

Example Chapter

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Chapter XX

Recent advances/contributions in the Suzuki-Miyaura reaction

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Abstract

Since the original reports of Suzuki-Miyaura on the coupling of vinyl or aryl boronic acids with vinyl or aryl halides a remarkable number of publications have either developed or applied this methodology in both an academic and industrial setting. This review covers recent developments in the area, focusing on new methodology, mechanistic implications and applications in medicinal, process and materials chemistry.

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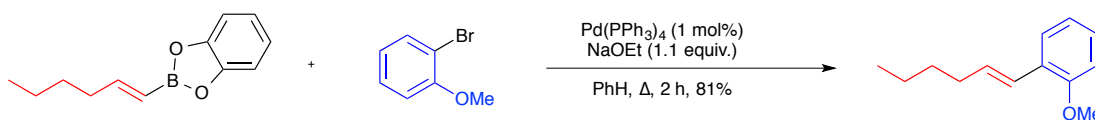
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X.1 Introduction

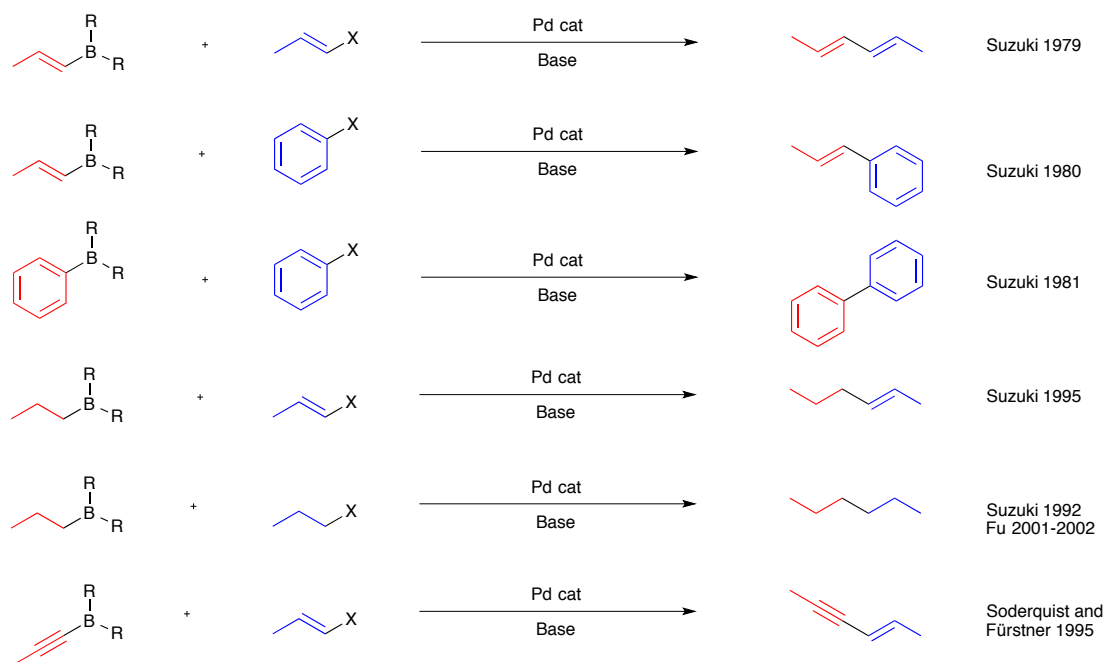
The Suzuki-Miyaura reaction is perhaps one of the most well known coupling protocols developed to date. A search of the literature reveals over 15000 citations¹ to work employing this coupling protocol that was first developed in 1979² and for which Akira Suzuki shared the Nobel prize in chemistry in 2010. The two seminal papers in 1979 coauthored by Suzuki and Miyaura describe the cross-coupling of vinyl boronic acids with vinyl bromides (Scheme 1)^{2a} or aryl halides (Scheme 2),^{2b} employing 1 mol% tetrakis(triphenylphosphene)palladium and a base such as sodium ethoxide. The stereoselectivity of the reactions were excellent with >99% retention of double bond geometry. The evolution of the various Suzuki coupling partners is shown in Scheme 3.



Scheme 1.

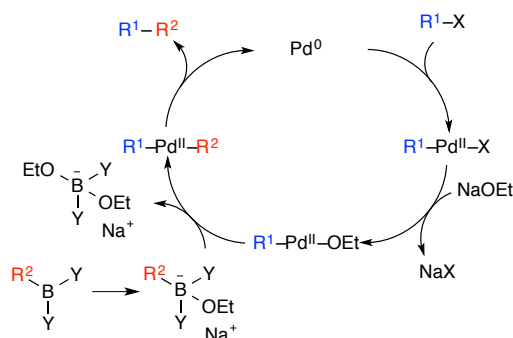


Scheme 2.



Scheme 3.

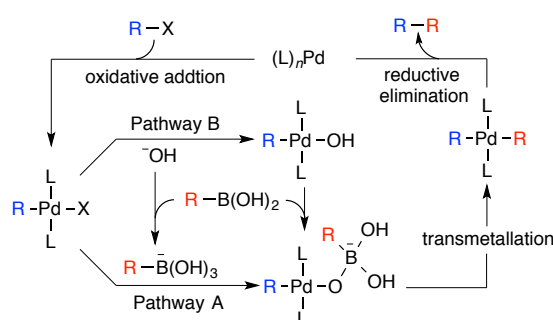
The generally accepted mechanism, employing palladium is shown in scheme 4. Oxidative addition of palladium (0) to the alkyl halide initially occurs to form an organopalladium (II) species, which on addition of a base affords intermediate (X), subsequent reaction with the boron-ate complex provides the organopalladium(II) species, the coupled product is then obtained through reductive elimination and the palladium (0) catalyst is restored.



Scheme 4.

Lennox and Lloyd-Jones have recently reported a review in which they compare and contrast mechanistic studies what they term as the “versatile transmetalation” process “which has allowed the Suzuki–Miyaura reaction to develop into such an important

coupling process in academic and industrial settings”.³ An in depth analysis of this important transmetallation centres around the propensity for either pathway A or B to be in operation (Scheme 5). Apparently there is little evidence for significant catalytic turnover through the boronate pathway A and the authors believe recent work from Hartwig⁴ and Amatore and Jutand⁵ provides “compelling and conclusive evidence” for the catalytic transit through pathway B, but only with any certainty for coupling of aryl boronic acids or selected esters, with simple aryl halides.



Scheme 5

This versatile reaction has found application in a wide variety chemical disciplines from the synthesis of biologically active compounds to materials for electronic devices (Figure 1). This is perhaps due in part to the wide variety of boronic acid derivatives that are commercially available or easily prepared. Not surprisingly there have been many review articles based around this Nobel prize winning methodology. The present review is by no means comprehensive but serves to update the reader on recent advances in the area.

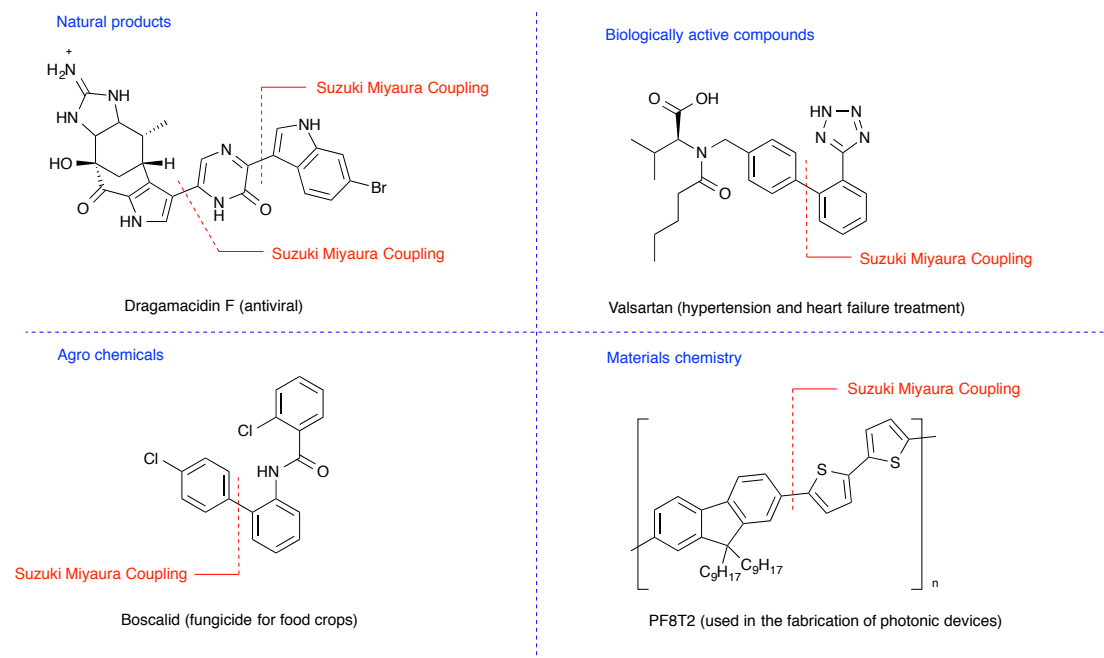


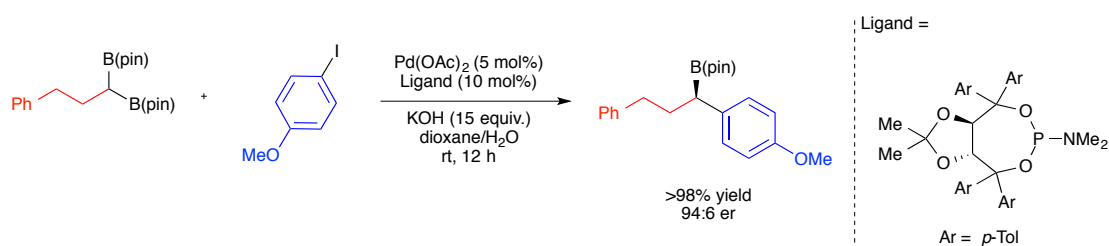
Figure 1.

X.2 Recent Methodology

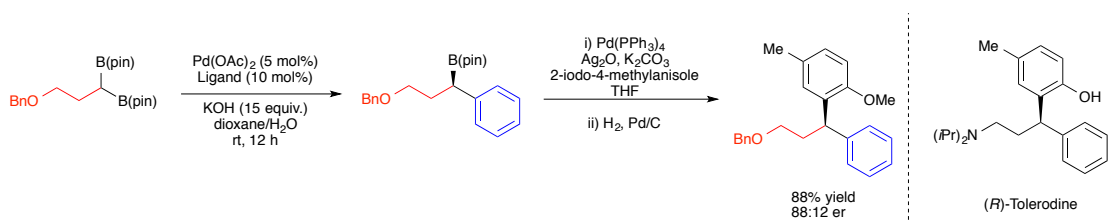
The original cross-coupling reactions of aryl and vinyl halides with boronic acid coupling partners has been extensively developed since the reactions inception. Over the past few years several interesting adaptations have expanded the scope of the original coupling protocol, below are just a few recent examples of systems that have harnessed the Suzuki-Miyaura protocol to access enantioenriched coupling products.

Morken and coworkers have reported a highly selective desymmetrisation of geminal bis(pincolboronates) using a catalytic enantioselective Suzuki-Miyaura coupling (Scheme 6).⁶ Detailed studies revealed that the transmetalation step is stereospecific and this step is likely to be stereochemistry determining. They also believe that the stereoselective transmetalation might occur either by a desymmetrization if both boronates are equivalent or by a dynamic kinetic resolution if the geminal boron atoms are not equivalent.

The applicability of the asymmetric cross-coupling reaction for the enantioselective construction of pharmaceutically relevant benzhydryl derivatives was exemplified through the construction of (*R*)-tolterodine (Detrol LA), a therapeutic used for the treatment of urinary incontinence (Scheme 7).

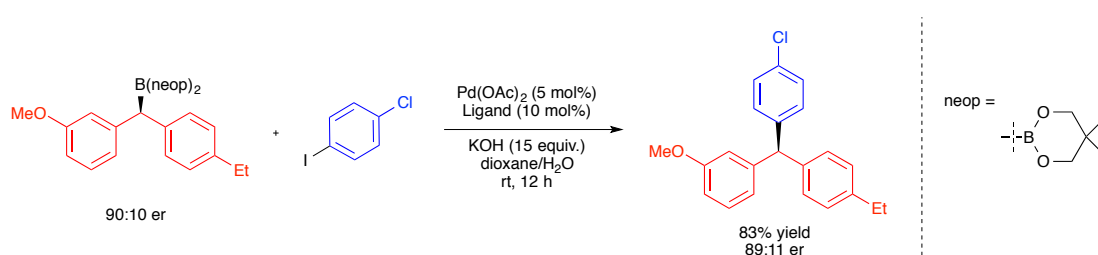


Scheme 6



Scheme 7

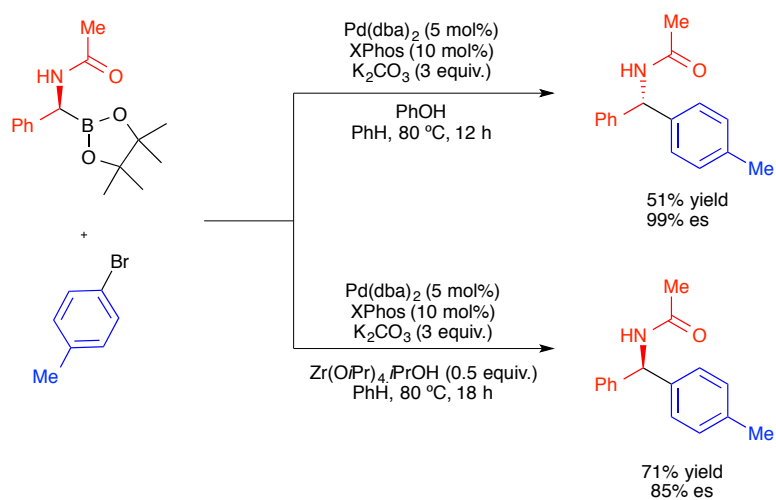
Crudden and coworkers have developed an elegant strategy to access enantiomerically enriched triarylmethanes,⁷ employing an enantioselective Suzuki-Miyaura coupling route (Scheme 8). Enantiomerically enriched dibenzylic boronic esters were prepared using *s*-BuLi and a chiral bisoxazoline ligand. These enantioenriched dibenzylic boronic esters were then cross-coupled using Pd(PPh₃)₄ to afford the desired triarylmethanes. High levels of stereochemical retention were observed over a wide range of substrates, with the level of enantiomeric ratio only governed by the ability to prepare the required dibenzylic boronic esters. The procedure was amenable to gram scale and was shown to proceed through retention of configuration.



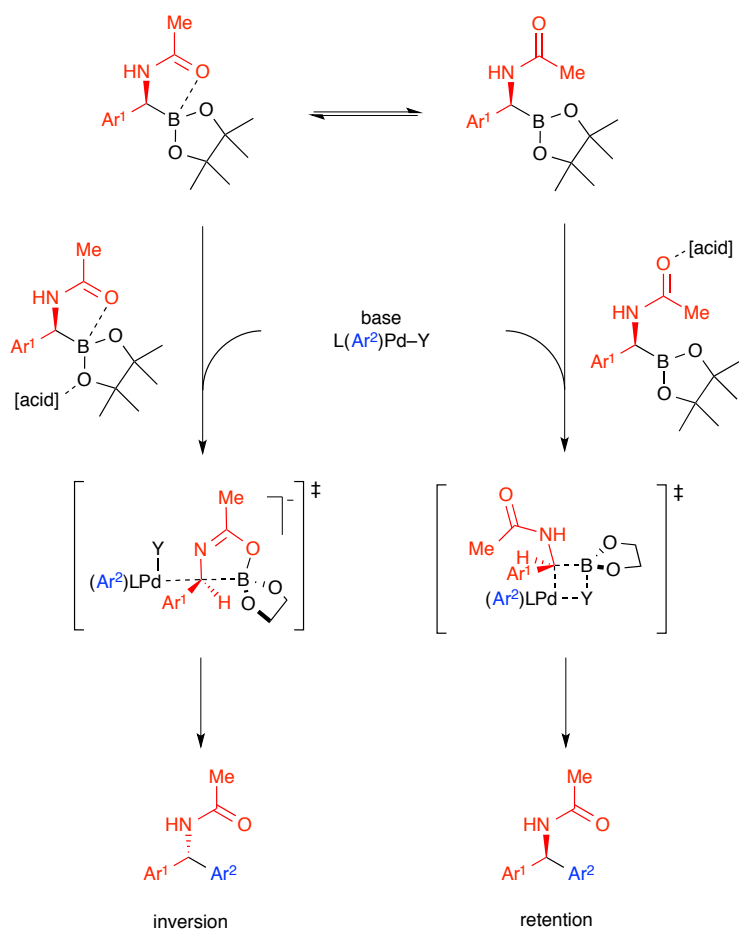
Scheme 8

An interesting route based on this type of stereochemical retention reaction has been reported by Ohmura and Suginome. By studying the effects of acidic additives on the stereochemical course in enantiospecific Suzuki-Miyaura coupling of α -(acetylamino)benzylboronic esters (Scheme 9). After a range of optimisation studies they were able to carry out reactions with up to 93% retention of configuration. By varying the conditions the reaction could be switched to give the product with up to 99% inversion of configuration. The authors propose that the acidic additives can activate two different pathways leading to either retention of configuration or inversion (Scheme 10). This likely occurs due to the rotamers derived from the amide

bond, when the amide carbonyl is available for coordination to the acid retention of configuration is available.

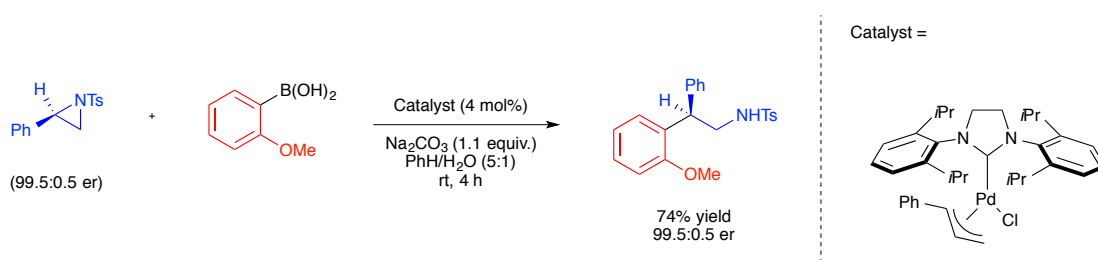


Scheme 9

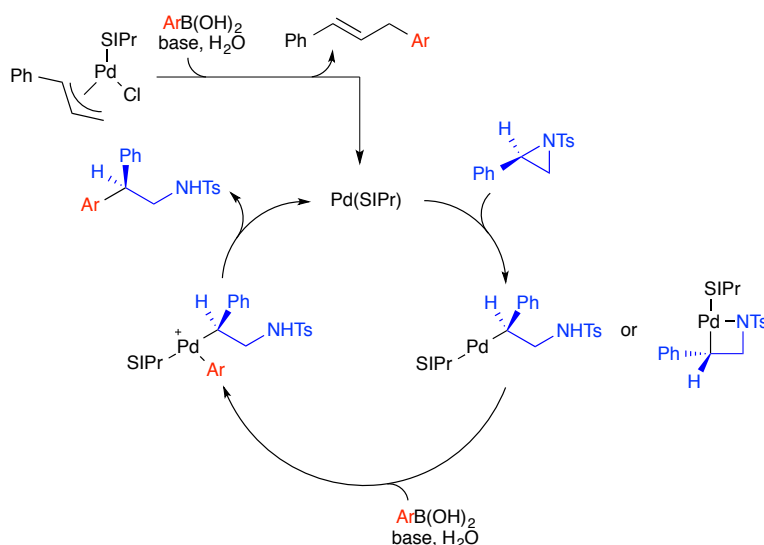


Scheme 10

Takeda and Minakata have reported a Pd-catalyzed enantiospecific and regioselective cross-coupling of 2-arylaziridines with arylboronic acids (Scheme 11).⁸ The reaction was found to work well with an NHC-ligated Palladium complex, which was able to out compete β -hydride elimination (Scheme 12). This coupling process allowed the preparation of configurationally defined 2-arylphenethylamine derivatives that are otherwise difficult to access in a simple operation by current conventional routes.



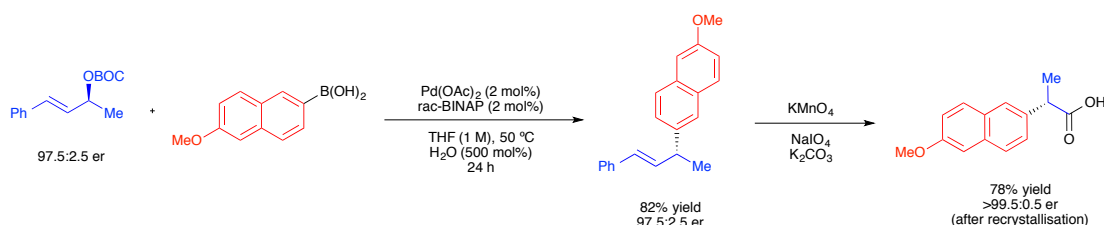
Scheme 11



Scheme 12

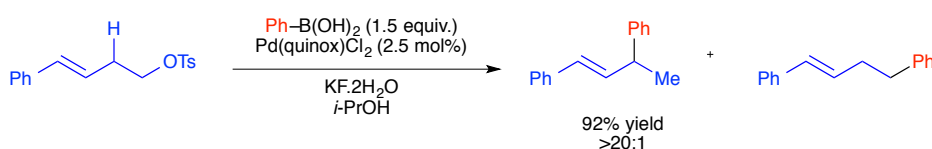
Several reports have emerged utilising an allylic C–H functionalisation strategy. Zhang and coworkers have reported the Suzuki–Miyaura coupling reaction of unsymmetric 1,3-disubstituted secondary allylic carbonates with arylboronic acids (Scheme 13).⁹ The coupling products were afforded with high yields and high regio-

and E/Z selectivities and good to excellent chemoselectivities. The stereochemical course of the coupling reaction, afforded the products with inversion of the original carbonate stereochemistry. The authors then applied this coupling method to the synthesis of (*S*)-naproxen.



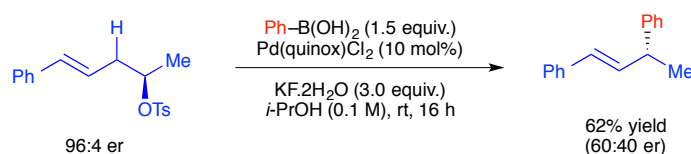
Scheme 13

Sigman and coworkers have developed a novel coupling strategy that capitalised on the slow oxidative addition to the metal centre for alkyl electrophiles and the subsequent competing β -hydride elimination prior to the cross-coupling event.¹⁰ The main challenge was in the identification of a catalytic system that could avoid the formation of the formal Suzuki–Miyaura product and instead afford a diene intermediate through oxidative addition and rapid β -hydride elimination. In addition, the catalyst would have to be able to reinsert the 1,3-diene intermediate in order to subsequently access the desired cross-coupled product (the relay Suzuki–Miyaura product). After a range of optimization experiments using phosphine and N,N-substituted ligands and various bases excellent yields of the desired products were obtained (optimized route shown in scheme 14). The reaction was amenable to a range of aryl boronic acid derivatives and even secondary tosylates could be effectively coupled with high yields and regiocontrol.



Scheme 14

The ability to carry out the reaction with secondary tosylates opened up the possibility for chirality transfer from the tosylate starting material to the desired products. However, a substantial erosion in enantiomeric ratio was observed when the methyl tosylate shown in scheme 15 was employed 96:4 er, was eroded to just 60:40 er. This loss in er was explained using conformational analysis with the hypothesis that the β -hydride elimination step would be responsible for the loss of stereochemical integrity as a result of the existence of an equilibrium between two Pd-alkyl conformational isomers (Figure 2). This was substantiated by replacing the methyl group in the substrate with a bulky isopropyl group, thus increasing the steric penalty of the gauche interaction, resulting in a selective β -hydride elimination (Scheme 16). No erosion of er was observed when employing this bulky substrate.



Scheme 15

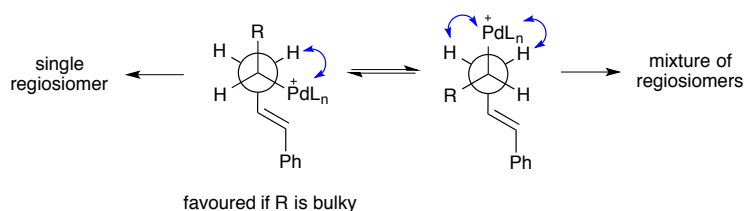
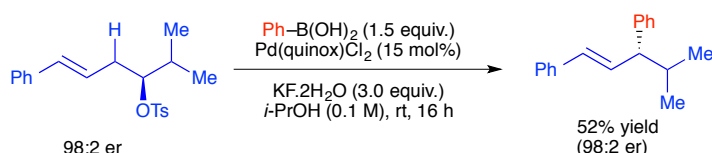


Figure 2



Scheme 16

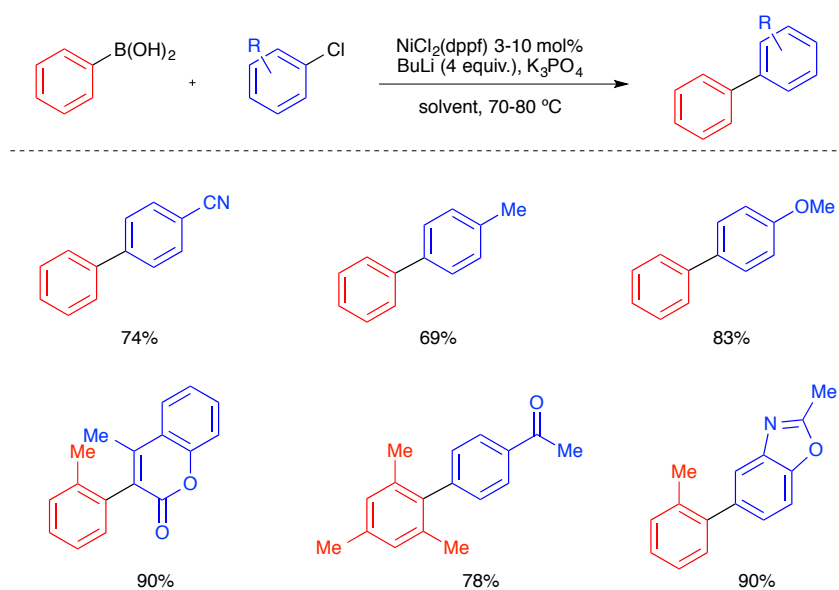
X.3 Alternative Metal Catalysts

The Suzuki-Miyaura coupling has traditionally been carried out using palladium as the metal catalyst, however, there have been several reports that employ alternative metals as catalysts for the coupling reaction. In fact a rather controversial report even disclosed the use of no metal catalyst,¹¹ however, on careful examination of the reaction conditions it was found that palladium contaminants down to a level of 50 ppb found in commercially available sodium carbonate were responsible for the generation of the biaryl rather than an alternative non-palladium-mediated reaction.¹²

X.3.1 NICKEL

The use of nickel catalysts as a replacement for palladium is attractive since it would be far more cost-effective as it is much cheaper and more earth abundant than palladium. But because nickel usually displays Ni(0)/Ni(II) as well as Ni(I)/Ni(III) oxidation states and is more nucleophilic than palladium, nickel cannot be simply considered as a direct substitute for palladium, it possesses distinctive catalytic properties that palladium does not have. One particular advantage to using nickel is its propensity to insert into C–Cl bonds more readily than palladium, this is advantageous since aryl chlorides are generally much cheaper than the corresponding aryl bromides or iodides.

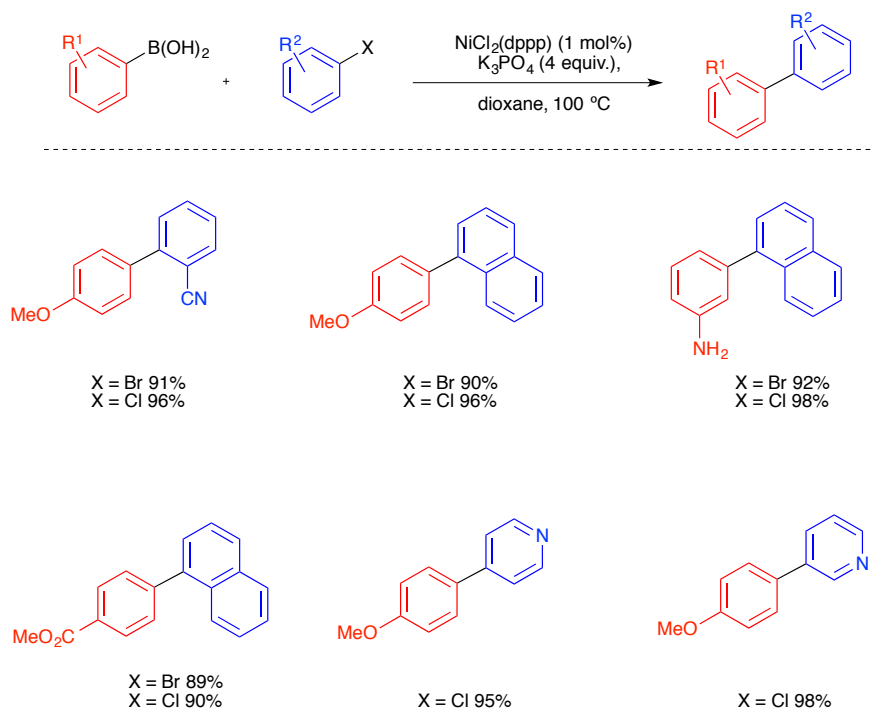
In 1996, Miyaura and co-workers reported the first nickel catalysed cross-coupling of aryl chlorides with boronic acids (Scheme 17).¹³ Various aryl chlorides with electron-withdrawing or electron-donating groups were tolerated when using between 3–10 mol% of Ni(0), prepared *in situ* by reduction of NiCl₂(dppf) with four equivalents of butyllithium or Dibal-H. This initial report spurred a range of new reports employing various nickel catalysts for cross-coupling reactions.¹⁴



Scheme 17

Han has comprehensively reviewed the use of nickel catalysts for the Suzuki-Miyaura cross-coupling reaction,¹⁵ and found that the nickel mediated process can tolerate a broad range of aryl electrophiles, for example, sulfamates, carbamates, carboxylates, ethers, carbonates, phosphoramides, phosphonium salts, phosphates, phenols, and broad range of alkyl substrates including both secondary and primary alkyl iodides, bromides, and chlorides. Many of these electrophiles have been found to be incompatible with traditional palladium catalysed processes.

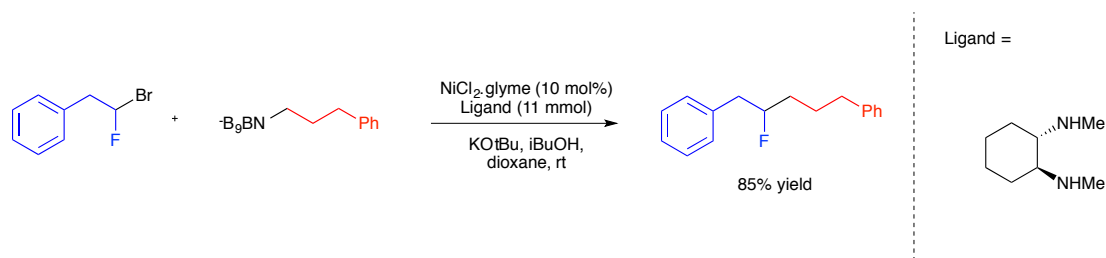
Han's group have also developed the use of what they believe is a much more effective and readily available nickel catalyst $[\text{NiCl}_2(\text{dppp})]$.¹⁶ This catalyst allowed for very general and efficient cross-coupling of a large range of aryl bromides as well as the less reactive aryl chlorides with a catalyst loadings down to 1 mol% or below (Scheme 18).



Scheme 18

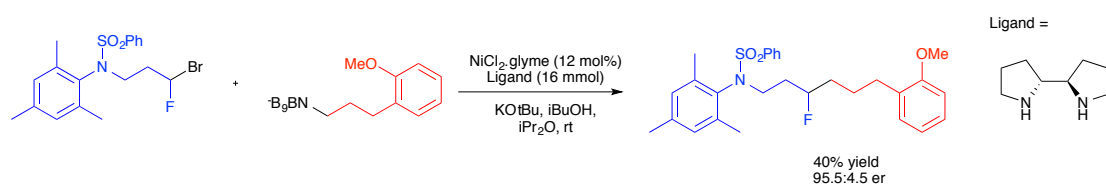
Gandelman and coworkers have reported the synthesis of secondary alkyl fluorides using a Suzuki-Miyaura cross-coupling of 1-halo-1-fluoroalkanes (Scheme 19).¹⁷

Geminal dihaloalkanes were used as starting materials and the report demonstrated that these simple 1-fluoro-1-haloalkanes with no adjacent functional groups could be used as electrophiles for the cross-coupling reaction. Their optimized system employed NiCl_2 .glyme and the alkylated 1,2-diaminocyclohexane ligand, which afforded a wide variety of fluorinated alkanes, as well as site-selective fluorinated analogs of bioactive molecules and known C-F containing compounds with interesting biomedical properties. A wide range of alkyl boranes were compatible but Gandelman and coworkers found that 9-BBN-based alkyl nucleophiles bearing functional groups such as aryls, ethers, esters, and amines reacted particularly well to give the desired cross-coupling products in high yields.



Scheme 19

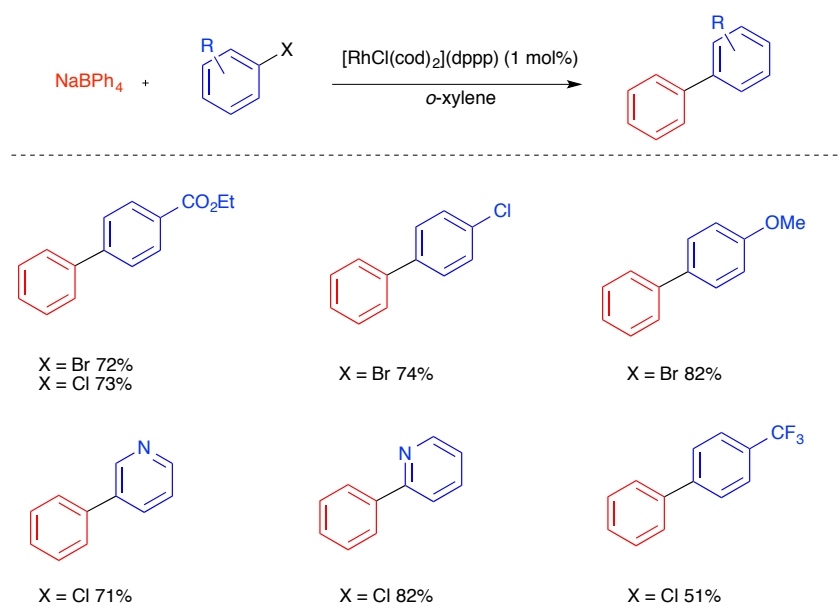
The direct asymmetric catalytic stereoconvergent synthesis of enantioenriched secondary alkyl fluorides from a racemic mixture of 1-fluoro-1-haloalkanes also proved feasible. For example, the cross-coupling of racemic sulfonamides and organoboranes using $\text{NiCl}_2\cdot\text{glyme}$ as a catalyst and the chiral bisamine ligand X occurred with high levels of enantiocontrol (95.5:4.5 er). However, the yield of the process requires some further optimization (Scheme 20).



Scheme 20

X.3.2 RHODIUM

Rhodium has been successfully used in a range of Suzuki-Miyaura type reactions. Satoh and Miura have reported the Suzuki–Miyaura-type cross-coupling of arylboron compounds with aryl halides in the presence of a rhodium-based catalyst system to produce the corresponding biaryls (Scheme 21).¹⁸ They also found, unexpectedly, that when employing benzonitrile as substrate under similar reaction conditions a multiple arylation is observed, in which nucleophilic arylation on the cyano group and subsequent ortho arylation via C–H bond cleavage is involved.



Scheme 21

Fürstner and coworkers have shown that rhodium-catalysts decorated with either phosphines or *N*-heterocyclic carbenes can be useful mediators for the addition of aryl- and alkenylboronic acids to aldehydes.¹⁹ Frost and co-workers have also reported the addition of arylboronic acids to aldehydes using [RhCl(ethylene)]₂ RuCl₃·3H₂O and [RhCl(cod)]₂ catalysts in the presence of the nitrogen-containing ligand.²⁰

Hayashi has reported a wide range of reactions employing rhodium with chiral binaphthylphosphine ligands, for example in the asymmetric 1,4-addition of boronic acids and triarylboranes to a variety of unsaturated starting materials; α,β -unsaturated ketones, esters, 1-alkenylphosphonates, nitroalkenes and 5,6-dihydro-2(1H)-pyridinones.²¹

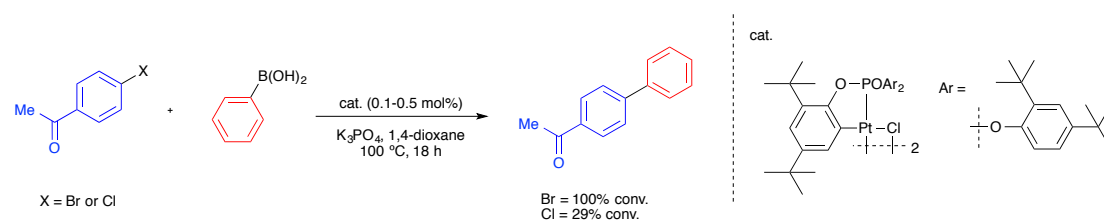
The Miyaura and Batey have also independently reported the use of rhodium catalysts for addition to aldehydes in the presence of phosphine ligands.²² Lautens has shown that [Rh(cod)Cl]₂ catalysed reactions of heterocyclic alkynes with arylboronic acids in the presence of water-soluble ligands such as sodium dodecylsulphate (SDS) and

sodium carbonate as bases affords trisubstituted alkenes in high regio-selectivity.²³

Supported rhodium(0) catalysts have also been reported to catalyse a range of cross-coupling reactions. For example, a layered double hydroxide (LDH) supported catalyst has been successfully used in the traditional Suzuki-Miyaura reaction to afford biaryl compounds in excellent yield.²⁴ The catalyst could be quantitatively recovered from the reaction mixture by simple filtration and reused for a number of runs with consistent activity in all the reactions. The catalyst was also simply prepared by treating LDH-CO₃ (Mg:Al = 3:1) with treated with RhCl₃.H₂O in doubly deionized water.

X.3.3 OTHER METAL SYSTEMS

Rhodium and nickel have been by far the most common metals aside from palladium employed in Suzuki-Miyura carbon-carbon bond forming reactions. Platinum has been used on several occasions, for example, Bedford and Hazelwood showed that platinum complexes with π -acidic, ortho-metalated triaryl phosphite and phosphinite ligands showed what they termed as “unexpectedly good activity” in Suzuki biaryl coupling reactions with aryl bromide substrates (Scheme 22). Application to aryl chlorides resulted in low conversion to the desired biaryl products.



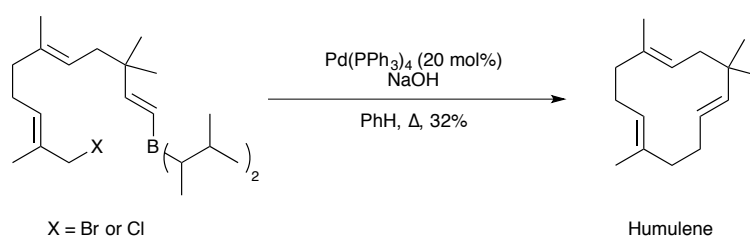
Scheme 22

Copper has also found wide use, however, it has generally only been found to be applicable to heteroatom-carbon coupling reactions when employing boronic acids as coupling partners, now known as the Chan-Lam Coupling.²⁵

X.4 Recent Applications:

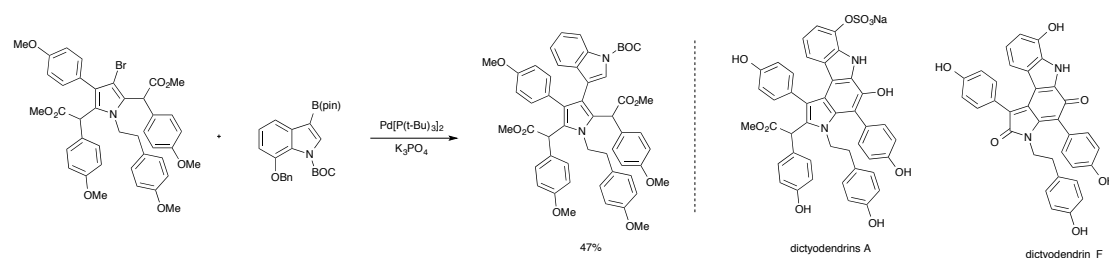
X.4.1 IN NATURAL PRODUCT SYNTHESIS

The use of the Suzuki-Miyaura reaction in the synthesis of natural products has been wide spread over the years and well reviewed. The intramolecular Suzuki-Miyaura reaction macrocyclisation to form macrocyclic natural products has been well reviewed by Fairlamb.²⁶ Interestingly the first report employing this type of approach for macrocyclic formation came from the group of Miyaura and Suzuki in their synthesis of humulene (Scheme 23).²⁷



Scheme 23

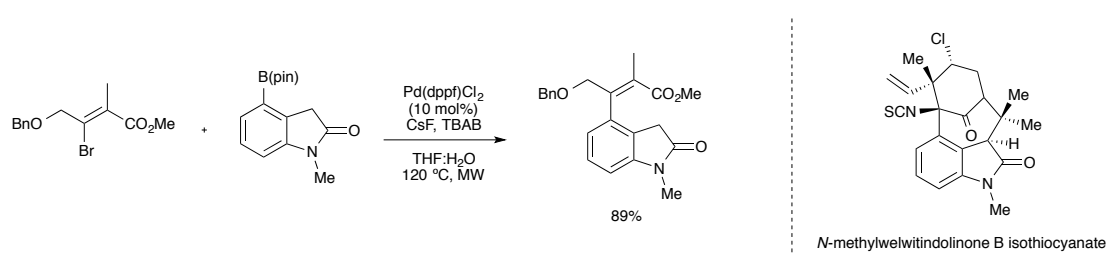
Below are a number of representative routes employing the Suzuki-Miyaura reaction from the past few years. Yamaguchi, Itami and Davies have reported the synthesis of the dictyodendrins A and F, which are active for cancer chemotherapy by telomerase inhibition, using C-H functionalization and a Suzuki-Miyaura coupling (Scheme 24).²⁸



Scheme 24

Shea and coworkers have reported an elegant route towards N-methylwelwitindolinone B isothiocyanate, employing a as a key step in coupling the aryl unit with the carbon

unit in order to build up the core of the bicyclic natural product framework (Scheme 25).²⁹



Scheme 25

Tang and coworkers have used an asymmetric Suzuki-Miyaura coupling reaction in their syntheses of the atropoisomeric natural products Korupensamines A, B and Michellamine B (Figure 3).³⁰ In their key enantioselective biaryl coupling step the presence of a polar- π interaction between the highly polarized BOP group and the extended π system of the arylboronic acid coupling partner was believed to be essential for high selectivity (Scheme 26). Synthesis of the heterodimer was also accomplished using this novel methodology.

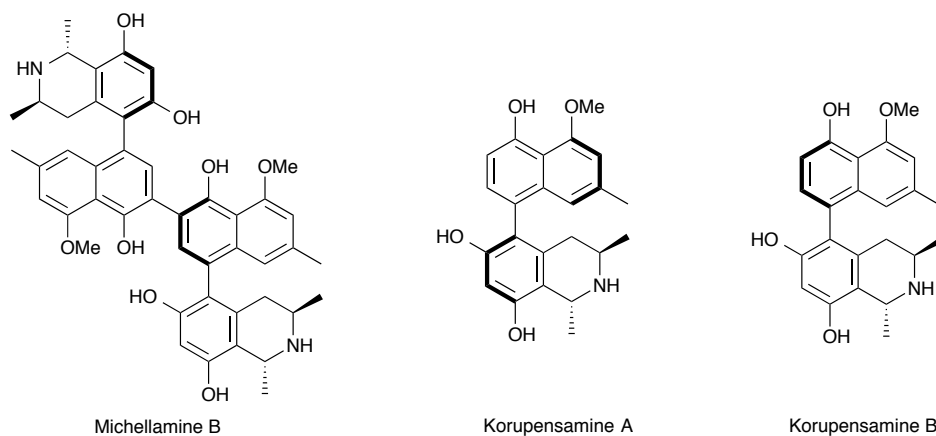
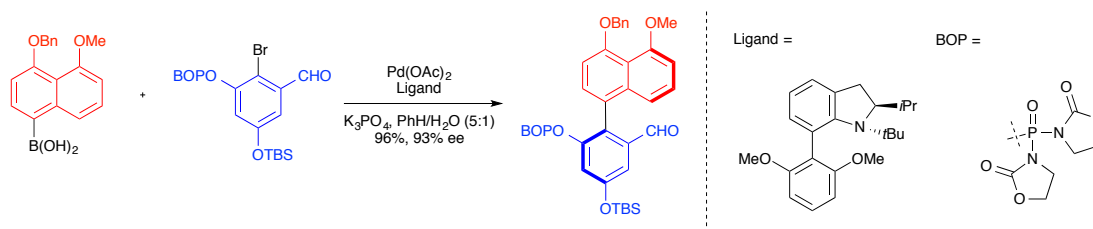


Figure 3

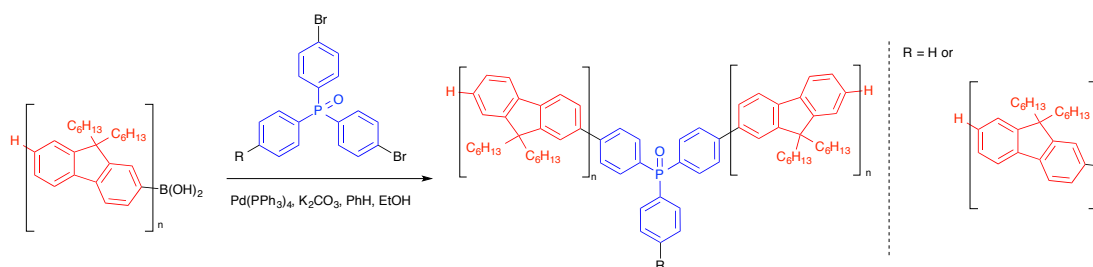


Scheme 26

X.4.2 IN MATERIALS CHEMISTRY

The Suzuki-Miyaura coupling has found widespread applications in materials chemistry, below are a few recent examples that harness the coupling protocol to produce novel materials.

Deep-blue organic light-emitting diodes have been produced that are based on multibranch oligofluorenes with a phosphine oxide centre.³¹ A series of these compounds were produced (Scheme 27) and the compounds showed excellent thermal stabilities, pronounced photoluminescence efficiencies, and good solution processability. Double-layered nondoped OLEDs based on these materials exhibited highly efficient deep-blue electroluminescence.



Scheme 27

Using a similar approach a range of stable emulsions of spherical and rod-like conjugated polymer nanoparticles were synthesized by Suzuki-Miyaura cross-coupling of 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester with a range of different dibromoarene monomers.³² Using this protocol the direct synthesis of conjugated polymer nanoparticles at room temperature was possible, to afford high

concentrations of conjugated polymers dispersed in water. These concentrations are within the range of organic solutions employed for organic electronic device fabrication. This room temperature emulsion polymerisation can be applied to a variety of suitably functionalised monomers. These novel materials (Figure 4) are to be used in the fabrication of OFET, OPV, and photonic devices.

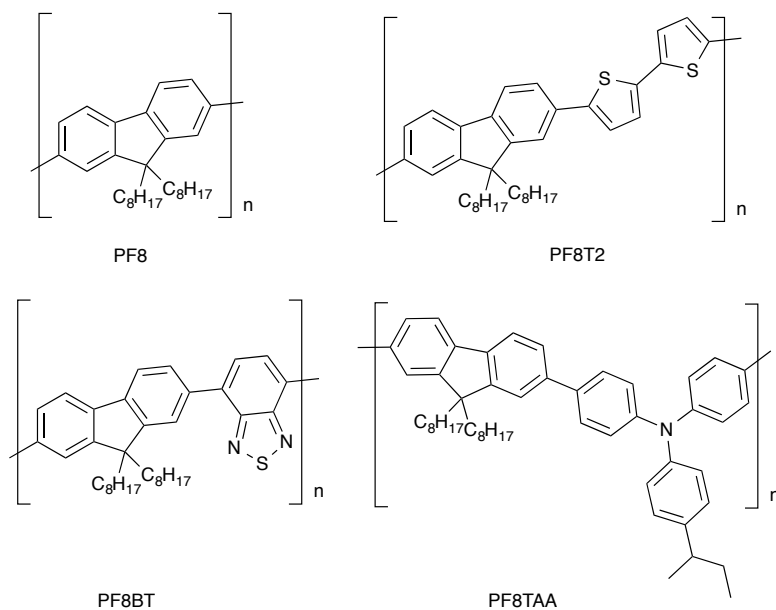


Figure 4

X.5 Conclusion

As can be seen from the above reports the Suzuki-Miyaura reaction has had and continues to have broad applicability across a wide manner of scientific disciplines, with a diverse series of applications spanning pharma and materials chemistry. There have been some fascinating developments of this process from its inception some 35 years ago. Suzuki and Miyaura have significantly added to their original report, with the ability to catalyse the coupling reaction with a variety of metals. Undoubtedly there have been significant advances in asymmetric catalysis since the Suzuki-Miyaura reaction was initially reported and groups from around the globe have harnessed this reaction to prepare enantioenriched compounds that would previously have been difficult or impossible to prepare without the original coupling protocol. Not surprisingly this has led to the synthesis of several natural products and biologically active compounds. Applications in materials chemistry are perhaps some of the most exciting as one would anticipate that Suzuki and Miyaura would not have dreamed of such applications for their work.

The application, modification and development of this cross-coupling methodology is surely set to continue apace and we look forward to the next step change developments in this area.

X.6 References

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