}_5\text{CO}_3$ (3 eq), $\text{THF}-\text{H}_2\text{O}$, 77°		85													
		<table><tr><th>Ar</th><th>X</th><th>Time (h)</th></tr><tr><td>4-MeC₆H₄</td><td>Br</td><td>12 (81)</td></tr><tr><td>4-MeOC₆H₄</td><td>Cl</td><td>20 (91)</td></tr></table>	Ar	X	Time (h)	4-MeC ₆ H ₄	Br	12 (81)	4-MeOC ₆ H ₄	Cl	20 (91)						
Ar	X	Time (h)															
4-MeC ₆ H ₄	Br	12 (81)															
4-MeOC ₆ H ₄	Cl	20 (91)															
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (2%), $\text{C}_5\text{H}_5\text{CO}_3$ (3 eq), $\text{CPME}-\text{H}_2\text{O}$, 90°		85													
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (2%), $\text{C}_5\text{H}_5\text{CO}_3$ (3 eq), $\text{THF}-\text{H}_2\text{O}$, 77°, 21 h		(82) 85													
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (2%), $\text{C}_5\text{H}_5\text{CO}_3$ (3 eq), $\text{CPME}-\text{H}_2\text{O}$, 90°, 15 h		(80) 85													
		<table><tr><th>Ar</th><th>R</th><th>Time (h)</th></tr><tr><td>4-MeOC₆H₄</td><td>H</td><td>20 (86)</td></tr><tr><td>4-CF₃C₆H₄</td><td>H</td><td>18 (87)</td></tr><tr><td>4-OHCC₆H₄</td><td>H</td><td>15 (87)</td></tr><tr><td>4-MeOC₆H₄</td><td>CN</td><td>14 (72)</td></tr></table>	Ar	R	Time (h)	4-MeOC ₆ H ₄	H	20 (86)	4-CF ₃ C ₆ H ₄	H	18 (87)	4-OHCC ₆ H ₄	H	15 (87)	4-MeOC ₆ H ₄	CN	14 (72)
Ar	R	Time (h)															
4-MeOC ₆ H ₄	H	20 (86)															
4-CF ₃ C ₆ H ₄	H	18 (87)															
4-OHCC ₆ H ₄	H	15 (87)															
4-MeOC ₆ H ₄	CN	14 (72)															

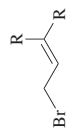
C₁₀

Pd(OAc)₂ (5%),
1,4-dioxane, 100°

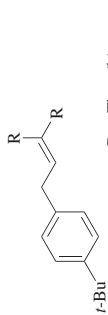


254

R		Time (h)	
H	Me	6	12
(84)	(71)		



Pd(OAc)₂ (5%),
1,4-dioxane, 100°

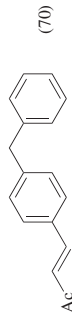


254

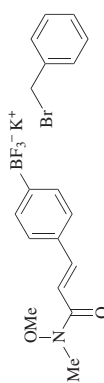
R		Time (h)	
H	Me	6	12
(85)	(83) ^b		



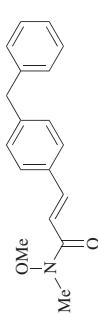
PdCl₂ (dppf)•CH₂Cl₂ (2%),
C₅CO₃ (3 eq), THF-H₂O,
77°, 16 h



85

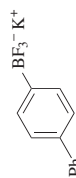
C₁₁

PdCl₂ (dppf)•CH₂Cl₂ (2%),
C₅CO₃ (3 eq),
CPME-H₂O, 90°, 19 h

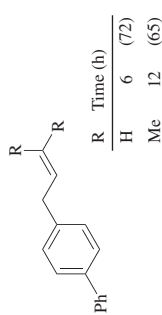


85

(74)

C₁₂

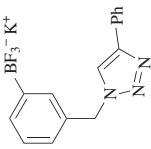
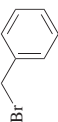
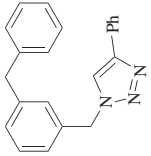
Pd(OAc)₂ (5%),
1,4-dioxane, 100°



254

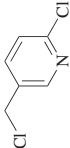
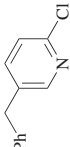
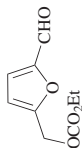
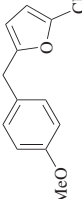
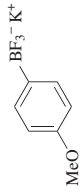
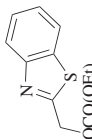
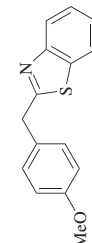
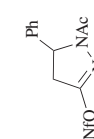
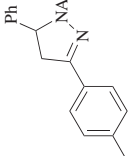
R		Time (h)	
H	Me	6	12
(72)	(65)		

TABLE 1D. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH ALLYLIC AND BENZYLIC ELECTROPHILES (Continued)

Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15} 		PdCl ₂ (dppf)•CH ₂ Cl ₂ (2%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, 77°, 16 h	 (86)	85

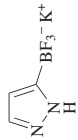
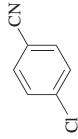
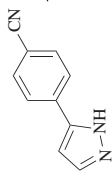
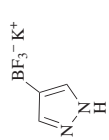
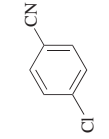
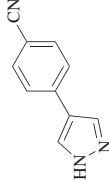
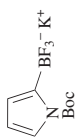
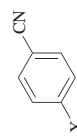
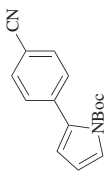
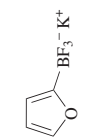
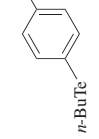
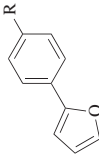
^a The yield of the crude product was determined by ¹H NMR.^b The yield of the product was determined by GC analysis.

TABLE 1E. CROSS-COUPLING OF ARYLTRIFLUOROBORATES WITH MISCELLANEOUS ELECTROPHILES

Aryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆ PhBF ₃ ⁻ K ⁺	<i>n</i> -C ₆ H ₁₃ Br	Pd (2.5 ppm), Na ₂ CO ₃ (3.7 eq), TBAB (1 eq), EtOH-H ₂ O, MW, 150°, 5 min	<i>n</i> -C ₆ H ₁₃ Ph (0)	214
	¹¹ MeI	Pd ₂ (dba) ₃ , P(<i>o</i> -tol) ₃ , K ₂ CO ₃ , DMF, 60°, 5 min	¹¹ MePh (13)	255
		Pd cat. 6 (0.1%), KOH (2 eq), TBAB (0.5 eq), acetone-H ₂ O, 50°, 9 h	 (77)	150
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (2%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, 77°, 24 h	 (trace)	85
C ₇ 		PdCl ₂ (dppf)•CH ₂ Cl ₂ (2%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, 77°, 24 h	 (trace)	85
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (9%), K ₂ CO ₃ (3 eq), LiCl (3 eq), toluene-H ₂ O, 100°, 18 h	 (87)	123

Please refer to the charts preceding the tables for structures indicated by the **bold numbers**.

TABLE 2A. CROSS-COUPLING OF HETEROARYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES

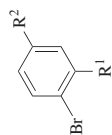
Heteroaryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.									
		Pd(OAc) ₂ (x%), RuPhos (y%), Na ₂ CO ₃ (z eq), EtOH, 85°, 48 h	 <table><tr><td>x</td><td>y</td><td>z</td></tr><tr><td>1</td><td>2</td><td>2 (26)</td></tr><tr><td>5</td><td>10</td><td>3 (84)</td></tr></table>	x	y	z	1	2	2 (26)	5	10	3 (84)	94
		x	y	z									
1	2	2 (26)											
5	10	3 (84)											
		Pd(OAc) ₂ (x%), RuPhos (y%), Na ₂ CO ₃ (z eq), EtOH, 85°, 48 h	 <table><tr><td>x</td><td>y</td><td>z</td></tr><tr><td>1</td><td>2</td><td>2 (20)</td></tr><tr><td>5</td><td>10</td><td>3 (37)</td></tr></table>	x	y	z	1	2	2 (20)	5	10	3 (37)	94
x	y	z											
1	2	2 (20)											
5	10	3 (37)											
		Pd(OAc) ₂ (1%), RuPhos (2%), Na ₂ CO ₃ (2 eq), EtOH, 85°, 5 h	 <table><tr><td>X</td></tr><tr><td>Br (90)</td></tr><tr><td>Cl (52)</td></tr></table>	X	Br (90)	Cl (52)	94						
		X											
Br (90)													
Cl (52)													
		Pd(PPh ₃) ₄ (10%), Ag ₂ O (2 eq), Et ₃ N (3 eq), MeOH, reflux, 90 min	 <table><tr><td>R</td></tr><tr><td>Cl (52)</td></tr><tr><td>H (40)</td></tr></table>	R	Cl (52)	H (40)	142						
R													
Cl (52)													
H (40)													

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

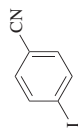
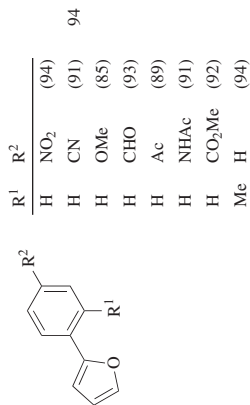
C₃

C₄

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

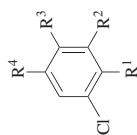
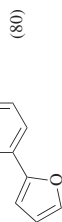


Pd(OAc)₂ (1%),
 RuPhos (2%),
 Na₂CO₃ (2 eq),
 EtOH, 85°, 8–36h



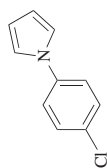
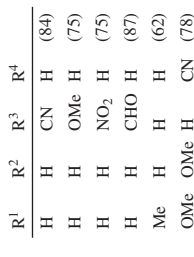
Pd(OAc)₂ (1%),
 RuPhos (2%),
 Na₂CO₃ (2 eq),
 EtOH, 85°, 8–36h

94



Pd(OAc)₂ (1%),
 RuPhos (2%),
 Na₂CO₃ (2 eq),
 EtOH, 85°, 8–36h

94



Pd(OAc)₂ (1%),
 RuPhos (2%),
 Na₂CO₃ (2 eq),
 EtOH, 85°, 8–36h

94

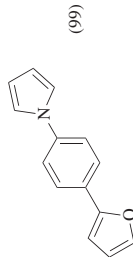
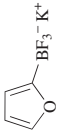
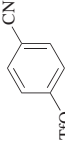
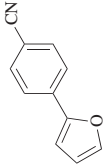
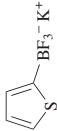
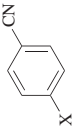
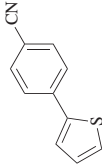
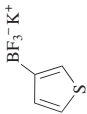
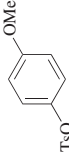
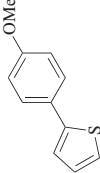
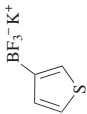
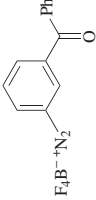
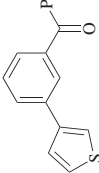
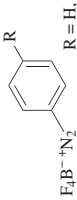
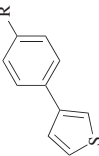
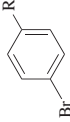
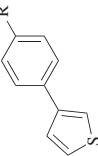


TABLE 2A. CROSS-COUPLING OF HETEROARYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Heteroaryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc) ₂ (1%), RuPhos (2%), Na ₂ CO ₃ (2 eq), EtOH, 85°, 8–36 h	 (82)	94
		Pd(OAc) ₂ (1%), RuPhos (2%), Na ₂ CO ₃ (2 eq), EtOH, 85°, 2 h	 X Br (98) Cl (83)	94
		Pd(OAc) ₂ (2%), L2 (4%), KOH (3 eq), MeOH, 60°, 5 h	 (27)	135
		Pd(OAc) ₂ (5%), 1,4-dioxane, 20°, 3 h	 (86)	13
		Pd cat. 2 (5%), 1,4-dioxane, rt, 19 h	 (24)	231
		Pd (2.5 ppm), Na ₂ CO ₃ (3.7 eq), TBAB (1 eq), EtOH–H ₂ O, MW, 150°, 5 min	 R OMe (8) Me (12) Ac (77)	214

C₄

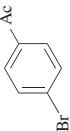
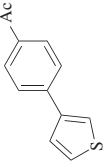
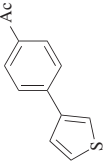
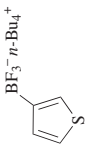
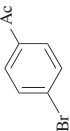
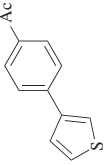
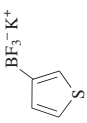
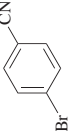
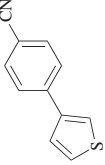
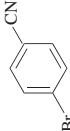
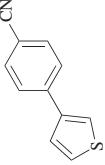
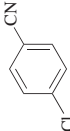
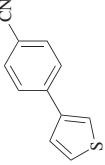
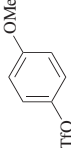
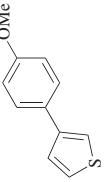
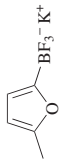
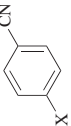
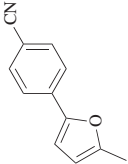
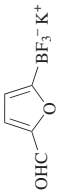
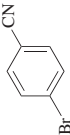
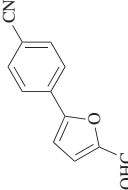
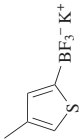
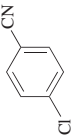
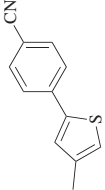
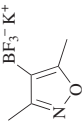
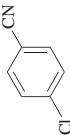
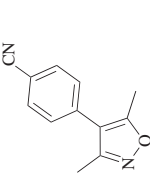
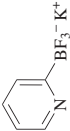
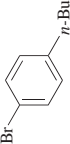
		PdCl ₂ (1.2%), K ₂ CO ₃ (3 eq), MW, 125°, 20 min		Solvent MeOH (57) MeOH-H ₂ O (79)	215
		BF ₃ ⁻ · <i>n</i> -Bu ₄ ⁺		(91)	12
		BF ₃ ⁻ ·K ⁺		(93)	46
				(93)	94
				(96)	94
				(79)	134

TABLE 2A. CROSS-COUPLING OF HETEROARYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Heteroaryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc) ₂ (1%), RuPhos (2%), Na ₂ CO ₃ (2 eq), EtOH, 85°, 8 h	 X Br (95) Cl (58)	94
		Pd(OAc) ₂ (3%), RuPhos (6%), Na ₂ CO ₃ (2 eq), EtOH, 85°, 48 h	 (39)	94
		Pd(OAc) ₂ (1%), RuPhos (2%), Na ₂ CO ₃ (2 eq), EtOH, 85°, 12 h	 (74)	94
		Pd(OAc) ₂ (1%), RuPhos (2%), Na ₂ CO ₃ (2 eq), EtOH, 85°, 12 h	 (71)	94
		Pd ₂ (dba) ₃ (1%), diphenylphosphine oxide (6%), base (3 eq), dioxane, 110°, 20 h	Base KF (0) ^a NaO <i>n</i> -Bu (10) ^a	97

C₅

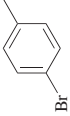
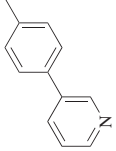
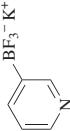
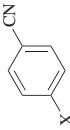
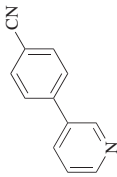
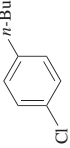
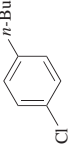
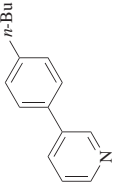
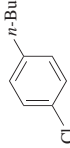
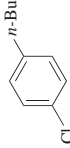
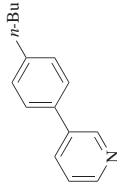
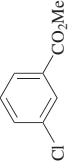
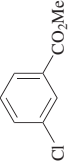
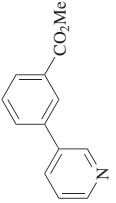
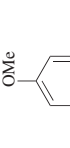
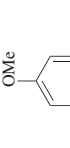
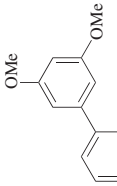
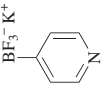
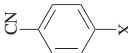
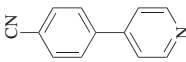
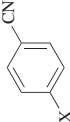
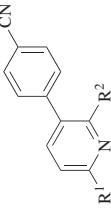
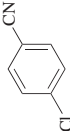
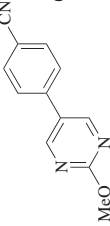
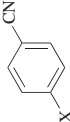
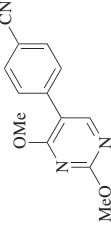
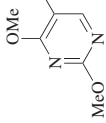
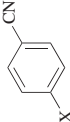
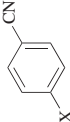
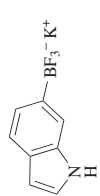
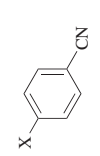
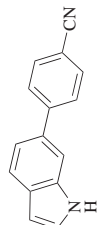
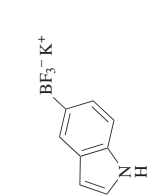
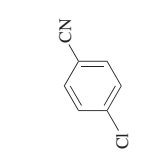
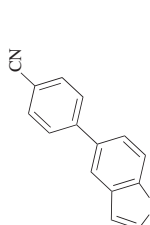
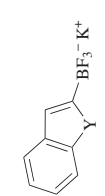
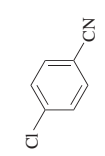
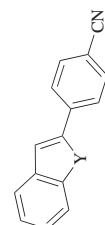
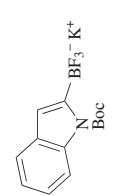
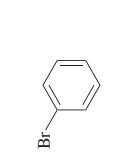
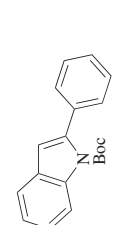
		$\text{Pd}(\text{OAc})_2$ (5%), dppb (5%), C_5CO_3 (1.25 eq), DME– H_2O , 50°, 24 h		12
		$\text{Pd}(\text{OAc})_2$ (3%), RuPhos (6%), Na_2CO_3 (2 eq), EtOH, 85°, 16 h		94
		$\text{Pd}(\text{OAc})_2$ (3%), SPhos (6%), K_2CO_3 (3 eq), EtOH, 72°, 22 h		87
		$\text{Pd}_2(\text{dba})_3$ (1%), PCy_3 (2.4%), K_3PO_4 (1.7 eq), dioxane– H_2O , 100°		93
		$\text{Pd}(\text{OAc})_2$ (3%), SPhos (6%), K_2CO_3 (3 eq), EtOH, 72°, 22 h		87
		$\text{Pd}(\text{OAc})_2$ (3%), SPhos (6%), K_2CO_3 (3 eq), EtOH, 72°, 22 h		87

TABLE 2A. CROSS-COUPLING OF HETEROARYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

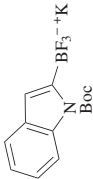
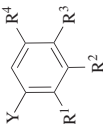
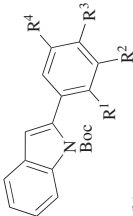
Heteroaryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 		Pd(OAc) ₂ (3%), RuPhos (6%), Na ₂ CO ₃ (2 eq), EtOH, 85°, 12 h	 X Br (90) Cl (96)	94
		Pd(OAc) ₂ (3%), RuPhos (6%), Na ₂ CO ₃ (2 eq), EtOH, 85°, 12 h	 R ¹ R ² X H F Br (73) H F Cl (49) F H Br (61) F H Cl (77)	94
		Pd(OAc) ₂ (3%), RuPhos (6%), Na ₂ CO ₃ (2 eq), EtOH, 85°, 12 h	 (96)	94
		Pd(OAc) ₂ (3%), RuPhos (6%), Na ₂ CO ₃ (2 eq), EtOH, 85°, 12 h	 X Br (88) Cl (86)	94
C_6 				
				

			$\text{Pd}(\text{OAc})_2$ (1%), RuPhos (2%), Na_2CO_3 (2 eq), EtOH, 85°, 8 h	$\frac{\text{X}}{\text{Br (96)}}$ Cl (83)	94
			$\text{Pd}(\text{OAc})_2$ (1%), RuPhos (2%), Na_2CO_3 (2 eq), EtOH, 85°, 6 h	(98)	94
			$\text{Pd}(\text{OAc})_2$ (1%), RuPhos (2%), Na_2CO_3 (2 eq), EtOH, 85°		94
			Pd Source (x%), ligand (y%), Na_2CO_3 (3 eq), DME-H ₂ O		256

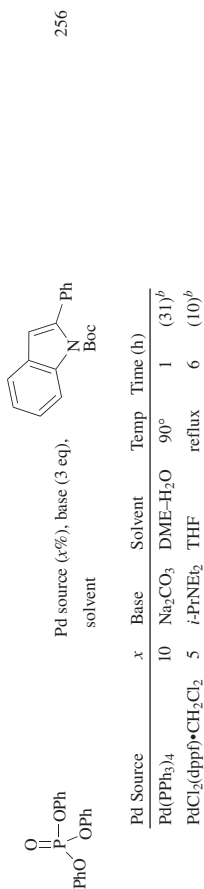
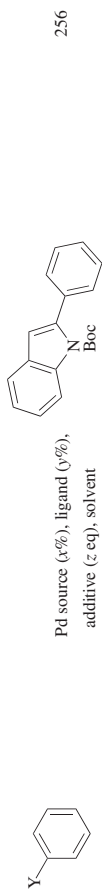
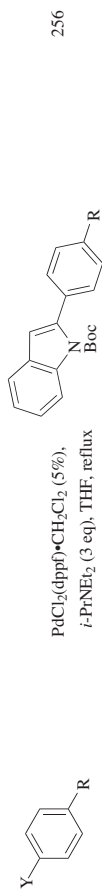
Y	Time (h)		
NBoc	6	7	12
S	(81)	(82)	(92)
O			

Pd Source	x	Ligand	y	Temp (°)	Time (h)
$\text{Pd}(\text{OAc})_2$	5	PPh ₃	10	90	1 (60)
$\text{PdCl}_2(\text{PPh}_3)_2$	10	none	—	90	1 (55)
$\text{Pd}(\text{PPh}_3)_4$	10	none	—	90	1 (92)
$\text{Pd}(\text{PPh}_3)_4$	10	none	—	50	4 (54)

TABLE 2A. CROSS-COUPLING OF HETEROARYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

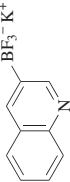
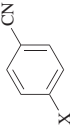
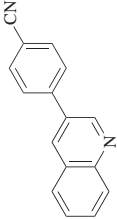
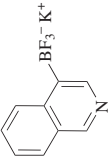
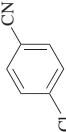
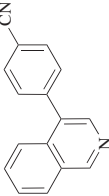
Heteroaryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.	
		Pd(PPh₃)₄ (10%), Na₂CO₃ (3 eq), DME-H₂O, 90°		256	
Y	R ¹	R ²	R ³	R ⁴	Time (h)
Br	H	H	F	H	5 (70)
Br	H	H	Me	H	4 (73)
Br	H	H	CF ₃	H	4 (62)
Br	H	H	CN	H	6 (73)
Br	H	H	OMe	H	3 (76)
Br	H	OMe	H	H	4 (70)
Br	F	H	H	H	6 (63)
Br	CN	H	H	H	6 (36)
Br	OMe	H	H	H	4 (51)
Br	H	Me	H	Me	4 (77)
I	H	H	H	H	1 (90)
Cl	H	H	H	H	1 (0)
OTf	H	H	H	H	1 (64)
SMe	H	H	H	H	1 (0)
BF ₄ ⁻ N ₂ ⁺	H	H	H	H	1 (22) ^b

C₈



Pd Source	x	Base	Solvent	Temp	Time (h)
Pd(PPh ₃) ₄	10	Na ₂ CO ₃	DME-H ₂ O	90°	1 (31) ^b
PdCl ₂ (dppf)•CH ₂ Cl ₂	5	<i>i</i> -PrNEt ₂	THF	reflux	6 (10) ^b

TABLE 2A. CROSS-COUPLING OF HETEROARYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Heteroaryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc) ₂ (3%), RuPhos (6%), Na ₂ CO ₃ (2 eq), EtOH, 85°, 12 h	 X Br (88) Cl (86)	94
		Pd(OAc) ₂ (3%), RuPhos (6%), Na ₂ CO ₃ (2 eq), EtOH, 85°, 24 h	 (85)	94

^a The yield of the product was determined by GC analysis.^b The yield of the crude product was determined by ¹H NMR.

TABLE 2B. CROSS-COUPLING OF HETEROARYLTRIFLUOROBORATES WITH HETEROARYL ELECTROPHILES

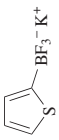
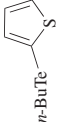
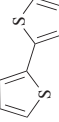
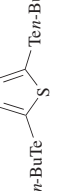
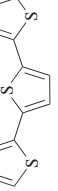
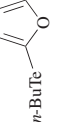
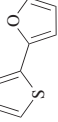
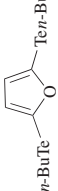
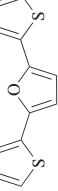
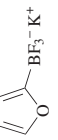
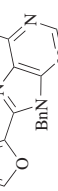
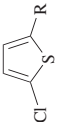
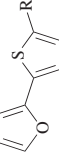
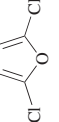
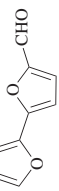
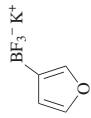
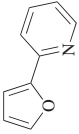
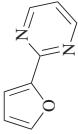
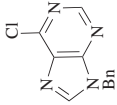
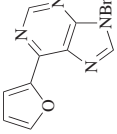
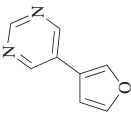
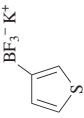
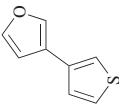
Heteroaryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc) ₂ (10%), dppf (20%), Ag ₂ O (2 eq), MeOH, rt, 1.5 h	 (0)	143
		Pd(OAc) ₂ (10%), dppf (20%), Ag ₂ O (2 eq), MeOH, rt, 1.5 h	 (0)	143
		Pd(OAc) ₂ (10%), dppf (20%), Ag ₂ O (2 eq), MeOH, rt, 1.5 h	 (34)	143
		Pd(OAc) ₂ (10%), dppf (20%), Ag ₂ O (2 eq), MeOH, rt, 1.5 h	 (0)	143
		Pd(PPh ₃) ₄ (4%), K ₂ CO ₃ (3 eq), MeCN-H ₂ O, MW, 150°, 5 min	 x $\frac{2}{4}$ (51) (73)	104
		Pd(OAc) ₂ (3%), RuPhos (6%), Na ₂ CO ₃ (2 eq), EtOH, 85°, 16 h	 R $\frac{Ac}{CHO}$ (77) (64)	94
		Pd(OAc) ₂ (3%), RuPhos (6%), Na ₂ CO ₃ (2 eq), EtOH, 85°, 16 h	 (81)	94

TABLE 2B. CROSS-COUPLING OF HETEROARYLTRIFLUOROBORATES WITH HETEROARYL ELECTROPHILES (Continued)

Heteroaryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 		Pd(OAc) ₂ (3%), RuPhos (6%), Na ₂ CO ₃ (2 eq), EtOH, 85°, 28 h	 (67)	94
		Pd(OAc) ₂ (3%), RuPhos (6%), Na ₂ CO ₃ (2 eq), EtOH, 85°, 16 h	 (92)	94
		Pd(PPh ₃) ₄ (4%), K ₂ CO ₃ (3 eq), MeCN-H ₂ O, MW, 150°, 5 min	 x 2 (52) 4 (95)	104
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (0.5%), Et ₃ N (3 eq), EtOH, reflux, 18 h	 (72)	46
$BF_3^- K^+$ 		PdCl ₂ (dppf)•CH ₂ Cl ₂ (1%), Et ₃ N (3 eq), EtOH, reflux, 10 h	 (24)	46

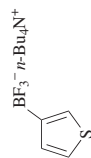
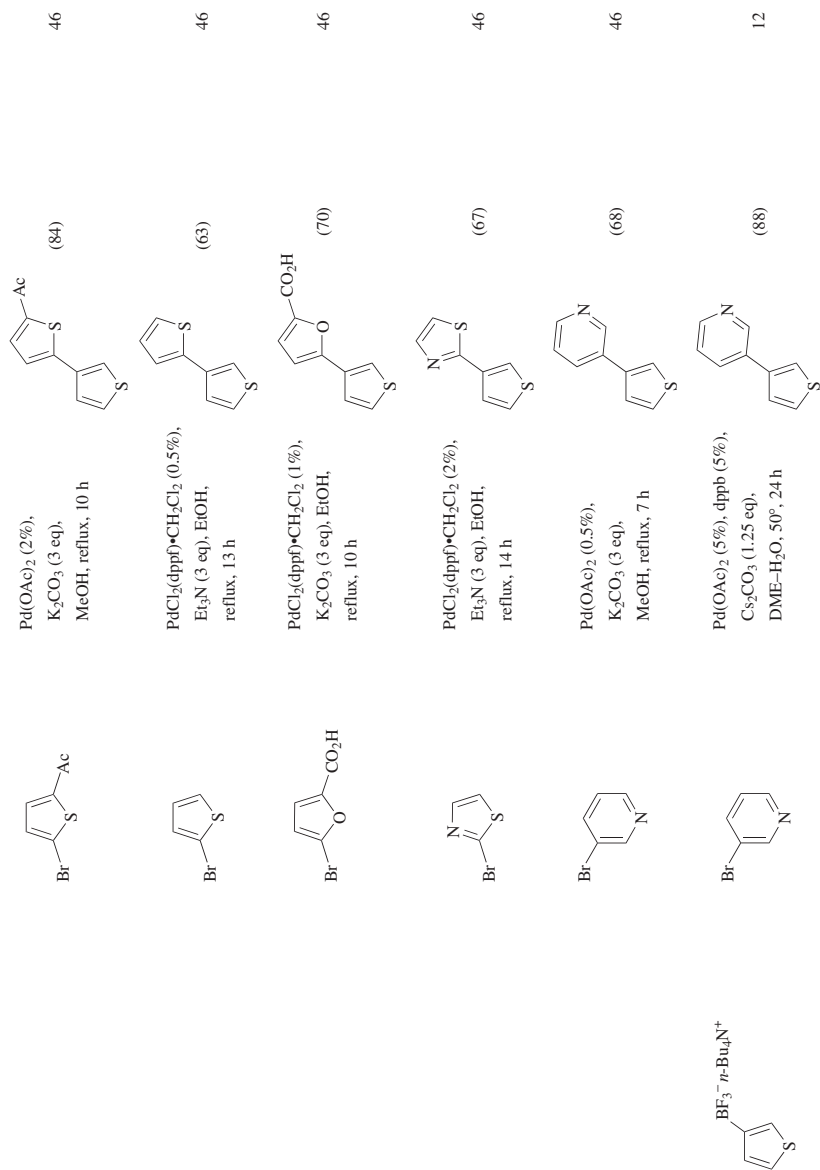


TABLE 2B. CROSS-COUPLING OF HETEROARYLTRIFLUOROBORATES WITH HETEROARYL ELECTROPHILES (Continued)

Heteroaryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc) ₂ (1%), K ₂ CO ₃ (3 eq), MeOH, reflux, 15 h	 (60)	46
		Pd(A ^{trip} Phos) ₂ Cl ₂ (2%), Et ₃ N (3 eq), PTS-H ₂ O, rt, 19 h	 (78)	257
		Pd(OAc) ₂ (0.5%), K ₂ CO ₃ (3 eq), MeOH, reflux, 7 h	 (64)	46
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (0.5%), Et ₃ N (3 eq), EtOH, reflux, 18 h	 (75)	46
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (1%), Et ₃ N (3 eq), EtOH, reflux, 10 h	 (77)	46

C₄

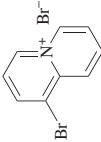
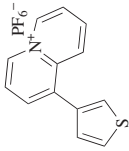
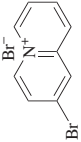
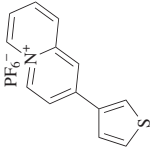
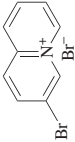
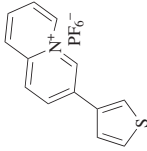
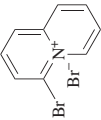
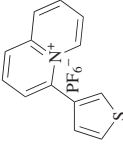
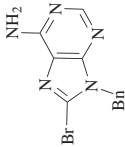
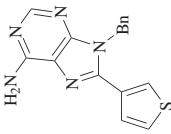
	1. Pd(OAc) ₂ (1%), K ₂ CO ₃ (3 eq), H ₂ O, 65°, 5 h 2. H ₄ NPF ₆		(76)	122
	1. Pd(OAc) ₂ (1%), K ₂ CO ₃ (3 eq), H ₂ O, 65°, 5 h 2. H ₄ NPF ₆		(98)	122
	1. Pd(OAc) ₂ (1%), K ₂ CO ₃ (3 eq), H ₂ O, 65°, 5 h 2. H ₄ NPF ₆		(83)	122
	1. Pd(OAc) ₂ (1%), K ₂ CO ₃ (3 eq), H ₂ O, 65°, 5 h 2. H ₄ NPF ₆		(56)	122
	Pd(PPh ₃) ₄ (2%), K ₂ CO ₃ (3 eq), MeCN-H ₂ O, MW, 150°, 5 min		(96)	104

TABLE 2B. CROSS-COUPLING OF HETEROARYLTRIFLUOROBORATES WITH HETEROARYL ELECTROPHILES (Continued)

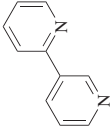
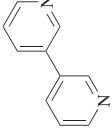
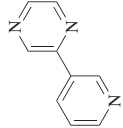
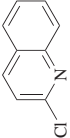
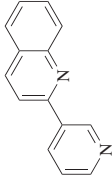
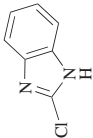
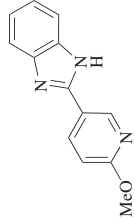
Heteroaryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (1%), K_2CO_3 (3 eq), EtOH, reflux, 12 h	 (83)	46
		$\text{Pd}(\text{OAc})_2$ (3%), RuPhos (6%), Na_2CO_3 (2 eq), EtOH, 85°, 12 h	 (52)	94
		$\text{Pd}(\text{OAc})_2$ (2%), K_2CO_3 (3 eq), MeOH, reflux, 12 h	 (40)	46
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (1%), Et_3N (3 eq), EtOH, reflux, 9 h	 (70) + (10)	46

C₄

		104
		235
		104
		104
		94
		143

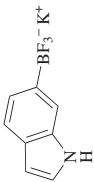
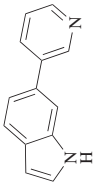
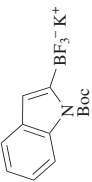
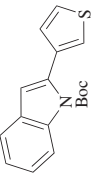
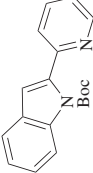
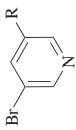
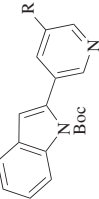
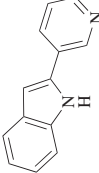
TABLE 2B. CROSS-COUPLING OF HETEROARYLTRIFLUOROBORATES WITH HETEROARYL ELECTROPHILES (Continued)

Heteroaryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc) ₂ (10%), dppf (20%), Ag ₂ O (2 eq), MeOH, rt, 1.5 h	 (0)	143
		Pd(OAc) ₂ (10%), dppf (20%), Ag ₂ O (2 eq), MeOH, rt, 1.5 h	 (0)	143
		Pd(OAc) ₂ (10%), dppf (20%), Ag ₂ O (2 eq), MeOH, rt, 1.5 h	 (0)	143
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (0.5%), Et ₃ N (3 eq), EtOH, reflux, 18 h	 (64)	46
		Pd(OAc) ₂ (3%), SPhos (6%), K ₂ CO ₃ (3 eq), EtOH, 72°, 22 h	 (75)	87

		Pd(OAc)₂ (3%), RuPhos (6%), Na₂CO₃ (2 eq), EtOH, 85°, 16 h	94
		Pd(OAc)₂ (3%), SPhos (6%), K₂CO₃ (3 eq), EtOH, 72°, 22 h	87
		Pd(OAc)₂ (3%), SPhos (6%), K₂CO₃ (3 eq), EtOH, 72°, 22 h	87
		Pd(OAc)₂ (5%), SPhos (10%), K₂CO₃ (3 eq), EtOH, 72°, 22 h	87
		PdCl₂(PPh₃)₂ or PdCl₂(dppf)•CH₂Cl₂, K₂CO₃, MeCN, MW, 150°, 30 min	223

C₆

TABLE 2B. CROSS-COUPLING OF HETEROARYLTRIFLUOROBORATES WITH HETEROARYL ELECTROPHILES (Continued)

Heteroaryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc) ₂ (3%), RuPhos (6%), Na ₂ CO ₃ (2 eq), EtOH, 85°, 16 h	 (93)	94
		Pd(PPh ₃) ₄ (10%), Na ₂ CO ₃ (3 eq), DME-H ₂ O, 90°, 3 h	 (95)	256
		Pd(PPh ₃) ₄ (10%), Na ₂ CO ₃ (3 eq), DME-H ₂ O, 90°, 3 h	 (75)	256
		Pd(PPh ₃) ₄ (10%), Na ₂ CO ₃ (3 eq), DME-H ₂ O, 90°, 3 h		R Time (h) H 3 (77) Br 5 (80) 256
		Pd(OAc) ₂ (3%), RuPhos (6%), Na ₂ CO ₃ (2 eq), EtOH, 85°, 16 h	 (57)	94

C₈

		$\text{Pd}(\text{PPh}_3)_4$ (10%), Na_2CO_3 (2.75 eq), $\text{DME-H}_2\text{O}$, 110°, 48h	258																								
C₁₁																											
			<table> <tr> <th>R¹</th><th>X</th><th>R²</th><th></th></tr> <tr> <td>H</td><td>Br</td><td>Me</td><td>(91)</td></tr> <tr> <td>H</td><td>Br</td><td>OMe</td><td>(85)</td></tr> <tr> <td>H</td><td>Br</td><td>NMe₂</td><td>(86)</td></tr> <tr> <td>OBn</td><td>Br</td><td>F</td><td>(87)</td></tr> <tr> <td>OBn</td><td>Cl</td><td>CF₃</td><td>(73)</td></tr> </table>	R ¹	X	R ²		H	Br	Me	(91)	H	Br	OMe	(85)	H	Br	NMe ₂	(86)	OBn	Br	F	(87)	OBn	Cl	CF ₃	(73)
R ¹	X	R ²																									
H	Br	Me	(91)																								
H	Br	OMe	(85)																								
H	Br	NMe ₂	(86)																								
OBn	Br	F	(87)																								
OBn	Cl	CF ₃	(73)																								
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$, Et_3N, EtOH, reflux	95																								
		$\text{Pd}_2(\text{dba})_3$, PCy_3, Et_3N, 1,4-dioxane, reflux	95																								

TABLE 2C. CROSS-COUPLING OF HETEROARYLTRIFLUOROBORATES WITH ALKENYL ELECTROPHILES

Heteroaryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(PPh ₃) ₄ (8%), Ag ₂ O (2 eq), MeOH, rt, ultrasound, 40 min		69
		Pd(PPh ₃) ₄ (10%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 90°, 10 h		161
		Pd(PPh ₃) ₄ (4.5%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 90°, 2.5 h		66
		PdCl ₂ (PPh ₃) ₂ (5%), K ₂ CO ₃ (2 eq), DMF-H ₂ O, 100°, 2 h		259
		Pd(PPh ₃) ₄ (4.5%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 90°, 2.5 h		66

C₄

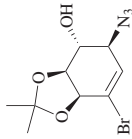
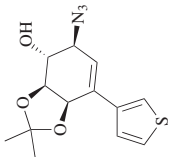
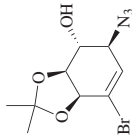
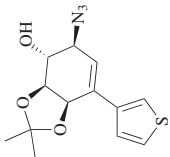
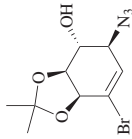
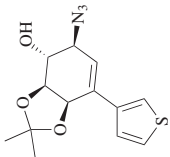
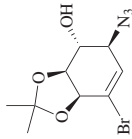
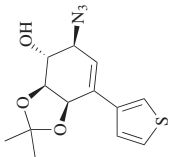
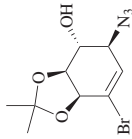
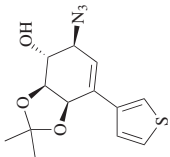
		$\text{Pd}(\text{PPh}_3)_4$ (6%), Cs_2CO_3 (3 eq), toluene-H_2O, 90°, 5.5 h	(50)	161
		$\text{Pd}(\text{PPh}_3)_4$ (4%), K_2CO_3 (3 eq), toluene-H_2O, 90°, 50 min	$\frac{x}{4.5 \text{ (>99)} \quad 0.5 \text{ (93)}}$	66
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (4%), K_2CO_3 (6 eq), toluene-H_2O, 90°, 3.5 h	(99)	260
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (2%), K_2CO_3 (6 eq), toluene-H_2O, 90°, 3.5 h	(91)	260
		$\text{Pd}_2(\text{dba})_3$ (2.5%), RuPhos (10%), Cs_2CO_3 (3 eq), $\text{THF}-\text{H}_2\text{O}$, 80°	(97)	148

TABLE 2C. CROSS-COUPLING OF HETEROARYLTRIFLUOROBORATES WITH ALKENYL ELECTROPHILES (Continued)

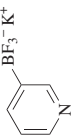
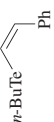
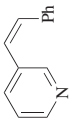
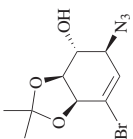
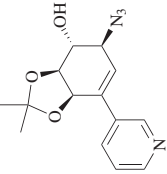
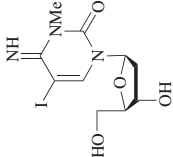
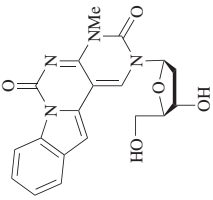
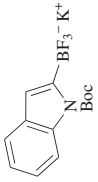
Heteroaryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₅		Pd(PPh ₃) ₄ (8%), Ag ₂ O (2 eq), MeOH, ultrasound, rt, 40 min	 (0)	69
		Pd(PPh ₃) ₄ (6%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 90°, 24 h	 (0)	161
		Pd(OAc) ₂ (3%), TPPTS (8%), Na ₂ CO ₃ (2.2 eq), MeOH-H ₂ O, 45°, 12 h	 (60)	145
 C ₈				

TABLE 2D. CROSS-COUPLING OF HETEROARYLTRIFLUOROBORATES WITH BENZYL ELECTROPHILES

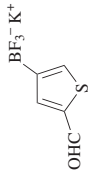
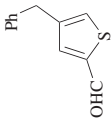
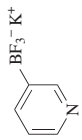
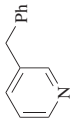
Heteroaryltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₅ 		PdCl ₂ (dppf)•CH ₂ Cl ₂ (2%), Cs ₂ CO ₃ (3 eq), CPME-H ₂ O, 90°, 14 h	 (72)	85
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (2%), Cs ₂ CO ₃ (3 eq), CPME-H ₂ O, 90°, 22 h	 (67)	85

TABLE 3A. CROSS-COUPLING OF ALKENYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES

$$\text{CH}_2=\text{CH}-\text{BF}_3^-\text{K}^+$$

$$\text{F}_4\text{B}^+\text{N}_2^-\text{C}_6\text{H}_4\text{CO}_2\text{Et}$$

Pd(OAc)₂ (5%),
1,4-dioxane, 20°, 1 h

$$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4\text{CO}_2\text{Et}$$

13

$$\text{F}_4\text{B}^+\text{N}_2^-\text{C}_6\text{H}_4\text{R}$$

Pd cat. **1** (0.1%),
[bmim][BF₄-MeOH], rt
10 min

$$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4\text{R}$$

R	Time (h)
H	(80)
Me	(83)

132

$$\text{F}_4\text{B}^+\text{N}_2^-\text{C}_6\text{H}_4\text{R}$$

Pd cat. **2** (5%),
1,4-dioxane, rt

$$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4\text{R}$$

R	Time (h)
NO ₂	3 (60)
Me	3.5 (36)
OMe	3 (41)
<i>t</i> -Bu	3.5 (43)

231

$$\text{F}_4\text{B}^+\text{N}_2^-\text{C}_6\text{H}_4\text{COPh}$$

Pd(OAc)₂ (5%),
1,4-dioxane, 20°, 5 min

$$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4\text{COPh}$$

(86)

133

$$\text{F}_4\text{B}^+\text{N}_2^-\text{C}_6\text{H}_2\text{R}^1\text{R}^2\text{R}^3$$

Pd₂(μ-OAc)₂(P(*o*-tol)₃)₂ (x%),
MeOH, 20°

$$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_2\text{R}^1\text{R}^2\text{R}^3$$

133

R ¹	R ²	R ³	x	Time (min)
H	H	Br	0.1	30 (70)
H	H	OMe	1	20 (81)
H	H	CO ₂ Et	0.1	120 (88)
H	H	OTf	0.5	60 (75)
H	COPh	H	5	instantaneous (81)
H	COPh	H	1	10 (86)
Me	H	H	0.5	20 (78)

Refs.

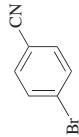
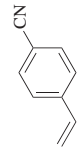
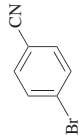
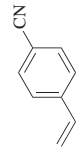
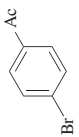
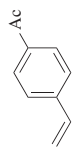
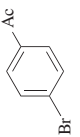
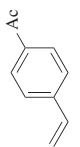
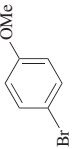
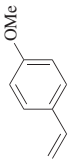
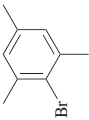
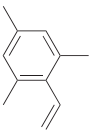
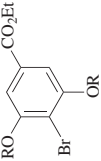
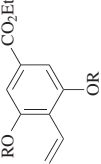
Alkenyltrifluoroborate

Electrophile

Conditions

Product(s) and Yield(s) (%)

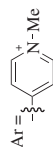
Refs.

	$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (2%), Et_3N (3 eq), <i>i</i> -PrOH– H_2O , reflux, 6 h		(76)	71
	$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (9%), C_5CO_3 (3 eq), THF– H_2O , reflux, 6 h		(69)	261
	$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (2%), Et_3N (1 eq), MeOH, reflux, 3 h		(90)	261
	$\text{Pd}(\text{OAc})_2$ (1%), TBAB, K_2CO_3 , H_2O , 120°		Time — 20 h (82) MW 20 min (89)	70
	Pd cat. (2%), ligand (6%), C_5CO_3 (3 eq), THF– H_2O , 85°			106
	$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (18%), C_5CO_3 (3 eq), THF– H_2O , 90°, 4 d		(32)	262
	$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (18%), C_5CO_3 (3 eq), THF– H_2O , 90°, 2 d		R H (24) TBS (18)	262

Pd cat.	Ligand	Time (h)
$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$	—	22 (63)
$\text{Pd}(\text{PPh}_3)_4$	—	40 (62)
$\text{Pd}(\text{OAc})_2$	PPh_3	45 (72)
PdCl_2	PPh_3	22 (72)

TABLE 3A. CROSS-COUPLING OF ALKENYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Alkenyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (18%), Cs_2CO_3 (3 eq), THF– H_2O , 90° , 7 d		262
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (18%), Cs_2CO_3 (3 eq), THF– H_2O , 90° , 4 d		262
		$\text{Pd}(\text{OAc})_2$, TPPTS, K_2CO_3 , MeCN– H_2O , 60 – 70° , 12 h		159



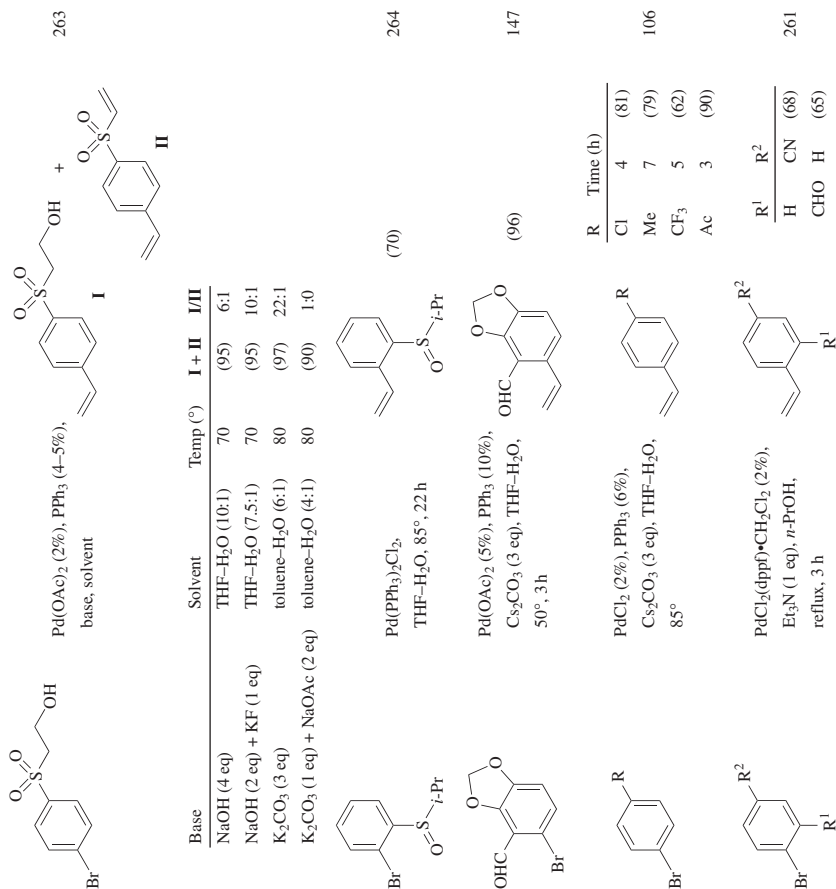
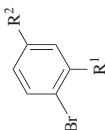
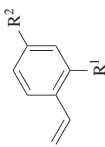
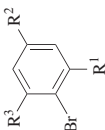
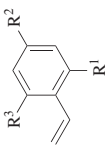
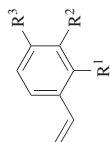
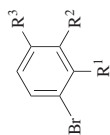


TABLE 3A. CROSS-COUPLING OF ALKENYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Alkenyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.																														
		Pd cat. 6 (1%), TBAB, K ₂ CO ₃ , H ₂ O, 120°		70																														
			<table><tr><th>R¹</th><th>R²</th><th>Time</th></tr><tr><td>H</td><td>CN</td><td>— 14 h (82)</td></tr><tr><td>H</td><td>OMe</td><td>— 24 h (67)</td></tr><tr><td>H</td><td>OMe</td><td>MW 20 min (63)</td></tr><tr><td>H</td><td>Ac</td><td>— 2 h (93)</td></tr><tr><td>H</td><td>Ac</td><td>— 3 h (72)</td></tr><tr><td>H</td><td>Ac</td><td>MW 20 min (92)</td></tr><tr><td>H</td><td>CO₂Et</td><td>— 8 h (71)</td></tr><tr><td>Me</td><td>H</td><td>— 14 h (65)</td></tr><tr><td>Me</td><td>H</td><td>MW 30 min (68)</td></tr></table>	R ¹	R ²	Time	H	CN	— 14 h (82)	H	OMe	— 24 h (67)	H	OMe	MW 20 min (63)	H	Ac	— 2 h (93)	H	Ac	— 3 h (72)	H	Ac	MW 20 min (92)	H	CO ₂ Et	— 8 h (71)	Me	H	— 14 h (65)	Me	H	MW 30 min (68)	
R ¹	R ²	Time																																
H	CN	— 14 h (82)																																
H	OMe	— 24 h (67)																																
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Me	H	MW 30 min (68)																																
		PdCl ₂ (2%), RuPhos (6%), Cs ₂ CO ₃ (3 eq), THF–H ₂ O, 85°, 22 h		<table><tr><th>R¹</th><th>R²</th><th>R³</th></tr><tr><td>H</td><td>NMe₂</td><td>H (93)</td></tr><tr><td>Me</td><td>Me</td><td>Me (81)</td></tr></table>	R ¹	R ²	R ³	H	NMe ₂	H (93)	Me	Me	Me (81)	106																				
R ¹	R ²	R ³																																
H	NMe ₂	H (93)																																
Me	Me	Me (81)																																



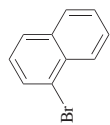
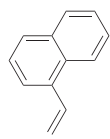
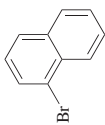
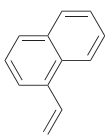
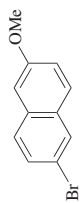
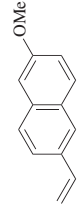
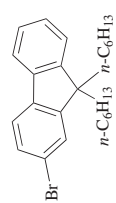
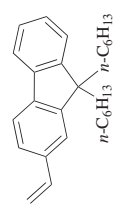
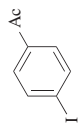
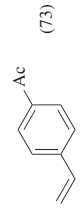
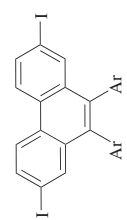
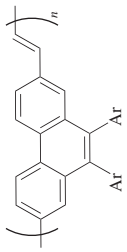
137

Pd/C (2%),
NaOAc•3H₂O (3 eq), 24 h

R ¹	R ²	R ³	Solvent	Temp (°)	
H	H	NO ₂	NMP	100	(78)
H	H	CN	NMP	100	(46) ^a
H	H	CN	NMP-H ₂ O	100	(9) ^a
H	H	Ac	NMP	100	(44) ^a
H	H	OBn	NMP	140	(28) ^a
H	H	OBn	NMP-H ₂ O	140	(26) ^a
H	NO ₂	H	NMP	100	(88) ^a
NO ₂	H	H	NMP	100	(53) ^a
NO ₂	H	H	NMP-H ₂ O	100	(18) ^a

TABLE 3A. CROSS-COUPLING OF ALKENYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Alkenyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																																
		PdCl_2 (2%), PPh_3 (6%), Cs_2CO_3 (3 eq), $\text{THF-H}_2\text{O}$, 85°, 22 h		<table><tr><th>R¹</th><th>R²</th><th>R³</th><th></th></tr><tr><td>H</td><td>H</td><td>Cl</td><td>(77)</td></tr><tr><td>H</td><td>H</td><td>NO₂</td><td>(84)</td></tr><tr><td>H</td><td>H</td><td>Me</td><td>(76)</td></tr><tr><td>H</td><td>H</td><td>CN</td><td>(83)</td></tr><tr><td>H</td><td>H</td><td>CF₃</td><td>(64)</td></tr><tr><td>H</td><td>H</td><td>CHO</td><td>(83)</td></tr><tr><td>H</td><td>H</td><td>OMe</td><td>(72)</td></tr><tr><td>H</td><td>H</td><td>CH₂OH</td><td>(82)</td></tr><tr><td>H</td><td>H</td><td>Ac</td><td>(85)</td></tr><tr><td>H</td><td>H</td><td>CO₂Me</td><td>(87)</td></tr><tr><td>H</td><td>H</td><td>NHAc</td><td>(78)</td></tr><tr><td>H</td><td>H</td><td>COPh</td><td>(85)</td></tr><tr><td>H</td><td>CN</td><td>H</td><td>(78)</td></tr><tr><td>H</td><td>OMe</td><td>H</td><td>(74)</td></tr><tr><td>H</td><td>Ac</td><td>H</td><td>(79)</td></tr><tr><td>Me</td><td>H</td><td>H</td><td>(82)</td></tr><tr><td>CN</td><td>H</td><td>H</td><td>(82)</td></tr><tr><td>OMe</td><td>H</td><td>H</td><td>(71)</td></tr><tr><td>Ac</td><td>H</td><td>H</td><td>(92)</td></tr></table>	R ¹	R ²	R ³		H	H	Cl	(77)	H	H	NO ₂	(84)	H	H	Me	(76)	H	H	CN	(83)	H	H	CF ₃	(64)	H	H	CHO	(83)	H	H	OMe	(72)	H	H	CH ₂ OH	(82)	H	H	Ac	(85)	H	H	CO ₂ Me	(87)	H	H	NHAc	(78)	H	H	COPh	(85)	H	CN	H	(78)	H	OMe	H	(74)	H	Ac	H	(79)	Me	H	H	(82)	CN	H	H	(82)	OMe	H	H	(71)	Ac	H	H	(92)
R ¹	R ²	R ³																																																																																		
H	H	Cl	(77)																																																																																	
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C ₂																																																																																				

		PdCl_2 (2%), PPh_3 (6%), Cs_2CO_3 (3 eq), THF- H_2O , 85°	Time (h) 22 (82) 8 (81)	106
		Pd cat. 6 (1%), TBAB, K_2CO_3 , H_2O , 120°	Time — 10 h (74) MW 20 min (78)	70
		Pd cat. 6 (1%), TBAB, K_2CO_3 , H_2O , 120°	Time — 14 h (57) MW 30 min (68)	70
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (5%), Et_3N (1 eq), <i>n</i> -PrOH, reflux, 4 h	(62)	265
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (2%), Et_3N (1 eq), <i>n</i> -PrOH, reflux, 3 h	(73)	261
		$\text{Pd}(\text{OAc})_2$ (5%), $\text{P}(o\text{-tol})_3$ (2.5%), Et_3N (2.5 eq), toluene-DMF, 120°, overnight	(71)	158

Ar = *n*-C₆H₁₃OC₆H₄-4

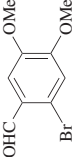
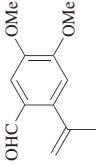
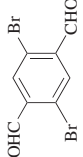
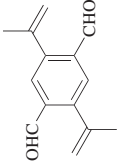
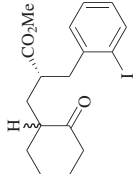
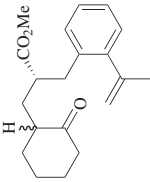
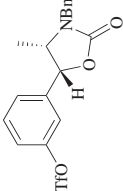
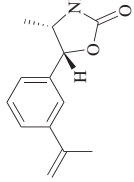
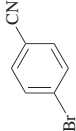
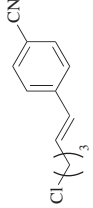
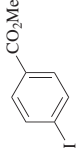
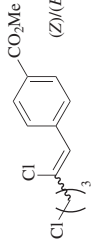
TABLE 3A. CROSS-COUPLING OF ALKENYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Alkenyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd/C (2%), NaOAc•3H ₂ O (3 eq), 24 h		137
	R ¹	Solvent	Temp (°)	
	H	NO ₂	80	(90) ^a
	H	Br	100	(68) ^a
	H	Br	NMP-H ₂ O	100 (81) ^a
	H	OMe	100	(58) ^a
	H	OMe	NMP-H ₂ O	100 (69)
	NO ₂	H	NMP	100 (75) ^a
	NO ₂	H	NMP-H ₂ O	100 (73)
	OH	H	NMP	100 (67)
	Me	H	NMP	100 (40) ^a
	Me	H	NMP-H ₂ O	100 (79) ^a
	OBn	H	NMP	100 (60)
		Pd(OAc) ₂ (5%), PPh ₃ (10%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, 70°, 4 h		107
	R	R	R	Me (72) i-Pr (74)
		Pd(OAc) ₂ (5%), PPh ₃ (10%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, 70°, 4 h		107
	R	R	R	Me (64) i-Pr (92)

		PdCl_2 (2%), PPh_3 (6%), Cs_2CO_3 (3 eq), $\text{THF-H}_2\text{O}$, 85°, 22 h	Y OTf (82) I (89) Cl (0)	106
			(65)	106
			(90)	220
		$\text{PdCl}_2(\text{dppf})\cdot\text{CH}_2\text{Cl}_2$ (9%), Cs_2CO_3 (3 eq), $\text{THF-H}_2\text{O}$, reflux, 6 h	R NO_2 (72) Ac (84)	261
		$\text{PdCl}_2(\text{dppf})\cdot\text{CH}_2\text{Cl}_2$ (2%), Et_3N (1 eq), <i>n</i> -PrOH, reflux, 3 h	R NO_2 (82) OMe (64) Ac (95)	261
		$\text{PdCl}_2(\text{dppf})\cdot\text{CH}_2\text{Cl}_2$ (5%), Et_3N (1.3 eq), EtOH, 80°, 4.5 h	(93)	103
		$\text{PdCl}_2(\text{dppf})\cdot\text{CH}_2\text{Cl}_2$, Et_3N (1.3 eq), MeOH, 50°, 10 h	(91)	266

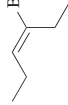
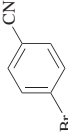
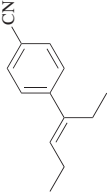
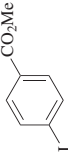
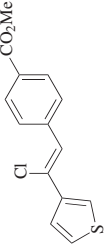
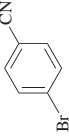
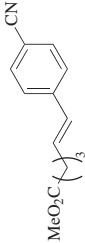
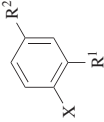
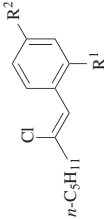
TABLE 3A. CROSS-COUPLING OF ALKENYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Alkenyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2 		Pd source (5%), solvent, 20°		237
		Pd Source	Solvent	
		Pd ₂ (μ-OAc) ₂ (<i>o</i> -tol) ₂ C ₆ H ₄ CH ₂	MeOH (0) ^b	
		Pd(PPh ₃) ₄	MeOH (14) ^b	
C_3 		PdCl ₂ (dppf)•CH ₂ Cl ₂ (2%), <i>t</i> -BuNH ₂ (3 eq), <i>i</i> -PrOH–H ₂ O, reflux, 24 h		71
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (2%), <i>t</i> -BuNH ₂ (3 eq), <i>i</i> -PrOH–H ₂ O, reflux, 5 h		71
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (2%), Et ₃ N (1 eq), <i>n</i> -PrOH, reflux, 5 h		261
		PdCl ₂ (dppf) (1%), <i>i</i> -Pr ₂ NH (2%), K ₂ CO ₃ , <i>n</i> -PrOH, 90°		267

		$\text{Pd}(\text{OAc})_2$ (5%), PPh_3 (10%), Cs_2CO_3 (3 eq), THF– H_2O , 50°, 3 h	(>99)	147
		$\text{Pd}(\text{OAc})_2$ (10%), PPh_3 (20%), Cs_2CO_3 (3 eq), THF– H_2O , reflux, 3 h	(84)	147
		$\text{Pd}(\text{OAc})_2$ (4.5%), PPh_3 (9%), Cs_2CO_3 (3 eq), THF– H_2O , 70°, 5 h	(78)	107
		$\text{PdCl}_2(\text{dppf})$ (1%), <i>i</i> -Pr ₂ NH (2%), K ₂ CO ₃ , <i>n</i> -PrOH, 90°	(95)	267
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (2%), <i>i</i> -BuNH ₂ (3 eq), <i>i</i> -PrOH– H_2O , reflux, 6 h	(52)	71
		$\text{Pd}_2(\text{dba})_3$ (1.5%), $\text{P}(\text{i-Bu})_3 \cdot \text{HBF}_4$ (3%), Cs_2CO_3 (3 eq), THF– H_2O , 120°, 12 h	(Z)/(E) = 62:38 (50)	148

C₅

TABLE 3A. CROSS-COUPLING OF ALKENYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Alkenyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 		PdCl ₂ (dppf)•CH ₂ Cl ₂ (2%), <i>t</i> -BuNH ₂ (3 eq), <i>i</i> -PrOH–H ₂ O, reflux, 7 h	 (70)	71
		Pd ₂ (dba) ₃ (1.5%), P(<i>t</i> -Bu) ₃ •HBF ₄ (3%), Cs ₂ CO ₃ (3 eq), THF–H ₂ O, 120°, 12 h	 (36)	148
C_7 		PdCl ₂ (dppf)•CH ₂ Cl ₂ (2%), <i>t</i> -BuNH ₂ (3 eq), <i>i</i> -PrOH–H ₂ O, reflux, 14 h	 (33)	71
		Pd ₂ (dba) ₃ (1.5%), P(<i>t</i> -Bu) ₃ •HBF ₄ (3%), Cs ₂ CO ₃ (3 eq), THF–H ₂ O, 120°	 (36)	148

X	R ¹	R ²	Time (h)
Br	H	H	12 (70)
Br	H	NO ₂	12 (46)
Br	H	OMe	36 (56)
Br	H	CO ₂ Me	48 (63)
I	NH ₂	H	12 (74)
Cl	OH	H	12 (0)

		$\text{Pd}_2(\text{dba})_3$ (1.5%), $\text{P}(t\text{-Bu})_3\cdot\text{HBF}_4$ (3%), Cs_2CO_3 (3 eq), $\text{THF}-\text{H}_2\text{O}$, 120°, 12 h		(58)	148																														
		Pd cat. (5%), ligand (5%), Cs_2CO_3 (3 eq), $\text{THF}-\text{H}_2\text{O}$			148																														
<table><tr><th>Pd cat.</th><th>x</th><th>Ligand</th><th>y</th><th>Temp (°)</th><th>Time (h)</th></tr><tr><td>$\text{Pd}_2(\text{dba})_3$</td><td>1.5</td><td>XantPhos</td><td>6</td><td>90</td><td>20 (85)</td></tr><tr><td>PdCl_2</td><td>5</td><td>$\text{P}(t\text{-Bu})_3\cdot\text{HBF}_4$</td><td>10</td><td>reflux</td><td>60 (72)</td></tr><tr><td>$\text{Pd}_2(\text{dba})_3$</td><td>2.5</td><td>$\text{P}(t\text{-Bu})_3\cdot\text{HBF}_4$</td><td>5</td><td>reflux</td><td>90 (81)</td></tr><tr><td>$\text{Pd}_2(\text{dba})_3$</td><td>1.5</td><td>$\text{P}(t\text{-Bu})_3\cdot\text{HBF}_4$</td><td>3</td><td>120</td><td>12 (92)</td></tr></table>						Pd cat.	x	Ligand	y	Temp (°)	Time (h)	$\text{Pd}_2(\text{dba})_3$	1.5	XantPhos	6	90	20 (85)	PdCl_2	5	$\text{P}(t\text{-Bu})_3\cdot\text{HBF}_4$	10	reflux	60 (72)	$\text{Pd}_2(\text{dba})_3$	2.5	$\text{P}(t\text{-Bu})_3\cdot\text{HBF}_4$	5	reflux	90 (81)	$\text{Pd}_2(\text{dba})_3$	1.5	$\text{P}(t\text{-Bu})_3\cdot\text{HBF}_4$	3	120	12 (92)
Pd cat.	x	Ligand	y	Temp (°)	Time (h)																														
$\text{Pd}_2(\text{dba})_3$	1.5	XantPhos	6	90	20 (85)																														
PdCl_2	5	$\text{P}(t\text{-Bu})_3\cdot\text{HBF}_4$	10	reflux	60 (72)																														
$\text{Pd}_2(\text{dba})_3$	2.5	$\text{P}(t\text{-Bu})_3\cdot\text{HBF}_4$	5	reflux	90 (81)																														
$\text{Pd}_2(\text{dba})_3$	1.5	$\text{P}(t\text{-Bu})_3\cdot\text{HBF}_4$	3	120	12 (92)																														
		$\text{PdCl}_2(\text{dppf})\cdot\text{CH}_2\text{Cl}_2$ (5%), <i>i</i>-Pr₂NEt (3 eq), <i>i</i>-PrOH-H₂O, MW, 100°, 15 min		<table><tr><th>R</th><th></th></tr><tr><td></td><td>NO₂ (82)</td></tr><tr><td></td><td>OMe (61)</td></tr></table>	R			NO ₂ (82)		OMe (61)	220																								
R																																			
	NO ₂ (82)																																		
	OMe (61)																																		
C ₈																																			
		$\text{PdCl}_2(\text{dppf})\cdot\text{CH}_2\text{Cl}_2$ (2%), <i>t</i>-BuNH₂ (3 eq), <i>i</i>-PrOH-H₂O, reflux, overnight		(80)	108																														
		$\text{Pd}_2(\mu\text{-OAc})_2\cdot$ $(\text{P}(o\text{-tol})_2)_2$ (5%), MeOH, 20°, 1–2 min		(96)	133																														

TABLE 3A. CROSS-COUPLING OF ALKENYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

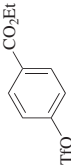
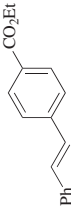
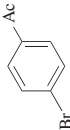
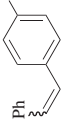
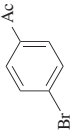
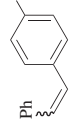
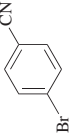
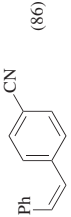
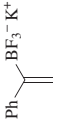
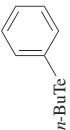
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Alkenyl/trifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc) ₂ , 1,4-dioxane, rt, 19 h	(58)	268
		Pd(PPh ₃) ₄ (8%), Ag ₂ O (2 eq), K ₂ CO ₃ (2 eq), MeOH, rt, ultrasound, 40 min		69
		Pd(PPh ₃) ₄ (8%), Ag ₂ O (2 eq), K ₂ CO ₃ (2 eq), MeOH, rt, ultrasound	(87)	69
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (2%), Et ₃ N (1 eq), <i>n</i> -PrOH, reflux, 8 h	(91)	261
		Pd(OAc) ₂ (1%), TBAB, K ₂ CO ₃ , H ₂ O, 120°		70
		Pd (2.5 ppm), Na ₂ CO ₃ (3.7 eq), TBAB (1 eq), EtOH-H ₂ O, MW, 150°, 5 min		214

C₈

	Pd cat. 6 (1%), TBAB, K ₂ CO ₃ , H ₂ O, 120°		70																											
		<table><tr><th>R¹</th><th>R²</th><th>Time</th></tr><tr><td>H</td><td>CN</td><td>— 14 h (84)</td></tr><tr><td>H</td><td>OMe</td><td>— 14 h (78)</td></tr><tr><td>H</td><td>OMe</td><td>MW 20 min (75)^c</td></tr><tr><td>H</td><td>Ac</td><td>— 3 h (91)</td></tr><tr><td>H</td><td>Ac</td><td>MW 20 min (93)^c</td></tr><tr><td>H</td><td>CO₂Et</td><td>— 8 h (81)</td></tr><tr><td>Me</td><td>H</td><td>— 14 h (88)</td></tr><tr><td>Me</td><td>H</td><td>MW 20 min (92)</td></tr></table>	R ¹	R ²	Time	H	CN	— 14 h (84)	H	OMe	— 14 h (78)	H	OMe	MW 20 min (75) ^c	H	Ac	— 3 h (91)	H	Ac	MW 20 min (93) ^c	H	CO ₂ Et	— 8 h (81)	Me	H	— 14 h (88)	Me	H	MW 20 min (92)	
R ¹	R ²	Time																												
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	Pd cat. 6 (1%), TBAB, K ₂ CO ₃ , H ₂ O, 120°		70																											
	Pd cat. 6 (1%), TBAB, K ₂ CO ₃ , H ₂ O		70																											
	Pd(OAc) ₄ (5%), K ₃ PO ₄ (6 eq), <i>n</i> -Bu ₄ NBr (0.5%), EtOH, 80°, 24 h		269																											
	PdCl ₂ (dppf)•CH ₂ Cl ₂ , Et ₃ N, <i>t</i> -PrOH–H ₂ O		270																											

TABLE 3A. CROSS-COUPLING OF ALKENYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Alkenyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (2%), CsOAc (2 eq), THF- H_2O , reflux	 (95)	236
		$\text{Pd}(\text{OAc})_2$ (1%), TBAB, K_2CO_3 , H_2O , 120° , 14 h	 (79) ^c (Z)/(E) = 80:20	70
		Pd cat. 6 (1%), TBAB, K_2CO_3 , H_2O , 120° , 14 h	 (55) (Z)/(E) = 80:20	70
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (2%), <i>t</i> - BuNH_2 (3 eq), <i>i</i> - PrOH - H_2O , reflux, 6 h	 (86)	71
		$\text{Pd}(\text{PPh}_3)_4$ (10%), base (3 eq), additive (2 eq), MeOH, ultrasound		144
		Base	Cs_2CO_3 Et_3N Et_3N K_2CO_3	(81) (84) (61) (60)

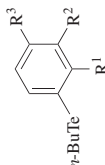
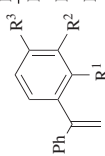
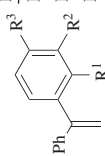
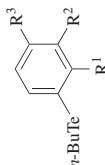
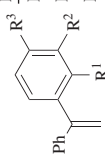
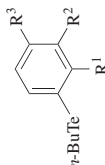
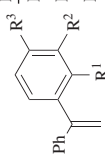
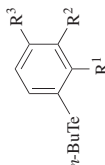
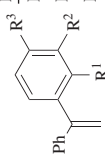
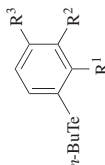
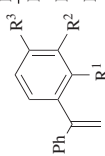
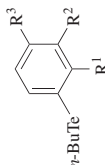
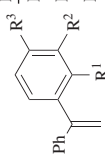
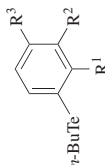
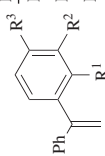
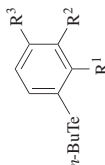
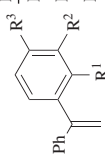
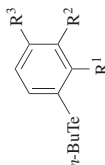
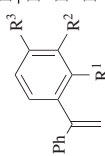
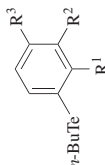
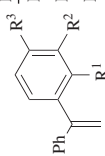
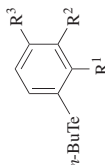
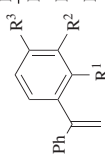
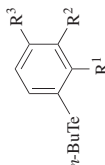
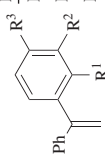
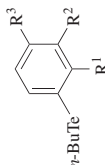
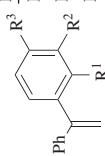
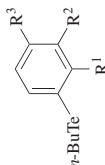
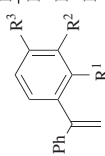
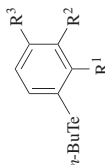
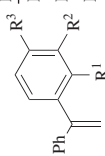
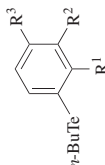
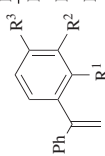
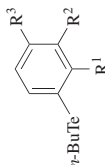
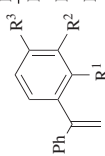
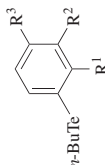
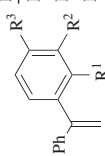
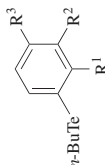
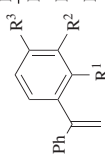
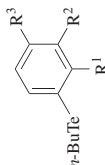
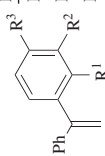
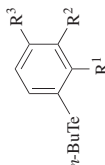
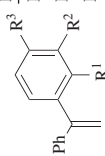
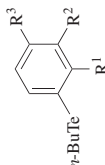
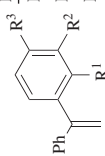
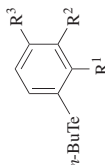
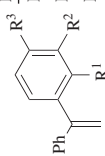
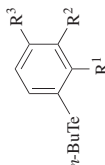
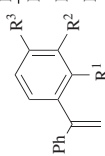
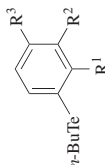
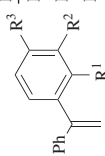
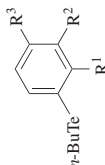
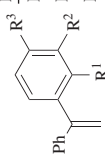
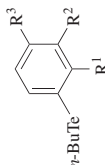
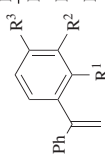
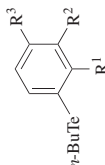
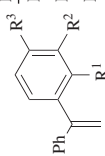
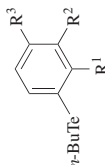
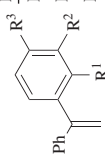
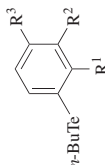
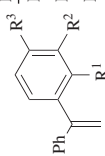
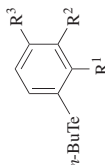
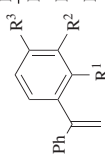
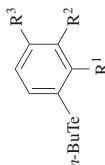
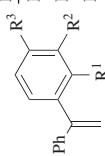
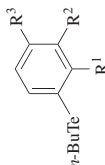
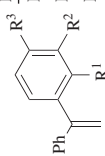
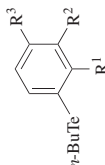
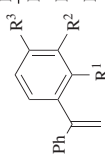
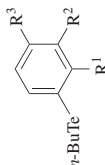
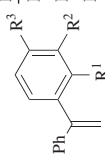
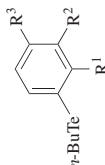
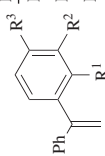
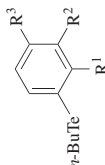
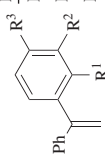
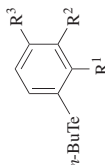
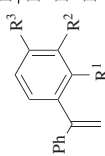
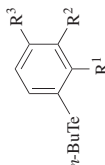
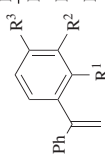
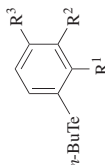
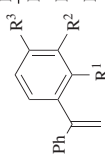
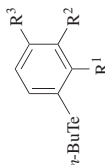
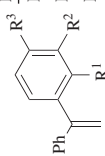
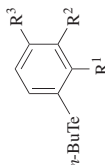
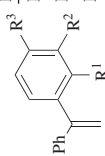
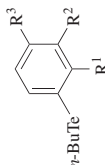
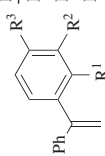
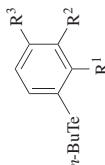
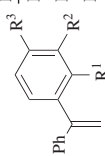
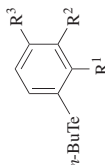
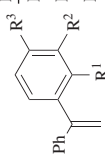
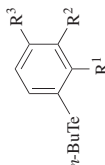
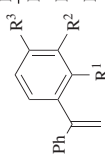
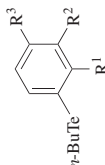
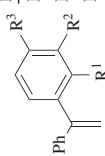
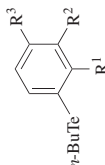
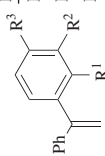
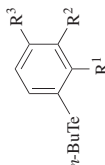
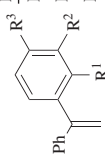
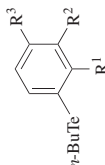
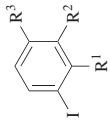
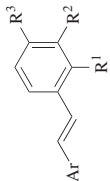
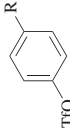
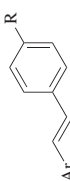
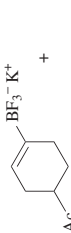
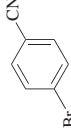
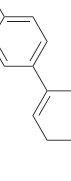
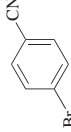
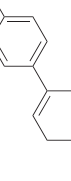
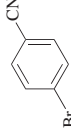
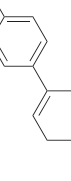
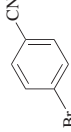
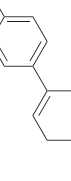
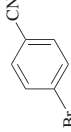
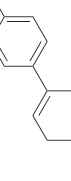
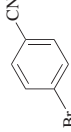
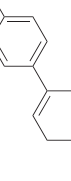
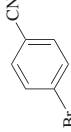
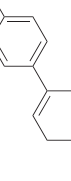
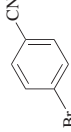
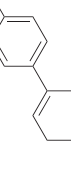
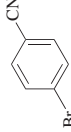
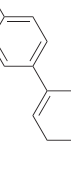
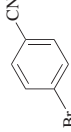
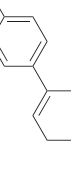
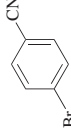
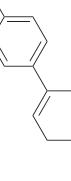
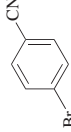
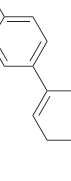
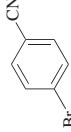
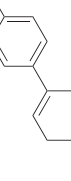
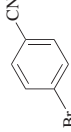
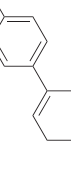
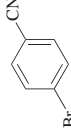
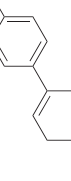
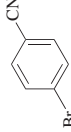
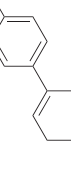
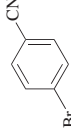
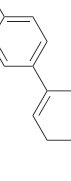
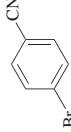
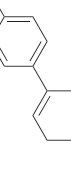
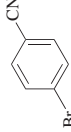
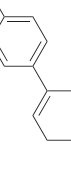
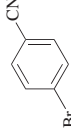
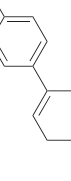
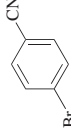
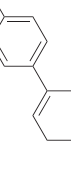
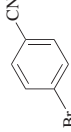
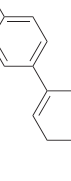
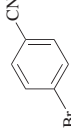
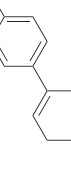
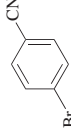
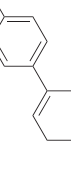
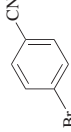
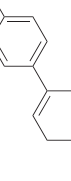
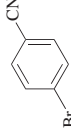
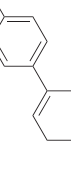
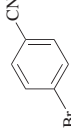
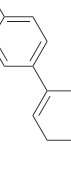
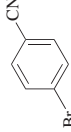
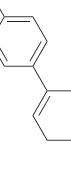
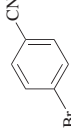
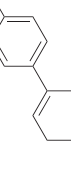
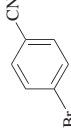
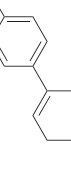
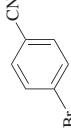
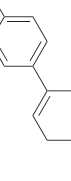
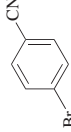
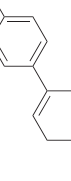
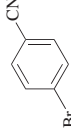
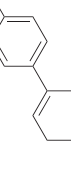
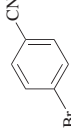
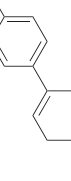
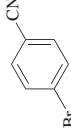
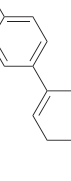
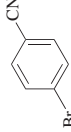
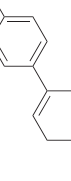
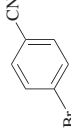
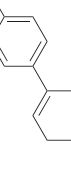
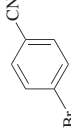
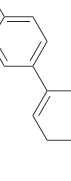
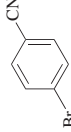
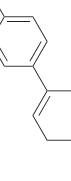
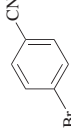
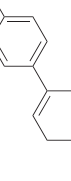
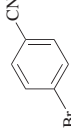
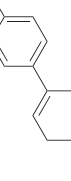
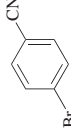
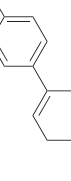
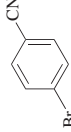
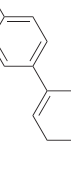
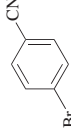
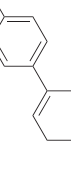
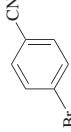
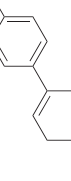
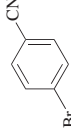
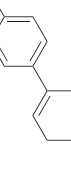
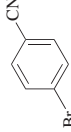
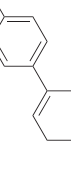
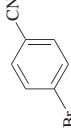
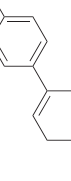
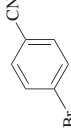
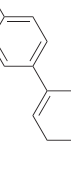
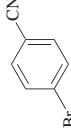
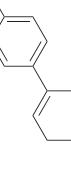
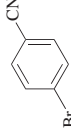
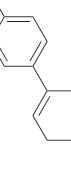
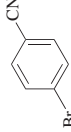
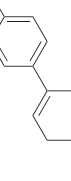
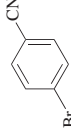
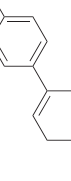
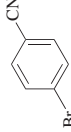
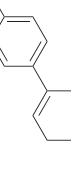
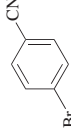
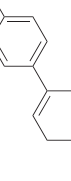
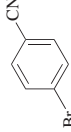
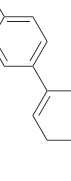
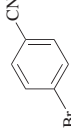
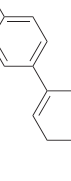
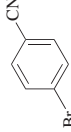
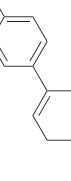
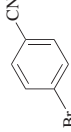
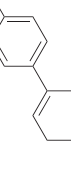
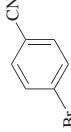
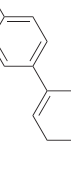
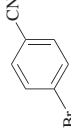
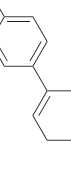
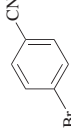
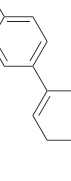
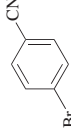
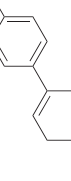
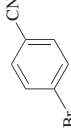
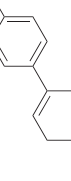
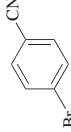
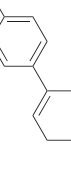
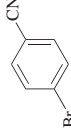
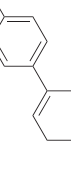
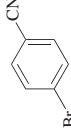
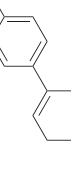
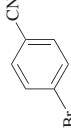
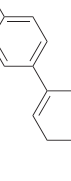
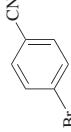
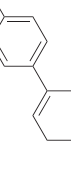
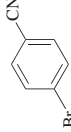
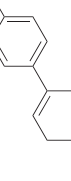
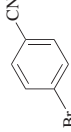
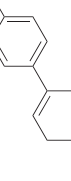
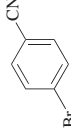
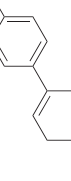
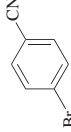
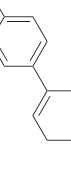
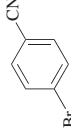
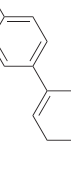
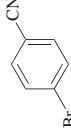
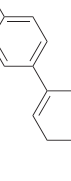
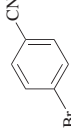
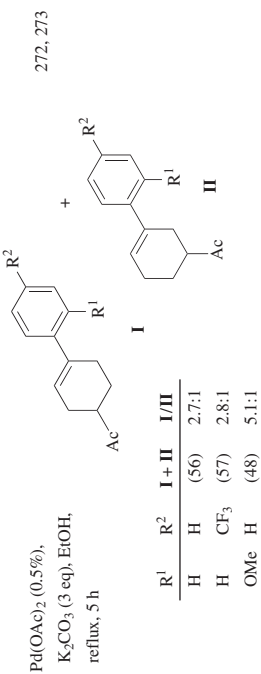
		R ¹	R ²	R ³	Time (min)	
<i>n</i> -BuTe		H	H	H	20	(80)
		H	H	Br	20	(91)
		H	H	Cl	20	(80)
		H	H	F	20	(79)
		H	H	OH	20	(87)
		H	H	Me	20	(82)
		H	H	OMe	20	(83)
		H	CF ₃	H	20	(85)
		Me	H	H	30	(76)
		Me	H	F	30	(74)
		X	R			
		Br	H		(70)	148
		Br	NO ₂		(46)	
		I	CO ₂ Me		(80)	
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						

TABLE 3A. CROSS-COUPLING OF ALKENYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Alkenyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.																																																							
		$\text{PdCl}_2(\text{dppf}) \bullet \text{CH}_2\text{Cl}_2$ (2%), <i>i</i>-PrNEt₂, <i>i</i>-PrOH–H₂O, MW, 100°, 10 min	 271																																																								
	Ar <table border="1"> <thead> <tr> <th>Ar</th><th>R¹</th><th>R²</th><th>R³</th><th>Ref.</th></tr> </thead> <tbody> <tr> <td>Ph</td><td>H</td><td>H</td><td>H</td><td>(67)</td></tr> <tr> <td>Ph</td><td>H</td><td>H</td><td>F</td><td>(61)</td></tr> <tr> <td>Ph</td><td>H</td><td>H</td><td>Cl</td><td>(99)</td></tr> <tr> <td>Ph</td><td>H</td><td>H</td><td>Ac</td><td>(91)</td></tr> <tr> <td>Ph</td><td>H</td><td>NO₂</td><td>H</td><td>(76)</td></tr> <tr> <td>Ph</td><td>OMe</td><td>H</td><td>H</td><td>(79)</td></tr> <tr> <td>Ph</td><td>Me</td><td>H</td><td>Me</td><td>(96)</td></tr> <tr> <td>Ph</td><td>Me</td><td>H</td><td>H</td><td>(92)</td></tr> <tr> <td>4-ClC₆H₄</td><td>H</td><td>NO₂</td><td>H</td><td>(87)</td></tr> <tr> <td>4-ClC₆H₄</td><td>H</td><td>H</td><td>OMe</td><td>(85)</td></tr> </tbody> </table>	Ar	R ¹	R ²	R ³	Ref.	Ph	H	H	H	(67)	Ph	H	H	F	(61)	Ph	H	H	Cl	(99)	Ph	H	H	Ac	(91)	Ph	H	NO ₂	H	(76)	Ph	OMe	H	H	(79)	Ph	Me	H	Me	(96)	Ph	Me	H	H	(92)	4-ClC ₆ H ₄	H	NO ₂	H	(87)	4-ClC ₆ H ₄	H	H	OMe	(85)			
Ar	R ¹	R ²	R ³	Ref.																																																							
Ph	H	H	H	(67)																																																							
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Ph	Me	H	Me	(96)																																																							
Ph	Me	H	H	(92)																																																							
4-ClC ₆ H ₄	H	NO ₂	H	(87)																																																							
4-ClC ₆ H ₄	H	H	OMe	(85)																																																							
		$\text{PdCl}_2(\text{dppf}) \bullet \text{CH}_2\text{Cl}_2$ (5%), <i>i</i>-Pr₂NEt (3 eq), <i>i</i>-PrOH–H₂O, MW, 100°, 15 min	 220																																																								
		$\text{Pd}(\text{OAc})_2$ (1.5%), K₂CO₃ (3 eq), EtOH, reflux, 5 h	 272, 273																																																								
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C₉

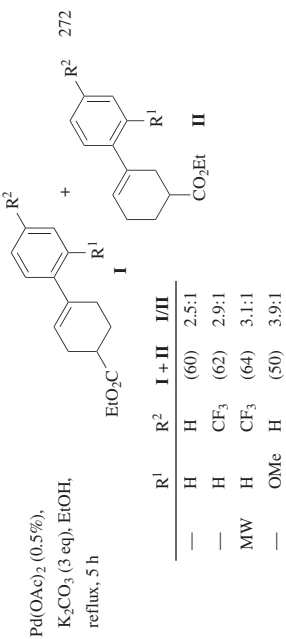
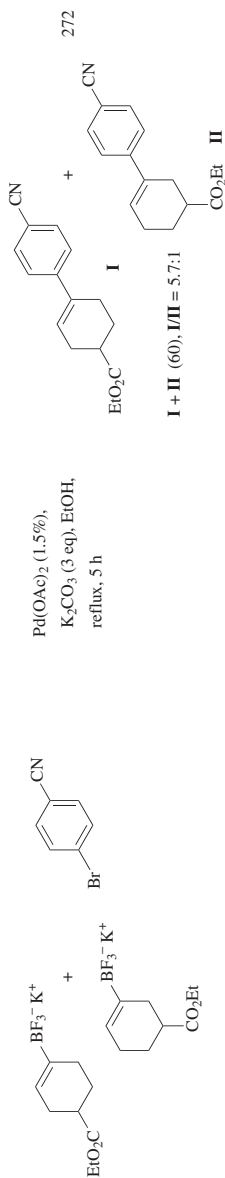


TABLE 3A. CROSS-COUPLING OF ALKENYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Alkenyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc) ₂ (0.5%), K ₂ CO ₃ (3 eq), EtOH, reflux	 I + II (53), I/II = 2.3:1	272
		Pd(OAc) ₂ (0.5%), K ₂ CO ₃ (3 eq), EtOH, reflux	 I + II (73), I/II = 4.4:1	273
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (2%), <i>i</i> -PrNEt ₂ , <i>i</i> -PrOH-H ₂ O, MW, 100°, 10 min	 n-C ₇ H ₁₅ (91)	271
		Pd ₂ (dba) ₃ (1.5%), P(<i>t</i> -Bu) ₃ •HBF ₄ (3%), C ₅ H ₅ CO ₃ (3 eq), THF-H ₂ O, 120°, 12 h	 (79)	148

C₉

$\text{PdCl}_2(\text{dppf}) \bullet \text{CH}_2\text{Cl}_2$ (2%),
i-PrNEt₃, *i*-PrOH–H₂O,
MW, 100°, 10 min

R ¹	R ²	
H	Cl	(92)
H	Ac	(95)
NO ₂	H	(81)

C₁₀

$\text{PdCl}_2(\text{dppf}) \bullet \text{CH}_2\text{Cl}_2$ (2%),
i-PrNEt₃, *i*-PrOH–H₂O,
MW, 100°, 10 min

(90)

C₁₀

$\text{PdCl}_2(\text{dppf}) \bullet \text{CH}_2\text{Cl}_2$ (2%),
base (3 eq), *i*-PrOH–H₂O,
reflux

R ¹	R ²	R ³	R ⁴	Base	Time (h)	
H	H	F	H	Et ₃ N	14	(59)
H	H	NO ₂	H	<i>t</i> -BuNH ₂	2	(71)
H	H	CN	H	<i>t</i> -BuNH ₂	6	(87)
H	H	CF ₃	H	<i>t</i> -BuNH ₂	10	(65)
H	H	Ac	H	<i>t</i> -BuNH ₂	6	(69)
H	OMe	H	H	<i>t</i> -BuNH ₂	6	(61)
CN	H	H	H	<i>t</i> -BuNH ₂	6	(75)
Me	H	Me	Me	Et ₃ N	14	(38)
Ac	H	H	H	<i>t</i> -BuNH ₂	14	(63)

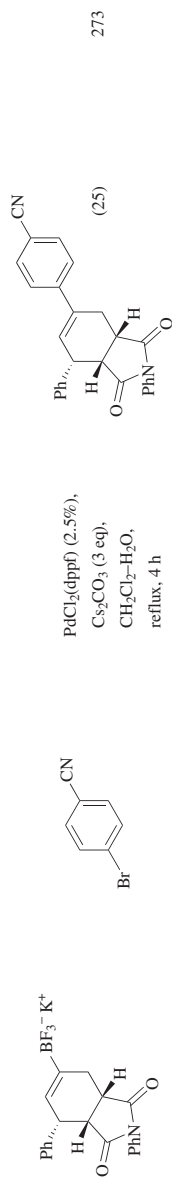
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C₁₀

TABLE 3A. CROSS-COUPLING OF ALKENYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Alkenyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.														
		Pd cat. 6 (1%), TBAB, K ₂ CO ₃ , H ₂ O, 120°, 14 h		70														
			<table><tr><th colspan="2">R</th><th>Time</th></tr><tr><td>OMe</td><td>—</td><td>22 h (81)</td></tr><tr><td>OMe</td><td>MW</td><td>20 min (91)^c</td></tr><tr><td>Ac</td><td>—</td><td>3 h (93)</td></tr><tr><td>Ac</td><td>MW</td><td>20 min (89)</td></tr></table>	R		Time	OMe	—	22 h (81)	OMe	MW	20 min (91) ^c	Ac	—	3 h (93)	Ac	MW	20 min (89)
R		Time																
OMe	—	22 h (81)																
OMe	MW	20 min (91) ^c																
Ac	—	3 h (93)																
Ac	MW	20 min (89)																
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (2%), <i>t</i> -BuNH ₂ (3 eq), <i>i</i> -PrOH–H ₂ O, reflux, 10 h		106														
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (2%), <i>t</i> -BuNH ₂ (3 eq), <i>i</i> -PrOH–H ₂ O, reflux		<table><tr><th colspan="2">R</th><th>Time (h)</th></tr><tr><td>OMe</td><td>6</td><td>(60)</td></tr><tr><td>Ac</td><td>2</td><td>(65)</td></tr></table>	R		Time (h)	OMe	6	(60)	Ac	2	(65)					
R		Time (h)																
OMe	6	(60)																
Ac	2	(65)																
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (2%), <i>t</i> -BuNH ₂ (3 eq), <i>i</i> -PrOH–H ₂ O, reflux		<table><tr><th colspan="2">R</th><th>Time (h)</th></tr><tr><td>NO₂</td><td>3</td><td>(76)</td></tr><tr><td>Ac</td><td>8</td><td>(60)</td></tr></table>	R		Time (h)	NO ₂	3	(76)	Ac	8	(60)					
R		Time (h)																
NO ₂	3	(76)																
Ac	8	(60)																
		Pd ₂ (dba) ₃ (1.5%), P(<i>t</i> -Bu) ₃ •HBF ₄ (3%), Cs ₂ CO ₃ (3 eq), THF–H ₂ O, 120°, 12 h		148														

C₁₄



^a The yield of the product was determined by GC analysis.

^b The yield of the crude product was determined by ¹⁹F NMR.

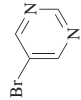
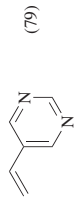
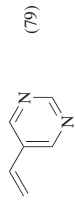
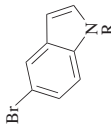
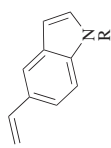
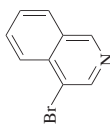
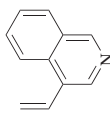
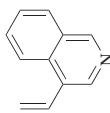
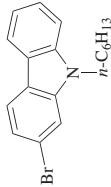
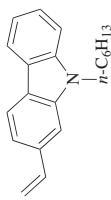
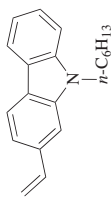
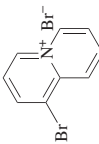
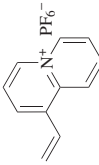
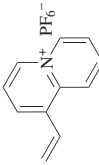
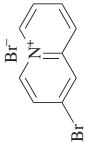
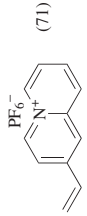
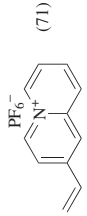
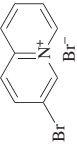
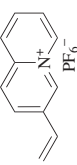
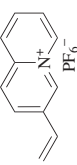
^c The yield of the crude product was determined by ¹H NMR.

^d The trifluoroborate derivative was prepared by a Diels-Alder reaction and was not isolated. The indicated yield is a two-step yield.

^e The trifluoroborate derivative was prepared by a Diels-Alder reaction and was not isolated. The indicated yield is a multi-step yield.

TABLE 3B. CROSS-COUPLING OF ALKENYLTRIFLUOROBORATES WITH HETEROARYL ELECTROPHILES

Alkenyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2 		$PdCl_2(dppf) \cdot CH_2Cl_2$ (2%), Et_3N (1 eq), <i>n</i> - $PrOH$, reflux, 3 h	 (60)	261
		Pd cat. 6 (1%), TBAB, K_2CO_3 , H_2O , 120°	 Time — 14 h (75) MW 20 min (86)	70
		$PdCl_2$ (2%), PPh_3 (6%), Cs_2CO_3 (3 eq), $THF-H_2O$, 85° , 22 h	 R — H (64) Ac (66)	106
		$PdCl_2$ (2%), PPh_3 (6%), Cs_2CO_3 (3 eq), $THF-H_2O$, 85° , 22 h	 (70)	106
		$Pd(OAc)_2$ (5%), PPh_3 (10%), Cs_2CO_3 (3 eq), $THF-H_2O$, 50° , 3 h	 (82)	147
		$PdCl_2$ (2%), PPh_3 (6%), Cs_2CO_3 (3 eq), $THF-H_2O$, 85° , 22 h	 (70)	106
		$PdCl_2$ (2%), PPh_3 (6%), Cs_2CO_3 (3 eq), $THF-H_2O$, 85° , 22 h	 (71)	106
		Pd cat. 6 (1%), TBAB, K_2CO_3 , H_2O , 120°	 Time — 14 h (52) MW 30 min (81)	70

			106
		(79)	
			106
		R	
		H (38)	
		Ts (88)	
		Boc (77)	
		Bn (71)	
			106
		(88)	
			265
		(41)	
			122
		(72)	
			122
		(71)	
			122
		(70)	

PdCl₂ (2%), PPh₃ (6%),
Cs₂CO₃ (3 eq),
THF-H₂O, 85°, 22 h

PdCl₂ (2%), PPh₃ (6%),
Cs₂CO₃ (3 eq), THF-H₂O,
85°, 22 h

PdCl₂ (2%), PPh₃ (6%),
Cs₂CO₃ (3 eq), THF-H₂O,
85°, 22 h

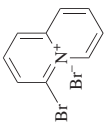
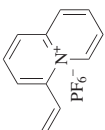
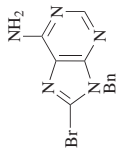
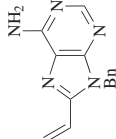
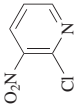
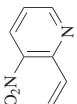
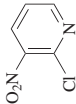
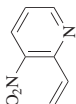
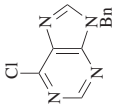
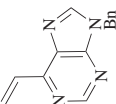
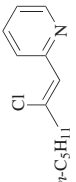
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Et₃N (1 eq), *n*-PrOH,
reflux, 14 h

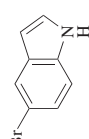
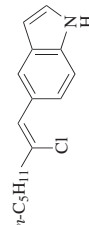
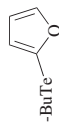
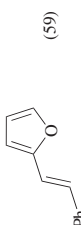
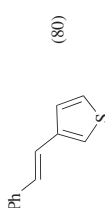
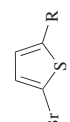
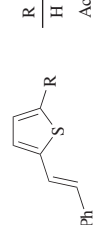
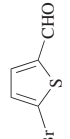
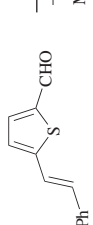
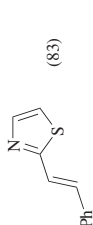
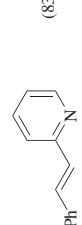
1. Pd(OAc)₂ (1%),
K₂CO₃ (3 eq), H₂O, 65°, 5 h
2. H₄NPF₆

1. Pd(OAc)₂ (1%),
K₂CO₃ (3 eq), H₂O, 65°, 5 h
2. H₄NPF₆

1. Pd(OAc)₂ (1%),
K₂CO₃ (3 eq),
H₂O, 65°, 5 h
2. H₄NPF₆

TABLE 3B. CROSS-COUPLING OF ALKENYLTRIFLUOROBORATES WITH HETEROARYL ELECTROPHILES (Continued)

Alkenyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂				
		1. Pd(OAc) ₂ (1%), K ₂ CO ₃ (3 eq), H ₂ O, 65°, 5 h 2. H ₄ NPF ₆	 (53)	122
		Pd(PPh ₃) ₄ (2%), K ₂ CO ₃ (3 eq), MeCN-H ₂ O, MW, 150°, 5 min	 (0)	104
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (2%), Et ₃ N (1 eq), <i>n</i> -PrOH, reflux, 3 h	 (62)	261
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (9%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, reflux, 6 h	 (64)	261
C ₇		Pd(PPh ₃) ₄ (2%), K ₂ CO ₃ (3 eq), MeCN-H ₂ O, MW, 150°, 5 min	 (97)	104
		Pd ₂ (dba) ₃ (1.5%), P(<i>t</i> -Bu) ₃ •HBF ₄ (3%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, 120°, 12 h	 (25)	148

		$\text{Pd}_2(\text{dba})_3$ (1.5%), $\text{P}(\text{-}i\text{-Bu})_3\text{•HBF}_4$ (3%), Cs_2CO_3 (3 eq), THF–H_2O, 120°, 36 h	(77)	148
		$\text{Pd}(\text{PPh}_3)_4$ (8%), Ag_2O (2 eq), K_2CO_3 (2 eq), MeOH, rt, ultrasound	(59)	69
		$\text{PdCl}_2(\text{dppf})\text{•CH}_2\text{Cl}_2$ (2%), $i\text{-BuNH}_2$ (3 eq), $i\text{-PrOH-H}_2\text{O}$, reflux, 5 h	(80)	71
		$\text{PdCl}_2(\text{dppf})\text{•CH}_2\text{Cl}_2$ (2%), $i\text{-BuNH}_2$ (3 eq), $i\text{-PrOH-H}_2\text{O}$, reflux, 3 h	R H (69) Ac (91)	71
		Pd cat. 6 (1%), TBAB, K_2CO_3, H_2O, 120°	Time — 12 h (80) MW 20 min (82)	70
		$\text{PdCl}_2(\text{dppf})\text{•CH}_2\text{Cl}_2$ (2%), Et_3N (3 eq), $i\text{-PrOH-H}_2\text{O}$, reflux, 3 h	(83)	71
		$\text{PdCl}_2(\text{dppf})\text{•CH}_2\text{Cl}_2$ (2%), Et_3N (1 eq), $n\text{-PrOH}$, reflux, 8 h	(83)	261

C₈



TABLE 3B. CROSS-COUPLING OF ALKENYLTRIFLUOROBORATES WITH HETEROARYL ELECTROPHILES (Continued)

Alkenyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(PPh ₃) ₄ (8%), Ag ₂ O (2 eq), K ₂ CO ₃ (2 eq), MeOH, rt, ultrasound		69
		Pd cat. 6 (1%), TBAB, K ₂ CO ₃ , H ₂ O, 120°		70
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (2%), <i>t</i> -BuNH ₂ (3 eq), <i>i</i> -PrOH–H ₂ O, reflux, 4 h		71
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (2%), <i>t</i> -BuNH ₂ (3 eq), <i>i</i> -PrOH–H ₂ O, reflux, 6 h		71
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (2%), <i>t</i> -BuNH ₂ (3 eq), <i>i</i> -PrOH–H ₂ O, reflux, 9 h		71
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (2%), <i>t</i> -BuNH ₂ (3 eq), <i>i</i> -PrOH–H ₂ O, reflux		71

C₈

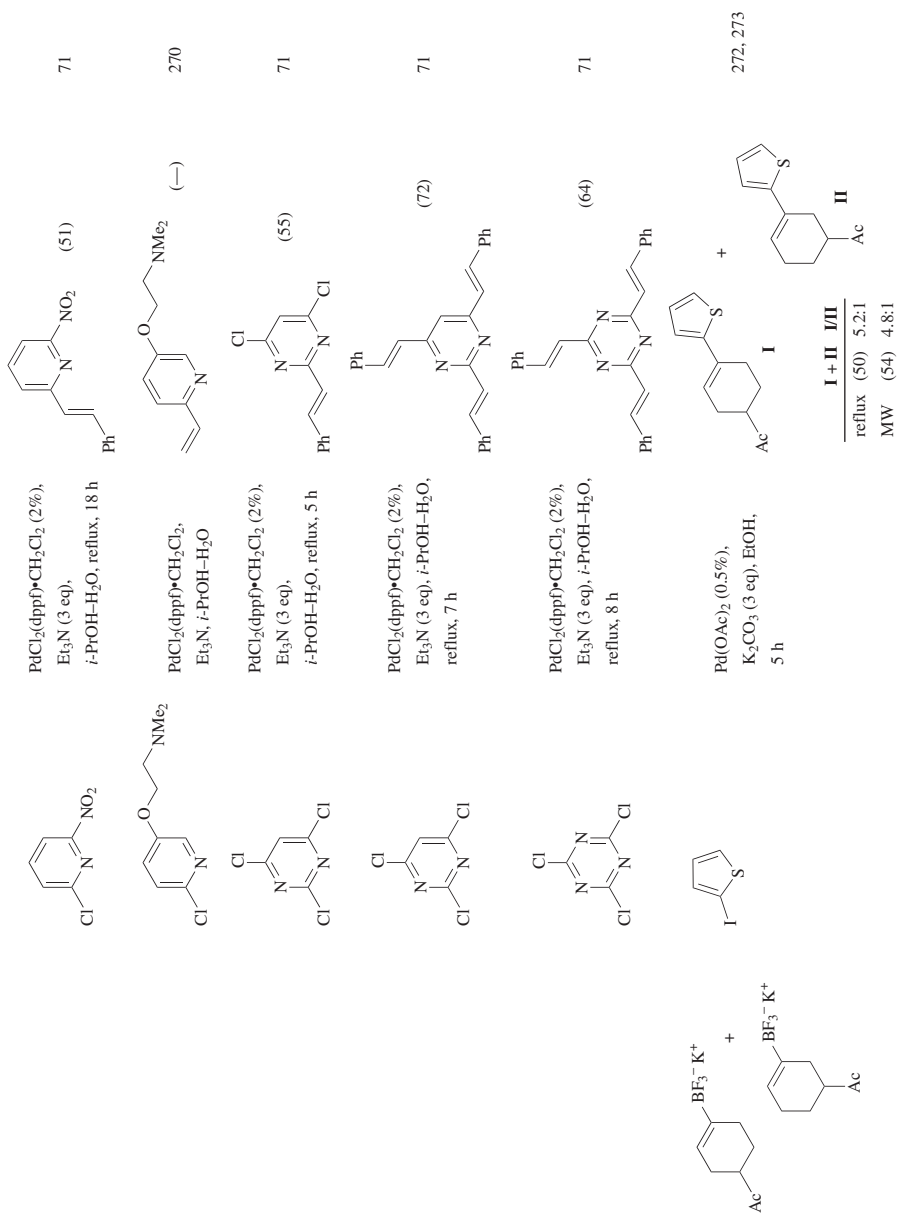
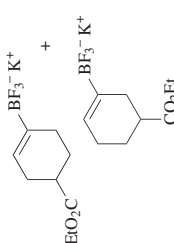
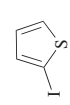
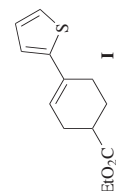
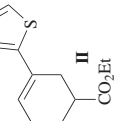
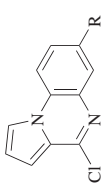
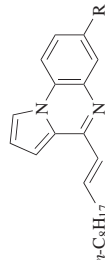
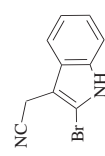
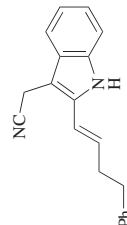


TABLE 3B. CROSS-COUPLING OF ALKENYLTRIFLUOROBORATES WITH HETEROARYL ELECTROPHILES (Continued)

Alkenyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C₉  + 		Pd(OAc)₂ (0.5%), K₂CO₃ (3 eq), EtOH, reflux, 5 h	 I +  II I + II (55), I/II = 3.8:1 272	
C₁₀ 		PdCl₂(dppf)•CH₂Cl₂, Cs₂CO₃, THF-H₂O, reflux	 <i>n</i>-C₈H₁₇ R H OMe 274 (66) (69)	
		Pd(OAc)₂ (5%), PPh₃ (10%), Cs₂CO₃ (3 eq), THF-H₂O, 70°, 3 h	 (90) 72	

^a The trifluoroborate derivative was prepared by a Diels-Alder reaction and was not isolated. The indicated yield is a two-step yield.

TABLE 3C. CROSS-COUPLING OF ALKENYLTRIFLUOROBORATES WITH ALKENYL ELECTROPHILES

Alkenyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$\text{PdCl}_2(\text{dppf}) \bullet \text{CH}_2\text{Cl}_2$ (9%), Cs_2CO_3 (3 eq), $\text{THF-H}_2\text{O}$, reflux, 6 h	(72)	261
		$\text{PdCl}_2(\text{dppf}) \bullet \text{CH}_2\text{Cl}_2$ (2%), Et_3N (1 eq), <i>n</i> - PrOH , reflux, 3 h	(74)	261
		$\text{Pd}(\text{OAc})_2$ (5%), PPh_3 (10%), Cs_2CO_3 (3 eq), $\text{THF-H}_2\text{O}$, 70°, 2.5 h	(73)	72
		$\text{PdCl}_2(\text{dppf}) \bullet \text{CH}_2\text{Cl}_2$ (9%), Cs_2CO_3 (3 eq), $\text{THF-H}_2\text{O}$, reflux, 9 h	(51)	162
		$\text{Pd}(\text{OAc})_2$ (5%), PPh_3 (10%), Cs_2CO_3 (3 eq), $\text{THF-H}_2\text{O}$, 50°		147
		$\text{PdCl}_2(\text{dppf}) \bullet \text{CH}_2\text{Cl}_2$ (25%), Cs_2CO_3 (20 eq), $\text{THF-H}_2\text{O}$, 80°, overnight	(61)	115

TABLE 3C. CROSS-COUPLING OF ALKENYLTRIFLUOROBORATES WITH ALKENYL ELECTROPHILES (Continued)

	Alkenyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.					
C ₂			Pd(OAc) ₂ (5%), PPh ₃ (10%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, 60°, 12 h	(73)	147					
			Pd ₂ (dba) ₃ (2.5%), RuPhos (10%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, 80°, 18-36 h	 R <table><tr><td>CO₂Me</td><td>(87)</td><td>—</td></tr><tr><td>NO₂</td><td>(69)</td><td>85:15</td></tr></table> n-C ₃ H ₁₁	CO ₂ Me	(87)	—	NO ₂	(69)	85:15
CO ₂ Me	(87)	—								
NO ₂	(69)	85:15								
C ₃			Pd(OAc) ₂ (10%), dppe (10%), <i>t</i> -BuNH ₂ , THF, reflux		275					
			PdCl ₂ (dppf)•CH ₂ Cl ₂ (2%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, reflux, 24 h	(91)	276					
			Pd(OAc) ₂ (5%), PPh ₃ (10%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, reflux, 24 h	(70)	147					
			Pd(OAc) ₂ (5%), PPh ₃ (10%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, rt, 15 h	(56)	147					

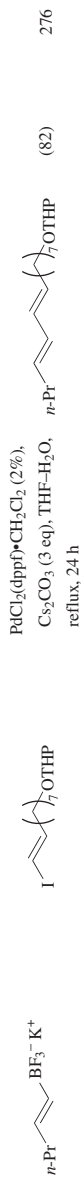
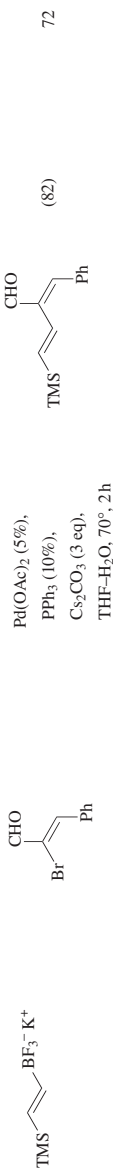
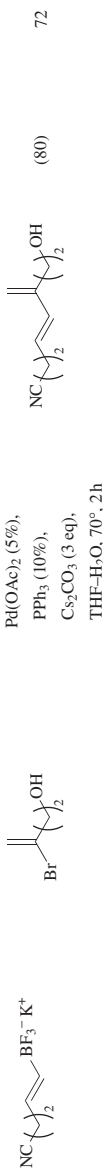
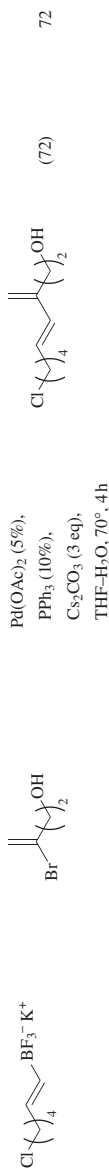
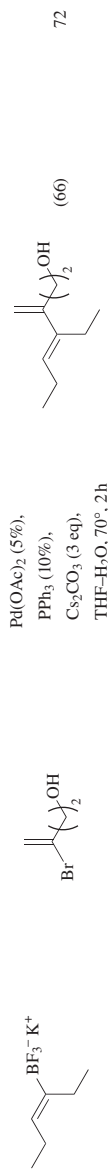
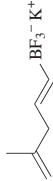
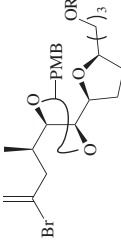
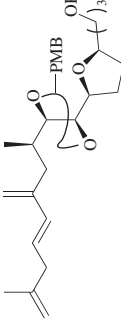
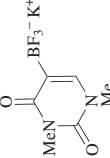
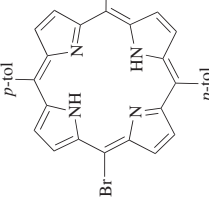
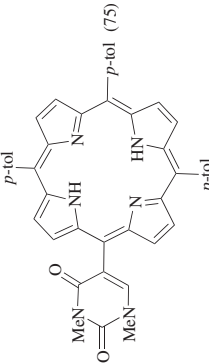
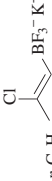
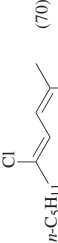
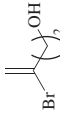
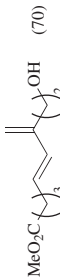
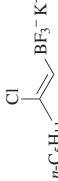
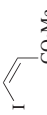
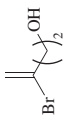
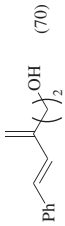
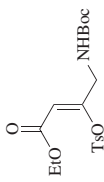
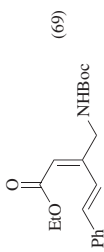
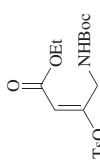
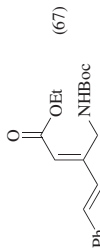
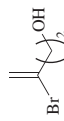
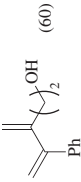
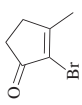
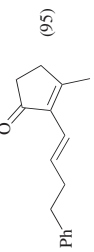
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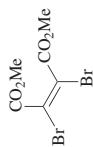
TABLE 3C. CROSS-COUPLING OF ALKENYLTRIFLUOROBORATES WITH ALKENYL ELECTROPHILES (Continued)

Alkenyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
 $\text{BF}_3^- \text{K}^+$	 $\text{R} = \text{TBDPS}$	$\text{Pd}(\text{OAc})_2$ (5%), PPh_3 (10%), Cs_2CO_3 (3 eq), $\text{THF-H}_2\text{O}$, reflux, 1.5 h	 $\text{R} = \text{TBDPS}$	163
 $\text{BF}_3^- \text{K}^+$	 $\text{R} = \text{TBDPS}$	$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (25%), Cs_2CO_3 (20 eq), $\text{THF-H}_2\text{O}$, 80°, overnight	 $\text{R} = \text{TBDPS}$	115
 $\text{BF}_3^- \text{K}^+$	 Br	$\text{Pd}_2(\text{dba})_3$ (1.5%), $\text{P}(\text{-}i\text{-Bu})_3 \cdot \text{HBF}_4$ (3%), Cs_2CO_3 (3 eq), $\text{THF-H}_2\text{O}$, 120°, 12 h	 Cl	148
 $\text{BF}_3^- \text{K}^+$	 Br	$\text{Pd}(\text{OAc})_2$ (5%), PPh_3 (10%), Cs_2CO_3 (3 eq), $\text{THF-H}_2\text{O}$, 70°, 2 h	 MeO_2C	72
 $\text{BF}_3^- \text{K}^+$	 I	$\text{Pd}(\text{P}(\text{-}i\text{-Bu})_3)_2$ (2.5%), Cs_2CO_3 (3 eq), $\text{THF-H}_2\text{O}$, 80°, 72 h	 Cl	148

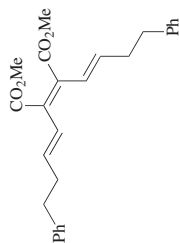
				Base	Additive
				Pd(PPh ₃) ₄ (20%), base (2 eq), additive (2 eq), MeOH, ultrasound, 20 min	K ₂ CO ₃ Ag ₂ O (65) Cs ₂ CO ₃ Ag ₂ O (67) 73 Et ₃ N Ag ₂ O (66) Et ₃ N AgOAc (84)
				Pd(PPh ₃) ₄ (20%), Et ₃ N (2 eq), AgOAc (2 eq), MeOH, ultrasound, 20 min	R ¹ R ² R ³ H H 4-BrC ₆ H ₄ (82) 73 H H <i>i</i> -Bu (70) H Ph H (85) Me Ph Cl (82) CH ₂ OH H H (57)
				Pd(PPh ₃) ₄ (20%), Et ₃ N (2 eq), AgOAc (2 eq), MeOH, ultrasound, 20 min	(67) 73
				Pd(PPh ₃) ₄ (20%), Et ₃ N (2 eq), AgOAc (2 eq), MeOH, ultrasound, 20 min	(48) 73
				Pd(PPh ₃) ₄ (20%), Et ₃ N (2 eq), AgOAc (2 eq), MeOH, ultrasound, 20 min	(79) 73

TABLE 3C. CROSS-COUPLING OF ALKENYLTRIFLUOROBORATES WITH ALKENYL ELECTROPHILES (Continued)

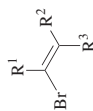
Alkenyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈				
		Pd(OAc) ₂ (5%), PPh ₃ (10%), Cs ₂ CO ₃ (3 eq), THF–H ₂ O, 70°, 2 h	 (70)	72
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (5%), Et ₃ N (1 eq), <i>n</i> -PrOH, 65°	 (69)	68
		PdCl ₂ (PPh ₃) ₂ (5%), aq Na ₂ CO ₃ (3.5 eq), THF, 60°, 14 h	 (67)	68
		Pd(OAc) ₂ (5%), PPh ₃ (10%), Cs ₂ CO ₃ (3 eq), THF–H ₂ O, 70°, 12 h	 (60)	72
C ₁₀				
		Pd(OAc) ₂ (5%), PPh ₃ (10%), Cs ₂ CO ₃ (3 eq), THF–H ₂ O, 70°, 8 h	 (95)	72



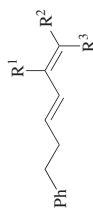
$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (5%),
 Cs_2CO_3 (3 eq),
 $\text{THF}-\text{H}_2\text{O}$, 70° , 5 h



72

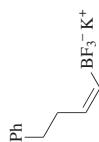


$\text{Pd}(\text{OAc})_2$ (5%),
 PPh_3 (10%),
 Cs_2CO_3 (3 eq),
 $\text{THF}-\text{H}_2\text{O}$, 70°

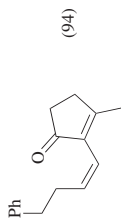


72

R^1	R^2	R^3	Time (h)
H	Me	Me	4 (70)
H	H	$(\text{CH}_2)_3\text{CN}$	2 (78)
Me	Me	Me	6 (95)
CHO	H	Ph	2 (88)
$(\text{CH}_2)_2\text{OH}$	H	H	2 (79)
$(\text{CH}_2)_2\text{OTIPS}$	H	H	2 (85)
$(\text{CH}_2)_2\text{OTBS}$	H	H	2 (80)
$(\text{CH}_2)_2\text{OTES}$	H	H	2 (80)



$\text{Pd}(\text{OAc})_2$ (5%),
 PPh_3 (10%),
 Cs_2CO_3 (3 eq),
 $\text{THF}-\text{H}_2\text{O}$, 70° , 12 h



72

TABLE 3C. CROSS-COUPLING OF ALKENYLTRIFLUOROBORATES WITH ALKENYL ELECTROPHILES (Continued)

Alkenyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.																				
C_{10} 		Pd source (9%), ligand (18%), base (3 eq), THF-H ₂ O, reflux, 14 h		72																				
				Pd Source	Ligand	Base	ds	Pd(PPh ₃) ₄	—	Cs ₂ CO ₃	>99 (81)	Pd(OAc) ₂	PPh ₃	Cs ₂ CO ₃	>99 (87)	Pd(OAc) ₂	PPh ₃	K ₂ CO ₃	98 (67)	Pd(OAc) ₂	PCy ₃	Cs ₂ CO ₃	95 (33)	
				Pd Source	Ligand	Base	ds																	
				Pd(PPh ₃) ₄	—	Cs ₂ CO ₃	>99 (81)																	
				Pd(OAc) ₂	PPh ₃	Cs ₂ CO ₃	>99 (87)																	
Pd(OAc) ₂	PPh ₃	K ₂ CO ₃	98 (67)																					
Pd(OAc) ₂	PCy ₃	Cs ₂ CO ₃	95 (33)																					
C_{11} 		Pd(OAc) ₂ (5%), PPh ₃ (10%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, 70°, 2 h		72																				
				(85)																				
C_{11} 		Pd ₂ (dba) ₃ , P(<i>t</i> -Bu) ₃ •HBF ₄ , Cs ₂ CO ₃ , THF-H ₂ O, 80°		148																				
				(76)																				

TABLE 3D. CROSS-COUPLING OF ALKENYLTRIFLUOROBORATES WITH ALLYLIC AND BENZYLIC ELECTROPHILES

Alkenyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂ 		Pd(OAc) ₂ (0.1%), TBAB, KOH, acetone-H ₂ O, 50°, 14 h	(51) ^a	70
		Pd cat. 6 (x%), TBAB, KOH, acetone-H ₂ O, 50°, 14 h	R x H 0.1 (75) OMe 1 (59)	70
		Pd cat. 6 (0.1%), TBAB, KOH, acetone-H ₂ O, 50°, 8 h	(83)	70
		Pd(OAc) ₂ (0.1%), TBAB (0.5 eq), KOH (2 eq), acetone-H ₂ O, 50°, 14 h	(66) ^a	70
		Pd cat. 6 (0.1%), TBAB (0.5 eq), KOH (2 eq), acetone-H ₂ O, 50°, 14 h	R H (61) Ph (84)	70
C ₈ 		Pd cat. 6 (0.1%), TBAB, KOH, acetone-H ₂ O, 50°	R H 14 (85) OMe 8 (89)	70

TABLE 3D. CROSS-COUPLING OF ALKENYLTRIFLUOROBORATES WITH ALLYLIC AND BENZYLIC ELECTROPHILES (Continued)

Alkenyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 		Pd(OAc) ₂ (0.1%), TBAB, KOH, acetone-H ₂ O, 50°, 14 h	 (78) ^d	70
		Pd cat. 6 (0.1%), TBAB, KOH, acetone-H ₂ O, 50°, 6 h	 (87)	70
		Pd(OAc) ₂ (0.1%), TBAB, KOH, acetone-H ₂ O, 50°, 14 h	 (93) ^d	70
		Pd cat. 6 (0.1%), TBAB, KOH, acetone-H ₂ O, 50°, 14 h	 R ¹ R ² H H (79) H Me (77) Ph H (68)	70
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (2%), <i>i</i> -PrNEt ₂ (3 eq), <i>i</i> -PrOH-H ₂ O, MW, 100°, 20 min	 R ¹ R ² R ³	151
			Ar X R ¹ R ² R ³ Ph Br H H H (65)	
			Ph I H H H (55)	
			Ph Cl H H H (81)	
			Ph Cl H Ph H (46)	
			Ph Cl H Me Me (54)	
			Ph Cl Me H H (64)	
			Ph Cl H Me H (51)	
			4-ClC ₆ H ₄ Cl H H (71)	

		Ar	R	
PdCl ₂ (dppf)•CH ₂ Cl ₂ (2%), <i>i</i> -PrNEt ₂ (3 eq), <i>i</i> -PrOH–H ₂ O, MW, 100°, 20 min		4-FC ₆ H ₄	H	(89)
		4-FC ₆ H ₄	Ph	(75)
		4-MeC ₆ H ₄	H	(79)
		4-MeC ₆ H ₄	Me	(81)

^a The yield of the crude product was determined by ¹H NMR.

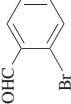
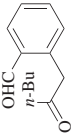
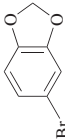
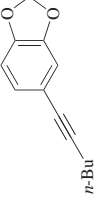
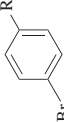
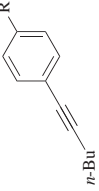
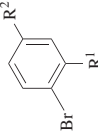
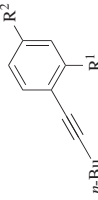
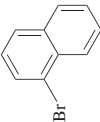
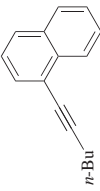
TABLE 3E. CROSS-COUPLING OF ALKENYLTRIFLUOROBORATES WITH MISCELLANEOUS ELECTROPHILES

Alkenyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2 		Pd cat. 6 (0.5%), TBAB, KOH, acetone-H ₂ O, 50°, 8h	 (81)	70
C_8 		Pd(PPh ₃) ₄ (10%), Et ₃ N (2 eq), AgOAc (1 eq), MeOH, ultrasound, 20 min	 (74)	149
		Pd(PPh ₃) ₄ (10%), Et ₃ N (2 eq), AgOAc (1 eq), MeOH, ultrasound, 20 min	 R Ph (73) <i>n</i> -C ₅ H ₁₁ (68) <i>n</i> -C ₆ H ₁₃ (71)	149
		Pd cat. 6 (0.1%), TBAB, KOH, acetone-H ₂ O, 50°, 14 h	 (81)	70

TABLE 4A. CROSS-COUPLING OF ALKYNYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES

Alkynyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂		PdCl ₂ (dppf)•CH ₂ Cl ₂ (9%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, reflux, 12 h	(60)	109
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (9%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, reflux, 12 h	(88)	109
C ₅		PdCl ₂ (dppf)•CH ₂ Cl ₂ (9%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, reflux, 12 h	(85)	109
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (5%), <i>i</i> -Pr ₂ NEt (3 eq), <i>t</i> -PrOH-H ₂ O, MW, 100°, 15 min	(94)	220
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (9%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, reflux, 12 h	(87)	109

TABLE 4A. CROSS-COUPLING OF ALKYNYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Alkynyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
$n\text{-Bu}-\text{C}\equiv\text{C}-\text{BF}_3^-\text{K}^+$		$\text{PdCl}_2(\text{dppf})\cdot\text{CH}_2\text{Cl}_2$ (9%), Cs_2CO_3 (3 eq), THF– H_2O , reflux, 12 h	 (53)	109
		$\text{PdCl}_2(\text{dppf})\cdot\text{CH}_2\text{Cl}_2$ (9%), Cs_2CO_3 (3 eq), solvent, reflux, 12 h	 (44) (75)	109
		$\text{PdCl}_2(\text{dppf})\cdot\text{CH}_2\text{Cl}_2$ (9%), Cs_2CO_3 (3 eq), THF– H_2O , reflux, 12 h	 R OH (48) Me (trace) CN (98) CH_2OH (76) CO_2H (73) NMe_2 (61)	109
		$\text{PdCl}_2(\text{dppf})\cdot\text{CH}_2\text{Cl}_2$ (9%), Cs_2CO_3 (3 eq), THF, reflux, 12 h	 R ¹ R ² H OH (trace) H Me (36) H NMe_2 (33) CHO H (89)	109
		Pd source (9%), base (3 eq) THF– H_2O (x/y), reflux, 12 h See subtable on p.215.		109

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Pd Source	Base	x/y
$\text{PdCl}_2(\text{dppf})\cdot\text{CH}_2\text{Cl}_2$	Cs_2CO_3	20:1 (87)
$\text{PdCl}_2(\text{PPh}_3)_2$	Cs_2CO_3	10:1 (22)
$\text{PdCl}_2(\text{dppf})\cdot\text{CH}_2\text{Cl}_2$	K_2CO_3	10:1 (40)
$\text{PdCl}_2(\text{dppf})\cdot\text{CH}_2\text{Cl}_2$	K_3PO_4	10:1 (42)
$\text{PdCl}_2(\text{dppf})\cdot\text{CH}_2\text{Cl}_2$	Cs_2CO_3	10:1 (43)
$\text{PdCl}_2(\text{dppf})\cdot\text{CH}_2\text{Cl}_2$	K_2CO_3	20:1 (87)

		X I (48) Cl (29)	109
		Y I (30) OTs (0) OMs (0) Cl (40)	109
		Solvent THF-H ₂ O (10:1) (68) THF-H ₂ O (20:1) (73) THF (87)	109
		R NO ₂ (98) Me (55) OMe (78) Ac (87)	109

	$\text{PdCl}_2(\text{dppf})\cdot\text{CH}_2\text{Cl}_2$ (9%), Cs_2CO_3 (3 eq), THF-H ₂ O, reflux, 12 h	
	$\text{PdCl}_2(\text{dppf})\cdot\text{CH}_2\text{Cl}_2$ (9%), Cs_2CO_3 (3 eq), THF, reflux, 60 h	
	$\text{PdCl}_2(\text{dppf})\cdot\text{CH}_2\text{Cl}_2$ (9%), Cs_2CO_3 (3 eq), solvent, reflux, 12 h	
	$\text{PdCl}_2(\text{dppf})\cdot\text{CH}_2\text{Cl}_2$ (9%), Cs_2CO_3 (3 eq), THF, reflux, 12 h	

TABLE 4A. CROSS-COUPLING OF ALKYNYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Alkynyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆		PdCl ₂ (dppf)•CH ₂ Cl ₂ (5%), <i>i</i> -Pr ₂ NEt (3 eq), <i>i</i> -PrOH-H ₂ O, MW, 100°, 15 min	 R CN (90) Me (79) OMe (65)	220
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (9%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, reflux, 12 h	 (69)	109
C ₈		PdCl ₂ (dppf)•CH ₂ Cl ₂ (2%), <i>i</i> -PrNEt ₂ , <i>i</i> -PrOH-H ₂ O, MW, 100°, 10 min	 (60)	220
		Pd source, base (3 eq), <i>i</i> -PrOH-H ₂ O, MW, 100°, 15 min	 R	220
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (5%) Pd ₂ dba ₃ •CH ₂ Cl ₂ Pd ₂ dba ₃ •CH ₂ Cl ₂ PdCl ₂ (dppf)•CH ₂ Cl ₂ (5%)	<i>i</i> -Pr ₂ NEt (96) Cs ₂ CO ₃ (50) K ₂ CO ₃ (60) <i>i</i> -Pr ₂ NEt (91)	

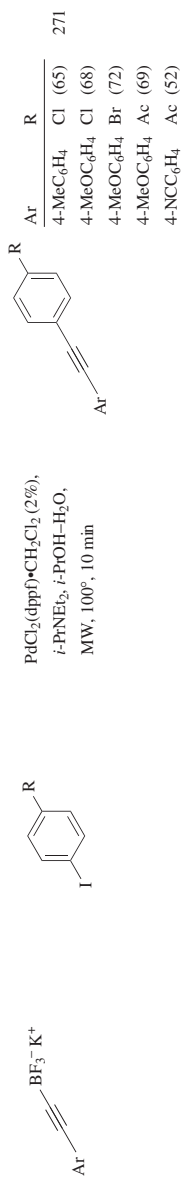
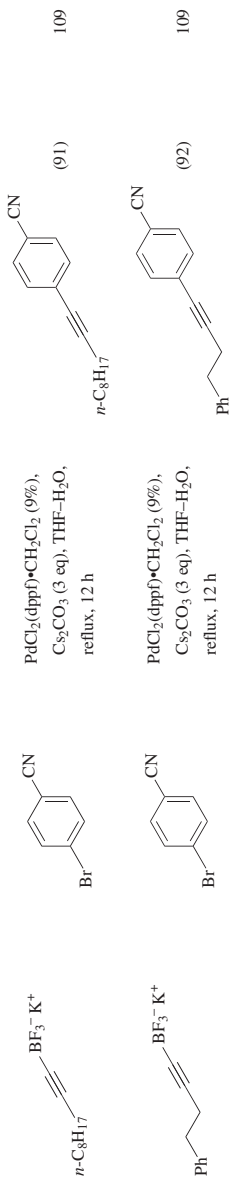
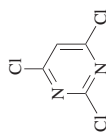
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TABLE 4B. CROSS-COUPLING OF ALKYNYLTRIFLUOROBORATES WITH HETEROARYL ELECTROPHILES

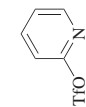
Alkynyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(%)	Refs.
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (9%), Cs_2CO_3 (3 eq), solvent, reflux, 12 h	 Solvent THF-H ₂ O (47) THF (88)	109
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (9%), Cs_2CO_3 (3 eq), THF-H ₂ O, reflux, 12 h	 (78)	109
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (9%), Cs_2CO_3 (3 eq), THF-H ₂ O, reflux, 12 h	 (30)	109
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (9%), Cs_2CO_3 (3 eq), solvent, reflux, 12 h	 Solvent THF-H ₂ O (46) THF (97)	109
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (9%), Cs_2CO_3 (3 eq), THF-H ₂ O, reflux, 12 h	 (85)	109
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (9%), Cs_2CO_3 (6 eq), THF-H ₂ O, reflux, 12 h	 (62)	109



$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (9%),
 Cs_2CO_3 (9 eq), THF– H_2O ,
 reflux, 12 h

109

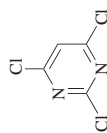
(70)



$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (9%),
 Cs_2CO_3 (3 eq), THF,
 reflux, 12 h

109

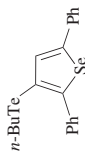
(31)



$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (27%),
 Cs_2CO_3 (3 eq), THF– H_2O ,
 reflux, 12 h

165

(74)



$\text{Pd}(\text{PPh}_3)_4$ (15%), Et_3N ,
 Ag_2O , MeOH, reflux, 24 h

141

(71)

TABLE 4B. CROSS-COUPLING OF ALKYNYLTRIFLUOROBORATES WITH HETEROARYL ELECTROPHILES (Continued)

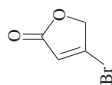
Alkynyl/trifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.						
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (27%), Cs_2CO_3 (3 eq), THF- H_2O , reflux, 12 h	 (35) 165							
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (27%), Cs_2CO_3 (3 eq), THF- H_2O , reflux, 12 h	 165 <table><tr><td>R^1</td><td>R^2</td></tr><tr><td>H</td><td>NMe₂</td></tr><tr><td>OMe</td><td>OMe</td></tr></table> (51) (45)	R^1	R^2	H	NMe ₂	OMe	OMe	
R^1	R^2									
H	NMe ₂									
OMe	OMe									

TABLE 4C. CROSS-COUPLING OF ALKYNYLTRIFLUOROBORATES WITH ALKENYL ELECTROPHILES

Alkynyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂		 Pd(PPh ₃) ₄ (10%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 90°, 24 h	 (0)	277
		 Pd(PPh ₃) ₄ (10%), Et ₃ N (2 eq), AgOAc (1 eq), MeOH, ultrasound, 20 min	 (77)	149
		 PdCl ₂ (dppf)•CH ₂ Cl ₂ (5%), THF, rt, 4 h	 (71)	110
		 Pd(PPh ₃) ₄ (10%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 90°, 24 h	 (0)	277
C ₃		 Pd(PPh ₃) ₄ (10%), Et ₃ N (2 eq), AgOAc (1 eq), MeOH, ultrasound, 20 min	 (70)	149

TABLE 4C. CROSS-COUPLING OF ALKYNYLTRIFLUOROBORATES WITH ALKENYL ELECTROPHILES (Continued)

Alkynyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₄ 		Pd(acac) ₂ (15%), CuI (30%), Et ₃ N (3 eq), MeOH, reflux, 8 h		75
C ₅ 		Pd(PPh ₃) ₄ (10%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 90°, 24 h		277
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (5%), THF, rt, 3 h		110
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (10%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, 50°, 2 h		111



$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (5%),
THF, rt, 3 h

(88)

110



$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (10%),
 Cs_2CO_3 (3 eq), THF-H₂O,
50°, 2 h

(74)

111



$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (10%),
 Cs_2CO_3 (3 eq), THF-H₂O,
50°, 2 h

(85)

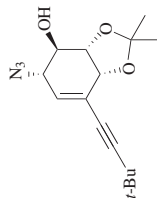
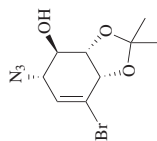
111



$\text{Pd}(\text{acac})_2$ (15%),
CuI (30%), Et₃N (3 eq),
MeOH, reflux, 8 h

(61)

75



$\text{Pd}(\text{PPh}_3)_4$ (10%), Cs_2CO_3 (3 eq),
toluene-H₂O, 90°, 4 h

(74)

277

C₆

TABLE 4C. CROSS-COUPLING OF ALKYNYLTRIFLUOROBORATES WITH ALKENYL ELECTROPHILES (Continued)

Alkynyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆ 		PdCl ₂ (dppf)•CH ₂ Cl ₂ (5%), THF, rt	 R Time (h) t-Bu 3 (95) n-Bu 4 (95)	110
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (5%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, 50°	 R Time (h) t-Bu 1 (97) n-Bu 1.5 (91)	110
C ₇ 		Pd(PPh ₃) ₄ (10%), Et ₃ N (2 eq), AgOAc (1 eq), MeOH, ultrasound, 20 min	 (74)	149
C ₈ 		Pd source (15%), CuI (30%), Et ₃ N (3 eq), MeOH, reflux, 8 h	 Pd Source Pd(OAc) ₂ (55) Pd(acac) ₂ (77) [Pd(allyl)Cl] ₂ (68) PdCl ₂ (C ₆ H ₅ CN) ₂ (66)	75
		Pd(acac) ₂ (15%), CuI (30%), Et ₃ N (3 eq), MeOH, reflux, 8 h	 R ¹ R ² H CH ₂ OH (58) CH ₂ OH H (51) CH ₂ OH CH ₂ OH (63)	75

		$\text{Pd}(\text{acac})_2$ (15%), CuI (30%), Et_3N (3 eq), MeOH, reflux, 8 h	(68)	75
		$\text{Pd}(\text{acac})_2$ (15%), CuI (30%), Et_3N (3 eq), MeOH, reflux, 8 h	(0)	75
		$\text{Pd}(\text{acac})_2$ (15%), CuI (30%), Et_3N (3 eq), MeOH, reflux, 8 h	(0)	75
		$\text{Pd}(\text{acac})_2$ (15%), CuI (30%), Et_3N (3 eq), MeOH, reflux, 8 h	(58)	75
		$\text{Pd}(\text{acac})_2$ (15%), CuI (30%), Et_3N (3 eq), MeOH, reflux, 8 h	(65)	75
		$\text{Pd}(\text{acac})_2$ (15%), CuI (30%), Et_3N (3 eq), MeOH, reflux, 8 h	(68)	75
		$\text{Pd}(\text{PPh}_3)_4$ (10%), Et_3N (2 eq), AgOAc (1 eq), MeOH, ultrasound, 20 min	(79)	149

TABLE 4C. CROSS-COUPLING OF ALKYNYLTRIFLUOROBORATES WITH ALKENYL ELECTROPHILES (Continued)

Alkynyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (5%), THF, rt, 6 h	 (91)	110
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (5%), Cs_2CO_3 (3 eq), THF– H_2O , 50°, 2 h	 (92)	110
		$\text{Pd}(\text{PPh}_3)_4$ (10%), Cs_2CO_3 (3 eq), toluene– H_2O , 90°, 8 h	 (69)	277
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (10%), Cs_2CO_3 (3 eq), THF– H_2O , 50°, 2 h	 R Ph 4- ClC_6H_4 $n\text{-C}_8\text{H}_{17}$	111
		$\text{Pd}(\text{PPh}_3)_4$ (10%), Et_3N (2 eq), AgOAc (1 eq), MeOH, ultrasound, 20 min	 (79)	149

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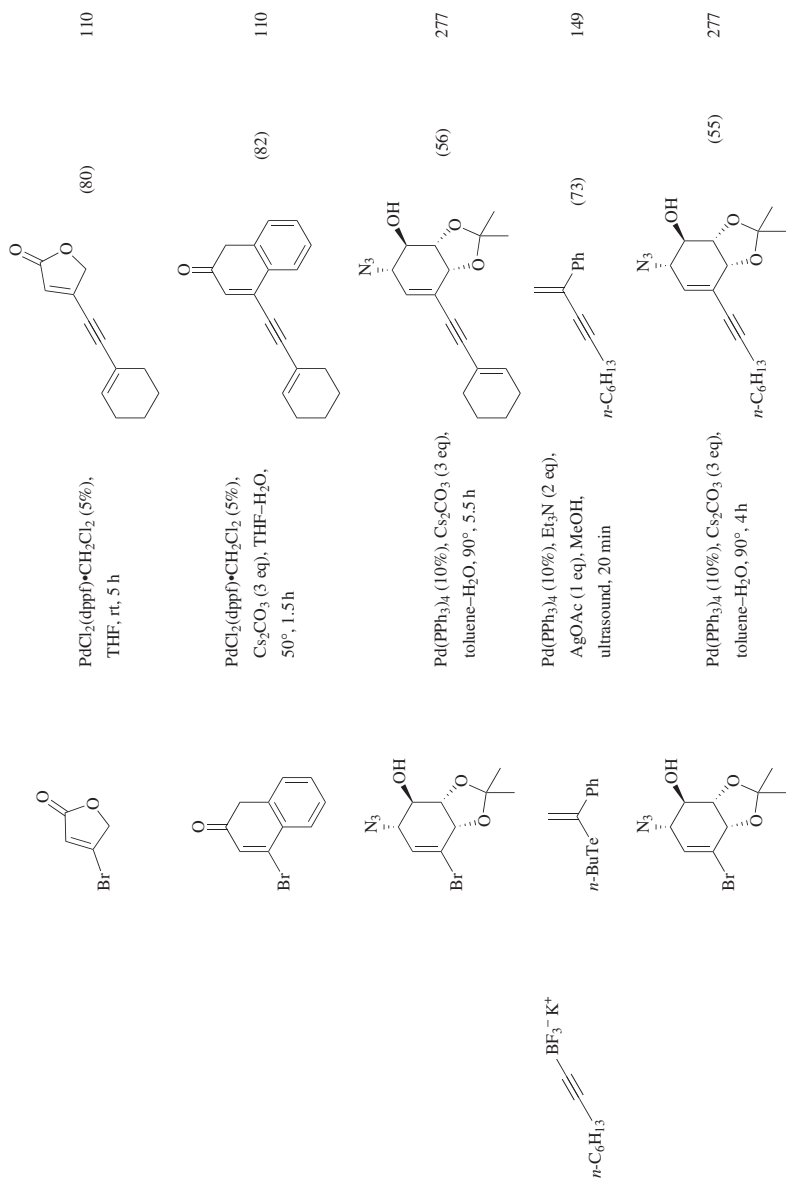
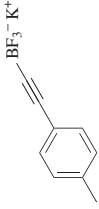
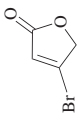
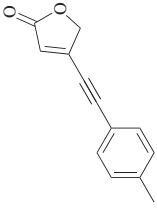
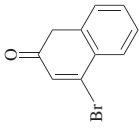
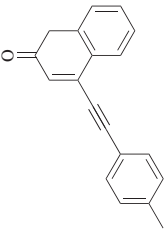
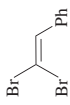
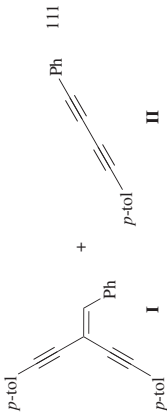
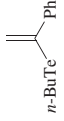
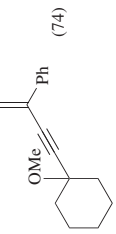


TABLE 4C. CROSS-COUPLING OF ALKYNYLTRIFLUOROBORATES WITH ALKENYL ELECTROPHILES (Continued)

Alkynyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (5%), THF, rt, 6 h	 (87)	110
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (5%), Cs_2CO_3 (3 eq), THF– H_2O , 50°, 2 h	 (85)	110
		Pd source (x%), $\text{C}_5\text{H}_5\text{CO}_3$ (3 eq), THF– H_2O , 50°		111
		$\text{Pd}(\text{PPh}_3)_4$ (10%), Et_3N (2 eq), AgOAc (1 eq), MeOH, ultrasound, 20 min	 (74)	149

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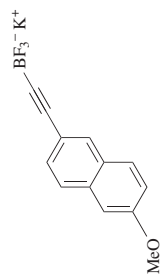
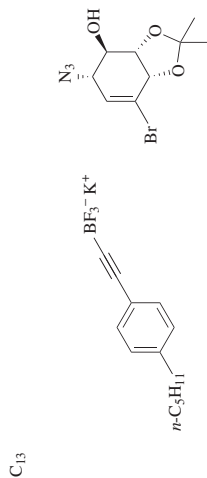
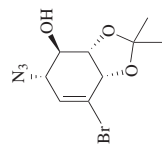
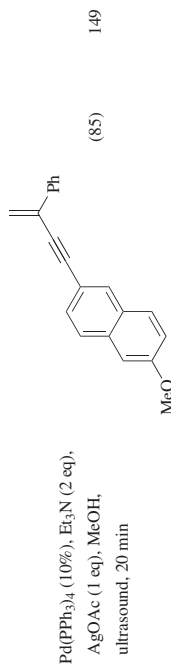
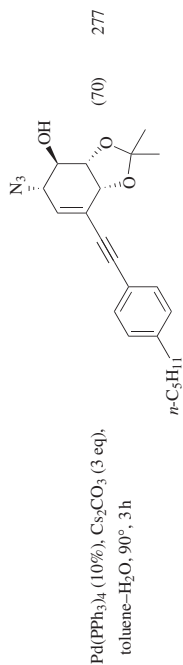
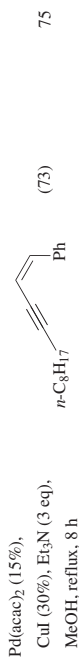
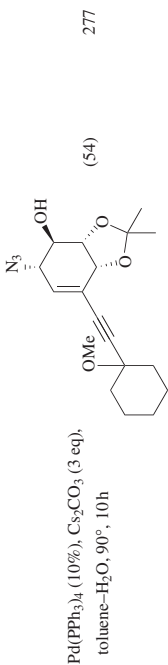
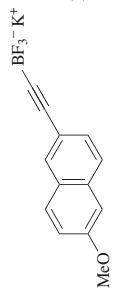
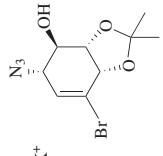
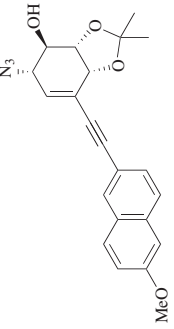


TABLE 4C. CROSS-COUPLING OF ALKYNYLTRIFLUOROBORATES WITH ALKENYL ELECTROPHILES (Continued)

Alkynyl/trifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(PPh ₃) ₄ (10%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 90°, 3 h	 (60) 277	

C₁₃

TABLE 5A. CROSS-COUPLING OF ALKYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES

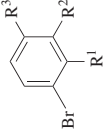
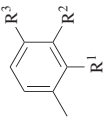
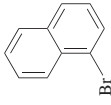
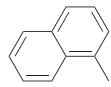
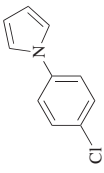
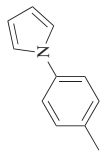
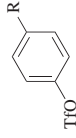
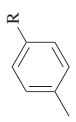
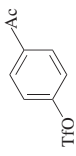
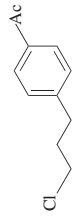
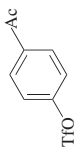
Alkyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁ MeBF ₃ ⁻ K ⁺		PdCl ₂ (dppf)•CH ₂ Cl ₂ (9%), Cs ₂ CO ₃ (3 eq), THF–H ₂ O, reflux, 16–18 h		(77) (68) (80) (67) (92) (57) (60) (83) (61)
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (9%), Cs ₂ CO ₃ (3 eq), THF–H ₂ O, reflux, 16–18 h		(85) 113
		Pd(OAc) ₂ (2%), RuPhos (4%), K ₂ CO ₃ (3 eq), toluene–H ₂ O, 80°, 36 h		(72) 114
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (9%), Cs ₂ CO ₃ (3 eq), THF–H ₂ O, reflux, 16–18 h		$\frac{\text{R}}{\text{NO}_2}$ (85) Ac (85) 113
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (9%), Cs ₂ CO ₃ (3 eq), THF–H ₂ O, reflux, 3 d		(72) 113
C ₃				
				

TABLE 5A. CROSS-COUPLING OF ALKYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Alkyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3 		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (9%), Cs_2CO_3 (3 eq), THF- H_2O , reflux, 3 d	 (70)	113
		$\text{Pd}(\text{OAc})_2$ (2%), RuPhos (4%), K_2CO_3 (3 eq), toluene- H_2O , 80°, 24 h	 (0)	114
		$\text{Pd}(\text{OAc})_2$ (2%), <i>n</i> -BuPAd ₂ (3%), Cs_2CO_3 (3 eq), toluene- H_2O , 100°, 72 h	 + R ¹ R ² I + II I:II R ¹ R ² I:II H OMe (77) 3.5:1 OMe H (78) 1:6	78
		$\text{Pd}(\text{OAc})_2$ (5%), <i>t</i> -Bu ₃ PPh (7.5%), Cs_2CO_3 (3 eq), toluene- H_2O , 100°, 72 h	 + R ¹ R ² I + II I:II R ¹ R ² I:II H OMe (79) 8.2:1 OMe H (57) 1.4:1	78
		$\text{Pd}(\text{OAc})_2$ (5%), RuPhos (10%), K_2CO_3 (3 eq), toluene- H_2O , 85°, 14 h	 (0)	121

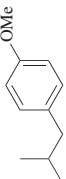
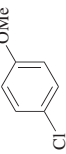
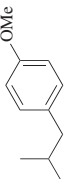
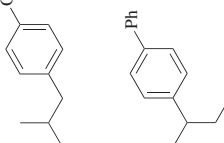
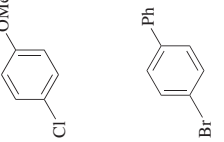
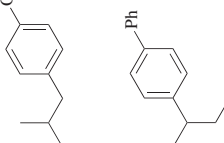
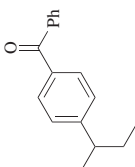
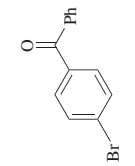
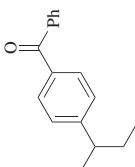
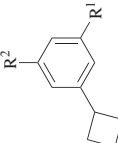
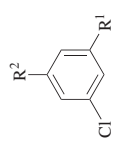
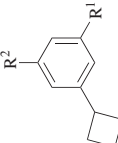
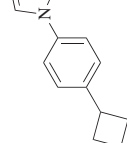
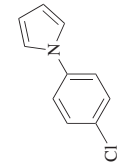
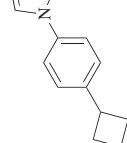
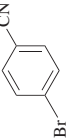
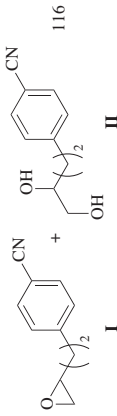
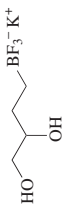
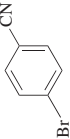
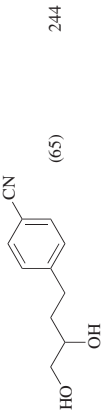
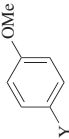
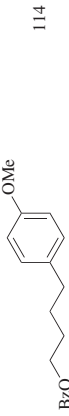
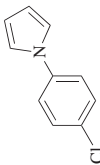
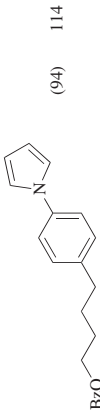
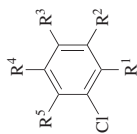
		Pd(OAc)₂ (2%), RuPhos (4%), K₂CO₃ (3 eq), toluene-H₂O, 80°, 36 h		(77)	114									
		Pd(OAc)₂ (7.5%), RuPhos (15%), K₃PO₄ (3 eq), toluene-H₂O, 115°, 72 h		(45)	278									
		Pd(OAc)₂ (7.5%), RuPhos (15%), K₃PO₄ (3 eq)		(51)	278									
		Pd(OAc)₂ (2%), <i>n</i>-BuPAd₂ (3%), Cs₂CO₃ (3 eq), toluene-H₂O, 100°, 24 h		<table><tr><td>R¹</td><td>R²</td></tr><tr><td>OMe</td><td>OMe</td></tr><tr><td>CO₂Me</td><td>H</td></tr></table>	R ¹	R ²	OMe	OMe	CO ₂ Me	H	<table><tr><td>(82)</td><td>(63)</td></tr></table>	(82)	(63)	112
R ¹	R ²													
OMe	OMe													
CO ₂ Me	H													
(82)	(63)													
		Pd(OAc)₂ (2%), <i>n</i>-BuPAd₂ (3%), Cs₂CO₃ (3 eq), toluene-H₂O, 100°, 24 h		(74)	112									

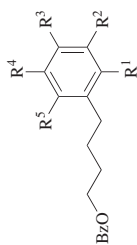
TABLE 5A. CROSS-COUPLING OF ALKYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Alkyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (9%), Cs_2CO_3 (3 eq), THF– H_2O (x/y), reflux	 116	
			I  II  x/y Time I II 10:1 8 h — (74) 40:1 3 d (80) —	
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (10%), Cs_2CO_3 (3 eq), THF– H_2O , reflux, 21 h	 244	
		$\text{Pd}(\text{OAc})_2$ (2%), RuPhos (4%), base (3 eq), toluene– H_2O , 80°, 36 h	 114	
			Y Base Br K_2CO_3 (88) I Cs_2CO_3 (80) Cl K_2CO_3 (92) OTf K_2CO_3 (75)	
		$\text{Pd}(\text{OAc})_2$ (2%), RuPhos (4%), K_2CO_3 (3 eq), toluene– H_2O , 80°, 24 h	 114	

C₄

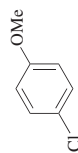


Pd(OAc)₂ (2%), RuPhos (4%),
K₂CO₃ (3 eq), toluene-H₂O,
80°, 24h

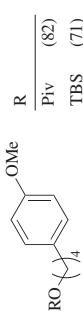


114

R ¹	R ²	R ³	R ⁴	R ⁵	
H	H	H	H	H	(81)
H	H	NO ₂	H	H	(96)
H	H	CF ₃	H	H	(90)
H	H	CN	H	H	(87)
H	H	CHO	H	H	(90)
H	H	Me	H	H	(82)
H	H	Ac	H	H	(87)
H	H	COPh	H	H	(89)
H	CO ₂ Me	H	H	H	(91)
H	OMe	H	OMe	H	(89)
OMe	H	H	H	H	(87)
Me	H	H	H	Me	(95)
Me	H	OMe	H	Me	(92)
OMe	OMe	H	CN	H	(80)

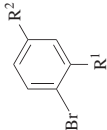
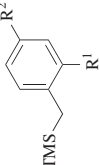
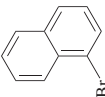
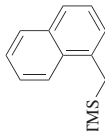
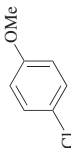
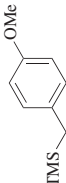
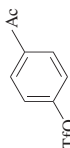
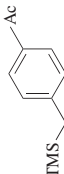


Pd(OAc)₂ (2%), RuPhos (4%),
K₂CO₃ (3 eq), toluene-H₂O,
80°, 36h

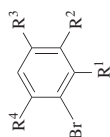
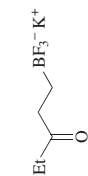


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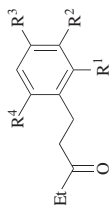
TABLE 5A. CROSS-COUPLING OF ALKYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Alkyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.	
$\text{TMS-CH}_2\text{-BF}_3^-\text{K}^+$		$\text{PdCl}_2(\text{dppf})\cdot\text{CH}_2\text{Cl}_2$ (9%), Cs_2CO_3 (3 eq), $\text{THF-H}_2\text{O}$, reflux, 6–8 h		R^1 R^2 H Ac (65) H C_{OPh} (60) H NHA_c (53) H CN (55) CN H (51)	113
		$\text{PdCl}_2(\text{dppf})\cdot\text{CH}_2\text{Cl}_2$ (9%), Cs_2CO_3 (3 eq), $\text{THF-H}_2\text{O}$, reflux, 6–8 h		(77)	113
		$\text{Pd}(\text{OAc})_2$ (2%), RuPhos (4%), K_2CO_3 (3 eq), toluene- H_2O , 80°, 36 h		(71)	114
		$\text{PdCl}_2(\text{dppf})\cdot\text{CH}_2\text{Cl}_2$ (9%), Cs_2CO_3 (3 eq), $\text{THF-H}_2\text{O}$, reflux, 6–8 h		(70)	113

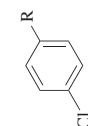
C₄



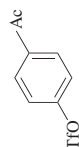
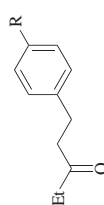
Pd(OAc)₂ (2.5%),
 RuPhos (5%), K₂CO₃ (3 eq),
 toluene-H₂O, 85°, 120



R ¹	R ²	R ³	R ⁴	Time (h)
H	CN	H	H	18 (87)
H	OMe	H	H	24 (87)
H	Ac	H	H	18 (87)
H	H	NO ₂	H	18 (93)
H	H	Me	H	24 (75)
H	H	CN	H	18 (88)
H	H	CHO	H	18 (78)
H	H	OMe	H	24 (86)
H	H	Ac	H	83 (83)
H	H	CO ₂ Me	H	18 (89)
H	H	NHAc	H	24 (78)
Me	H	Me	Me	24 (76)



Pd(OAc)₂ (2.5%),
 RuPhos (5%), K₂CO₃ (3 eq),
 toluene-H₂O, 85°, 18 h, 120



Pd(OAc)₂ (2.5%),
 RuPhos (5%), K₂CO₃ (3 eq),
 toluene-H₂O, 85°, 18 h, 120

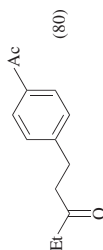
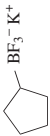
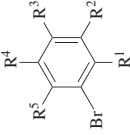
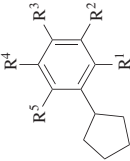
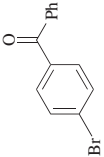
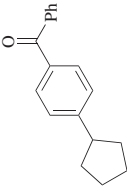
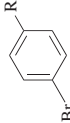
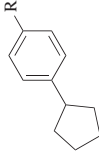
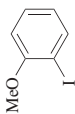
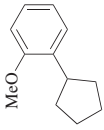


TABLE 5A. CROSS-COUPLING OF ALKYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Alkyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₅		 Pd(OAc) ₂ (2%), <i>n</i> -BuPAd ₂ (3%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 100°, 24 h		78
		Pd(OAc) ₂ (7.5%), RuPhos (15%), K ₃ PO ₄ (3 eq), toluene-H ₂ O, 115°, 44 h		278
		Pd(OAc) ₂ (7.5%), RuPhos (15%), K ₃ PO ₄ (3 eq), toluene-H ₂ O, 115°		278
		Pd(OAc) ₂ (2%), <i>n</i> -BuPAd ₂ (3%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 100°, 72 h		78

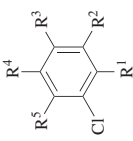
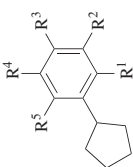
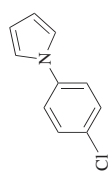
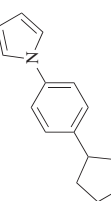
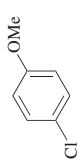
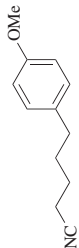
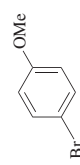
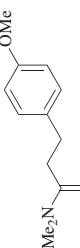
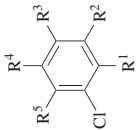
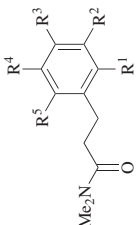
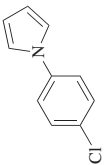
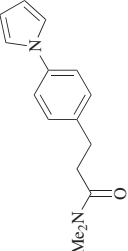
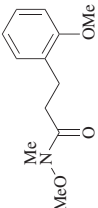
		78																																																												
$\text{Pd}(\text{OAc})_2$ (2%), <i>n</i>-BuPAd₂ (3%), Cs_2CO_3 (3 eq), toluene-H₂O, 100°, 24 h																																																														
	<table><tr><th>R¹</th><th>R²</th><th>R³</th><th>R⁴</th><th>R⁵</th><th></th></tr><tr><td>H</td><td>H</td><td>NO₂</td><td>H</td><td>H</td><td>(89)</td></tr><tr><td>H</td><td>H</td><td>CN</td><td>H</td><td>H</td><td>(—)</td></tr><tr><td>H</td><td>H</td><td>CF₃</td><td>H</td><td>H</td><td>(82)</td></tr><tr><td>H</td><td>H</td><td>OMe</td><td>H</td><td>H</td><td>(88)</td></tr><tr><td>H</td><td>H</td><td>Ac</td><td>H</td><td>H</td><td>(51)</td></tr><tr><td>H</td><td>CO₂Me</td><td>H</td><td>H</td><td>H</td><td>(89)</td></tr><tr><td>H</td><td>OMe</td><td>H</td><td>OMe</td><td>H</td><td>(92)</td></tr><tr><td>OMe</td><td>H</td><td>H</td><td>H</td><td>H</td><td>(87)</td></tr><tr><td>Me</td><td>H</td><td>OMe</td><td>H</td><td>Me</td><td>(82)</td></tr></table>	R ¹	R ²	R ³	R ⁴	R ⁵		H	H	NO ₂	H	H	(89)	H	H	CN	H	H	(—)	H	H	CF ₃	H	H	(82)	H	H	OMe	H	H	(88)	H	H	Ac	H	H	(51)	H	CO ₂ Me	H	H	H	(89)	H	OMe	H	OMe	H	(92)	OMe	H	H	H	H	(87)	Me	H	OMe	H	Me	(82)	
R ¹	R ²	R ³	R ⁴	R ⁵																																																										
H	H	NO ₂	H	H	(89)																																																									
H	H	CN	H	H	(—)																																																									
H	H	CF ₃	H	H	(82)																																																									
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H	CO ₂ Me	H	H	H	(89)																																																									
H	OMe	H	OMe	H	(92)																																																									
OMe	H	H	H	H	(87)																																																									
Me	H	OMe	H	Me	(82)																																																									
		78																																																												
	$\text{Pd}(\text{OAc})_2$ (2%), <i>n</i>-BuPAd₂ (3%), Cs_2CO_3 (3 eq), toluene-H₂O, 100°, 24 h	(94)																																																												
		114																																																												
		120																																																												

TABLE 5A. CROSS-COUPLING OF ALKYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Alkyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
$\text{Me}_2\text{N}-\text{C}(=\text{O})-\text{CH}_2-\text{CH}_2-\text{BF}_3^-\text{K}^+$		Pd(OAc) ₂ (5%), RuPhos (10%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 85°, 14 h		121
	R^1 R^2 R^3 R^4 R^5		H H H H H (75) H H NO_2 H H (85) H H CF_3 H H (76) H H CN H H (81) H H CHO H H (87) H H OMe H H (86) H H Ac H H (94) H OMe H OMe H (78) H CO_2Me H H H (81) CN H H H H (83) Me H H H H (75) OMe H H H H (79) Me H H H Me (76)	
		Pd(OAc) ₂ (5%), RuPhos (10%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 85°, 14 h		121
$\text{MeO}-\text{N}(\text{Me})-\text{C}(=\text{O})-\text{CH}_2-\text{CH}_2-\text{BF}_3^-\text{K}^+$		Pd(OAc) ₂ (5%), RuPhos (10%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 85°, 14 h		121

C₅

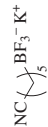
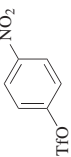
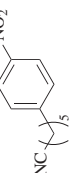
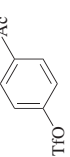
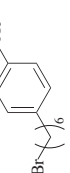
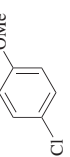
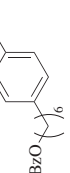
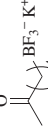
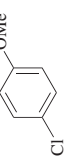
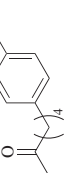
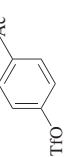
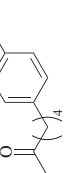
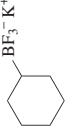
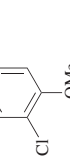
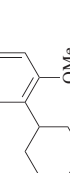
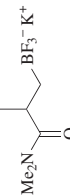
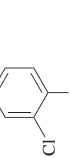
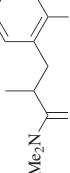
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (9%), Cs_2CO_3 (3 eq), THF-H ₂ O, reflux, 18 h		(73)	58
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (9%), Cs_2CO_3 (3 eq), THF-H ₂ O, reflux, 18 h		(61)	58
		$\text{Pd}(\text{OAc})_2$ (2%), RuPhos (4%), K_2CO_3 (3 eq), toluene-H ₂ O, 80°, 24 h		(91)	114
		$\text{Pd}(\text{OAc})_2$ (2%), RuPhos (4%), K_2CO_3 (3 eq), toluene-H ₂ O, 80°, 36 h		(78)	114
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (9%), Cs_2CO_3 (3 eq), THF-H ₂ O, reflux, 18 h		(79)	58
		$\text{Pd}(\text{OAc})_2$ (5%), <i>n</i> -Bu ₄ PAu ₂ (7.5%), Cs_2CO_3 (3 eq), toluene-H ₂ O, 100°, 72 h		(79)	78
		$\text{Pd}(\text{OAc})_2$ (5%), RuPhos (10%), K_2CO_3 (3 eq), toluene-H ₂ O, 85°, 14 h		(60)	121

TABLE 5A. CROSS-COUPLING OF ALKYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Alkyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc) ₂ (2.5%), RuPhos (5%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 85°, 24 h	 (70)	120
		Pd(OAc) ₂ (5%), RuPhos (10%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 85°, 14 h	 (65)	121
		Pd(OAc) ₂ (2%), RuPhos (4%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 80°, 24 h	 R ¹ R ² H CO ₂ Me (>69) OMe H (>62)	279
		Pd(OAc) ₂ (2%), RuPhos (4%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 80°, 24 h	 R CN (>68) CHO (>72)	279
		Pd(OAc) ₂ (2%), RuPhos (4%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 80°, 24 h	 CO ₂ Me (>80)	279

C₇

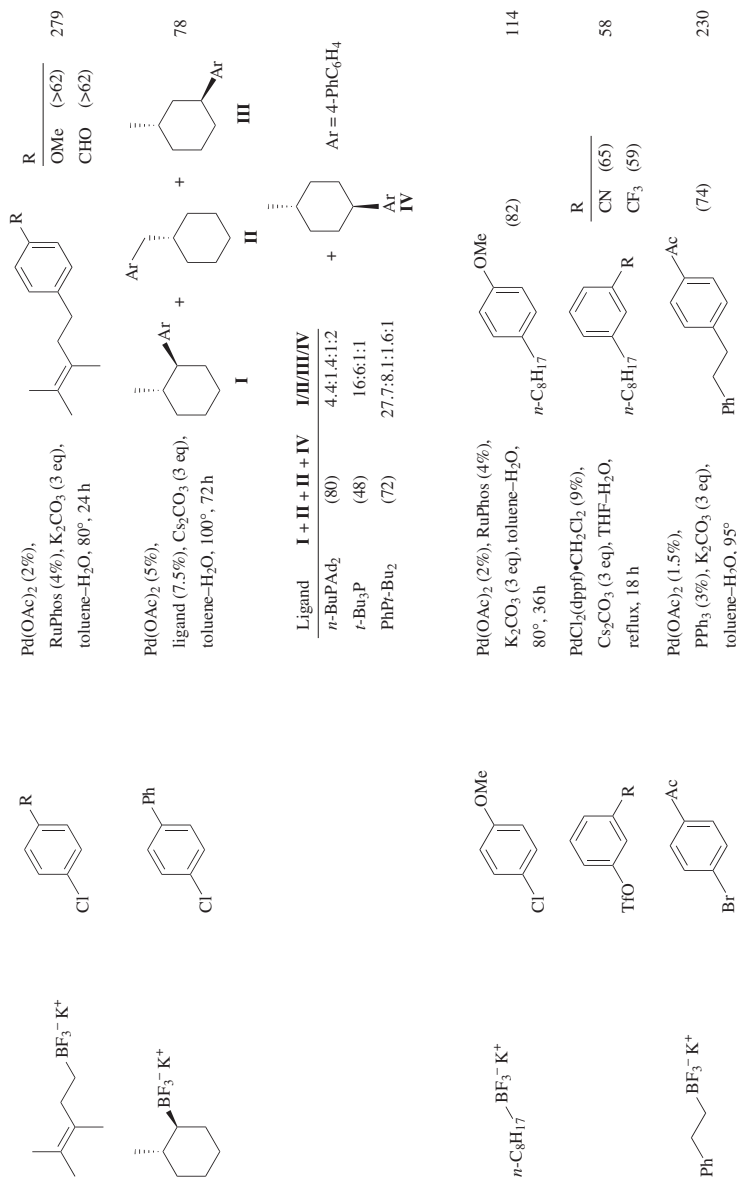


TABLE 5A. CROSS-COUPLING OF ALKYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

C₈

Alkyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.																												
		Pd (2.5 ppm), Na ₂ CO ₃ (3.7 eq), TBAB (1 eq), EtOH–H ₂ O, MW, 150°, 5 min	 (0)	214																												
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (9%), Cs ₂ CO ₃ (3 eq), THF–H ₂ O, reflux, 18 h to 3 d	 (25) ^b	113																												
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (9%), Cs ₂ CO ₃ (3 eq), THF–H ₂ O, reflux, 18 h to 3 d	<table><tr><th>R¹</th><th>R²</th><th>R³</th><th>R⁴</th></tr><tr><td>H</td><td>H</td><td>OH</td><td>H (trace)</td></tr><tr><td>H</td><td>H</td><td>OMe</td><td>H (45)</td></tr><tr><td>H</td><td>OMe</td><td>H</td><td>H (86)</td></tr><tr><td>H</td><td>H</td><td>NMe₂</td><td>H (0)</td></tr><tr><td>Me</td><td>H</td><td>H</td><td>H (82)</td></tr><tr><td>Me</td><td>H</td><td>Me</td><td>Me (68)</td></tr></table>	R ¹	R ²	R ³	R ⁴	H	H	OH	H (trace)	H	H	OMe	H (45)	H	OMe	H	H (86)	H	H	NMe ₂	H (0)	Me	H	H	H (82)	Me	H	Me	Me (68)	113
	R ¹	R ²	R ³	R ⁴																												
H	H	OH	H (trace)																													
H	H	OMe	H (45)																													
H	OMe	H	H (86)																													
H	H	NMe ₂	H (0)																													
Me	H	H	H (82)																													
Me	H	Me	Me (68)																													
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (9%), Cs ₂ CO ₃ (3 eq), THF–H ₂ O, reflux, 18 h to 3 d	 (0)	113																												
		Pd(OAc) ₂ (2%), RuPhos (4%), K ₂ CO ₃ (3 eq), toluene–H ₂ O, 80°, 24 h	 (87)	114																												
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (9%), Cs ₂ CO ₃ (3 eq), THF–H ₂ O, reflux, 18 h to 3 d	 (12) ^b	113																												

		PdCl₂(dppf)•CH₂Cl₂ (9%), Cs₂CO₃ (3 eq), THF–H₂O, reflux, 18 h		58
		Pd(OAc)₂ (2.5%), RuPhos (5%), K₂CO₃ (3 eq), toluene–H₂O, 85°, 14 h		119
		Pd(OAc)₂ (2.5%), RuPhos (5%), K₂CO₃ (3 eq), toluene–H₂O, 85°, 14 h		119
		PdCl₂(dppf)•CH₂Cl₂ (9%), Cs₂CO₃ (3 eq), THF–H₂O, reflux, 18 h		58
		Pd(OAc)₂ (2%), RuPhos (4%), K₂CO₃ (3 eq), toluene–H₂O, 80°, 24 h		279

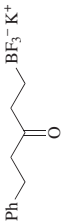
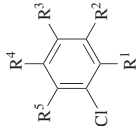
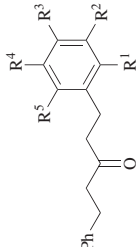
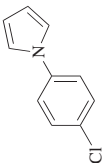
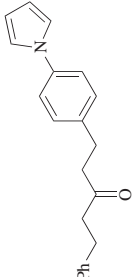
C₉

TABLE 5A. CROSS-COUPLING OF ALKYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

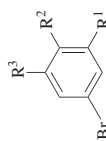
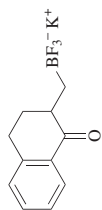
Alkyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc) ₂ (2.5%), RuPhos (5%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 85°, 14 h		R H (55) F (64) 119
		Pd(OAc) ₂ (2.5%), RuPhos (5%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 85°, 14 h		(trace) 119
		Pd(OAc) ₂ (5%), RuPhos (10%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 85°, 14 h		(84) 121
		Pd(OAc) ₂ (2%), RuPhos (4%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 85°, 24 h		(0) 114
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (9%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, reflux, 3 d		(66) 113
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (9%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, reflux, 3 d		(70) 113

		$\text{Pd}(\text{OAc})_2$ (2%), RuPhos (4%), K_2CO_3 (3 eq), toluene-H ₂ O, 80°, 36 h		(70)	114																					
		$\text{Pd}(\text{OAc})_2$ (5%), RuPhos (10%), K_2CO_3 , toluene-H ₂ O, 80°, 23 h		(74)	280																					
		$\text{Pd}(\text{OAc})_2$ (2.5%), RuPhos (5%), K_2CO_3 (3 eq), toluene-H ₂ O, 85°, 14 h		(60)	119																					
		$\text{Pd}(\text{OAc})_2$ (2.5%), RuPhos (5%), K_2CO_3 (3 eq), toluene-H ₂ O, 85°, 14 h		(60)	119																					
		$\text{Pd}(\text{OAc})_2$ (2%), RuPhos (4%), K_2CO_3 (3 eq), toluene-H ₂ O, 80°, 24 h		(>73)	279																					
		$\text{Pd}(\text{OAc})_2$ (2%), RuPhos (4%), K_2CO_3 (3 eq), toluene-H ₂ O, 80°, 24 h		279																						
				<table><tr><th>R¹</th><th>R²</th><th>R³</th><th></th></tr><tr><td>H</td><td>Ac</td><td>CHO</td><td>(>79)</td></tr><tr><td>OMe</td><td>H</td><td>OMe</td><td>(>75)</td></tr><tr><td>OMe</td><td>H</td><td>CHO</td><td>(>81)</td></tr><tr><td>OMe</td><td>H</td><td>Ac</td><td>(>78)</td></tr></table>	R ¹	R ²	R ³		H	Ac	CHO	(>79)	OMe	H	OMe	(>75)	OMe	H	CHO	(>81)	OMe	H	Ac	(>78)		
R ¹	R ²	R ³																								
H	Ac	CHO	(>79)																							
OMe	H	OMe	(>75)																							
OMe	H	CHO	(>81)																							
OMe	H	Ac	(>78)																							

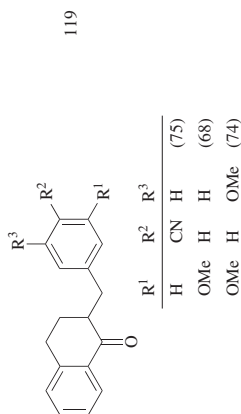
TABLE 5A. CROSS-COUPLING OF ALKYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Alkyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																																				
		Pd(OAc) ₂ (2.5%), RuPhos (5%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 85°, 14 h	 <table> <tr> <th>R¹</th><th>R²</th><th>R³</th><th>R⁴</th><th>R⁵</th><th></th></tr> <tr> <td>H</td><td>H</td><td>H</td><td>H</td><td>H</td><td>(83)</td></tr> <tr> <td>H</td><td>H</td><td>NO₂</td><td>H</td><td>H</td><td>(75)</td></tr> <tr> <td>H</td><td>H</td><td>CN</td><td>H</td><td>H</td><td>(73)</td></tr> <tr> <td>H</td><td>H</td><td>CHO</td><td>H</td><td>H</td><td>(94)</td></tr> <tr> <td>H</td><td>H</td><td>CF₃</td><td>H</td><td>H</td><td>(82)</td></tr> <tr> <td>H</td><td>H</td><td>OMe</td><td>H</td><td>H</td><td>(78)</td></tr> <tr> <td>H</td><td>H</td><td>Ac</td><td>H</td><td>H</td><td>(80)</td></tr> <tr> <td>H</td><td>OMe</td><td>H</td><td>OMe</td><td>H</td><td>(89)</td></tr> <tr> <td>H</td><td>CO₂Me</td><td>H</td><td>H</td><td>H</td><td>(89)</td></tr> <tr> <td>CN</td><td>H</td><td>H</td><td>H</td><td>H</td><td>(81)</td></tr> <tr> <td>Me</td><td>H</td><td>H</td><td>H</td><td>H</td><td>(70)</td></tr> <tr> <td>OMe</td><td>H</td><td>H</td><td>H</td><td>H</td><td>(88)</td></tr> <tr> <td>Me</td><td>H</td><td>H</td><td>H</td><td>Me</td><td>(67)</td></tr> </table>	R ¹	R ²	R ³	R ⁴	R ⁵		H	H	H	H	H	(83)	H	H	NO ₂	H	H	(75)	H	H	CN	H	H	(73)	H	H	CHO	H	H	(94)	H	H	CF ₃	H	H	(82)	H	H	OMe	H	H	(78)	H	H	Ac	H	H	(80)	H	OMe	H	OMe	H	(89)	H	CO ₂ Me	H	H	H	(89)	CN	H	H	H	H	(81)	Me	H	H	H	H	(70)	OMe	H	H	H	H	(88)	Me	H	H	H	Me	(67)	119
R ¹	R ²	R ³	R ⁴	R ⁵																																																																																				
H	H	H	H	H	(83)																																																																																			
H	H	NO ₂	H	H	(75)																																																																																			
H	H	CN	H	H	(73)																																																																																			
H	H	CHO	H	H	(94)																																																																																			
H	H	CF ₃	H	H	(82)																																																																																			
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		Pd(OAc) ₂ (2.5%), RuPhos (5%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 85°, 14 h	 (89)	119																																																																																				

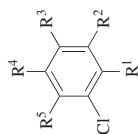
C₁₁



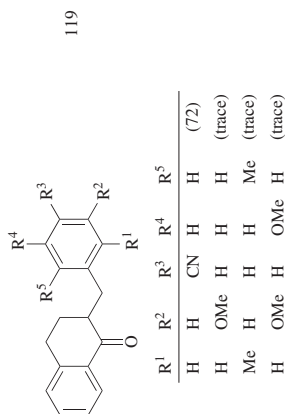
Pt(OAc)₂ (2.5%),
RuPhos (5%),
K₂CO₃ (3 eq),
toluene-H₂O, 85°, 14 h



119



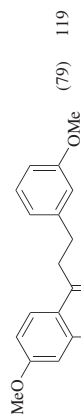
Pt(OAc)₂ (2.5%),
RuPhos (5%),
K₂CO₃ (3 eq),
toluene-H₂O, 85°, 14 h



119



Pt(OAc)₂ (2.5%),
RuPhos (5%),
K₂CO₃ (3 eq),
toluene-H₂O, 85°, 14 h



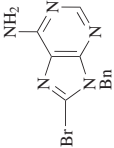
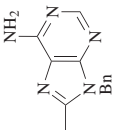
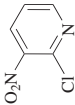
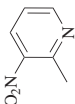
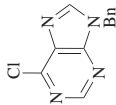
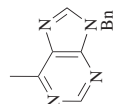
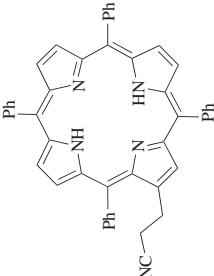
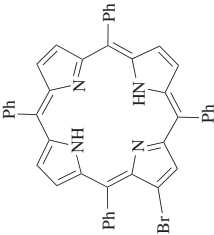
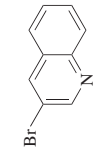
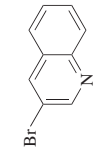
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TABLE 5A. CROSS-COUPLING OF ALKYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Alkyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₁		Pd(OAc) ₂ (2.5%), RuPhos (5%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 85°, 14 h		(87) 119
C ₁₃		Pd(OAc) ₂ (2.5%), RuPhos (5%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 85°, 14 h		(81) 119

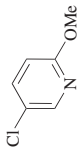
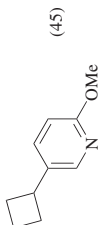
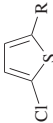
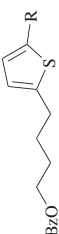
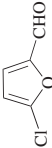
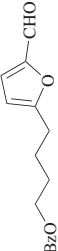
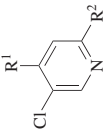
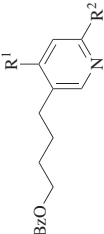
^aThe trifluoroborate derivative comes from the hydroboration/cross-coupling reaction of the corresponding 1,2-dibora species.^bThe yield of the product was determined by GC analysis.

TABLE 5B. CROSS-COUPLING OF ALKYLTRIFLUOROBORATES WITH HETEROARYL ELECTROPHILES

Alkyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁ MeBF ₃ ⁻ K ⁺		Pd(OAc) ₂ (10%), TPPTS, Cs ₂ CO ₃ (3 eq), MeCN-H ₂ O, MW, 150°, 5 min	 (0)	104
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (9%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, reflux, 16–18 h	 (32)	113
		Pd(OAc) ₂ (10%), TPPTS, Cs ₂ CO ₃ (3 eq), MeCN-H ₂ O, MW, 150°, 5 min	 (44)	104
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (25%), Cs ₂ CO ₃ (20 eq), THF-H ₂ O, 80°	 (70)	115
C ₃ NC-CH ₂ -CH ₂ -BF ₃ ⁻ K ⁺		Pd(OAc) ₂ (7.5%), RuPhos (15%), K ₃ PO ₄ (3 eq), toluene-H ₂ O, 115°, 48 h	 (37)	278
C ₄				

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

TABLE 5B. CROSS-COUPLING OF ALKYLTRIFLUOROBORATES WITH HETEROARYL ELECTROPHILES (Continued)

Alkyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc) ₂ (2%), <i>n</i> -BuPAd ₂ (3%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 100°, 24 h	 (45)	112
		Pd(OAc) ₂ (2%), RuPhos (4%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 80°, 24 h	 (81)	114
		Pd(OAc) ₂ (2%), RuPhos (4%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 80°, 24 h	 R	114 (96) (76) (71)
		Pd(OAc) ₂ (2%), RuPhos (4%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 80°, 24 h	 (83)	114
		Pd(OAc) ₂ (2%), RuPhos (4%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 80°, 24 h	 R ¹ R ²	114
			H H (93)	
			H F (73)	
			H OMe (97)	
			CHO H (85)	

C₄

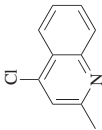
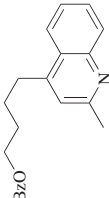
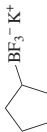
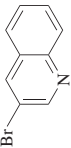
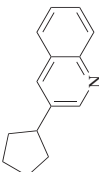
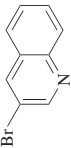
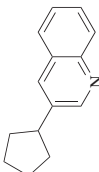
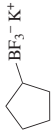
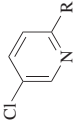
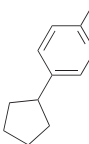
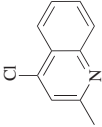
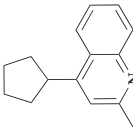
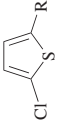
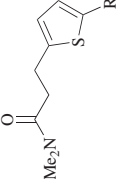
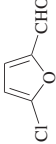
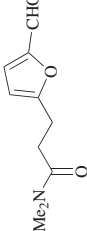
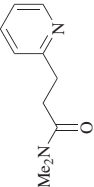
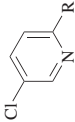
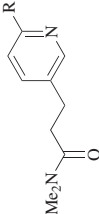
		Pd(OAc)₂ (2%), RuPhos (4%), K₂CO₃ (3 eq), toluene-H₂O, 80°, 24 h	114												
		Pd(OAc)₂ (2.5%), RuPhos (5%), K₂CO₃ (3 eq), toluene-H₂O, 85°, 18 h	120												
		Pd(OAc)₂ (x%), ligand (2x%), K₃PO₄ (3 eq), toluene-H₂O, 115°	278												
		<table><tr><th>x</th><th>Ligand</th><th></th></tr><tr><td>7.5</td><td>RuPhos</td><td>(40)</td></tr><tr><td>20</td><td>SPhos</td><td>(15)</td></tr></table>	x	Ligand		7.5	RuPhos	(40)	20	SPhos	(15)				
x	Ligand														
7.5	RuPhos	(40)													
20	SPhos	(15)													
		Pd(OAc)₂ (x%), RuPhos (2x%), K₃PO₄ (3 eq), toluene-H₂O, 115°, 88 h	278												
		<table><tr><th>x</th><th>Ligand</th><th>Time (h)</th></tr><tr><td>7.5</td><td>RuPhos</td><td>20 (40)</td></tr><tr><td>7.5</td><td>RuPhos</td><td>88 (60)</td></tr><tr><td>20</td><td>SPhos</td><td>20 (25)</td></tr></table>	x	Ligand	Time (h)	7.5	RuPhos	20 (40)	7.5	RuPhos	88 (60)	20	SPhos	20 (25)	78
x	Ligand	Time (h)													
7.5	RuPhos	20 (40)													
7.5	RuPhos	88 (60)													
20	SPhos	20 (25)													

TABLE 5B. CROSS-COUPLING OF ALKYLTRIFLUOROBORATES WITH HETEROARYL ELECTROPHILES (Continued)

Alkyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc) ₂ (2%), <i>n</i> -BuPAd ₂ (3%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 100°, 24 h	 R H (57) F (77) OMe (92)	78
		Pd(OAc) ₂ (2%), <i>n</i> -BuPAd ₂ (3%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 100°, 24 h	 (88)	78
		Pd(OAc) ₂ (2.5%), SPhos (5%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 85°, 14 h	 R H (79) CHO (66)	121
		Pd(OAc) ₂ (2.5%), SPhos (5%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 85°, 14 h	 CHO (73)	121
		Pd(OAc) ₂ (2.5%), SPhos (5%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 85°, 14 h	 (trace)	121
		Pd(OAc) ₂ (2.5%), SPhos (5%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 85°, 14 h	 R H (50) F (60) OMe (87)	121

C₅

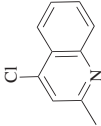
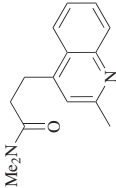
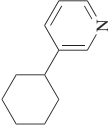
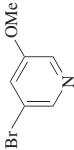
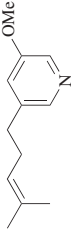
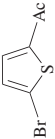
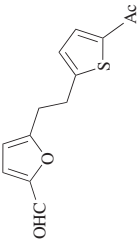
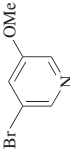
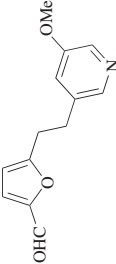
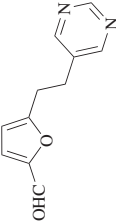
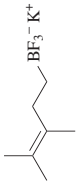
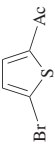
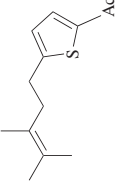
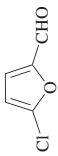
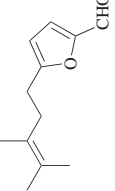
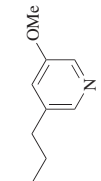
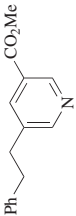
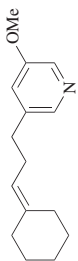
C ₆			Pd(OAc) ₂ (2.5%), SPhos (5%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 85°, 14 h	(72)	121
			Pd(OAc) ₂ (5%), <i>n</i> -BuPdAd ₂ (7.5%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 100°, 72 h	(87)	78
			Pd(OAc) ₂ (2%), RuPhos (4%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 80°, 24 h	(>69)	279
			Pd(OAc) ₂ (2%), RuPhos (4%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 80°, 24 h	(>75)	279
C ₇			Pd(OAc) ₂ (2%), RuPhos (4%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 80°, 24 h	(>56)	279
			Pd(OAc) ₂ (2%), RuPhos (4%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 80°, 24 h	(>60)	279

TABLE 5B. CROSS-COUPLING OF ALKYLTRIFLUOROBORATES WITH HETEROARYL ELECTROPHILES (Continued)

Alkyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇				
		Pd(OAc) ₂ (2%), RuPhos (4%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 80°, 24 h	 (>79)	279
		Pd(OAc) ₂ (2%), RuPhos (4%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 80°, 24 h	 (>79)	279
C ₈				
		Pd(OAc) ₂ (2%), RuPhos (4%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 80°, 24 h	 (>80)	279
C ₉		PdCl ₂ (dppf)•CH ₂ Cl ₂ (5%), K ₃ PO ₄ (4 eq), DMF-THF, 70°, 6 h	 (60)	161
		Pd(OAc) ₂ (2%), RuPhos (4%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 80°, 24 h	 (>81)	279

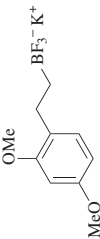
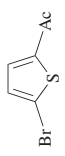
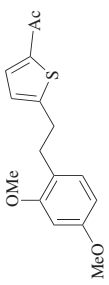
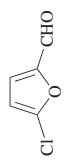
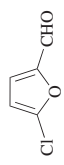
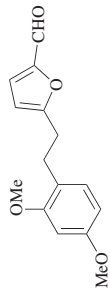
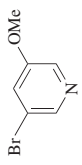
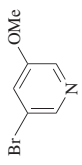
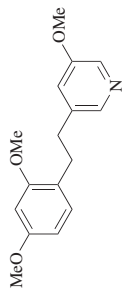
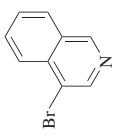
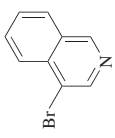
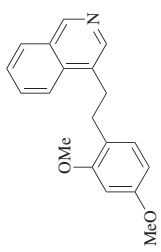
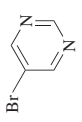
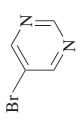
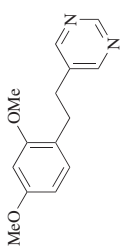
		$\text{Pd}(\text{OAc})_2$ (2%), RuPhos (4%), K_2CO_3 (3 eq), toluene–H ₂ O, 80°, 24 h		(>83)	279
		$\text{Pd}(\text{OAc})_2$ (2%), RuPhos (4%), K_2CO_3 (3 eq), toluene–H ₂ O, 80°, 24 h		(>84)	279
		$\text{Pd}(\text{OAc})_2$ (2%), RuPhos (4%), K_2CO_3 (3 eq), toluene–H ₂ O, 80°, 24 h		(>82)	279
		$\text{Pd}(\text{OAc})_2$ (2%), RuPhos (4%), K_2CO_3 (3 eq), toluene–H ₂ O, 80°, 24 h		(>72)	279
		$\text{Pd}(\text{OAc})_2$ (2%), RuPhos (4%), K_2CO_3 (3 eq), toluene–H ₂ O, 80°, 24 h		(>75)	279

TABLE 5B. CROSS-COUPLING OF ALKYLTRIFLUOROBORATES WITH HETEROARYL ELECTROPHILES (Continued)

Alkyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₁ 		Pd(OAc) ₂ (2.5%), RuPhos (5%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 85°, 14 h		(60) 119
		Pd(OAc) ₂ (2.5%), RuPhos (5%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 85°, 14 h		(0) 119
		Pd(OAc) ₂ (2.5%), RuPhos (5%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 85°, 14 h		R H (72) 119 F (73) OMe (87)
		Pd(OAc) ₂ (2.5%), RuPhos (5%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 85°, 14 h		(60) 119
		Pd(OAc) ₂ (2.5%), RuPhos (5%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 85°, 14 h		(65) 119
		Pd(OAc) ₂ (2.5%), RuPhos (5%), K ₂ CO ₃ (3 eq), toluene-H ₂ O, 85°, 14 h		(43) 119

^a The trifluoroborate derivative comes from the hydroboration/cross-coupling reaction of the corresponding 1,2-dibora species.

TABLE 5C. CROSS-COUPLING OF ALKYLTRIFLUOROBORATES WITH ALKENYL ELECTROPHILES

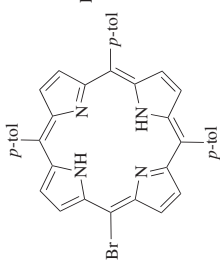
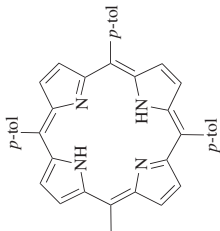
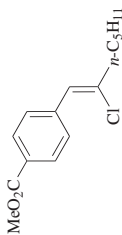
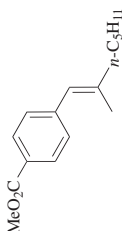
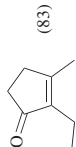
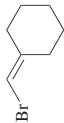
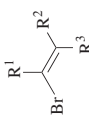
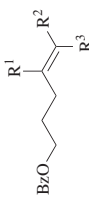
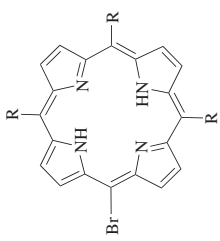
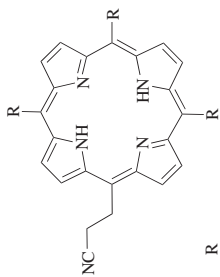
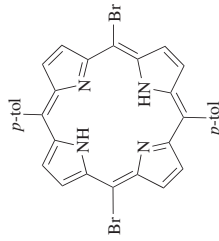
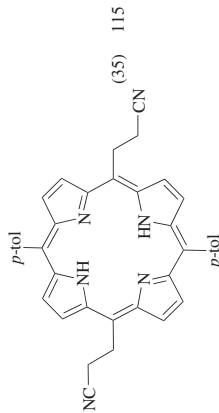
Alkyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁ MeBF ₃ ⁻ K ⁺		PdCl ₂ (dppf)•CH ₂ Cl ₂ (25%), Cs ₂ CO ₃ (20 eq), THF-H ₂ O, 80°, overnight	 (29)	115
		Pd ₂ (dba) ₃ (2.5%), RuPhos (10%), Cs ₂ CO ₃ (3 eq), THF, 80°, 18–36 h	 (67)	148
C ₂ BF ₃ ⁻ K ⁺		PdCl ₂ (dppf)•CH ₂ Cl ₂ (10%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 80°, 4 h	 (83)	76
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (10%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 80°, 5 h	 (82)	76

TABLE 5C. CROSS-COUPLING OF ALKYLTRIFLUOROBORATES WITH ALKENYL ELECTROPHILES (Continued)

Alkyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.																
$\text{BzOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{BF}_3^- \text{K}^+$		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (10%), Cs_2CO_3 (3 eq), toluene- H_2O , 80°		76																
			<table><tr><th>R¹</th><th>R²</th><th>R³</th><th>Time (h)</th></tr><tr><td>CHO</td><td>H</td><td>Ph</td><td>12 (69)</td></tr><tr><td>Ph</td><td>H</td><td>H</td><td>3 (54)</td></tr><tr><td>Ph</td><td>Ph</td><td>Ph</td><td>3 (91)</td></tr></table>	R ¹	R ²	R ³	Time (h)	CHO	H	Ph	12 (69)	Ph	H	H	3 (54)	Ph	Ph	Ph	3 (91)	
R ¹	R ²	R ³	Time (h)																	
CHO	H	Ph	12 (69)																	
Ph	H	H	3 (54)																	
Ph	Ph	Ph	3 (91)																	
$\text{NCCH}_2\text{CH}_2\text{CH}_2\text{BF}_3^- \text{K}^+$		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (25%), Cs_2CO_3 (20 eq), THF- H_2O , 80°, overnight		115																
			<table><tr><th>R</th></tr><tr><td>4-MeC₆H₄ (73)</td></tr><tr><td>c-C₆H₁₁ (25)</td></tr></table>	R	4-MeC ₆ H ₄ (73)	c-C ₆ H ₁₁ (25)														
R																				
4-MeC ₆ H ₄ (73)																				
c-C ₆ H ₁₁ (25)																				
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (25%), Cs_2CO_3 (40 eq), THF- H_2O , 80°, overnight		115																

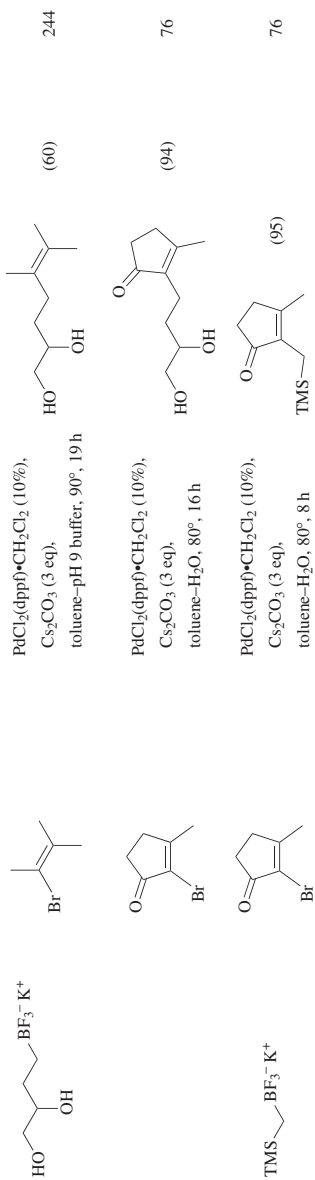
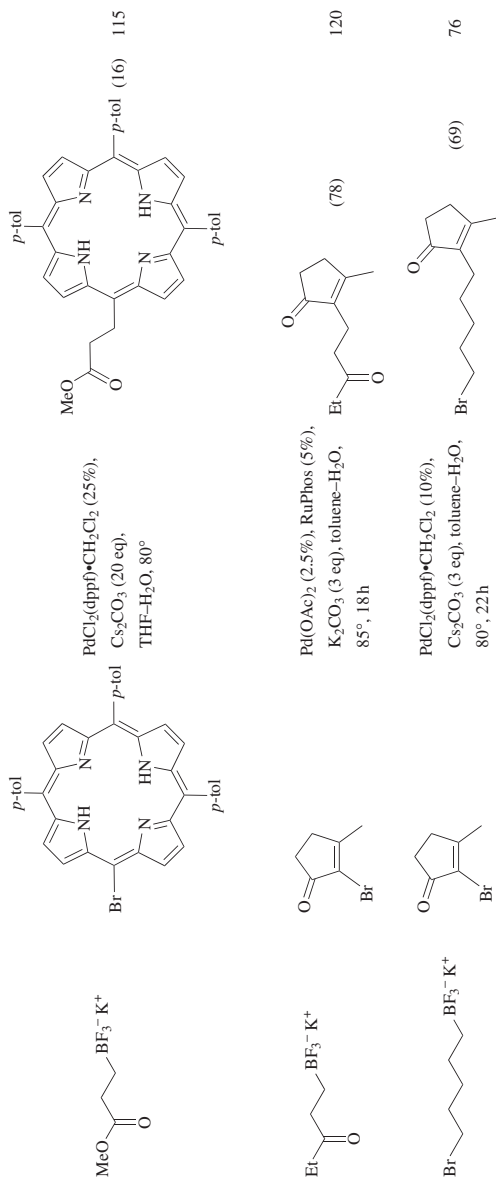
C₄C₅

TABLE 5C. CROSS-COUPLING OF ALKYLTRIFLUOROBORATES WITH ALKENYL ELECTROPHILES (Continued)

	Alkyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.													
C ₅			$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (25%), C_5CO_3 (20 eq), THF-H ₂ O, 80°, overnight		115													
C ₆			$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (10%), C_5CO_3 (3 eq), toluene-H ₂ O, 80°, 7 h		76													
			$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (9%), C_5CO_3 (3 eq), THF-H ₂ O, reflux, 18 h		58													
			$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (10%), C_5CO_3 (3 eq), toluene-H ₂ O, 80°		76													
				<table><tr><th>R¹</th><th>R²</th><th>R³</th><th>Time (h)</th></tr><tr><td>Me</td><td>Me</td><td>Me</td><td>3 (93)</td></tr><tr><td>H</td><td>H</td><td>(CH₂)₄OTBS</td><td>2 (78)</td></tr></table>	R ¹	R ²	R ³	Time (h)	Me	Me	Me	3 (93)	H	H	(CH ₂) ₄ OTBS	2 (78)		
R ¹	R ²	R ³	Time (h)															
Me	Me	Me	3 (93)															
H	H	(CH ₂) ₄ OTBS	2 (78)															
			$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (x%), base (3 eq), toluene-H ₂ O, 80°		<table><tr><th>x</th><th>Base</th><th>Time (h)</th></tr><tr><td>10</td><td>C₅CO₃</td><td>7 (74)</td></tr><tr><td>5</td><td>C₅CO₃</td><td>24 (68)</td></tr><tr><td>10</td><td>K₂CO₃</td><td>7 (39)</td></tr></table>	x	Base	Time (h)	10	C ₅ CO ₃	7 (74)	5	C ₅ CO ₃	24 (68)	10	K ₂ CO ₃	7 (39)	76
x	Base	Time (h)																
10	C ₅ CO ₃	7 (74)																
5	C ₅ CO ₃	24 (68)																
10	K ₂ CO ₃	7 (39)																

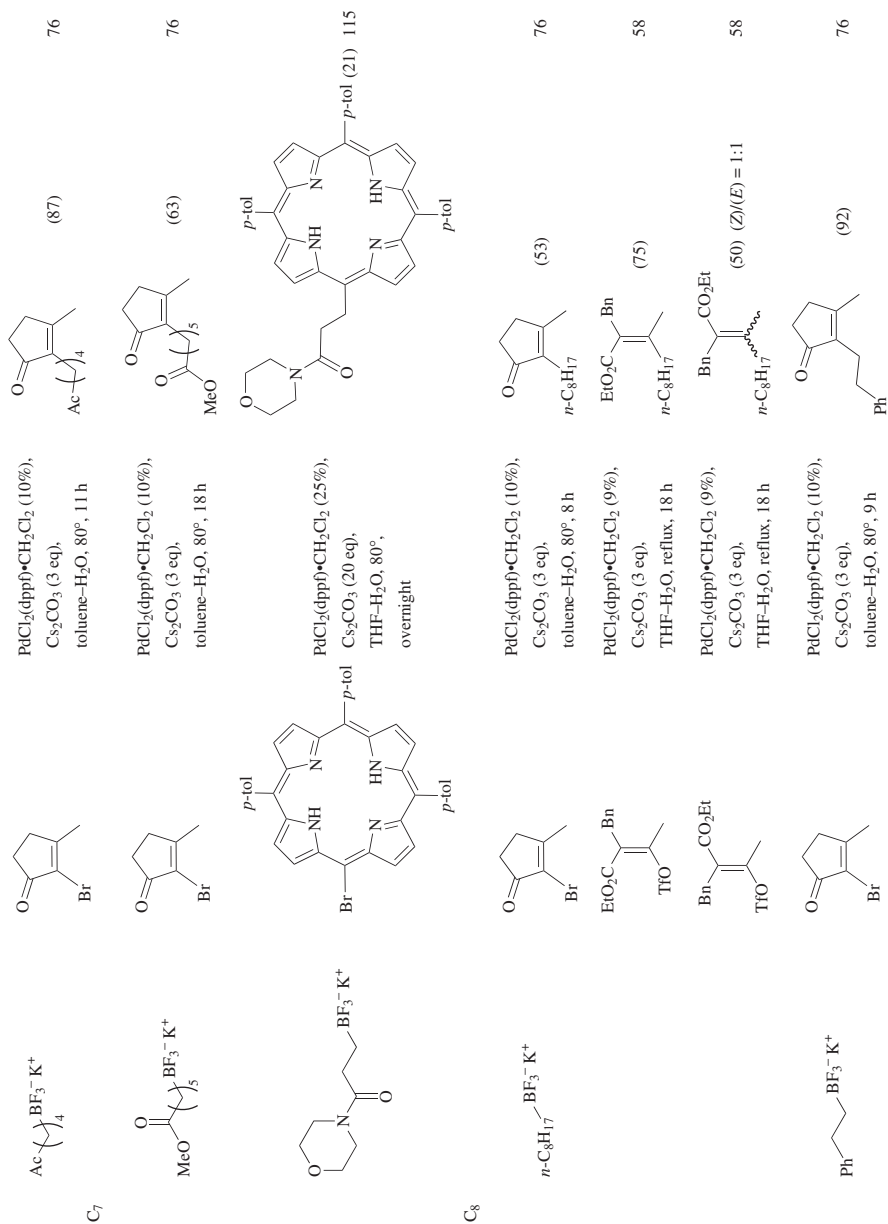


TABLE 5C. CROSS-COUPLING OF ALKYLTRIFLUOROBORATES WITH ALKENYL ELECTROPHILES (Continued)

Alkyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₉		PdCl ₂ (dppf)•CH ₂ Cl ₂ (10%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 80°, 12 h	 (41)	76
		Pd(PPh ₃) ₄ (10%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 80°, 12 h	 (90)	76
C ₁₀		PdCl ₂ (dppf)•CH ₂ Cl ₂ (10%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 80°, 18 h	 (63)	76
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (10%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 80°, 24 h	 (>74)	279
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (10%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 80°, 24 h	 (>72)	279
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (10%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 80°, 24 h	 (>32)	279

^a The trifluoroborate derivative comes from the hydroboration/cross-coupling reaction of the corresponding 1,2-dibora species.

TABLE 5D. CROSS-COUPLING OF ALKYLTRIFLUOROBORATES WITH IMIDOYL ELECTROPHILES

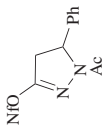
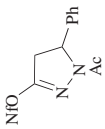
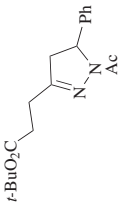
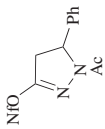
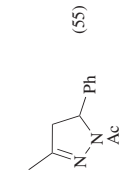
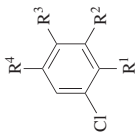
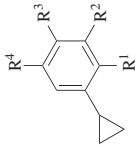
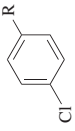
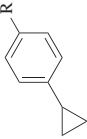
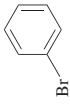
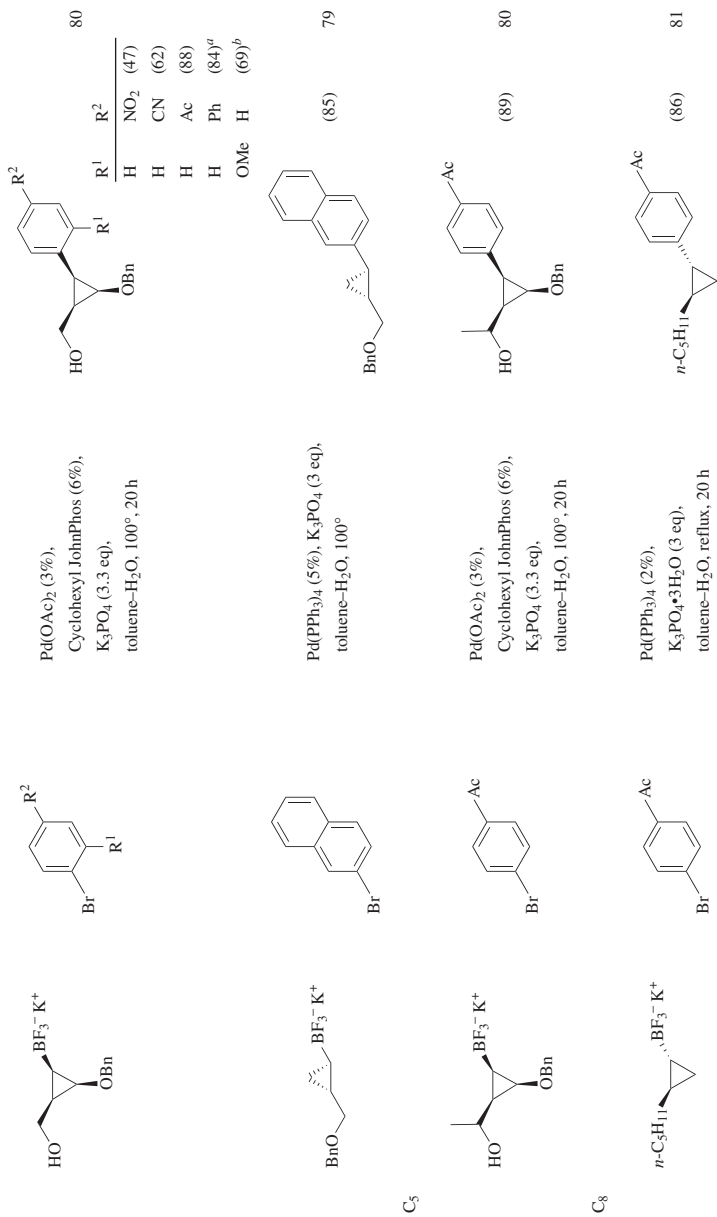
	Alkyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁	MeBF ₃ ⁻ K ⁺		PdCl ₂ (dppf)•CH ₂ Cl ₂ (9%), K ₂ CO ₃ (3 eq), LiCl (3 eq), toluene-H ₂ O, 100°, 18 h	 (0)	123
C ₇	<i>t</i> -BuO ₂ C—CH ₂ —CH ₂ —BF ₃ ⁻ K ⁺		PdCl ₂ (dppf)•CH ₂ Cl ₂ (9%), K ₂ CO ₃ (3 eq), LiCl (3 eq), toluene-H ₂ O, 100°, 18 h	 (32)	123
C ₈	Ph—CH ₂ —CH ₂ —CH ₂ —BF ₃ ⁻ K ⁺		PdCl ₂ (dppf)•CH ₂ Cl ₂ (9%), K ₂ CO ₃ (3 eq), LiCl (3 eq), toluene-H ₂ O, 100°, 18 h	 (55)	123

TABLE 6A. CROSS-COUPLING OF CYCLOPROPYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES

Cyclopropyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc) ₂ (3%), XPhos (6%), K ₂ CO ₃ (3 eq), CPME-H ₂ O, 100°		112
		Pd(OAc) ₂ (3%), XPhos (6%), K ₂ CO ₃ (3 eq), THF-H ₂ O, 80°, 24 h		112
		Pd(PPh ₃) ₄ (5%), K ₃ PO ₄ (3 eq), toluene-H ₂ O, 100°		79



C₅

C₈

TABLE 6A. CROSS-COUPLING OF CYCLOPROPYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Cyclopropyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.								
C ₈		Pd(PPh ₃) ₄ (2%), K ₃ PO ₄ ·3H ₂ O (3 eq), toluene-H ₂ O, reflux, 20 h		81								
	<table><tr><th>R¹</th><th>R²</th></tr><tr><td>H</td><td>Ac</td></tr><tr><td>OMe</td><td>H</td></tr></table> (87) (79)		R ¹	R ²	H	Ac	OMe	H				
R ¹	R ²											
H	Ac											
OMe	H											
C ₉		Pd(PPh ₃) ₄ (2%), K ₃ PO ₄ ·3H ₂ O (3 eq), toluene-H ₂ O, reflux, 20 h		81								
			<table><tr><th>R¹</th><th>R²</th></tr><tr><td>H</td><td>Ac</td></tr><tr><td>H</td><td>Ph</td></tr><tr><td>OMe</td><td>H</td></tr></table> (88) (80) (76)	R ¹	R ²	H	Ac	H	Ph	OMe	H	
	R ¹		R ²									
H	Ac											
H	Ph											
OMe	H											
C ₁₀		Pd(PPh ₃) ₄ (2%), K ₃ PO ₄ ·3H ₂ O (3 eq), toluene-H ₂ O, reflux, 20 h		81								

^a These products were isolated as a 12:88 ratio between the protodeboronated cyclopropane and the desired product.^b These products were isolated as a 22:78 ratio between the protodeboronated cyclopropane and the desired product.

TABLE 6B. CROSS-COUPLING OF CYCLOPROPYLTRIFLUOROBORATES WITH HETEROARYL ELECTROPHILES

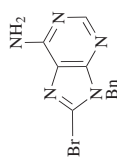
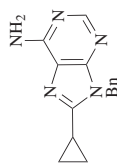
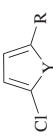
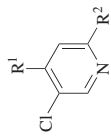
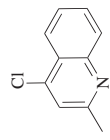
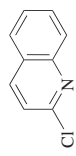
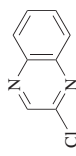
Cyclopropyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc) ₂ (3%), <i>n</i> -BuPdAd ₂ (3%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 100°, 24 h	 (48)	104
		Pd(OAc) ₂ (2%), <i>n</i> -BuPdAd ₂ (3%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 100°, 24 h	Y R S CHO (99) S Ac (90) O CHO (78)	112
		Pd(OAc) ₂ (2%), <i>n</i> -BuPdAd ₂ (3%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 100°, 24 h	R ¹ R ² H OMe (85) CHO H (52)	112
		Pd(OAc) ₂ (2%), <i>n</i> -BuPdAd ₂ (3%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 100°, 24 h	(95)	112
		Pd(OAc) ₂ (2%), <i>n</i> -BuPdAd ₂ (3%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 100°, 24 h	(70)	112
		Pd(OAc) ₂ (2%), <i>n</i> -BuPdAd ₂ (3%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 100°, 24 h	(79)	112

TABLE 6B. CROSS-COUPLING OF CYCLOPROPYLTRIFLUOROBORATES WITH HETEROARYL ELECTROPHILES (Continued)

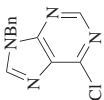
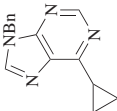
Cyclopropyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
 $\text{BF}_3^- \text{K}^+$		$\text{Pd}(\text{OAc})_2$ (3%), <i>n</i> -BuPdAd ₂ (3%), Cs_2CO_3 (3 eq), toluene- H_2O , 100°, 24 h	 (75)	104

TABLE 7A. CROSS-COUPLING OF BENZYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES

	Benzyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇			$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (9%), C_2CO_3 (3 eq), THF-H ₂ O, reflux, 18 h	 R H (91) ^a Ac (96) NO ₂ (89) Cl (57)	58
C ₈			$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (9%), C_2CO_3 (3 eq), THF-H ₂ O, reflux, 18 h	 X Br (70) I (16)	58
			$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (9%), C_2CO_3 (3 eq), THF-H ₂ O, reflux, 18 h	 (4)	58

^a The yield of the product was determined by GC analysis.

TABLE 7B. CROSS-COUPLING OF BENZYLTRIFLUOROBORATES WITH HETEROARYL ELECTROPHILES

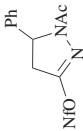
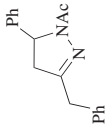
Benzyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
$\text{Ph-CH}_2\text{-BF}_3^-\text{K}^+$		1. $\text{Pd}(\text{OAc})_2$ (1%), K_2CO_3 (3 eq), H_2O , 65° , 5 h 2. H_4NPF_6	 (48)	122
		1. $\text{Pd}(\text{OAc})_2$ (1%), K_2CO_3 (3 eq), H_2O , 65° , 5 h 2. H_4NPF_6	 (64)	122
		1. $\text{Pd}(\text{OAc})_2$ (1%), K_2CO_3 (3 eq), H_2O , 65° , 5 h 2. H_4NPF_6	 (39)	122
		1. $\text{Pd}(\text{OAc})_2$ (1%), K_2CO_3 (3 eq), H_2O , 65° , 5 h 2. H_4NPF_6	 (67)	122
		1. $\text{Pd}(\text{OAc})_2$ (1%), K_2CO_3 (3 eq), H_2O , 65° , 5 h 2. H_4NPF_6	 (0)	223

C₇

TABLE 7C. CROSS-COUPLING OF BENZYLTRIFLUOROBORATES WITH ALKENYL ELECTROPHILES

Benzyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇ 		PdCl ₂ (dppf)•CH ₂ Cl ₂ (9%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, reflux, 18 h	(89)	58
		Pd(PPh ₃) ₂ Cl ₂ (5%), aq Na ₂ CO ₃ (3.5 eq), THF, 60°	(31)	68
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (10%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, 60°	(50)	68

TABLE 7D. CROSS-COUPLING OF BENZYLTRIFLUOROBORATES WITH IMIDOYL ELECTROPHILES

Benzyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
$\text{Ph}-\text{CH}_2-\text{BF}_3^-\text{K}^+$		PdCl ₂ (dppf)•CH ₂ Cl ₂ (9%), K ₂ CO ₃ (3 eq), LiCl (3 eq), toluene–H ₂ O, 100°, 18 h	 (73)	123

C₇

TABLE 8A. CROSS-COUPLING OF ALLYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES

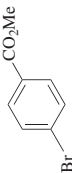
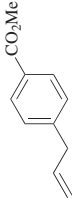
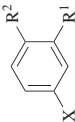
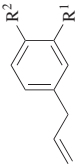
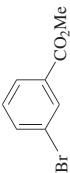
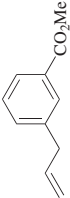
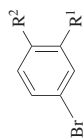
Allyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.																																																			
		Pd(OAc) ₂ (3%), Walphos (3.6%), K ₂ CO ₃ (3 eq), THF reflux, 22 h	 (99)	125																																																			
		PdCl ₂ (D- <i>i</i> -BPF) (3%), K ₂ CO ₃ (3 eq), <i>i</i> -PrOH-H ₂ O, MW 120°	 281																																																				
		<table><tr><th>X</th><th>R¹</th><th>R²</th><th>Time (min)</th></tr><tr><td>Br</td><td>Cl</td><td>H</td><td>30 (71)</td></tr><tr><td>Br</td><td>H</td><td>Cl</td><td>20 (94)</td></tr><tr><td>I</td><td>Br</td><td>H</td><td>40 (71)</td></tr><tr><td>I</td><td>Cl</td><td>H</td><td>45 (84)</td></tr><tr><td>I</td><td>H</td><td>H</td><td>35 (77)</td></tr><tr><td>I</td><td>H</td><td>I</td><td>50 (95)</td></tr><tr><td>I</td><td>H</td><td>Cl</td><td>40 (79)</td></tr><tr><td>I</td><td>H</td><td>Br</td><td>30 (95)</td></tr><tr><td>I</td><td>H</td><td>F</td><td>30 (85)</td></tr><tr><td>I</td><td>H</td><td>CF₃</td><td>50 (77)</td></tr><tr><td>I</td><td>H</td><td>CN</td><td>30 (81)</td></tr><tr><td>I</td><td>H</td><td>Me</td><td>20 (95)</td></tr></table>	X	R ¹	R ²	Time (min)	Br	Cl	H	30 (71)	Br	H	Cl	20 (94)	I	Br	H	40 (71)	I	Cl	H	45 (84)	I	H	H	35 (77)	I	H	I	50 (95)	I	H	Cl	40 (79)	I	H	Br	30 (95)	I	H	F	30 (85)	I	H	CF ₃	50 (77)	I	H	CN	30 (81)	I	H	Me	20 (95)	
X	R ¹	R ²	Time (min)																																																				
Br	Cl	H	30 (71)																																																				
Br	H	Cl	20 (94)																																																				
I	Br	H	40 (71)																																																				
I	Cl	H	45 (84)																																																				
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I	H	Cl	40 (79)																																																				
I	H	Br	30 (95)																																																				
I	H	F	30 (85)																																																				
I	H	CF ₃	50 (77)																																																				
I	H	CN	30 (81)																																																				
I	H	Me	20 (95)																																																				
		Pd(OAc) ₂ (3%), D- <i>i</i> -BPF (3.6%), K ₂ CO ₃ (3 eq), THF, reflux, 22 h	 (38)	124																																																			

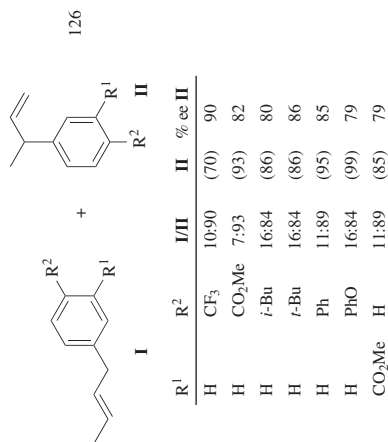
TABLE 8A. CROSS-COUPLING OF ALLYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Allyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc) ₂ (3%), ligand (3%), K ₂ CO ₃ (3 eq), THF-H ₂ O, 20 h, reflux	+ I II 124	
		Ligand I/II dppm 22:78 (35) ^a dppe 63:37 (17) ^a dppf <1:99 (68) ^a D- <i>r</i> -BPF <1:99 (87)		
		Pd(PPh ₃) ₄ (3%), K ₂ CO ₃ (3 eq), THF-H ₂ O, 20 h, reflux	+ I II 124	
		Pd(OAc) ₂ (3%), C ₃ PF ₅ - <i>t</i> -Bu (3.6%), K ₂ CO ₃ (3 eq), MeOH-H ₂ O, 80°, 4.5 h	+ I II I/II = 22:78 (42) ^a II = (97) 80% ee	126

C₄

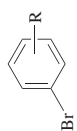
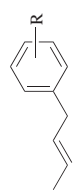
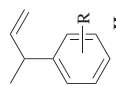


$\text{Pd}(\text{OAc})_2$ (3%), $\text{CyPF-}i\text{-Bu}$ (3.6%),
 K_2CO_3 (3 eq), $\text{H}_2\text{O-MeOH}$,
 80° , 22 h

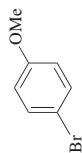


R ¹	R ²	I/II	II	% ee II
H	CF ₃	10:90	(70)	90
H	CO ₂ Me	7:93	(93)	82
H	<i>i</i> -Bu	16:84	(86)	80
H	<i>t</i> -Bu	16:84	(86)	86
H	Ph	11:89	(95)	85
H	PhO	16:84	(99)	79
CO ₂ Me	H	11:89	(85)	79

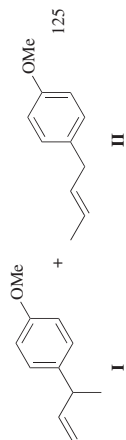
TABLE 8A. CROSS-COUPLING OF ALLYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Allyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.																																																			
		Pd(OAc) ₂ (3%), D- <i>r</i> -BPF (3.6%), K ₂ CO ₃ (3 eq), THF, reflux, 22 h	 I  II 124																																																				
	R		<table><tr><th>R</th><th>I + II</th><th>I/II</th></tr><tr><td>4-NH₂</td><td>(80)</td><td><1:99</td></tr><tr><td>4-NHBz</td><td>(96)</td><td><1:99</td></tr><tr><td>4-MeO</td><td>(90)</td><td><1:99</td></tr><tr><td>3-MeO</td><td>(85)</td><td><1:99</td></tr><tr><td>2-MeO</td><td>(84)</td><td><1:99</td></tr><tr><td>4-<i>i</i>-Bu</td><td>(88)</td><td>2:98</td></tr><tr><td>2,6-Me</td><td>(87)</td><td><1:99</td></tr><tr><td>4-CO₂Me</td><td>(92)</td><td><1:99</td></tr><tr><td>3-CO₂Me</td><td>(92)</td><td><1:99</td></tr><tr><td>2-CO₂Me</td><td>(92)</td><td><1:99</td></tr><tr><td>4-CN</td><td>(77)</td><td><1:99</td></tr><tr><td>4-CF₃</td><td>(83)</td><td><1:99</td></tr><tr><td>4-O₂N</td><td>(80)</td><td><1:99</td></tr><tr><td>4-Ac</td><td>(94)^b</td><td><1:99</td></tr><tr><td>2-naphthyl</td><td>(93)</td><td><1:99</td></tr><tr><td>4-<i>i</i>-Bu</td><td>(91)</td><td>0:100</td></tr></table>	R	I + II	I/II	4-NH ₂	(80)	<1:99	4-NHBz	(96)	<1:99	4-MeO	(90)	<1:99	3-MeO	(85)	<1:99	2-MeO	(84)	<1:99	4- <i>i</i> -Bu	(88)	2:98	2,6-Me	(87)	<1:99	4-CO ₂ Me	(92)	<1:99	3-CO ₂ Me	(92)	<1:99	2-CO ₂ Me	(92)	<1:99	4-CN	(77)	<1:99	4-CF ₃	(83)	<1:99	4-O ₂ N	(80)	<1:99	4-Ac	(94) ^b	<1:99	2-naphthyl	(93)	<1:99	4- <i>i</i> -Bu	(91)	0:100	
R	I + II	I/II																																																					
4-NH ₂	(80)	<1:99																																																					
4-NHBz	(96)	<1:99																																																					
4-MeO	(90)	<1:99																																																					
3-MeO	(85)	<1:99																																																					
2-MeO	(84)	<1:99																																																					
4- <i>i</i> -Bu	(88)	2:98																																																					
2,6-Me	(87)	<1:99																																																					
4-CO ₂ Me	(92)	<1:99																																																					
3-CO ₂ Me	(92)	<1:99																																																					
2-CO ₂ Me	(92)	<1:99																																																					
4-CN	(77)	<1:99																																																					
4-CF ₃	(83)	<1:99																																																					
4-O ₂ N	(80)	<1:99																																																					
4-Ac	(94) ^b	<1:99																																																					
2-naphthyl	(93)	<1:99																																																					
4- <i>i</i> -Bu	(91)	0:100																																																					

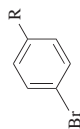
C₄



Pd(OAc)₂ (3%), ligand (3%),
K₂CO₃ (3 eq), THF-H₂O,
reflux, 20 h



Ligand	I + II	I/II
PPh ₃	(42) ^a	78:22
dppm	(35) ^a	78:22
dppe	(17) ^a	37:63
dppp	(37) ^a	>99:1
dppf	(68) ^a	>99:1
DPEphos	(21) ^a	>99:1
Xantphos	(10) ^a	>99:1
DBFPhos	(10) ^a	>99:1
D-1-BPF	(87)	>99:1



Pd(OAc)₂ (3%), D-*t*-BPF (3.6%),
K₂CO₃ (3 eq), THF
reflux, 22 h

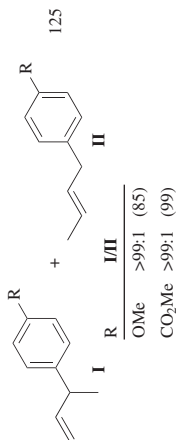
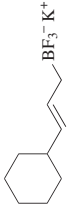
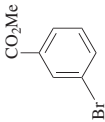
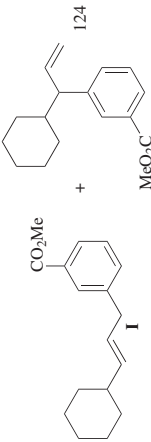
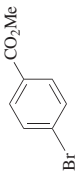
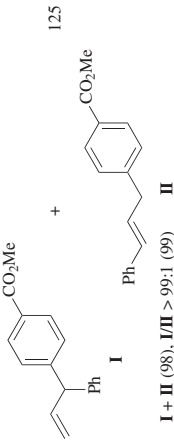


TABLE 8A. CROSS-COUPLING OF ALLYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Allyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.			
		Pd(OAc) ₂ (3%), ligand (3.6%), K ₂ CO ₃ (3 eq), solvent, reflux, 22 h	 + 	125			
		Ligand	Solvent	I + II	I/II	% ee II	
		(R)-BINAP	THF	(86)	32:68	3	—
		(S,S)-Et-Ferrocenyl-TANE	THF	(84)	69:31	12	—
		L5	THF	(98)	7:93	31	(R)
		(R,S)-CyPF- <i>t</i> -Bu	THF	(96)	8:92	63	(R)
		(R,S)-CyPF- <i>t</i> -Bu	THF-H ₂ O	(93)	5:95	82	(R)
		(R,S)-CyPF- <i>t</i> -Bu	MeOH-H ₂ O	(93)	7:93	82	(R)
		PdCl ₂ (D- <i>t</i> -BPPF) (3%), K ₂ CO ₃ (3 eq), <i>i</i> -PrOH-H ₂ O, MW, 120°	 + 	I + II	R	I + II	
				Cl	(54)		
				Br	(41)		
				Me	(77)		
		Pd(OAc) ₂ (3%), CyPF- <i>t</i> -Bu (3.6%), K ₂ CO ₃ (3 eq), H ₂ O-MeOH, 80°, 4.5 h	 + 	I + II	I/II = 12:88		
					II = (90) 83% ee		

TABLE 8A. CROSS-COUPLING OF ALLYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Allyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc) ₂ (3%), D- <i>r</i> -BPPF (3.6%), K ₂ CO ₃ (3 eq), THF, reflux, 22 h	 I + II (98), I/II < 1:99 I (Z)/(E) = 80:20	124
		Pd(OAc) ₂ (3%), D- <i>r</i> -BPPF (3.6%), K ₂ CO ₃ (3 eq), THF, reflux, 22 h	 I + II (98), I/II > 99:1 (99)	125

^a The yield of the crude product was determined by ¹H NMR.^b This yield was obtained under optimized conditions.

TABLE 8B. CROSS-COUPLING OF ALLYLTRIFLUOROBORATES WITH ALKENYL ELECTROPHILES

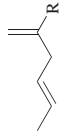
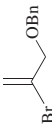
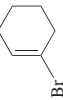
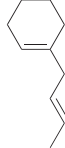
Allyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc) ₂ (3%), CyPF- <i>t</i> -Bu (3.6%), K ₂ CO ₃ (3 eq), H ₂ O-MeOH, 80°, 22 h	 (47)	126
		Pd(OAc) ₂ (3%), D- <i>t</i> -BPF (3.6%), K ₂ CO ₃ (3 eq), THF, reflux, 22 h	 I +  II R I + II I/II Ph (75) <1:99 CH₂OCH₂Bn (66) <1:99	124
		Pd(OAc) ₂ (3%), CyPF- <i>t</i> -Bu (3.6%), K ₂ CO ₃ (3 eq), H ₂ O-MeOH, 80°, 22 h	 (76)	126
		Pd(OAc) ₂ (3%), D- <i>t</i> -BPF (3.6%), K ₂ CO ₃ (3 eq), THF, reflux, 22 h	 I +  II I + II (98), I/II < 1:99	124

TABLE 9A. CROSS-COUPLING OF AMINOMETHYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES

	Aminomethyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂			Pd(OAc) ₂ (3%), XPhos (6%), C ₅ CO ₃ (3 eq), THF-H ₂ O, 80°, 18–24h	X Br (81) Cl (95)	128 127
C ₅			Pd(OAc) ₂ (3%), XPhos (6%), C ₅ CO ₃ (3 eq), THF-H ₂ O, 80°, 18–24h	X Br (85) Cl (84)	128 127
			Pd(OAc) ₂ (3%), XPhos (6%), C ₅ CO ₃ (3 eq), THF-H ₂ O, 80°, 18–24h	X Br (72) Cl (74)	128 127
			Pd(OAc) ₂ (3%), XPhos (6%), C ₅ CO ₃ (3 eq), THF-H ₂ O, 80°, 18–24h	X Br (81) Cl (75)	128 127
			Pd(OAc) ₂ (3%), XPhos (6%), C ₅ CO ₃ (3 eq), THF-H ₂ O, 80°, 18–24h	(82)	127

C₆

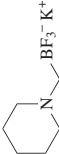
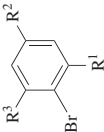
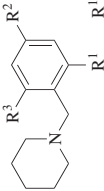
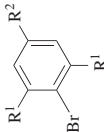
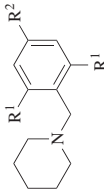
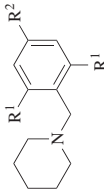
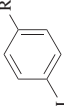
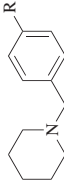
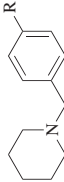
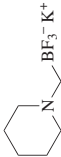
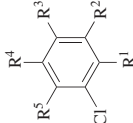
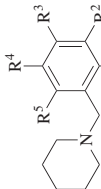
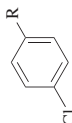
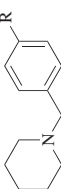
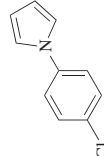
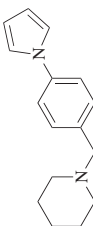
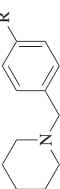
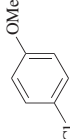
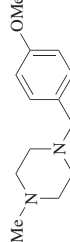
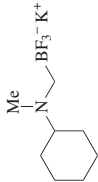
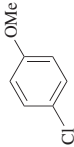
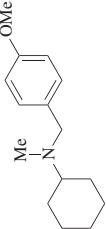
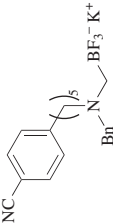
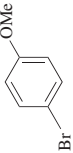
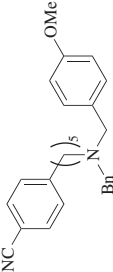
			Pd(OAc)₂ (3%), XPhos (6%), C₅CO₃ (3 eq), THF-H₂O, 80°, 22–24 h	128																																												
				<table><tr><th>R¹</th><th>R²</th><th>R³</th><th></th></tr><tr><td>H</td><td>NO₂</td><td>H</td><td>(68)</td></tr><tr><td>H</td><td>CN</td><td>H</td><td>(83)</td></tr><tr><td>H</td><td>CHO</td><td>H</td><td>(66)</td></tr><tr><td>H</td><td>OMe</td><td>H</td><td>(80)</td></tr><tr><td>H</td><td>CO₂Me</td><td>H</td><td>(83)</td></tr><tr><td>H</td><td>NMe₂</td><td>H</td><td>(72)</td></tr><tr><td>H</td><td>NHAc</td><td>H</td><td>(80)</td></tr><tr><td>H</td><td>COPh</td><td>H</td><td>(72)</td></tr><tr><td>Me</td><td>Me</td><td>Me</td><td>(69)</td></tr><tr><td>OMe</td><td>OMe</td><td>H</td><td>(75)</td></tr></table>	R ¹	R ²	R ³		H	NO ₂	H	(68)	H	CN	H	(83)	H	CHO	H	(66)	H	OMe	H	(80)	H	CO ₂ Me	H	(83)	H	NMe ₂	H	(72)	H	NHAc	H	(80)	H	COPh	H	(72)	Me	Me	Me	(69)	OMe	OMe	H	(75)
R ¹	R ²	R ³																																														
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				<table><tr><th>R</th><th></th></tr><tr><td>H</td><td>(83)</td></tr><tr><td>Ac</td><td>(82)</td></tr></table>	R		H	(83)	Ac	(82)																																						
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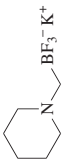
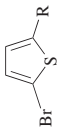
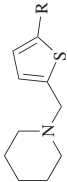
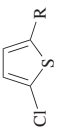
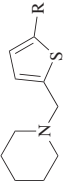
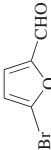
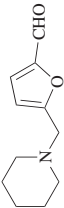
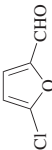
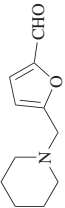
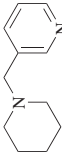
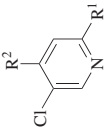
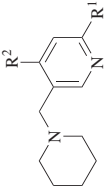
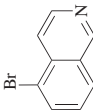
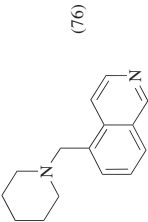
TABLE 9A. CROSS-COUPLING OF AMINOMETHYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

C ₆	Aminomethyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.																																										
			Pd(OAc) ₂ (3%), XPhos (6%), Cs ₂ CO ₃ (3 eq), THF–H ₂ O, 80°, 18–24 h		127																																										
				<table><tr><th>R¹</th><th>R²</th><th>R³</th><th>R⁴</th><th>R⁵</th><th></th></tr><tr><td>H</td><td>H</td><td>H</td><td>H</td><td>H</td><td>(85)</td></tr><tr><td>H</td><td>H</td><td>OMe</td><td>H</td><td>H</td><td>(94)</td></tr><tr><td>H</td><td>OMe</td><td>H</td><td>OMe</td><td>H</td><td>(99)</td></tr><tr><td>H</td><td>CO₂Me</td><td>H</td><td>H</td><td>H</td><td>(91)</td></tr><tr><td>Me</td><td>H</td><td>H</td><td>H</td><td>H</td><td>(63)</td></tr><tr><td>Me</td><td>H</td><td>H</td><td>H</td><td>Me</td><td>(66)</td></tr></table>	R ¹	R ²	R ³	R ⁴	R ⁵		H	H	H	H	H	(85)	H	H	OMe	H	H	(94)	H	OMe	H	OMe	H	(99)	H	CO ₂ Me	H	H	H	(91)	Me	H	H	H	H	(63)	Me	H	H	H	Me	(66)	
R ¹	R ²	R ³	R ⁴	R ⁵																																											
H	H	H	H	H	(85)																																										
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Me	H	H	H	Me	(66)																																										
			Pd(OAc) ₂ (3%), XPhos (6%), Cs ₂ CO ₃ (3 eq), CPME–H ₂ O, 95°, 18–24 h		127																																										
			Pd(OAc) ₂ (3%), XPhos (6%), Cs ₂ CO ₃ (3 eq), THF–H ₂ O, 80°, 18–24 h		127																																										
			Pd(OAc) ₂ (3%), XPhos (6%), Cs ₂ CO ₃ (3 eq), THF–H ₂ O, 80°, 18–24 h		127																																										
			Pd(OAc) ₂ (3%), XPhos (6%), Cs ₂ CO ₃ (3 eq), THF–H ₂ O, 80°, 18–24 h		127																																										

C ₇			Pd(OAc)₂ (3%), XPhos (6%), C₅H₅CO₂ (3 eq), THF-H₂O, 80°, 18–24 h		(75)	127
C ₁₃			Pd(OAc)₂ (3%), XPhos (6%), C₅H₅CO₂ (3 eq), THF-H₂O, 80°, 24 h		(>71)	225

^a The trifluoroborate derivative comes from the hydroboration/cross-coupling of a dibora species.

TABLE 9B. CROSS-COUPLING OF AMINOMETHYLTRIFLUOROBORATES WITH HETEROARYL ELECTROPHILES

Aminomethyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 		Pd(OAc) ₂ (3%), XPhos (6%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, 80°, 18–24 h	 R H (62) Ac (77)	128
		Pd(OAc) ₂ (3%), XPhos (6%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, 80°, 18–24 h	 R H (65) CHO (78) Ac (93)	127
		Pd(OAc) ₂ (3%), XPhos (6%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, 80°, 18–24 h	 (80)	128
		Pd(OAc) ₂ (3%), XPhos (6%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, 80°, 18–24 h	 (82)	127
		Pd(OAc) ₂ (3%), XPhos (6%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, 80°, 18–24 h	 (63)	128
		Pd(OAc) ₂ (3%), XPhos (6%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, 80°, 18–24 h	 R ¹ R ² H H (77) H CHO (60) OMe H (87)	127
		Pd(OAc) ₂ (3%), XPhos (6%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, 80°, 18–24 h	 (76)	128

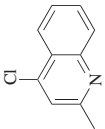
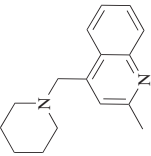
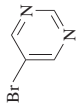
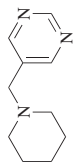
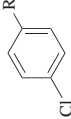
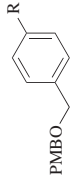
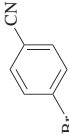
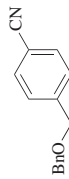
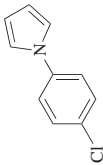
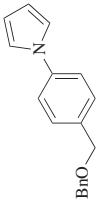
	$\text{Pd}(\text{OAc})_2$ (3%), XPhos (6%), Cs_2CO_3 (3 eq), THF-H_2O, 80°, 18–24h		(97)	127
	$\text{Pd}(\text{OAc})_2$ (3%), XPhos (6%), Cs_2CO_3 (3 eq), THF-H_2O, 80°, 18–24h		(84)	128

TABLE 10A. CROSS-COUPLING OF ALKOXYMETHYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES

Alkoxyethyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
$\text{PMBOCH}_2\text{BF}_3^-\text{K}^+$ $\text{BnOCH}_2\text{BF}_3^-\text{K}^+$		$\text{Pd}(\text{OAc})_2$ (3%), RuPhos (6%), Cs_2CO_3 (3 eq), dioxane– H_2O , 100° , 24 h	 R CN (72) OMe (74)	129
		$\text{Pd}(\text{OAc})_2$ (3%), ligand, Cs_2CO_3 (3 eq), dioxane– H_2O , 100° , 24 h	 CN Ligand RuPhos (6%) (76) SPhos (6%) (58) (S)-BINAP (3%) (76) DPEPhos (3%) (68) $\text{Fc}(\text{-i-Pr})_2$ (3%) (73)	129
		$\text{Pd}(\text{OAc})_2$ (3%), RuPhos (6%), Cs_2CO_3 (3 eq), dioxane– H_2O , 100° , 24 h	 (85)	129

C₁

TABLE 10A. CROSS-COUPLING OF ALKOXYMETHYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Alkoxyethyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁				129
C ₆				129
C ₆				129
C ₆				129

C ₇			Pd(OAc) ₂ (3%), RuPhos (6%), Cs ₂ CO ₃ (3 eq), dioxane-H ₂ O, 100°, 24 h		129
C ₁₄			Pd(OAc) ₂ (3%), RuPhos (6%), Cs ₂ CO ₃ (3 eq), dioxane-H ₂ O, 100°, 24 h		225

^a The trifluoroborate derivative comes from the hydroboration/cross-coupling of a dibora species.

TABLE 10B. CROSS-COUPLING OF ALKOXYMETHYLTRIFLUOROBORATES WITH HETEROARYL ELECTROPHILES

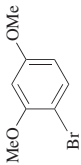
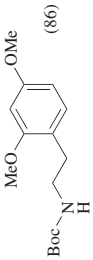
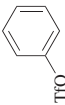
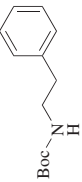
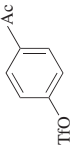
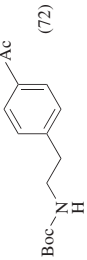
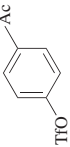
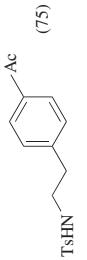
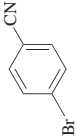
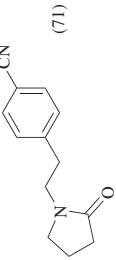
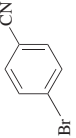
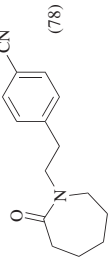
Alkoxyethyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_1 		Pd(OAc) ₂ (3%), RuPhos (6%), Cs ₂ CO ₃ (3 eq), dioxane-H ₂ O, 100°, 24 h	(40)	129
		Pd(OAc) ₂ (3%), RuPhos (6%), Cs ₂ CO ₃ (3 eq), dioxane-H ₂ O, 100°, 24 h	(50)	129
		Pd(OAc) ₂ (3%), RuPhos (6%), Cs ₂ CO ₃ (3 eq), dioxane-H ₂ O, 100°, 24 h	(54)	129
		Pd(OAc) ₂ (3%), RuPhos (6%), Cs ₂ CO ₃ (3 eq), dioxane-H ₂ O, 100°, 24 h	(70)	129
		Pd(OAc) ₂ (3%), RuPhos (6%), Cs ₂ CO ₃ (3 eq), dioxane-H ₂ O, 100°, 24 h	(51)	129

TABLE 11A. CROSS-COUPLING OF AMINOETHYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES

Aminoethyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.																																																
		$\text{PdCl}_2(\text{dppf}) \bullet \text{CH}_2\text{Cl}_2$ (5%), Cs_2CO_3 (3 eq), toluene– H_2O , 80° , 12 h	 (71)	130																																																
		$\text{PdCl}_2(\text{dppf}) \bullet \text{CH}_2\text{Cl}_2$ (5%), Cs_2CO_3 (3 eq), toluene– H_2O , 80° , 12 h	 <table><tr><th>R^1</th><th>R^2</th><th>R^3</th><th></th></tr><tr><td>H</td><td>H</td><td>NO_2</td><td>(84)</td></tr><tr><td>H</td><td>H</td><td>Cl</td><td>(70)</td></tr><tr><td>H</td><td>H</td><td>Me</td><td>(71)</td></tr><tr><td>H</td><td>H</td><td>CF_3</td><td>(88)</td></tr><tr><td>H</td><td>H</td><td>CN</td><td>(75)</td></tr><tr><td>H</td><td>H</td><td>CHO</td><td>(87)</td></tr><tr><td>H</td><td>H</td><td>Ac</td><td>(89)</td></tr><tr><td>H</td><td>H</td><td>CO_2Me</td><td>(86)</td></tr><tr><td>H</td><td>Ac</td><td>H</td><td>(91)</td></tr><tr><td>CN</td><td>H</td><td>H</td><td>(70)</td></tr><tr><td>OMe</td><td>H</td><td>OMe</td><td>(55)</td></tr></table>	R^1	R^2	R^3		H	H	NO_2	(84)	H	H	Cl	(70)	H	H	Me	(71)	H	H	CF_3	(88)	H	H	CN	(75)	H	H	CHO	(87)	H	H	Ac	(89)	H	H	CO_2Me	(86)	H	Ac	H	(91)	CN	H	H	(70)	OMe	H	OMe	(55)	131
R^1	R^2	R^3																																																		
H	H	NO_2	(84)																																																	
H	H	Cl	(70)																																																	
H	H	Me	(71)																																																	
H	H	CF_3	(88)																																																	
H	H	CN	(75)																																																	
H	H	CHO	(87)																																																	
H	H	Ac	(89)																																																	
H	H	CO_2Me	(86)																																																	
H	Ac	H	(91)																																																	
CN	H	H	(70)																																																	
OMe	H	OMe	(55)																																																	

TABLE 11A. CROSS-COUPLING OF AMINOETHYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

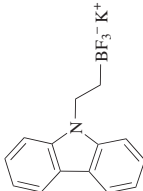
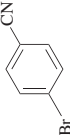
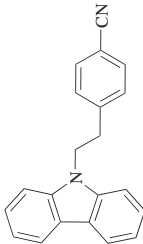
Aminoethyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.																																													
		Pd(OAc) ₂ (5%), RuPhos (10%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 95°, 12 h		131																																													
			<table><tr><th>R¹</th><th>R²</th><th>R³</th><th>R⁴</th><th></th></tr><tr><td>H</td><td>H</td><td>H</td><td>H</td><td>(86)</td></tr><tr><td>H</td><td>H</td><td>H</td><td>Me</td><td>(82)</td></tr><tr><td>H</td><td>H</td><td>Me</td><td>H</td><td>(75)</td></tr><tr><td>H</td><td>H</td><td>OMe</td><td>H</td><td>(80)</td></tr><tr><td>H</td><td>H</td><td>NHAc</td><td>H</td><td>(46)</td></tr><tr><td>H</td><td>H</td><td>OMe</td><td>OMe</td><td>(79)</td></tr><tr><td>H</td><td>OMe</td><td>H</td><td>H</td><td>(86)</td></tr><tr><td>Me</td><td>H</td><td>Me</td><td>Me</td><td>(85)</td></tr></table>	R ¹	R ²	R ³	R ⁴		H	H	H	H	(86)	H	H	H	Me	(82)	H	H	Me	H	(75)	H	H	OMe	H	(80)	H	H	NHAc	H	(46)	H	H	OMe	OMe	(79)	H	OMe	H	H	(86)	Me	H	Me	Me	(85)	
	R ¹	R ²	R ³	R ⁴																																													
	H	H	H	H	(86)																																												
	H	H	H	Me	(82)																																												
	H	H	Me	H	(75)																																												
	H	H	OMe	H	(80)																																												
	H	H	NHAc	H	(46)																																												
	H	H	OMe	OMe	(79)																																												
	H	OMe	H	H	(86)																																												
Me	H	Me	Me	(85)																																													
	PdCl ₂ (dppf)•CH ₂ Cl ₂ (5%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 80°, 12 h		<table><tr><th>Y</th></tr><tr><td>I (60)</td></tr><tr><td>OTf (82)</td></tr></table>	Y	I (60)	OTf (82)	131																																										
Y																																																	
I (60)																																																	
OTf (82)																																																	
	Pd(OAc) ₂ (5%), RuPhos (10%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 95°, 12 h		(85)	131																																													
	PdCl ₂ (dppf)•CH ₂ Cl ₂ (5%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 80°, 12 h		(73)	130																																													
	PdCl ₂ (dppf)•CH ₂ Cl ₂ (5%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 80°, 12 h		(79)	131																																													

		$\text{Pd}(\text{OAc})_2$ (5%), RuPhos (10%), Cs_2CO_3 (3 eq), toluene-H_2O, 95°, 12 h	131
		$\text{Pd}(\text{OAc})_2$ (5%), RuPhos (10%), Cs_2CO_3 (3 eq), toluene-H_2O, 95°, 12 h	131
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (5%), Cs_2CO_3 (3 eq), toluene-H_2O, 80°, 12 h	131
		$\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (9%), Cs_2CO_3 (3 eq), THF-H_2O, reflux, 3 d	113
		$\text{Pd}(\text{OAc})_2$ (5%), RuPhos (10%), Cs_2CO_3 (3 eq), toluene-H_2O, 80°, 12 h	130
		$\text{Pd}(\text{OAc})_2$ (5%), RuPhos (10%), Cs_2CO_3 (3 eq), toluene-H_2O, 80°, 12 h	130

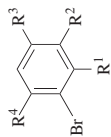
C₆

C₈

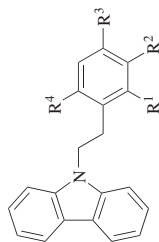
TABLE 11A. CROSS-COUPLING OF AMINOETHYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Aminoethyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.																				
		Pd source (5%), ligand (10%), base (3 eq), toluene-H ₂ O, 80°, 12 h		130																				
<table><tr><th>Pd Source</th><th>Ligand</th><th>Base</th><th></th></tr><tr><td>PdCl₂(dppf)•CH₂Cl₂</td><td>—</td><td>Cs₂CO₃</td><td>(90)</td></tr><tr><td>PdCl₂(dppf)•CH₂Cl₂</td><td>—</td><td>K₂CO₃</td><td>(69)</td></tr><tr><td>Pd(OAc)₂</td><td>PPh₃</td><td>Cs₂CO₃</td><td>(78)</td></tr><tr><td>PdCl₂</td><td>PPh₃</td><td>Cs₂CO₃</td><td>(56)</td></tr></table>					Pd Source	Ligand	Base		PdCl ₂ (dppf)•CH ₂ Cl ₂	—	Cs ₂ CO ₃	(90)	PdCl ₂ (dppf)•CH ₂ Cl ₂	—	K ₂ CO ₃	(69)	Pd(OAc) ₂	PPh ₃	Cs ₂ CO ₃	(78)	PdCl ₂	PPh ₃	Cs ₂ CO ₃	(56)
Pd Source	Ligand	Base																						
PdCl ₂ (dppf)•CH ₂ Cl ₂	—	Cs ₂ CO ₃	(90)																					
PdCl ₂ (dppf)•CH ₂ Cl ₂	—	K ₂ CO ₃	(69)																					
Pd(OAc) ₂	PPh ₃	Cs ₂ CO ₃	(78)																					
PdCl ₂	PPh ₃	Cs ₂ CO ₃	(56)																					

C₁₄

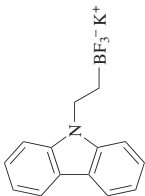
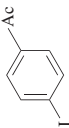
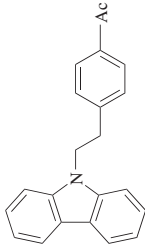
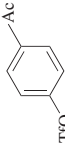
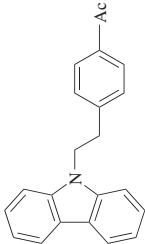


$\text{PdCl}_2(\text{dppf}) \bullet \text{CH}_2\text{Cl}_2$ (5%),
 Cs_2CO_3 (3 eq), toluene– H_2O ,
 80° , 12 h



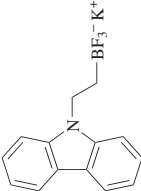
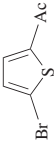
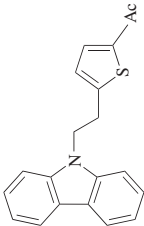
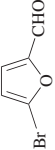
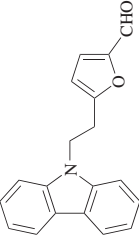
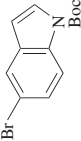
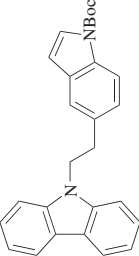
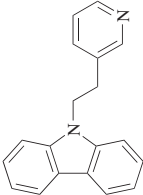
R ¹	R ²	R ³	R ⁴
H	H	H	H (89)
H	H	Cl	H (73)
H	H	NO ₂	H (79)
H	H	Me	H (81)
H	H	CF ₃	H (74)
H	H	CHO	H (84)
H	H	OMe	H (70)
H	H	Ac	H (82)
H	H	NHAc	H (73)
H	H	COPh	H (79)
H	OMe	H	H (68)
H	Ac	H	H (79)
H	H	CO ₂ Me	H (84)
Me	H	H	H (79)
CN	H	H	H (85)
Me	H	Me	Me (88)

TABLE 11A. CROSS-COUPLING OF AMINOETHYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES (Continued)

Aminoethyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (5%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 80°, 12 h	 (79)	130
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (5%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 80°, 12 h	 (77)	130

C₁₄

TABLE 11B. CROSS-COUPLING OF AMINOETHYLTRIFLUOROBORATES WITH HETEROARYL ELECTROPHILES (Continued)

Aminoethyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc) ₂ (2%), RuPhos (4%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 80°, 12 h	 (71)	130
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (5%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 80°, 12 h	 (62)	130
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (5%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 80°, 12 h	 (63)	130
		PdCl ₂ (dppf)•CH ₂ Cl ₂ (5%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 80°, 12 h	 (69)	130

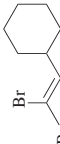
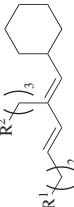
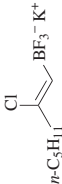
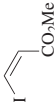
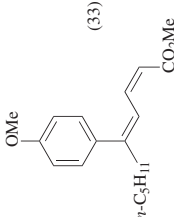
C₁₄

TABLE 12A. CROSS-COUPLING OF MISCELLANEOUS TRIFLUOROBORATES WITH HETEROARYL ELECTROPHILES

Trifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.														
		$\text{Pd}(\text{PPh}_3)_4$ (10%), K_2CO_3, DMF-H_2O, MW, 150°, 15 min	<table><tr><td>R</td><td>(97)</td></tr><tr><td>H</td><td>(—)</td></tr><tr><td>HO</td><td>(56)</td></tr><tr><td><i>n</i>-BuO</td><td>(64)</td></tr><tr><td><i>n</i>-C₆H₁₃O</td><td>(51)</td></tr><tr><td>BnO</td><td>(27)</td></tr><tr><td>TsO</td><td>(27)</td></tr></table>	R	(97)	H	(—)	HO	(56)	<i>n</i> -BuO	(64)	<i>n</i> -C ₆ H ₁₃ O	(51)	BnO	(27)	TsO	(27)	282
R	(97)																	
H	(—)																	
HO	(56)																	
<i>n</i> -BuO	(64)																	
<i>n</i> -C ₆ H ₁₃ O	(51)																	
BnO	(27)																	
TsO	(27)																	
		$\text{Pd}(\text{PPh}_3)_4$ (10%), K_2CO_3, DMF-H_2O, MW, 150°, 15 min	(63)	282														

C₂₀

TABLE 12B. CROSS-COUPLING OF MISCELLANEOUS TRIFLUOROBORATES WITH ALKENYL ELECTROPHILES

Trifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.																																																												
C₅₋₁₀ 		1. Pd(PPh ₃) ₄ (7%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, temp ₁ , time ₁ 2. R ² (CH ₂) ₃ BF ₃ ⁻ K ⁺ , PdCl ₂ (dppf)•CH ₂ Cl ₂ (5%), Cs ₂ CO ₃ (3 eq), 80°, time ₂	 74																																																													
		<table><tr><th>R¹</th><th>R²</th><th>Temp₁ (°)</th><th>Time₁ (h)</th><th>Time₂ (h)</th><th></th></tr><tr><td>NCCH₂</td><td>PivOCH₂</td><td>60</td><td>2</td><td>2.5</td><td>(91)</td></tr><tr><td>NCCH₂</td><td>AcCH₂</td><td>60</td><td>2</td><td>3.5</td><td>(87)</td></tr><tr><td>ClCH₂</td><td>PivOCH₂</td><td>60</td><td>2</td><td>2.5</td><td>(90)</td></tr><tr><td>ClCH₂</td><td>AcCH₂</td><td>60</td><td>2</td><td>4</td><td>(89)</td></tr><tr><td>Ph</td><td>PivOCH₂</td><td>60</td><td>1</td><td>2.5</td><td>(90)</td></tr><tr><td>Ph</td><td>AcCH₂</td><td>60</td><td>1</td><td>5</td><td>(89)</td></tr><tr><td><i>n</i>-C₆H₁₃</td><td>PivOCH₂</td><td>80</td><td>5</td><td>2.5</td><td>(90)</td></tr><tr><td><i>n</i>-C₆H₁₃</td><td>AcCH₂</td><td>80</td><td>5</td><td>5</td><td>(87)</td></tr><tr><td><i>n</i>-C₆H₁₃</td><td>Ph</td><td>80</td><td>5</td><td>1</td><td>(85)</td></tr></table>	R ¹	R ²	Temp ₁ (°)	Time ₁ (h)	Time ₂ (h)		NCCH ₂	PivOCH ₂	60	2	2.5	(91)	NCCH ₂	AcCH ₂	60	2	3.5	(87)	ClCH ₂	PivOCH ₂	60	2	2.5	(90)	ClCH ₂	AcCH ₂	60	2	4	(89)	Ph	PivOCH ₂	60	1	2.5	(90)	Ph	AcCH ₂	60	1	5	(89)	<i>n</i> -C ₆ H ₁₃	PivOCH ₂	80	5	2.5	(90)	<i>n</i> -C ₆ H ₁₃	AcCH ₂	80	5	5	(87)	<i>n</i> -C ₆ H ₁₃	Ph	80	5	1	(85)		
R ¹	R ²	Temp ₁ (°)	Time ₁ (h)	Time ₂ (h)																																																												
NCCH ₂	PivOCH ₂	60	2	2.5	(91)																																																											
NCCH ₂	AcCH ₂	60	2	3.5	(87)																																																											
ClCH ₂	PivOCH ₂	60	2	2.5	(90)																																																											
ClCH ₂	AcCH ₂	60	2	4	(89)																																																											
Ph	PivOCH ₂	60	1	2.5	(90)																																																											
Ph	AcCH ₂	60	1	5	(89)																																																											
<i>n</i> -C ₆ H ₁₃	PivOCH ₂	80	5	2.5	(90)																																																											
<i>n</i> -C ₆ H ₁₃	AcCH ₂	80	5	5	(87)																																																											
<i>n</i> -C ₆ H ₁₃	Ph	80	5	1	(85)																																																											
C₇ 		1. Pd ₂ (dba) ₃ (1.5%), P(<i>t</i> -Bu) ₃ •HBF ₄ (3%), Cs ₂ CO ₃ (3 eq), THF-H ₂ O, 120°, 12 h 2. 4-MeOC ₆ H ₄ BF ₃ ⁻ K ⁺ , Pd ₂ (dba) ₃ (2.5%), P(<i>t</i> -Bu) ₃ •HBF ₄ (3%), 100°, 48 h	 (33) 148																																																													

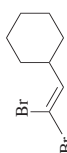
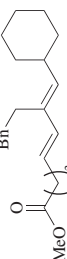
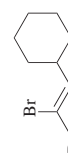
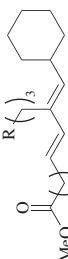
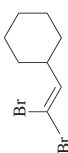
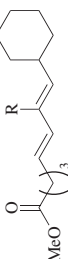
		1. Pd(PPh₃)₄ (7%), Cs₂CO₃ (3 eq), toluene-H₂O, temp₁, time₁ 2. Cs₂CO₃ (3 eq), BnCH₂BF₃⁻K⁺, 80°, time₂		74																		
		<table> <tr> <th>Temp₁ (°)</th><th>Time₁ (h)</th><th>Time₂ (h)</th><th></th></tr> <tr> <td>80</td><td>1.25</td><td>1</td><td>(85)</td></tr> <tr> <td>60</td><td>2</td><td>2.5</td><td>(84)</td></tr> <tr> <td>60</td><td>2</td><td>2.5</td><td>(89)</td></tr> </table>	Temp ₁ (°)	Time ₁ (h)	Time ₂ (h)		80	1.25	1	(85)	60	2	2.5	(84)	60	2	2.5	(89)				
Temp ₁ (°)	Time ₁ (h)	Time ₂ (h)																				
80	1.25	1	(85)																			
60	2	2.5	(84)																			
60	2	2.5	(89)																			
		1. Pd(PPh₃)₄ (7%), Cs₂CO₃ (3 eq), toluene-H₂O, 60°, 2 h 2. R(CH₂)₃BF₃⁻K⁺, Cs₂CO₃ (3 eq), 80°, time₂		74																		
		<table> <tr> <th>R</th><th>Time₂ (h)</th><th></th></tr> <tr> <td>PivOCH₂</td><td>2</td><td>(89)</td></tr> <tr> <td>BzOCH₂</td><td>2</td><td>(90)</td></tr> <tr> <td>NCCH₂</td><td>3</td><td>(89)</td></tr> <tr> <td>MeCOCH₂</td><td>3</td><td>(89)</td></tr> <tr> <td>PhS</td><td>1.5</td><td>(90)</td></tr> </table>	R	Time ₂ (h)		PivOCH ₂	2	(89)	BzOCH ₂	2	(90)	NCCH ₂	3	(89)	MeCOCH ₂	3	(89)	PhS	1.5	(90)		
R	Time ₂ (h)																					
PivOCH ₂	2	(89)																				
BzOCH ₂	2	(90)																				
NCCH ₂	3	(89)																				
MeCOCH ₂	3	(89)																				
PhS	1.5	(90)																				
		1. Pd(PPh₃)₄ (7%), Cs₂CO₃ (3 eq), toluene-H₂O, 60°, 2 h 2. PdCl₂(dppf)•CH₂Cl₂ (5%), Cs₂CO₃ (3 eq), RBF₃⁻K⁺, 80°, time₂		74																		
		<table> <tr> <th>R</th><th>Time₂ (h)</th><th></th></tr> <tr> <td>Me</td><td>2.5</td><td>(84)</td></tr> <tr> <td>Et</td><td>2.5</td><td>(82)</td></tr> <tr> <td>CH₂CH(CH₂)₃</td><td>1</td><td>(83)</td></tr> </table>	R	Time ₂ (h)		Me	2.5	(84)	Et	2.5	(82)	CH ₂ CH(CH ₂) ₃	1	(83)								
R	Time ₂ (h)																					
Me	2.5	(84)																				
Et	2.5	(82)																				
CH ₂ CH(CH ₂) ₃	1	(83)																				

TABLE 12B. CROSS-COUPLING OF MISCELLANEOUS TRIFLUOROBORATES WITH ALKENYL ELECTROPHILES (Continued)

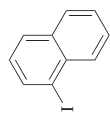
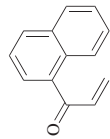
Trifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇		1. Pd(PPh ₃) ₄ (7%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 60°, 1 h 2. PivO(CH ₂) ₄ BF ₃ ⁻ K ⁺ , Cs ₂ CO ₃ (3 eq), 80°, 3 h		74
			$\frac{R}{n\text{-C}_7\text{H}_{15}}$ (E,E)/(E,Z) 92:8 (85) 94:6 (87)	
		1. Pd(PPh ₃) ₄ (7%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 60°, 1 h 2. PivO(CH ₂) ₄ BF ₃ ⁻ K ⁺ , Cs ₂ CO ₃ (3 eq), 80°, 3 h		74
C ₁₇		1. Pd(PPh ₃) ₄ (7%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 60°, 1 h 2. PivO(CH ₂) ₄ BF ₃ ⁻ K ⁺ , Cs ₂ CO ₃ (3 eq), 80°, 3 h		74
			(86) (E,E)/(E,Z) = 92:8	
		1. Pd(PPh ₃) ₄ (7%), Cs ₂ CO ₃ (3 eq), toluene-H ₂ O, 60°, 1 h 2. PivO(CH ₂) ₄ BF ₃ ⁻ K ⁺ , Cs ₂ CO ₃ (3 eq), 80°, 3 h		74
				(90)
				74
				(90)
				(90)
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				(90)
				(90)

TABLE 12C. CROSS-COUPLING OF MISCELLANEOUS TRIFLUOROBORATES WITH ARYL ELECTROPHILES

Trifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.	
		1. Pd ₂ (dba) ₃ (1.5%), P(<i>t</i> -Bu) ₃ •HBF ₄ (3%), C ₅ O ₃ (3 eq), THF-H ₂ O, 120°, 12 h 2. R ³ BF ₃ K ⁺ , Pd ₂ (dba) ₃ (2.5%), P(<i>t</i> -Bu) ₃ •HBF ₄ (3%), 100°, 48 h		148	
	X	R ¹	R ²	R ³	(56) (Z)/(E) = 60:40
	Br	<i>n</i> -C ₃ H ₁₁	NO ₂	CH=CH ₂	(42)
	I	<i>n</i> -C ₃ H ₁₁	CO ₂ Me	CH=CH ₂	(—)
	I	<i>n</i> -C ₃ H ₁₁	CO ₂ Me	Me	(26)
	I	<i>n</i> -C ₃ H ₁₁	CO ₂ Me	Ph	(38)
	I	<i>n</i> -C ₃ H ₁₁	CO ₂ Me	4-MeOC ₆ H ₄	(44)
	I	Ph	CO ₂ Me	4-MeOC ₆ H ₄	(43)
	I	3-Me-4-FC ₆ H ₃	CO ₂ Me	3-thienyl	

TABLE 13. CARBONYLATIVE CROSS-COUPLING OF ALKENYLTRIFLUOROBORATES WITH ARYL ELECTROPHILES

Alkenyltrifluoroborate	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.																																				
		CO (20 bar), Pd(OAc) ₂ (2%), PPh ₃ (6%), Na ₂ CO ₃ (1.1 eq), THF, 80°, 20 h	 (0)	283																																				
		CO (20 bar), Pd(OAc) ₂ (2%), PPh ₃ (6%), base (1.1 eq), solvent, 80°, 20 h	 Base Solvent	283																																				
		CO (20 bar), Pd(OAc) ₂ (2%), PPh ₃ (6%), Na ₂ CO ₃ (1.1 eq), THF, 80°, 20 h	 R ¹ R ² R ³	283																																				
<table><tr><th>Base</th><th>Solvent</th><th>Yield (%)</th></tr><tr><td>K₂CO₃</td><td>THF</td><td>(32)^a</td></tr><tr><td>K₂CO₃</td><td>toluene</td><td>(0)^a</td></tr><tr><td>K₂CO₃</td><td>DMF</td><td>(22)^a</td></tr><tr><td>K₂CO₃</td><td>dioxane</td><td>(21)^a</td></tr><tr><td>Na₂CO₃</td><td>THF</td><td>(59)^a</td></tr><tr><td>NaOAc</td><td>THF</td><td>(34)^a</td></tr><tr><td>KF</td><td>THF</td><td>(8)^a</td></tr><tr><td>KOt-Bu</td><td>THF</td><td>(0)^a</td></tr></table>					Base	Solvent	Yield (%)	K ₂ CO ₃	THF	(32) ^a	K ₂ CO ₃	toluene	(0) ^a	K ₂ CO ₃	DMF	(22) ^a	K ₂ CO ₃	dioxane	(21) ^a	Na ₂ CO ₃	THF	(59) ^a	NaOAc	THF	(34) ^a	KF	THF	(8) ^a	KOt-Bu	THF	(0) ^a									
Base	Solvent	Yield (%)																																						
K ₂ CO ₃	THF	(32) ^a																																						
K ₂ CO ₃	toluene	(0) ^a																																						
K ₂ CO ₃	DMF	(22) ^a																																						
K ₂ CO ₃	dioxane	(21) ^a																																						
Na ₂ CO ₃	THF	(59) ^a																																						
NaOAc	THF	(34) ^a																																						
KF	THF	(8) ^a																																						
KOt-Bu	THF	(0) ^a																																						
<table><tr><th>R¹</th><th>R²</th><th>R³</th><th>Yield (%)</th></tr><tr><td>H</td><td>H</td><td>Br</td><td>(45)</td></tr><tr><td>H</td><td>H</td><td>Cl</td><td>(42)</td></tr><tr><td>H</td><td>Cl</td><td>Cl</td><td>(60)</td></tr><tr><td>Me</td><td>H</td><td>H</td><td>(40)</td></tr><tr><td>H</td><td>Me</td><td>H</td><td>(70)</td></tr><tr><td>H</td><td>H</td><td>Me</td><td>(72)</td></tr><tr><td>H</td><td>H</td><td>Ac</td><td>(40)</td></tr><tr><td>H</td><td>H</td><td>CO₂Et</td><td>(68)</td></tr></table>					R ¹	R ²	R ³	Yield (%)	H	H	Br	(45)	H	H	Cl	(42)	H	Cl	Cl	(60)	Me	H	H	(40)	H	Me	H	(70)	H	H	Me	(72)	H	H	Ac	(40)	H	H	CO ₂ Et	(68)
R ¹	R ²	R ³	Yield (%)																																					
H	H	Br	(45)																																					
H	H	Cl	(42)																																					
H	Cl	Cl	(60)																																					
Me	H	H	(40)																																					
H	Me	H	(70)																																					
H	H	Me	(72)																																					
H	H	Ac	(40)																																					
H	H	CO ₂ Et	(68)																																					

	CO (20 bar), Pd(OAc) ₂ (2%), PPh ₃ (6%), Na ₂ CO ₃ (1.1 eq), THF, 80 °, 20 h		(35)	283

^aThe yield of the product was determined by GC analysis.

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