A Platinum Open Access Journal for Organic Chemistry

Review

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Recent applications of domino Suzuki-Miyaura coupling as an important tool in the modern organic synthesis

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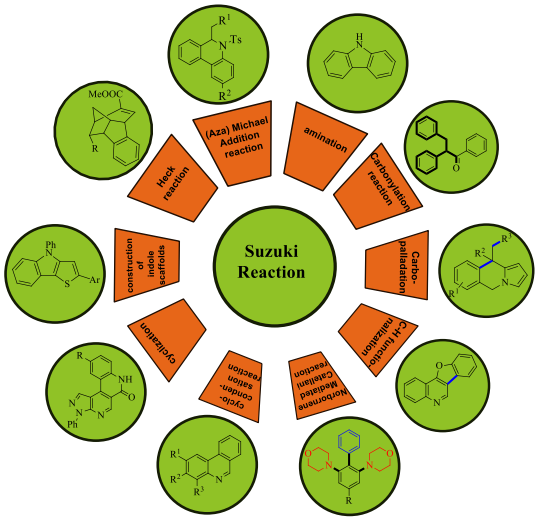
Received 01-10-2025 **Accepted** 04-02-2025 **Published on line** 04-30-2025

Abstract

Domino Suzuki-Miyaura couplings have been widely employed as an important tool in the construction of various C-C and C-heteroatom bonds in recent times. Suzuki-Miyaura coupling in combination with other strategies like acylation, amination, arylation, carbonylative coupling, carbopalladation, C-H functionalization, condensations, Heck reaction, Michael reaction, etc. have been widely utilized in diverse organic synthesis. In this review, there is a particular focus on Pd- and Ni-catalyzed domino Suzuki-Miyaura couplings and a detailed overview on the preparation of a of plethora organic compounds through the construction of variety of C-C and C-heteroatom bonds found in the literature since 2014 to date is given.



Keywords: Domino Suzuki-Miyaura coupling, C-C and C-heteroatom bonds, Heck reaction, C-H functionalization, carbopalladation

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1. Introduction

According to Tietze, a domino reaction is a reaction that involves at least two consecutive bond-making transformations in the same flask. It strictly means that domino reactions do not allow a change in reaction conditions by adding extra reagents, catalysts, or others. In these reactions, the functionality obtained by bond making or breaking in the preceding step is required for the subsequenttransformations.[1-2] Herein, the initial production of intermediate like a carbocation or a carbanion is not considered as a step. However, diene generation by a retro-Diels-Alder process, followed by cycloaddition, is counted as a domino reaction.[3] Multicomponent reactions are often found to consist a sub moiety of domino reactions among at least three components involved. Consequently, multicomponent reactions are also classified as domino reactions.[4] Other examples of domino reactions are the incorporations of cationic, radical, anionic, metal-catalyzed and photochemical reactions frequently found in recent literature.[5] Experimentalists suggested that if reagents or catalysts are added only to effect the commencement of a sequence, it is called a domino reaction. On the other hand, the addition is required to propagate the next step in consecutive reaction. Hence, domino reactions differ from consecutive tandem or cascade reactions. However, Nicolaou mentioned that the term domino is indistinguishably used for consecutive reactions in the literature.[6] These reactions are highly efficient compared to stepwise reactions by minimizing the amount of reagents, solvents, energy and adsorbents, consequently, the production of waste is also reduced.[7]

In a Suzuki-Miyaura (SM) reaction, an organoboron compound is coupled with an organic halide or pseudo halide in the presence of a transition-metal, mainly a palladiumcatalyst.[8] A diverse of organoboron compounds, prepared from various substrates, are found to be tolerant of several functional groups during the transformations. In addition, boron substrates are stable in water and air as well as exhibit low toxicities.[9] SM reactions even been conducted in water using nano-palladium metal that the reaction conditions become mild and benign, the reaction only requires short times and proceeds efficiently in conjunction with a facile separation of by-products. The broad advantages of SM coupling have made the technique a potent tool for the efficient formation of C-C bonds inaryl-aryl, aryl-alkyl, vinyl-aryl and alkyl-alkyl linkages since its establishment

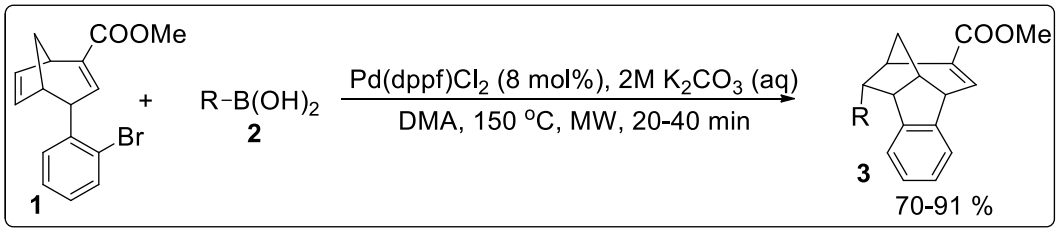
in 1979.[10] Theawarding of the Nobel Prize in Chemistry in 2010 for the development of the SM coupling reaction (alongside Heck and Negishi coupling reactions) bears testimony to its excellence.[11]

In this review, attention will be given to those domino reactions that involve at least one Suzuki-Miyaura (SM) coupling as a key step to make C-C bond published from 2014 onwards. A classic example is the preparation of benzo[c]chromenes by a domino SM coupling-oxa-Michael addition reported by our laboratory.[12] The synthesis starts with the Pd-nanoparticle-catalyzed SM coupling between 2-hydroxyarylboronic acid and β-(2-bromoaryl)-α,β-unsaturated carbonyls and ends with the intramolecular oxa-Michael addition. The other combinations will be explored in details, for example, aminations lead to the formation of carbazole and biaryl tertiary amines. The production of fluoranthenes and naphthothiophenes by the sequence of SM-coupling-arylation are other classic examples. In addition, a study of this coupling together with other strategies like carbonylative coupling, carbopalladation, C-H functionalization, cyclocondensation, dicarbofunctionalization, 4π-electrocyclic ring opening, elimination, hydroacylation or (aza-)Michael has been described in detail.

2. Domino Suzuki-Miyaura Coupling

2.1. Domino Heck/Suzuki coupling

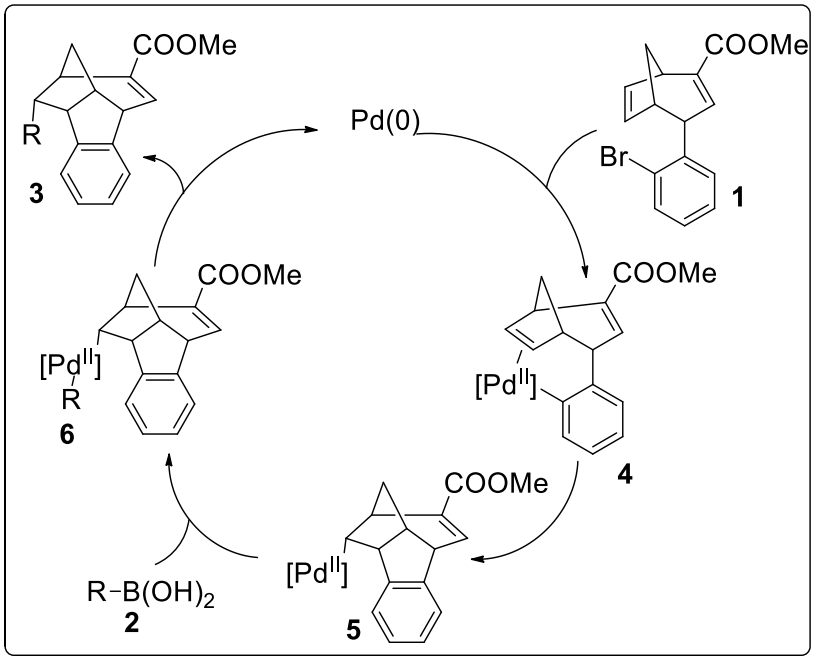
This section is intended to illustrate the importance of the combination of the Heck coupling reaction and SM coupling reaction. In recent times, domino**-**Heck-Suzuki coupling reactions are utilized as an important tool to produce structurally diverse molecules. In 2014, Alza and co-workers reported a synthetic route to construct a tetracyclic system rich in sp^3 carbons for the first time. They tested the coupling between a variety of aryl- as well as N-and S-heteroaryl-bicyclics **1** with boronic acids **2** in several conditions. However, the use of $Pd(dppf)Cl_2$ as catalyst, DMA as solvent and K_2CO_3 base led to the formation of the tetracyclic skeleton**3** efficiently with Suzuki coupling between sp^3-sp^2 carbons (Scheme-1).[13]



Scheme 1. Synthesis of a tetracyclic ring system.

A tentative reaction pathway was proposed for the domino Heck-Suzuki reaction (Scheme 2). Initially, aryl bromide **1** undergoes oxidative addition to Pd(0) to give **4**. Then, the adjacent olefinic bond is involved in a *syn*-migratory insertion of the carbopalladation type to produce **5**, which on subsequent transmetalation with boronic acid **2** gives **6**. Finally, reductive elimination delivers the domino product **3**.

In continuation of this type of domino reactions, the report by Kusunuru and others can be illustrated in which they achieved high diastereoselectivity in diarylation of glycals **7** with arylboronic acids **8** (Scheme-3).[14] The scope of the domino reaction was widely explored employing various glycals with arylboronic acids to produce diverse diarylated products **9**. In this reaction, TEMPO was used as a promoter which plays a significant role to prevent *syn*-as well as *anti*-elimination.



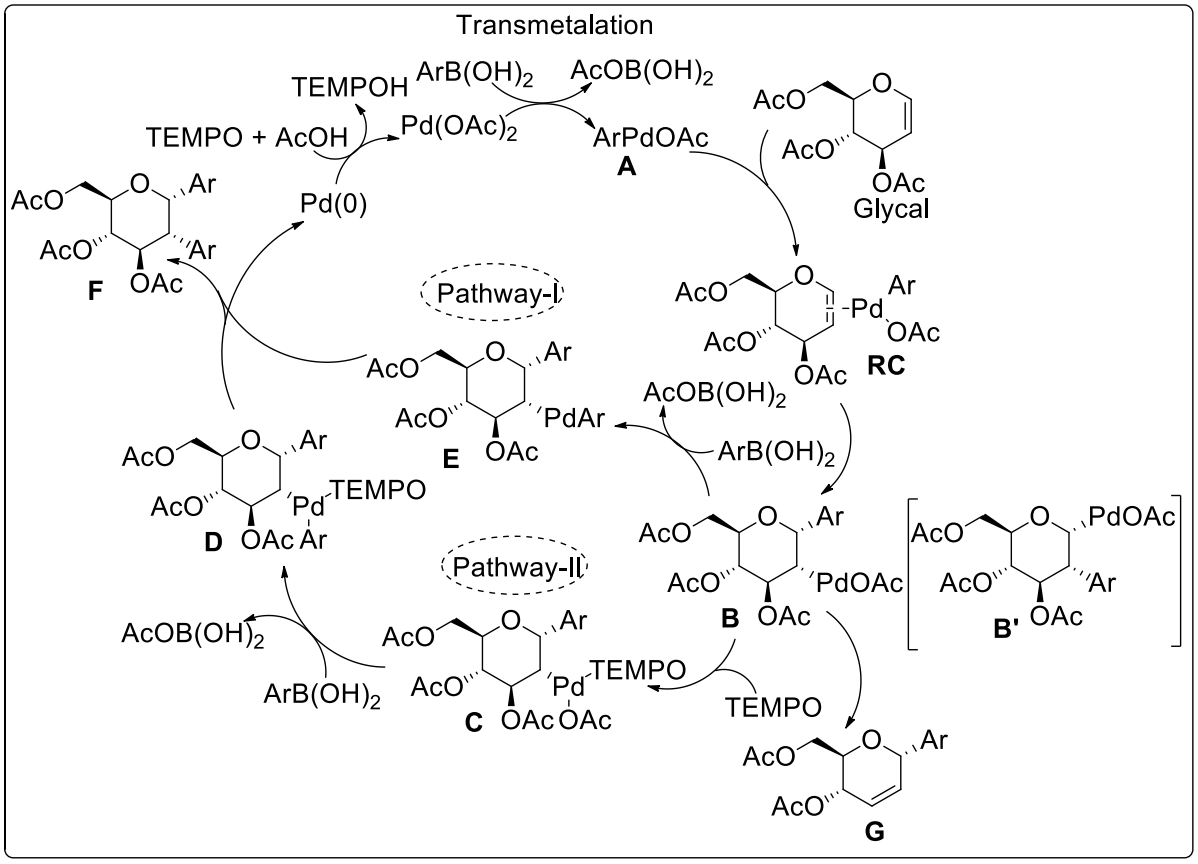
Scheme 2. Tentative mechanism for the synthesis of tetracyclic scaffold **3**.

Scheme 3. TEMPO-promoted diarylation of glycals.

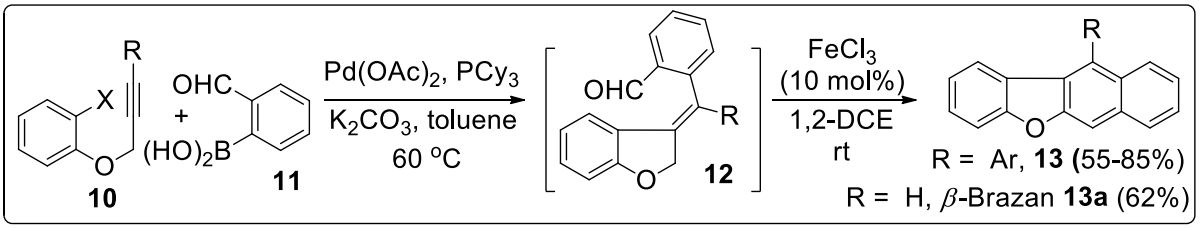
In addition, detailed spectroscopic data was studied to determine the stereochemistry of the aryl groups as cis(*α*-*α*) at C(1)/C(2) as well as the mechanistic course of the reaction pathway depicted in Scheme 4. Initially, they proposed two pathways for the diarylation with four main steps, likely (i) transmetalation to give **A**, (ii) syn addition of to generate **B**, (iii) exchange of aryl, (iv) a second arylation along with reductive elimination to generate **F**. DFT calculations helped the authors to conclude that the complex **RC** favours arylation at C(1) over C(2) to produce **B** rather than **B'**. Then, there was a possibility of obtaining the product **G** from **B** via anti elimination. However, the reaction gives diaryl product solely with probable intermediate **E**. But the energy calculation helped to conclude that the formation of the diaryl product was not obtained via **E**. Next, quantum chemical calculations were carried out on **C** and **D** obtained in the presence of TEMPO. This study clearly exhibited that getting **D** from **B** is energetically favorable over that of **E** from **B**. Hence, the presence of TEMPO lowers the energy required to give diaryl product **F**.

This domino strategy was extensively explored by Paul and co-workers, who reported a straightforward synthesis of diverse tetracyclic dibenzofuran analogues. In this reaction, benzene derivatives **10** follows a sequence of Heck-Suzuki coupling in presence of 2-formylphenylboronic acid **11** and a Pd-catalyst to give intermediate **12**, which on subsequent Fe(III)-catalyzed isomerization and aromatization delivers tetracyclic dibenzofurans **13** (Scheme 5). Moreover, the utility of this approach was demonstrated by the successful synthesis of the natural product β-brazan **13a**.[15]

Then, they have shown a plausible course of the reaction in details. However, considering the subject of this report, it appears appropriate to discuss the mechanistic course (Scheme 6) of the domino Heck/Suzuki reaction step only. At the beginning, Pd(0)/PCy_3 undergoes oxidative addition of **10**, which on subsequent *syn*-carbopalladation gives complex **10a**. Then, transmetalation with **11** provides intermediate **10b**. Finally, reductive elimination delivers the domino product **12** with *syn***-** as well as mixture of *syn*-and *anti*-configuration. It is believed that the *syn*-isomer is transformed into the *anti*-isomer during carbopalladation involving zwitterions **10c** or **10d**, which permit free rotation around the C-C bond.

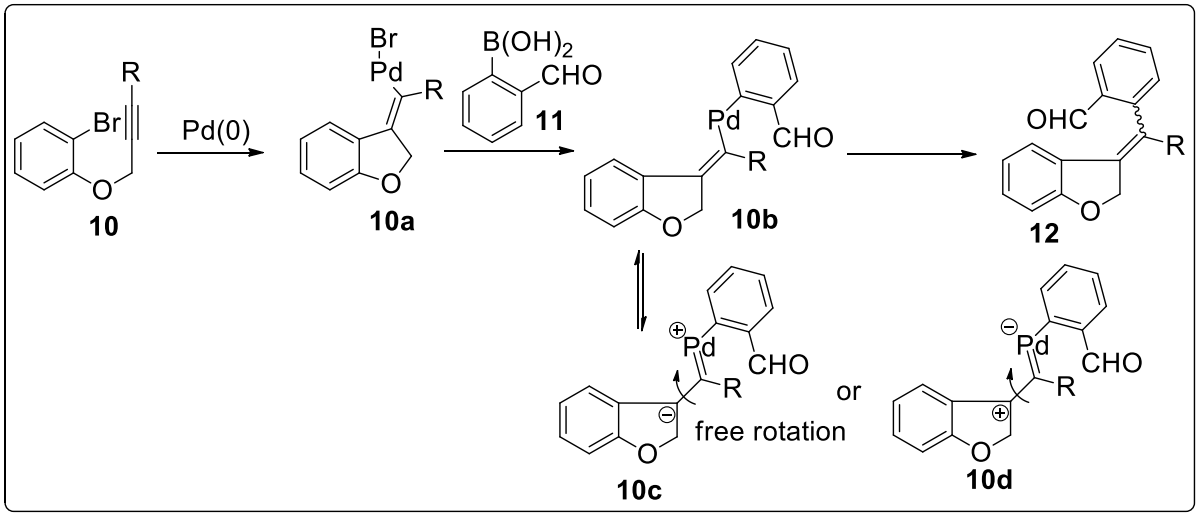


Scheme 4. Possible mechanistic course of diarylation.

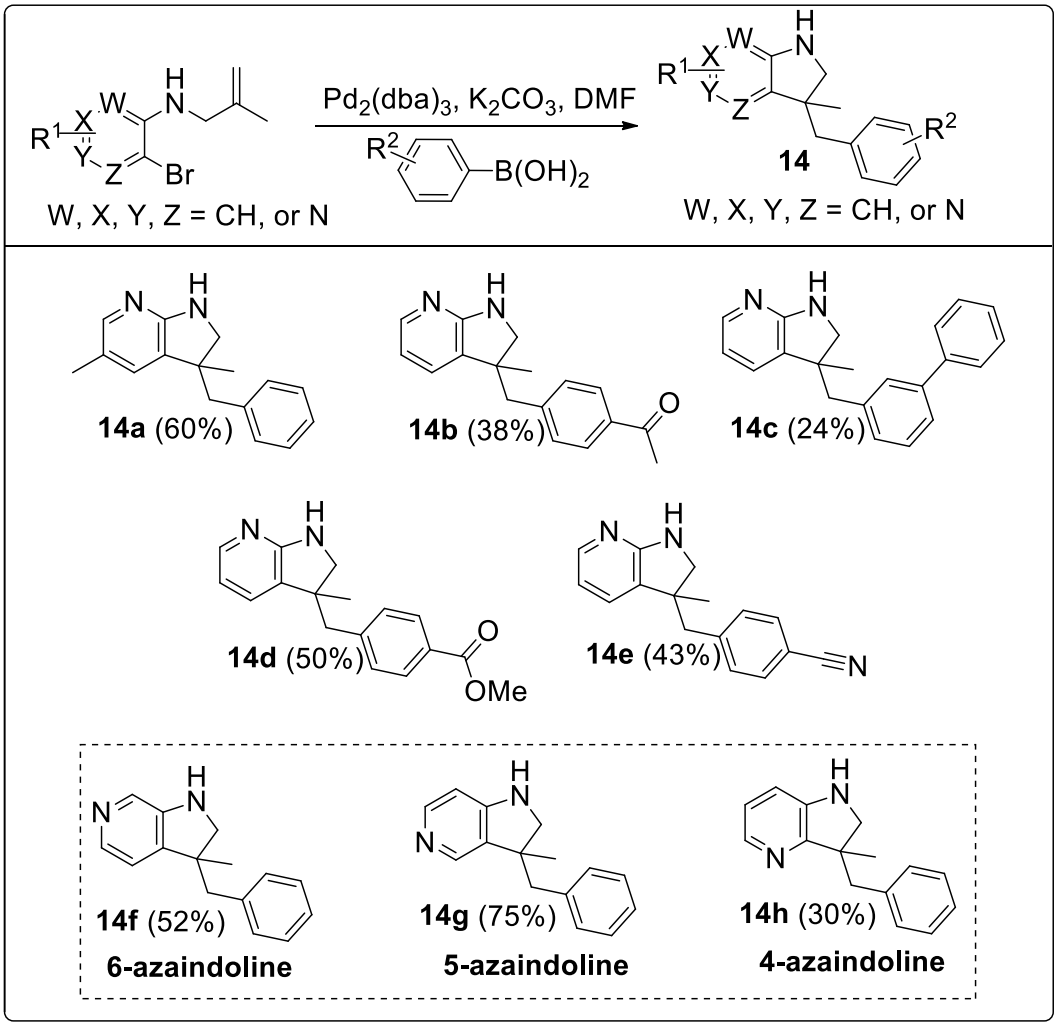


Scheme 5. Two steps synthesis of tetracyclic dibenzofurans.

In 2017, this domino approach was employed by Schempp and others in the synthesis of 3,3'-azaindolines **14**.[16] Herein, the reaction gives the product **14** via a sequence of Heck reaction-Suzuki coupling (Scheme 7). Moreover, the importance of the combined strategy is proved with the production all four isomers of 3,3'-azaindoline.



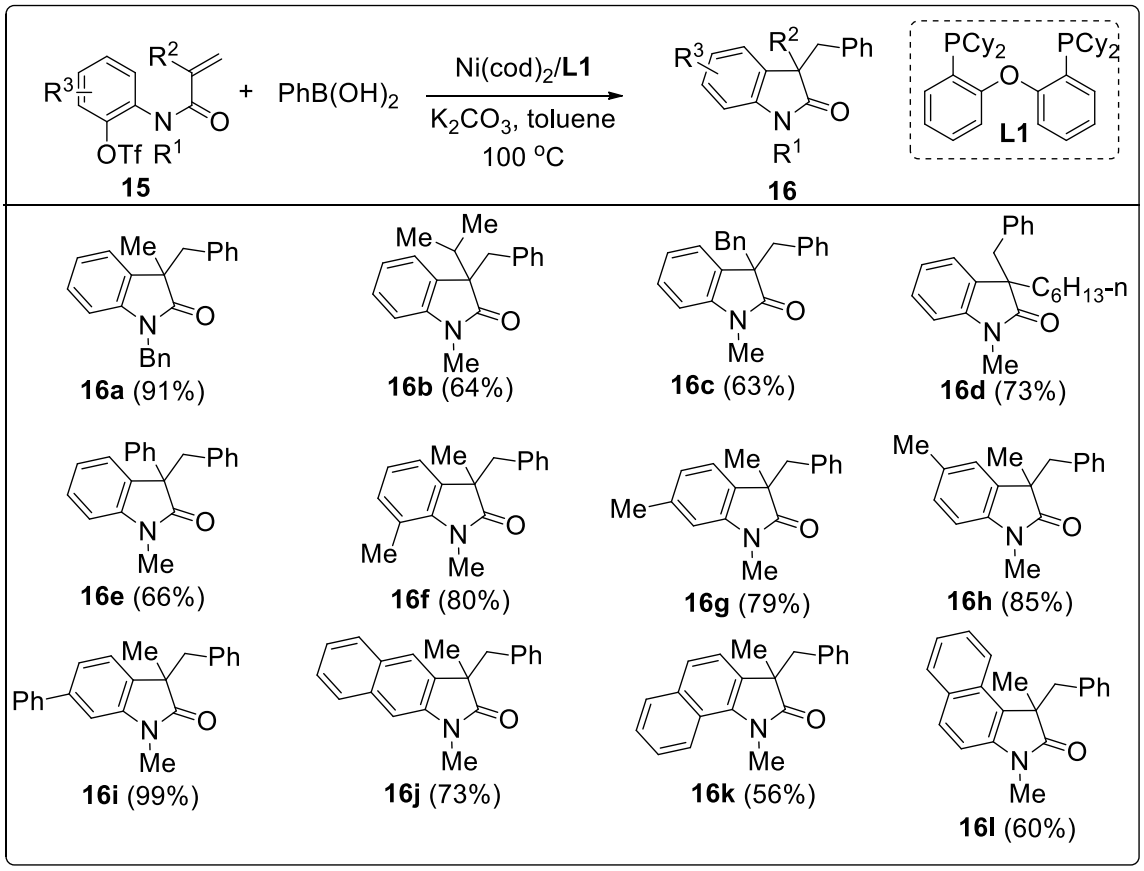
Scheme 6. Plausible mechanism to get a mixture of *syn*-and *anti*-isomers.



Scheme 7. Domino Heck reaction/Suzuki coupling to produce 3,3′-azaindolines.

Usually, palladium-catalysts are introduced in the transmetalation step for Heck, Suzuki and other coupling reactions. However, researchers are always interested to find a substitute for Pd-catalyst to reduce the cost of the reaction. In this regard, the best discovery is nickel catalyst which is less expensive, nontoxic and sustainable.[17] Moreover, its relatively smaller size makes oxidative addition easier. Although a nickel-catalyzed Heck reaction was already reported in 1980,[18] reactions with Ni-catalysts are still challenging.

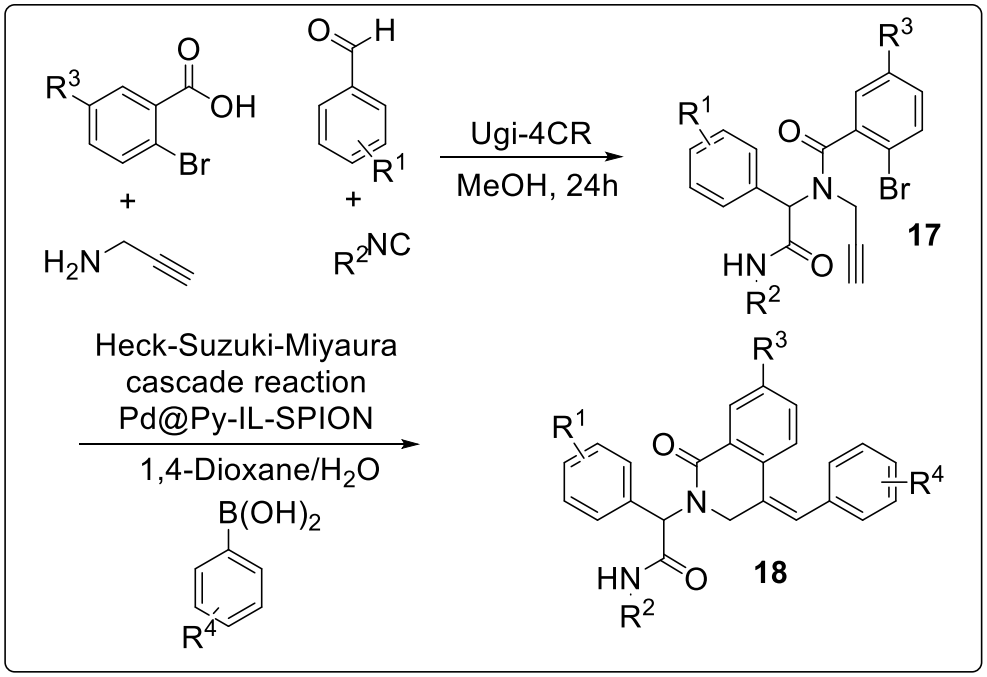
In 2018, 3,3-disubstitutedoxindoles **16** were synthesized in a cheaper way introducing nickel as catalyst by Li and co-workers. In this reaction, a cross coupling occurs between aryl triflates **15** and boronic acids via Csp^2-O cleavage of unreactive esters, and subsequent Heck reaction and Suzuki coupling (Scheme 8).[19]



Scheme 8. Ni-Catalyzed domino Heck reaction-Suzuki coupling.

In 2019, a general procedure was reported by Asgari and co-workers in which Pd@Py-IL-SPION was introduced as catalyst to obtain arylidene-isoquinolinones with stilbene scaffold **18**.[20] Ynamides **17** prepared by Ugi four-component reaction undergoes Heck-Suzuki-Miyaura cascade reaction in presence of boronic acids in a highly stereoselective fashion to give **18** (Scheme 9). The stereoselectivity of the product arises from the syn-addition to the triple bond.

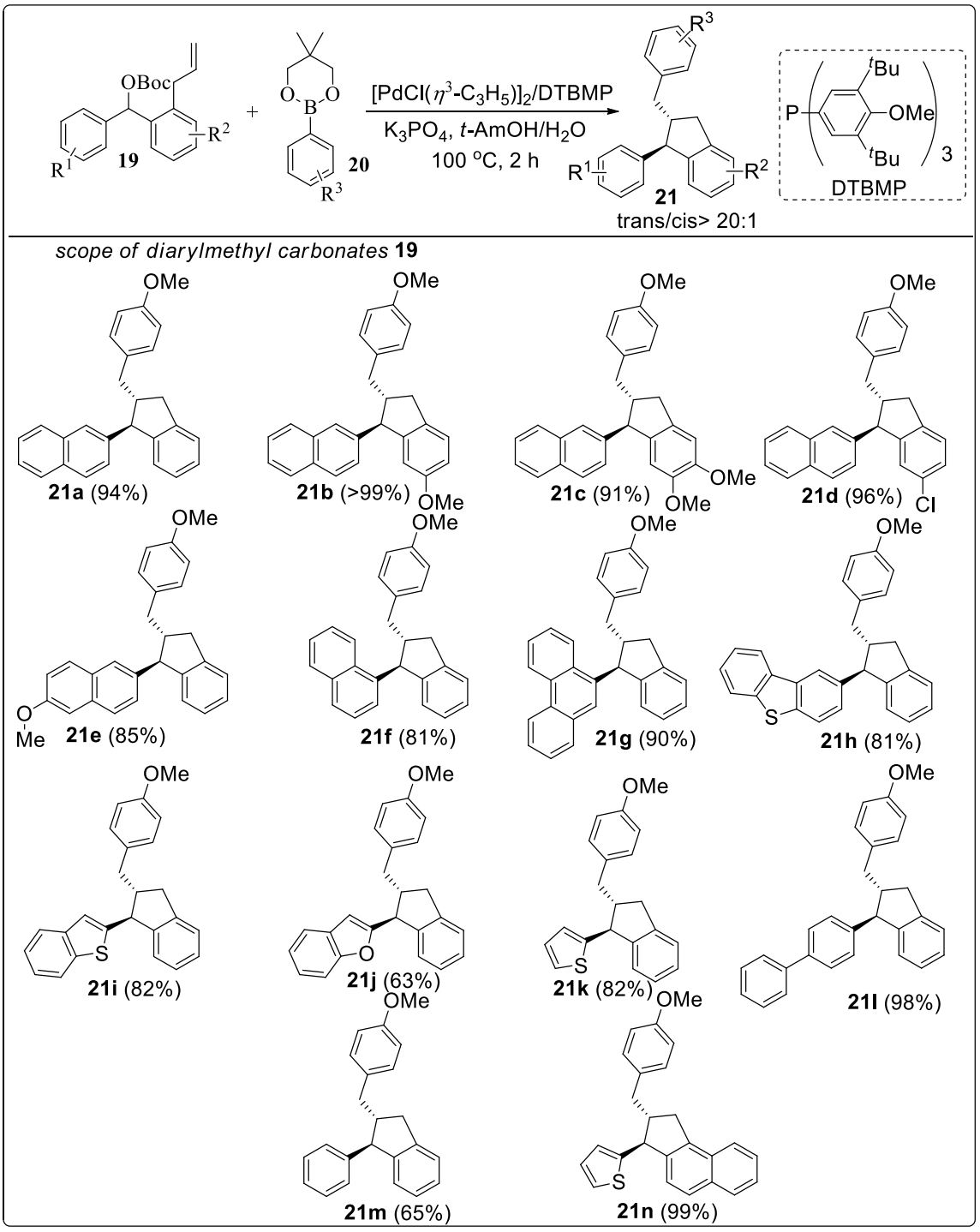
As an illustration of this domino approach, the report by Matsude and others in 2020 can be depicted in which 1,2-disubstituted indanes **21** were prepared chemo- and diastereoselectively from diarylmethyl carbonates **19** by the reaction with arylboronates **20** (Scheme 10).[21] The synthesis was completed by following a Heck-Suzuki cascade reaction in the presence of a Pd/DTBMP catalyst. In this protocol, trans selectivity as well as tolerance of several functional groups are also observed. In addition, insertion of chiral substrates results in enantiospecificity and stereoinvertivity in the products.



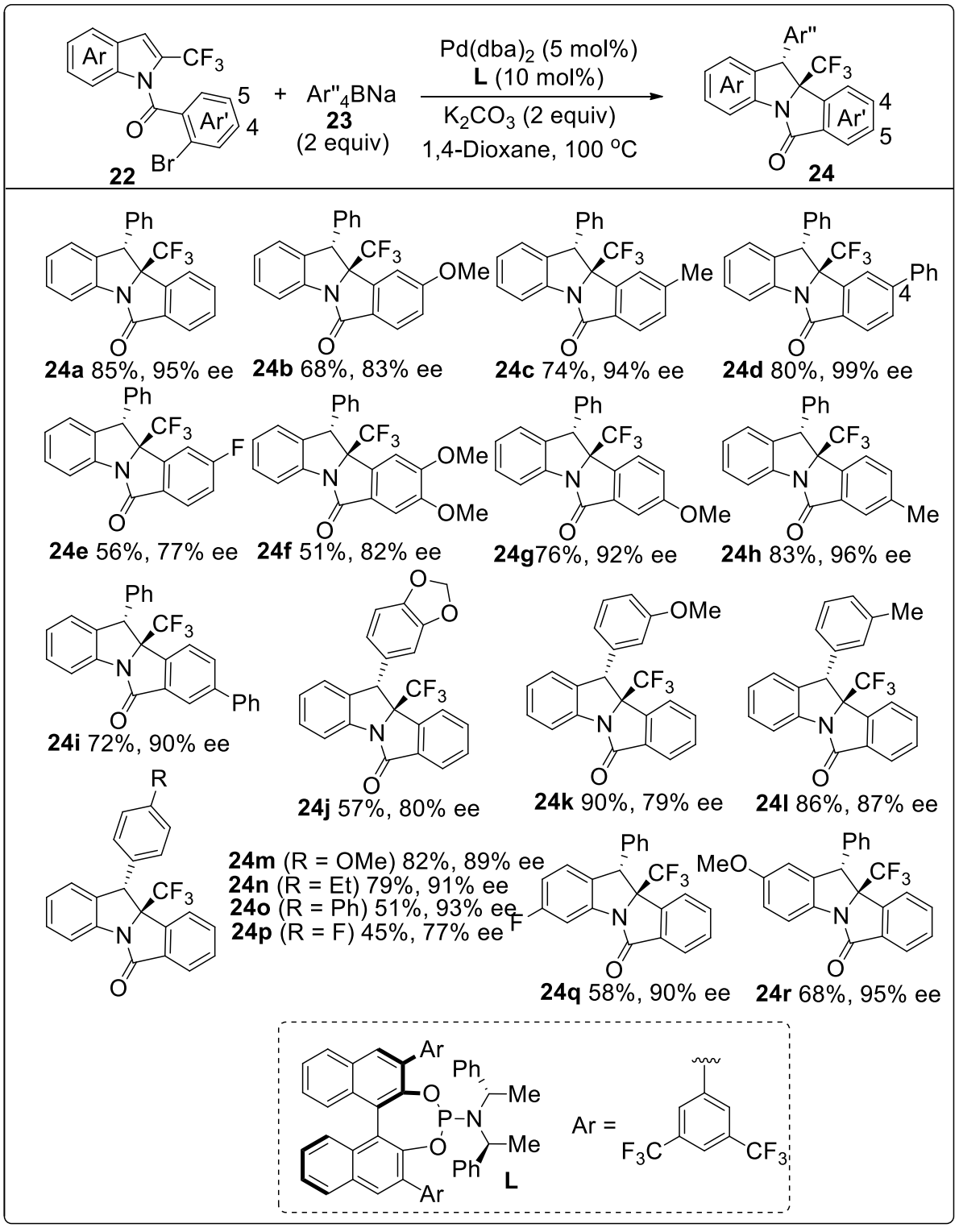
Scheme 9. Pd@Py-IL-SPION-catalyzed synthesis of arylidene-isoquinolinones.

In 2022, a facile approach to a dearomative domino Heck/Suzuki coupling of 2-CF_3-indoles was described by Liang and others.[22] In this dearomative reaction, *N*-(*o*-bromoaryloyl)-2-CF_3-indoles **22** reacts with Ar_4BNa **23** in the presence of a $Pd(dba)_2$/(*R,S,S*)-**L** catalyst to provide plethora indolines **24** with two adjacent stereocenters(Scheme 11). It was also observed that the presence of methoxy (**24b**, **24f**, **24g**) and methyl (**24c**, **24h**) groups delivers indolines with high ee. However, excellent ee result with C-4 or C-5 chloro-substituted substrates (**24d, 24i**) in which one more Suzuki coupling occurs with **23**.

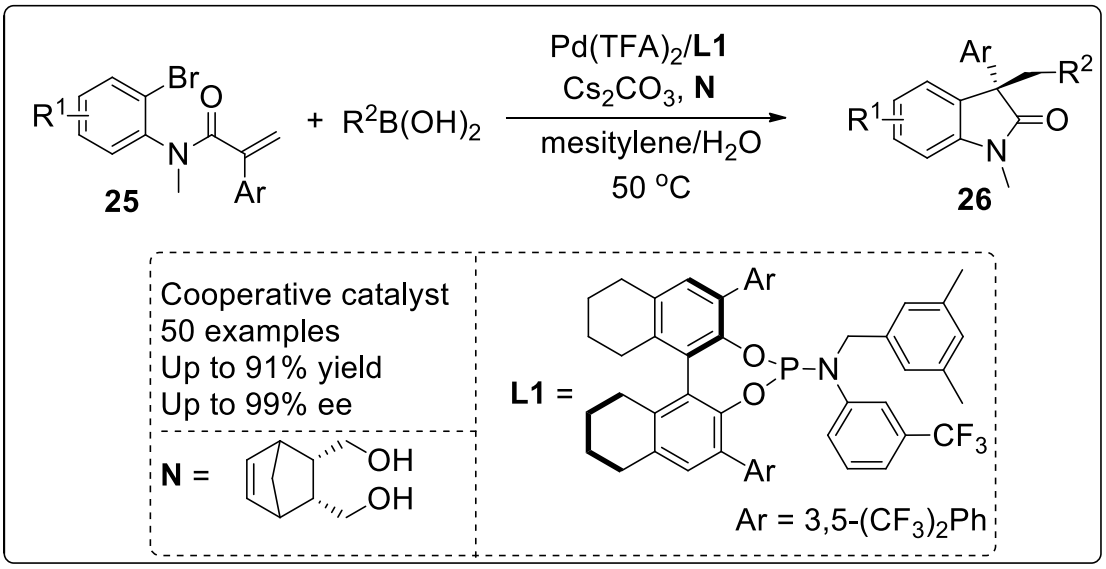
Later in the same year, a general methodology was disclosed by Chen and co-workers for a cascade of asymmetric Heck-Suzuki coupling of *N*-(2-bromophenyl)acrylamides **25**.[23] The reaction between amides **25** and arylboronic acids in the presence of a chiral ligand like phosphoramidite **L1** and *endo*-5-norbornene-2,3-dimethanol **N** produces variety of 3,3-disubstituted oxindoles **26** with very high enantioselectivities (Scheme 12).



Scheme 10. Pd/DTBMP-catalyzed synthesis of 1,2-disubstituted indanes.

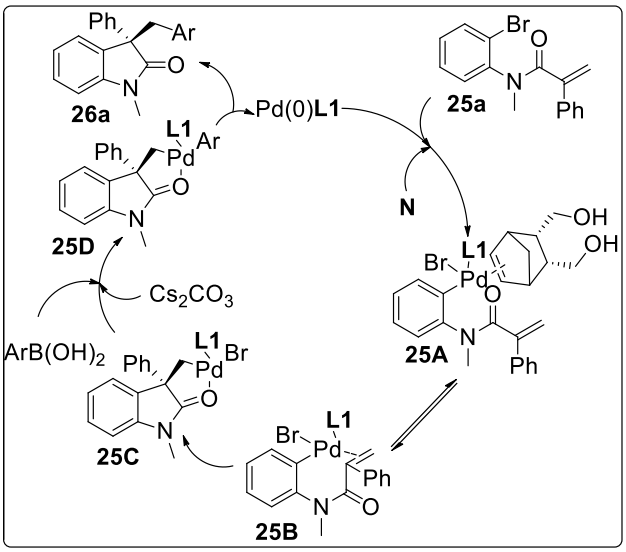


Scheme 11. Domino Heck/Suzuki coupling in the construction of chiral indolines.



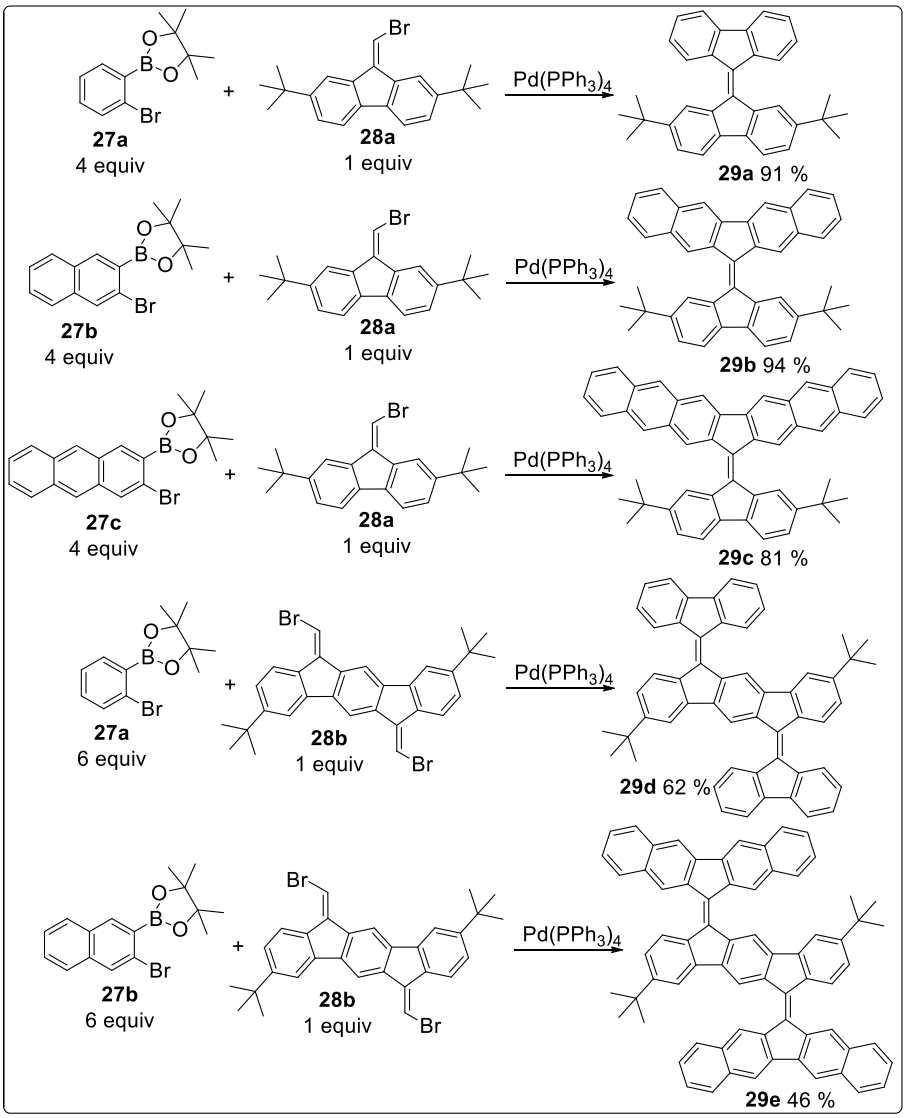
Scheme 12. Asymmetric Heck-Suzuki coupling of *N*-(2-bromophenyl)acrylamides.

From various experimental results it was obvious that the*endo*-5-norbornene-2,3-dimethanol **N** plays a crucial role in the prevention of transmetalation of aryl-Pd complex rather than having controlling effect on enantioselectivities. Then, a tentative reaction course for the asymmetric cascade reaction was explored as depicted in Scheme 13. At the beginning, aryl bromide of acrylamide **25a** undergoes oxidative addition to a Pd(0)/**L1** and **N** to give intermediate **25A**. Next, C-C double bond coordinates intramolecularly to the Pd center via interchange of alkenes reversibly producing intermediate **25B**. Subsequently, the alkyl-Pd intermediate **25C** is obtained via migratory insertion of **25B** in an enantioselective manner. Finally, **25C** undergoes transmetalation with arylboronic acids to generate intermediate **25D**, which on subsequent reductive elimination gives the final product **26a** with the regeneration of the active palladium(0)/**L1** catalyst.



Scheme 13. Tentative mechanism for asymmetric synthesis of oxindoles.

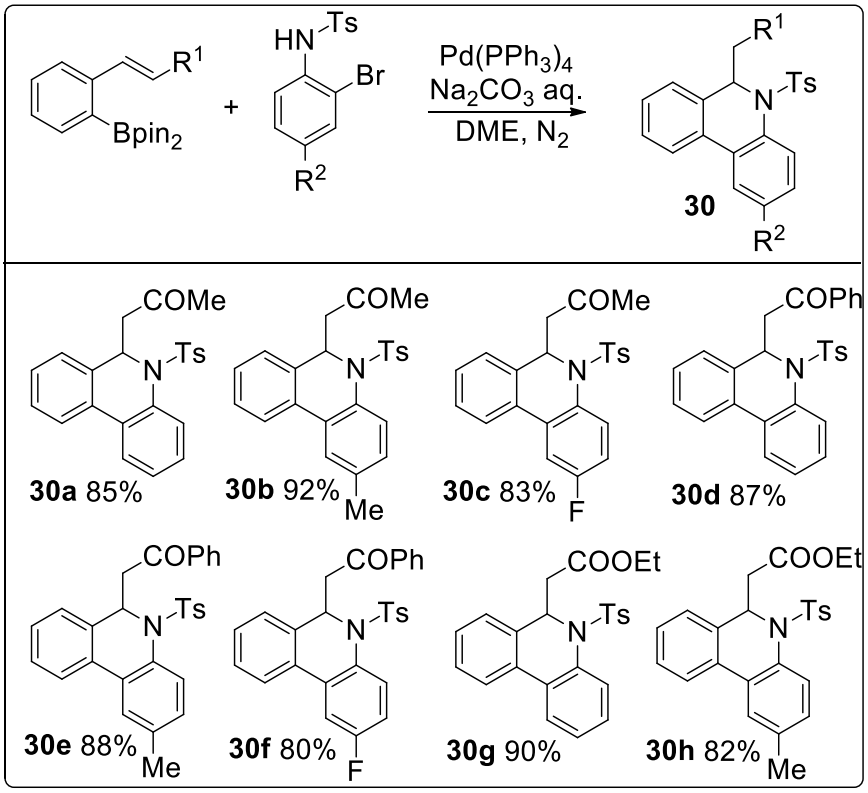
In 2023, a facile method has been developed by Zhu and co-workers to prepare a variety of bifluorenylidenes (9,9'BF) via a Pd-catalyzed cascade multistep reaction of Suzuki coupling and followed by Heck cyclization.[24] In this approach, the synthesis of the desired 9,9'BFderivatives **29** from the precursors pinacol ester of (2-bromoaryl)boronic acid **27** and vinyl bromides **28** is obtained in 81-94% yields by involving two successive Suzuki cross-coupling as well as one Heck cyclization as represented in Scheme 14.



Scheme 14. Synthesis of bifluorenylidenes via Suzuki coupling and Heck cyclization.

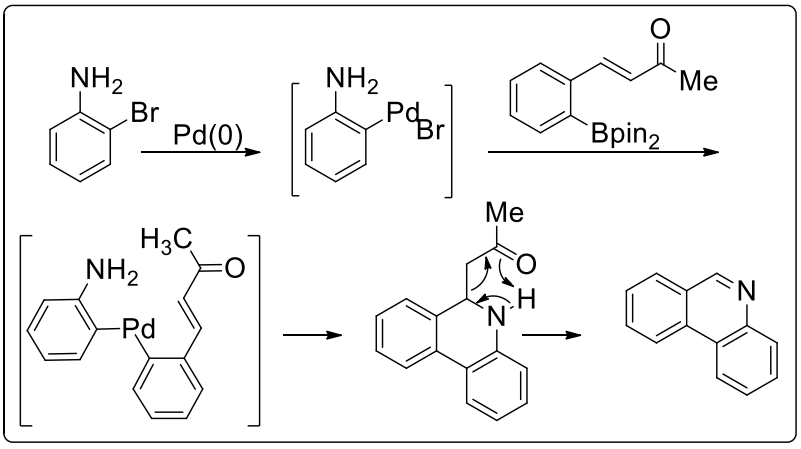
2.2. Domino Suzuki/ (Aza) Michael addition reaction

Transition metals have been immensely employed as efficient catalysts to prepare various cyclic compounds involving the formation of multiple bonds in one-pot processes. Oxygen- and nitrogen-bearing cyclic structures are found in numerous naturally occurring products. Therefore, reports for the sequential formation of C-C and C-N or C-O bonds are found regularly in literature. In 2014, an efficient strategy was established by Bao and others to produce 6-substituted phenanthridines **30** in one-pot.[25] The reaction is believed to be completed by a sequence of Pd-catalyzed Suzuki coupling and subsequent aza-Michael in an intramolecular way (Scheme 15).



Scheme 15. Synthesis of phenanthridines by Suzuki/Aza-Michael cascade.

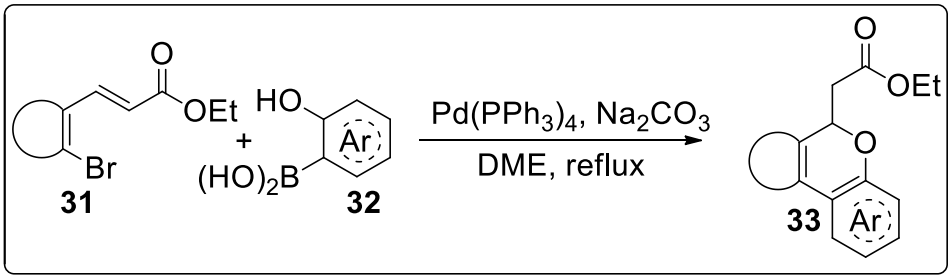
The previous reports[26-27] as well as results found in this reaction helps to draw mechanistic course for the preparation of phenanthridines with decomposition (Scheme 16). The reaction proceeds through the oxidative addition by Pd(0) to the C-Br bond of 2-bromoaniline. Then, transmetalation followed by decomposition leads to the formation of phenanthridines.



Scheme 16. Plausible mechanism for the formation of phenanthridines.

In 2016, a novel method was discovered by Zhu and co-workers to deliver O-heterocycles by Pd-catalyzed domino Suzuki cross-coupling/oxa-Michael addition.[28] The domino reaction between compound **31** and 2-hydroxyarylboronic acid **32** gives a rapid synthesis of novel O-heterocycles **33** (Scheme 17). The tandem reaction

starts with an intermolecular Suzuki cross-coupling and ends with an intramolecular oxa-Michael addition. Similar approaches were developed by Ahmed and others in 2013.[12]



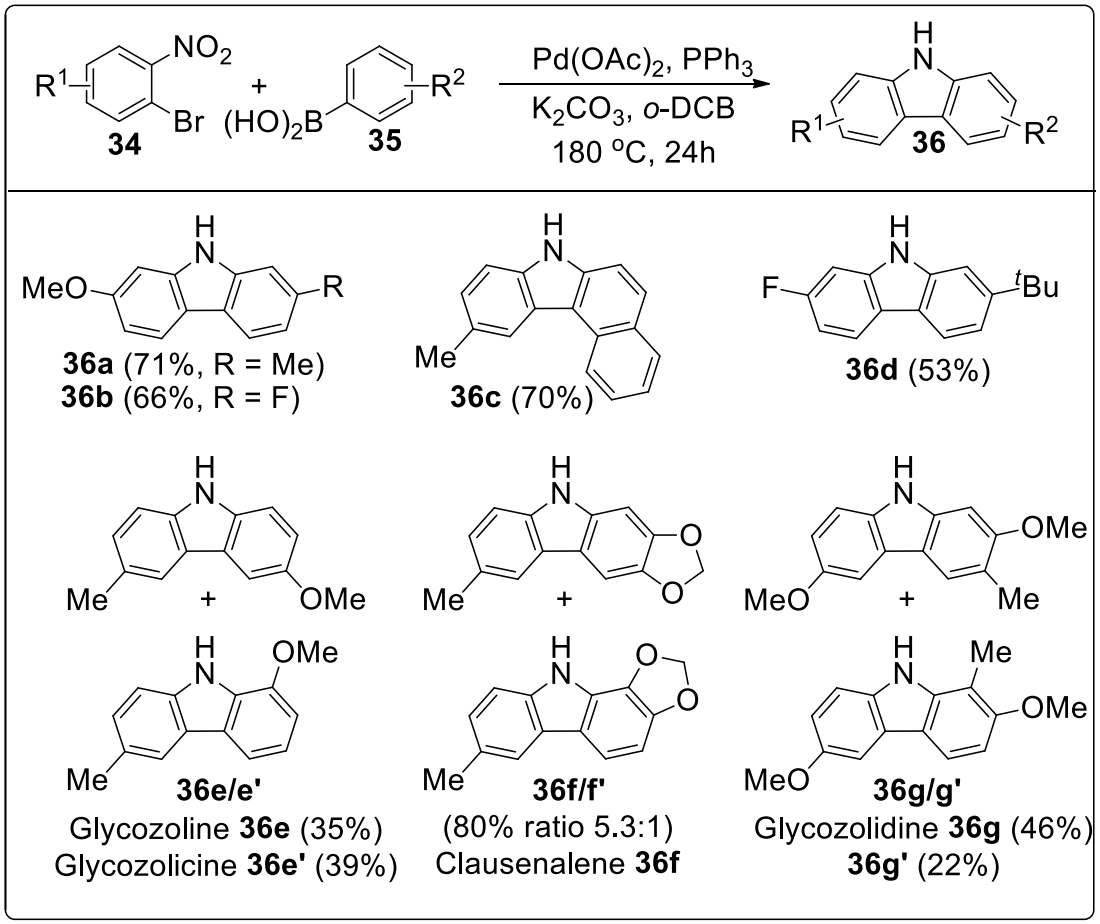
Scheme 17. Synthesis of O-heterocycles by cascade Suzuki coupling/oxa-Michael addition.

2.3. Domino Suzuki coupling/amination

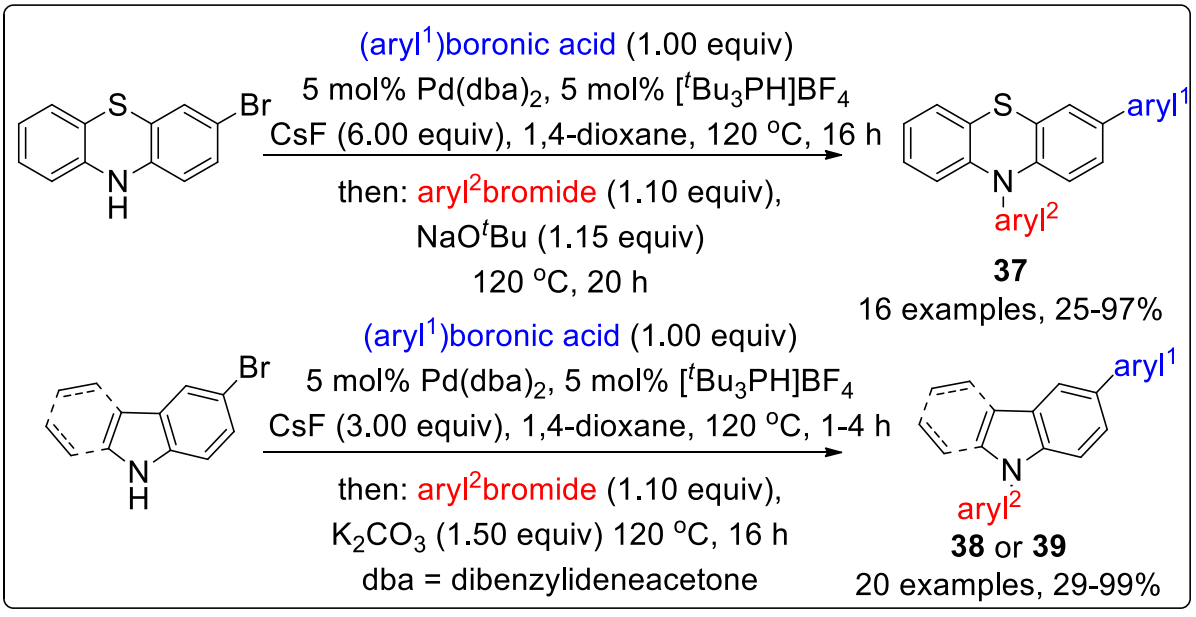
The preparation of C-C and C-N bonds by cascade reactions is fundamental significance in the formation of various *N*-containing heterocycles having biological activities. Pd-catalyzed Buchwald-Hartwig reaction effectsthe construction of aromatic C-N bonds efficiently.[29-30] In this regard, an efficient method for the preparation of carbazoles by Goo and others in 2015 can be referred to.[31] The reaction between 2-halonitrobenzenes **34** and arylboronic acids **35**in 1,2-dichlorobenzene, *o*-DCB delivers carbazoles **36** via a tandem of Suzuki coupling as well as the Cadogan reaction (Scheme 18). The scope of this approach was demonstrated by preparing various bioactive natural carbazole based alkaloids like glycozoline **36e** glycozolicine **36e'**, clausenalene **36f** and glycozolidine **36g**.

To categorize the following instance as a domino reaction, we should have a clear understanding about the reaction. From the Tietze's definition, it is known that the domino reactions do not permit a change in the reaction conditions with the addition of extra reagents, catalysts or others.[1-2] In contrast, the addition is required in other consecutive reactions like tandem or cascade reactions to propagate the next step. Hence, the domino reactions basically differ from these consecutive reactions. However, in modern days, Nicolaou suggested that the domino reaction is indistinguishably used with other consecutive reactions.[6]

In 2020, a concise and highly practical one-pot strategy was developed by Mayer and co-workers to afford diverse heterocycles in onepot.[32] This is a multicomponent reaction which starts with Suzuki coupling and ends with a Buchwald-Hartwig amination (Scheme 19). The modular approach gives heterocycles like 3,10-diaryl 10*H*-phenothiazines **37**, 1,5-diaryl 1*H*-indoles **38** and 3,9-diaryl 9*H*-carbazoles **39** efficiently from readily available substrates. The great advantage of this reaction is that the addition one-time Pd-catalyst is sufficient to achieve both coupling reactions. Actually, in this reaction, the complete transformations were obtained with the extra addition of aryl^{2}bromide, and NaO^{t}Bu or K_2CO_3 which clearly changed the reaction conditions. As a result, this particular reaction should not be an illustration of proper domino reaction. Nevertheless, the reaction was referred to as a domino reaction in accordance with the Nicolaou's definition rather than the Tietze's statement.



Scheme 18. Synthesis of carbazoles via Suzuki coupling/Cadogan cyclization cascade.

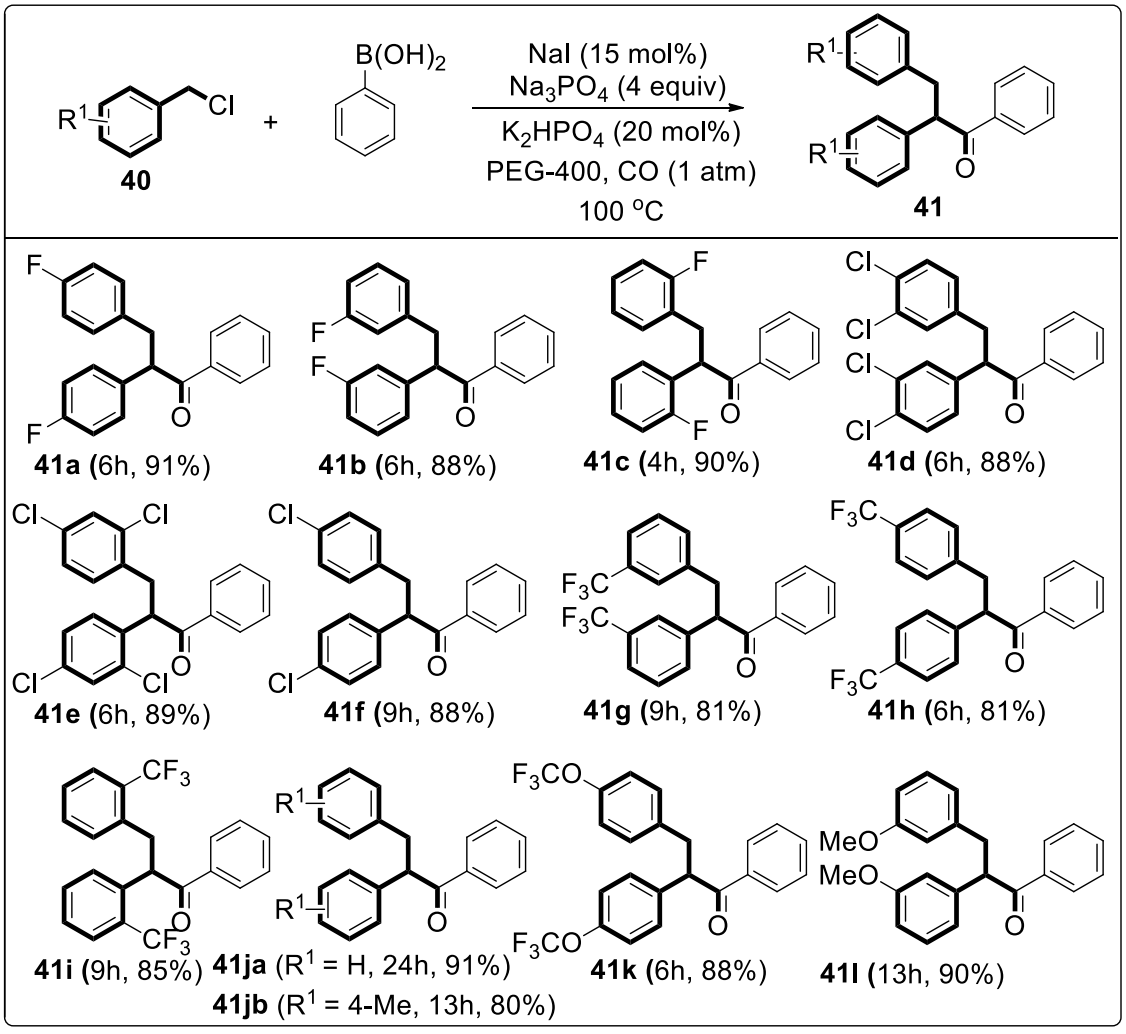


Scheme 19. Domino Suzuki coupling/Buchwald-Hartwig amination reaction.

2.4. Suzuki coupling-carbonylation reaction

Palladium catalysts are employed extensively in the carbonylation reactions by utilizing gaseous CO directly. The use of CO, acting as a C_1 source, makes the reactions cheaper. A variety of organic molecules are synthesized by introducing different types of CO moiety into the substrate molecule.[33-35] In this regard, carbonylative Suzuki cross-coupling is found regularly in literature in which various transition metals are employed particularly to activate aryl halides. However, the combined cross-coupling with benzyl or alkyl halides are rarely reported. This is due to the low reactivity of C(sp^3) halides with Pd(0).

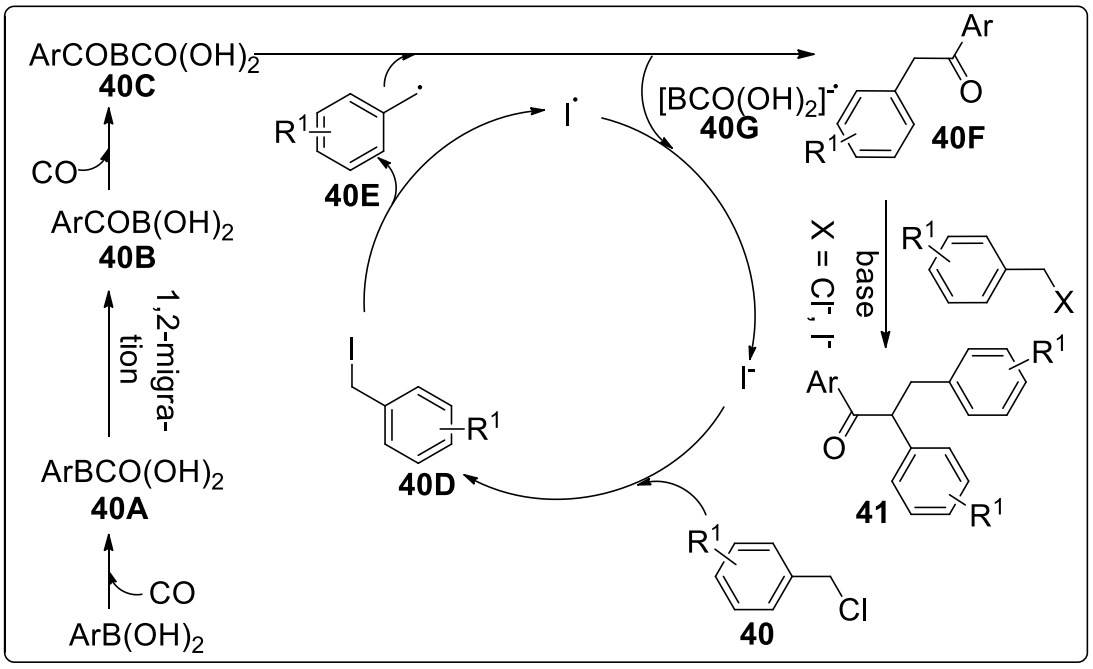
In 2016, a conceptually recognizable method was invented by Jin and others to afford 1,2,3-triarylpropan-1-one **41** efficiently.[36] In this reaction, less reactive benzyl chlorides **40** undergo carbonylation/benzylation in a domino manner with arylboronic acids in presence of NaI catalyst under medium CO gas pressure (Scheme 20). This is notable development over well-established Pd-catalyzed carbonylation in which easily available, inexpensive and highly air stable NaI is serving as catalyst making the reaction milder with avoiding the use of ligands. Hence, they have provided an approach for carbonylative coupling of C(sp^3) halides in absence of a transition metal.



Scheme 20. NaI-mediated carbonylation/benzylation cascade reaction.

Then, based on experimental results and previous reports, a free radical reaction pathway for the domino reaction is depicted in Scheme 21. At first, the reaction between arylboronic acid and CO gives the intermediate

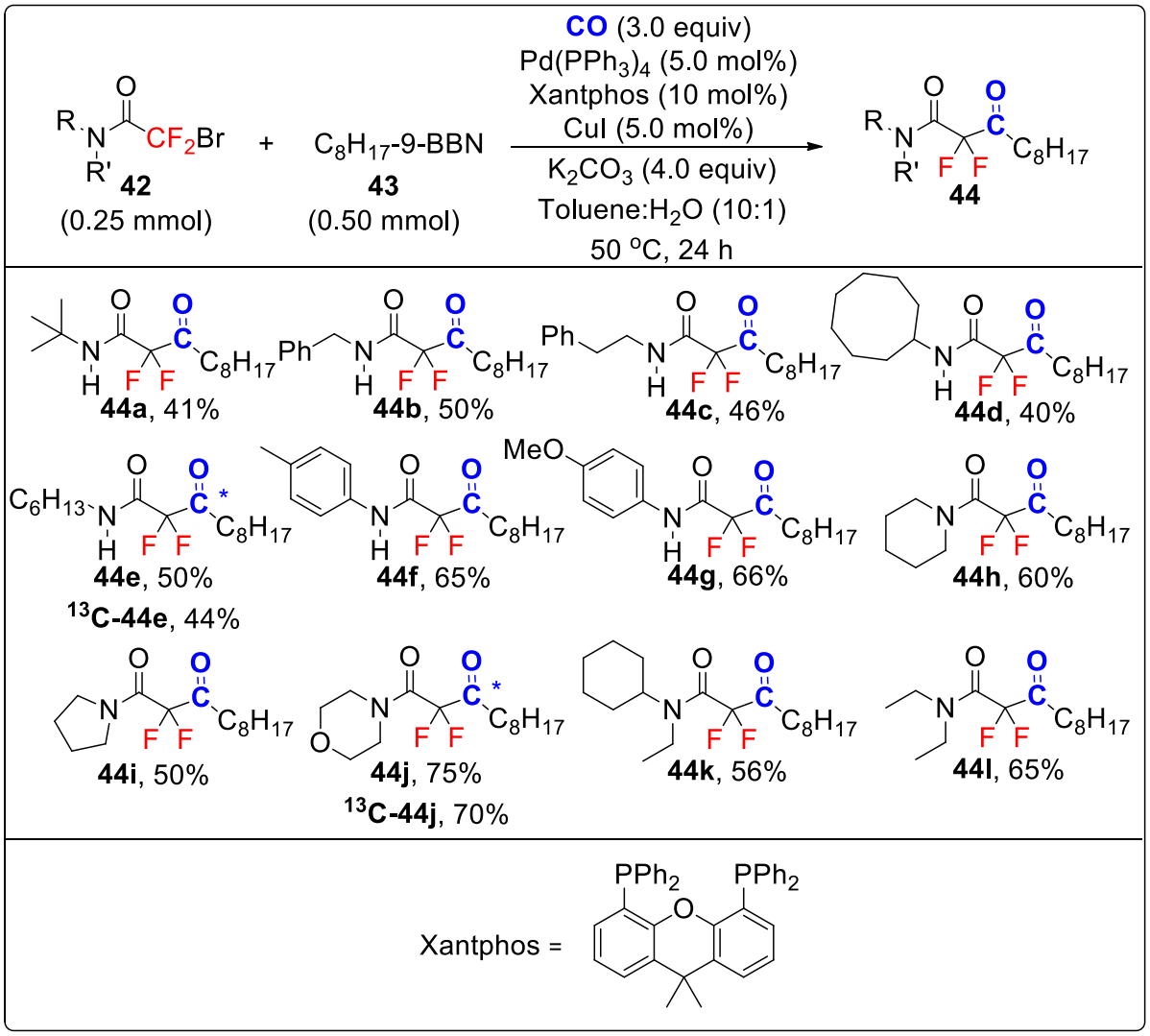
40A, which on subsequent 1,2-migratory insertion of carbonyl generates the intermediate **40B**. Next, **40B** undergoes carbonylation with CO to produce **40C**. The exchange of Cl of benzyl chloride **40** by NaI, benzyl iodide **40D** is obtained. Then, **40D** readily decomposes into highly reactive benzyl radical **40E** along with iodine radical. Next, the interception of **40E by 40C** gives1,2-diarylethanone **40F** with the release of the [$BCO(OH)_2$] radical anion **40G**. Finally, **40F** affords the expected product **41** through benzylation in presence of base and [$BCO(OH)_2$] radical anion **40G** reacts with iodine ion to give iodide ion and completes the cycle.



Scheme 21. Mechanistic pathway for iodine-promoted domino reaction.

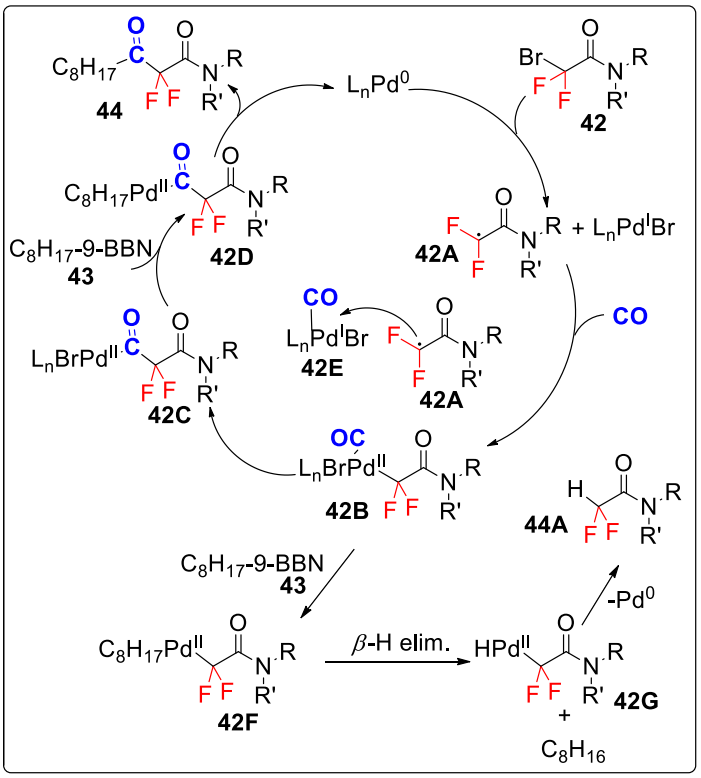
In 2018, a simple protocol for the synthesis of α,α-difluoro-β-alkyl-β-ketoamides **44** was discovered by Yin and co-workers.[37] This is a palladium-promoted carbonylative Suzuki reaction between bromodifluoroacetamides **42** and alkylborons **43** with COgen as the source of CO (Scheme 22). This method delivers diverse esters as well as amides bearing fluoroalkylated chains successfully. In addition, various heterocycles substituted by difluoro moieties have been obtained by modifying the products. Moreover, ^{13}C-labeled ketoamides **44**, diols along with heterocycles can be generated by introducing ^{13}C-COgen.

Based on other reports, they have proposed a tentative mechanistic course for the carbonylative reaction involving the transfer of a single electron (Scheme 23). Initially, Pd(0) abstracts a bromine radical from **42**and generates radical **42A** along with $L_nPd^{I}Br$. The complex **42B** is obtained by combining the radical **42A** with $L_nPd^{I}Br$ under carbon monoxide atmosphere which is then transforms to Pd(II) complex **42C**. The transmetalation between **42C** and alkyl-9-BBN **43** gives the complex **42D** which on subsequent reductive elimination produces the final product **44**. Alternately, the complex **42C** could be generated directly by combining the radical **42A** with a CO ligated Pd(I) species **42E**. Again, **42B** may undergo transmetalation directly rather than CO insertion giving **42F** which is then accompanying β-H elimination to provide Pd(II) species **42G**. Finally, reductive elimination gives the product **44**.

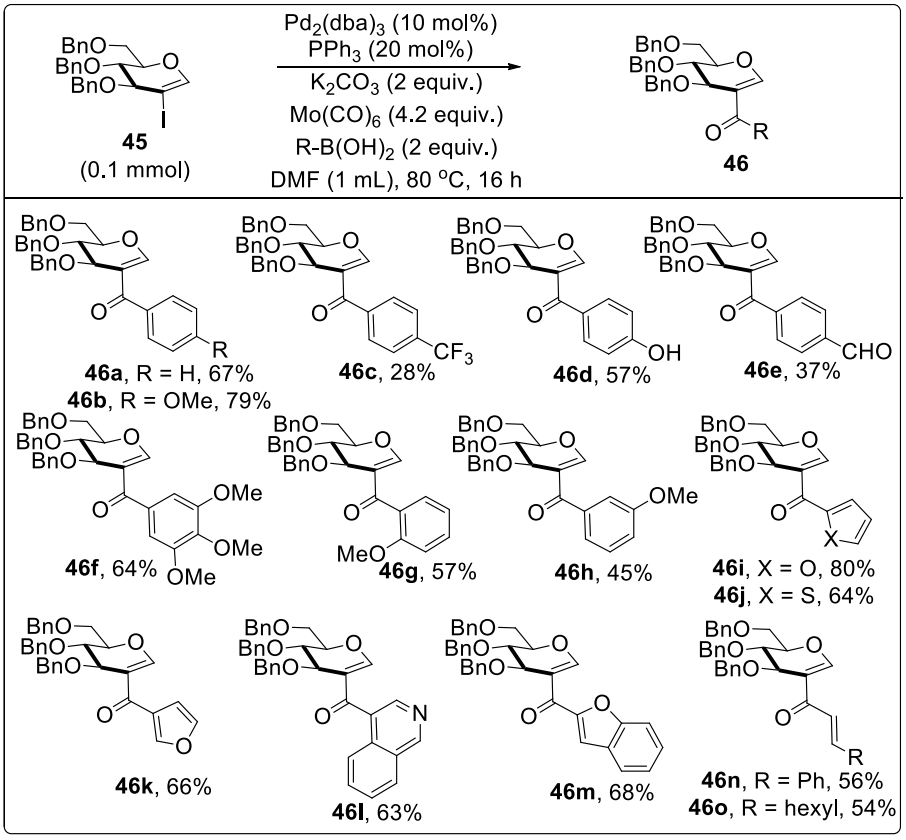


Scheme 22. Pd-promoted carbonylative Suzuki coupling to afford α,α-difluoro-β-alkyl-β-ketoamides.

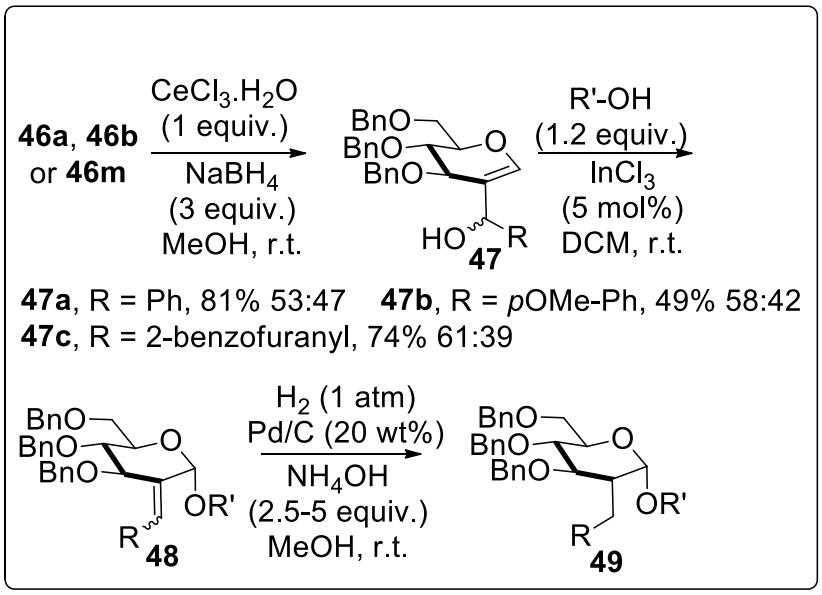
In 2019, this domino carbonylation and Suzuki-Miyaura reaction approach was widely explored by de Robichon and others to produce 2-ketoglycals **46**.[38] It is the presentation of a Pd-catalyzed reaction between 2-iodoglycal **45** and various alkenyl-as well as arylboronic acids as depicted in Scheme 24. When gaseous CO was added by cannulation, product **46**was only formed in trace amounts. On the other hand, the use of $Mo(CO)_6$ enhances the yield of the product **46** upto 67%. Moreover, other observations helped them to conclude that $Mo(CO)_6$ plays two roles: as a catalyst and as the source of CO. In addition, the scope of this synthetic route was successfully exploited by transforming the newly obtained carbonyl linked product **46** into compounds **49** present as the backbones in several biologically active molecules via reduction with $NaBH_4$ (**47**), indium-promoted substitution by allylic group (**48**) and hydrogenation (Scheme 25).



Scheme 23. Plausible mechanism for the synthesis of α,α-difluoro-β-alkyl-β-ketoamides.



Scheme 24. Pd-and $Mo(CO)_6$-catalyzed preparation of 2-ketoglycals.



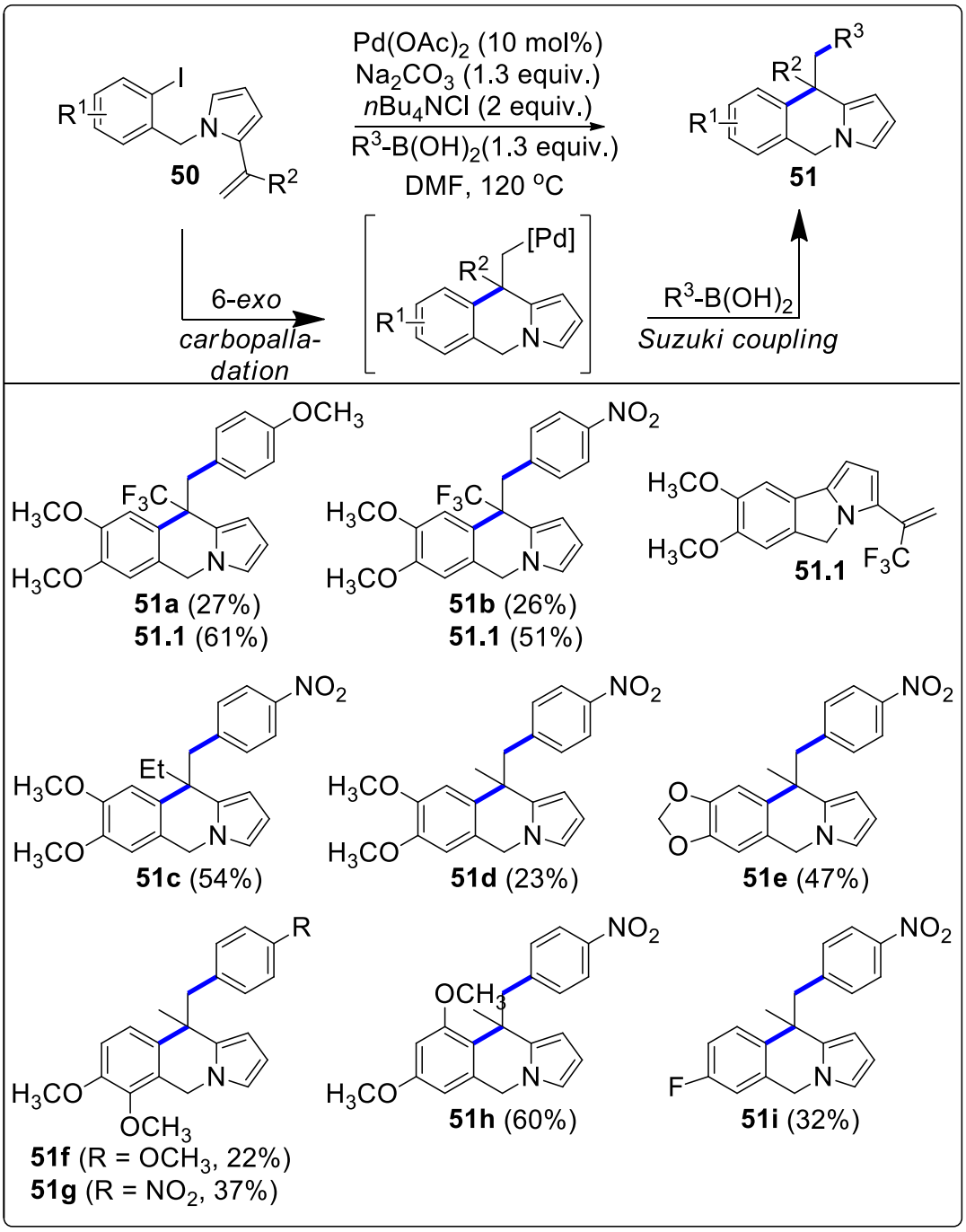
Scheme 25. Transformation of 2-ketoglycals into **49** present as scaffolds in bioactive molecules.

2.5. Carbopalladation/Suzuki cross-coupling

Transition metal-catalyzed domino carbopalladation/Suzuki reactions are powerful tools to make C-C bonds that give diverse carbocycles as well as heterocycles with quaternary stereocenters via tandem cyclizations.[39-40] In this cascade reaction, the Suzuki coupled product is obtained by the reaction between the initially produced *σ*-alkylpalladium (II) complex and boronic acids/esters. The great achievement of this tandem reaction is that the carbopalladation step can be conducted on alkynes, benzofurans and cyclopenta[*b*]indoles. This carbopalladation stepis regularly found in reports particularly with alkenes.[41]

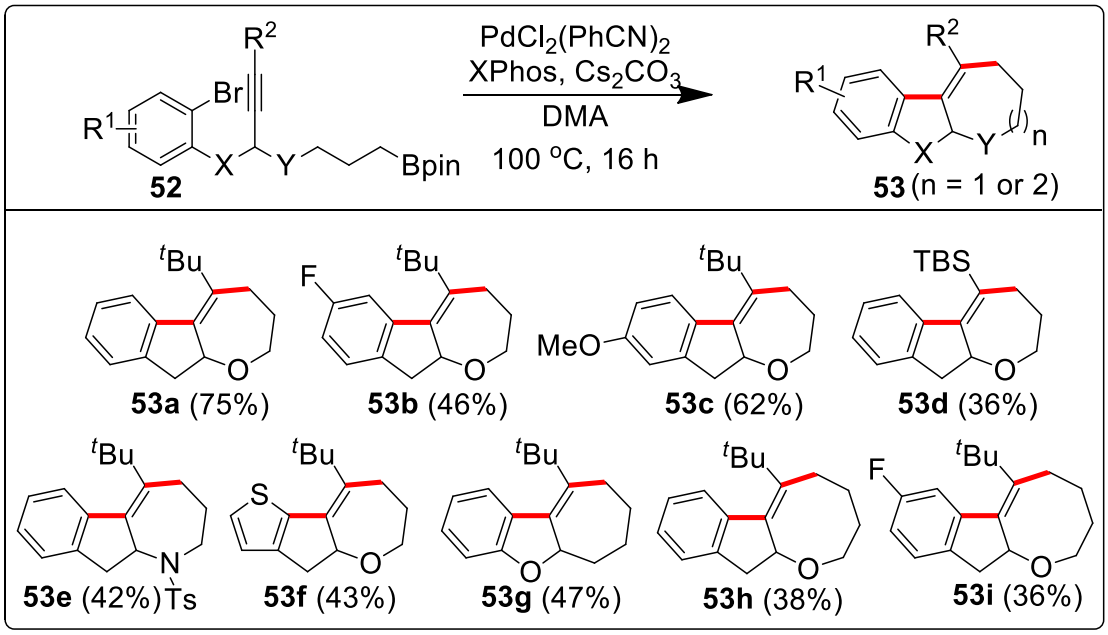
The Barbolla group[42] discovered a convergent way to pyrrolo[1,2-*b*]isoquinolines **51** via a 6-*exo* carbopalladation step of *N*-(2-iodobenzyl)-2-(alkenyl)-1*H*-pyrroles **50** and subsequent Suzuki coupling (Scheme 26). In this cascade, arylboronic acid helps to trap σ-alkylpalladium species to give C-10 disubstituted pyrroloisoquinolines **51**. It was observed that the reaction in absence of phosphane source favors the intramolecular 6-*exo* carbopalladation over the intermolecular Suzuki reaction. However, the 7-*endo* reaction was found to be in competition with 6-*exo* process and was suppressed by employing phosphane ligands like tri(furan-2-yl)phosphane. Finally, *n*-Bu_4NCl was introduced to play a crucial role in 6-*exo* carbo-palladation, suppressing the possibility of a direct Suzuki reaction. On investigation, it was noticed that the aryl iodide underwent arylation directly in an intramolecular manner with the C-5 position of pyrrole to deliver compound **51.1** as the major product in the presence of the substituent like CF_3 having electron-withdrawing effect in alkene.

In 2020, the Reding group[43] have represented a novel cascade reaction comprising with intramolecular *anti*-carbopalladation along with subsequent terminal Suzuki reaction to afford various seven- along with eight-membered cycles **53** (Scheme 27). In this reaction, two new bonds namely C(sp^2)-C(sp^2) and C(sp^2)-C(sp^3) are obtained that gives tetrasubstituted olefinic bond. The great advantage of using substituted alkyne motif of compounds **52** helps to form the double bond with *anti*-geometry avoiding the elimination of *β*-hydride.

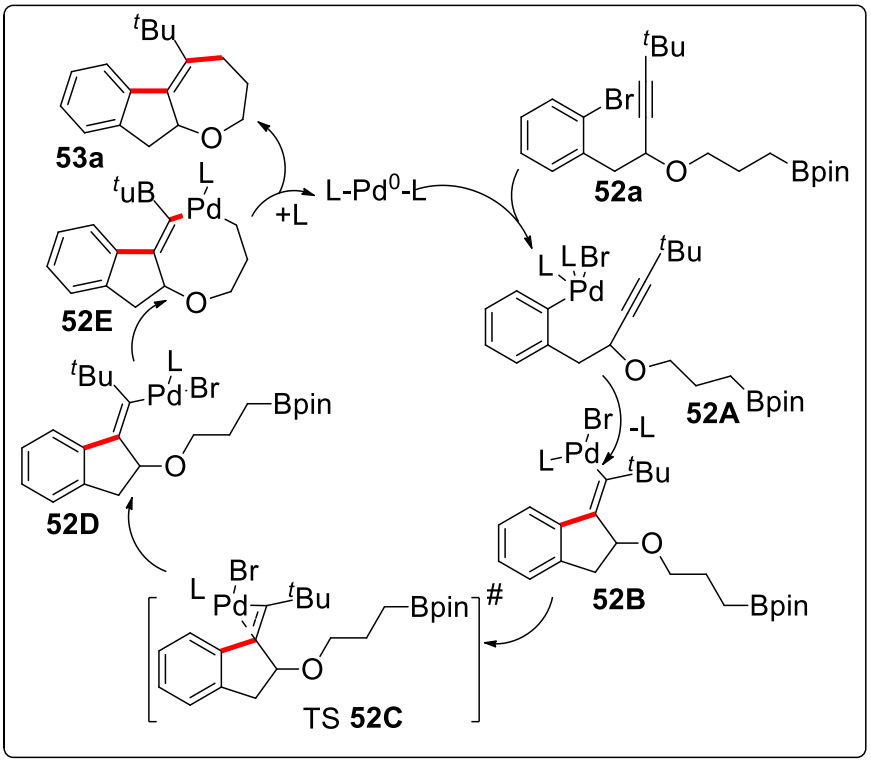


Scheme 26. Preparation of pyrroloisoquinolines **51**.

Then, they have proposed a mechanism for the construction the oligocycles as depicted in Scheme 28. Initially, oxidative addition occurs at theC-Br bond of **52a** by Pd(0) to generate **52A**, which on subsequent *syn*-carbopalladation with alkyne delivers intermediate **52B**. Next, intermediate **52D** is formed by *cis*/*trans*-isomerization via η^2-vinyl TS **52C**. Palladacycle **52E** is produced by Suzuki coupling which upon reductive elimination gives the product **53a** with the regeneration of Pd(0).



Scheme 27. Domino *anti*-carbopalladation/terminal Suzuki coupling.

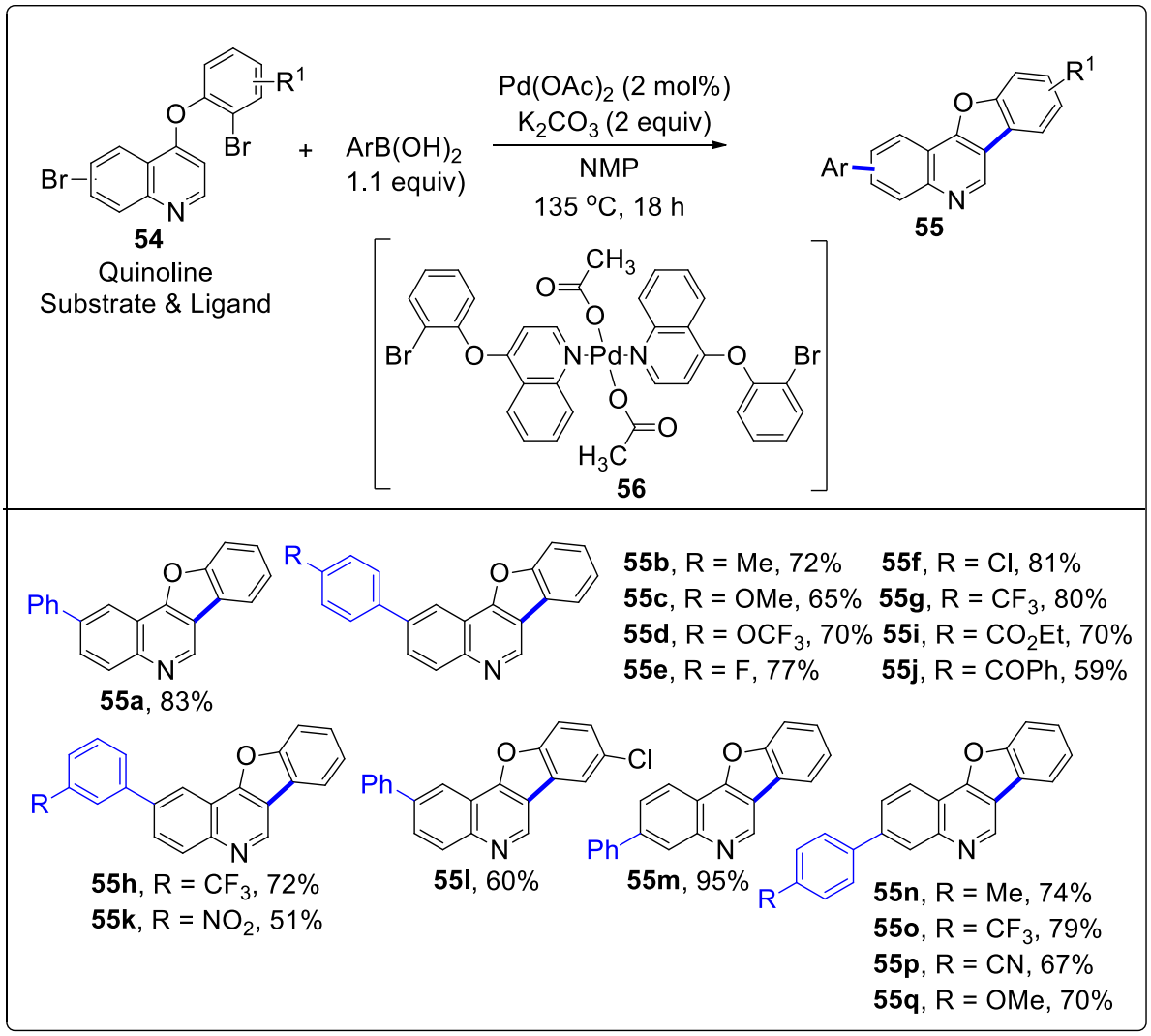


Scheme 28. Tentative mechanism for domino *anti*-carbopalladation and Suzuki coupling.

2.6. Suzuki coupling/C-H functionalization

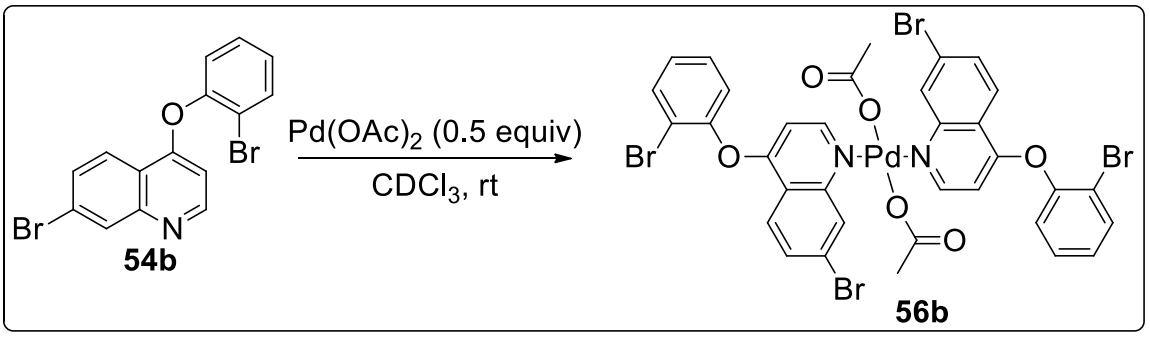
In recent times, C-H functionalization/bond activation catalyzed by transition metals has emerged as a potent tool to obtain molecular complexity as well as structural diversity in newly synthesized molecules. This strategy, together with cross-coupling reactions like Suzuki coupling, has been advantageously employed to form multiple C-C bonds in various carbo- and heterocycles. Hence, the combined method turns out to be an efficient, environmentally benign and cheap process giving variety of C-H activations.

In this context, the method established by Shanahan group[44] for the Suzuki coupling /C-H functionalization on quinoline motif can be represented. Herein, when the dibromoquinoline **54** reacted with various phenylboronic acids, a Suzuki coupling/direct arylation cascade was obtained leading to the formation of benzofuroquinolines **55** in moderate to high yield (Scheme 29). An advantage in this approach is that the chlorine substituent remained unaffected in the products **55f** and **55l**, which can be employed in the further synthetic applications. Moreover, benzofuropyridine present as a backbone in plethora biologically active molecules was synthesized in 69% yield. Initially, precatalyst **56** is generated, which drives the reaction effectively avoiding the use of any additional ligand as well as inert atmosphere required for a Suzuki coupling in the presence of heterocycles as a coupling partner. The formation of the precatalyst **56** was proven by isolation and characterization doing the reaction in $CDCl_3$and in the absence of arylboronic acid (Scheme 30).

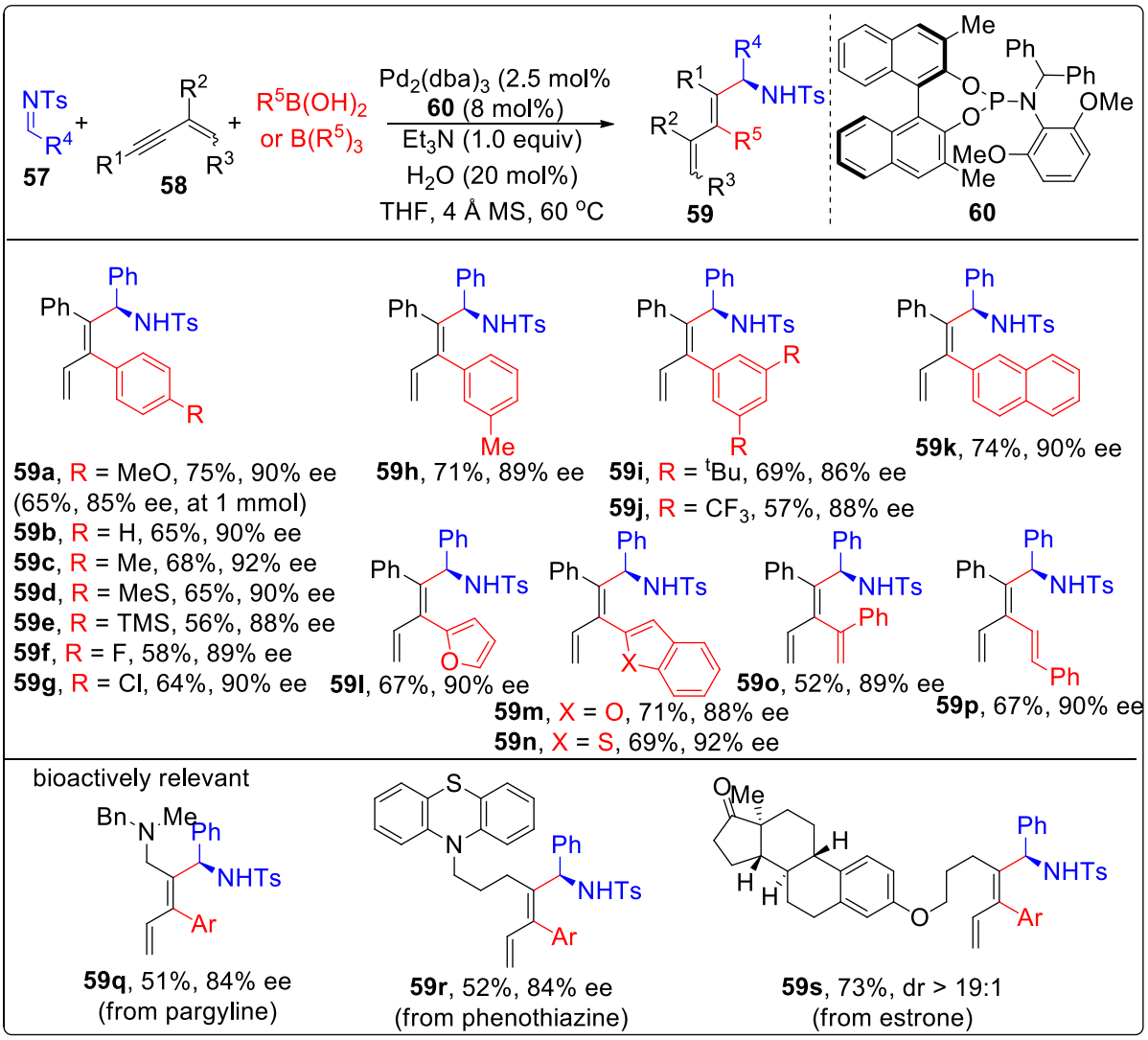


Scheme 29. Domino Suzuki coupling reaction/direct arylation.

In 2021, He and co-workers[45] have reported a Pd(0) complex-mediated stereo- and regioselective reaction between N-sulfonylimines **57** and 3-enynes **58**. This is an unprecedented reaction in which the generated Pd(II) complex undergoes a tandem Suzuki coupling with organoboronic species (Scheme 31). The reaction proceeds through the chemoselective formation of η^2-coordinated complex with the alkene motif of the 1,3-enynes **58**.

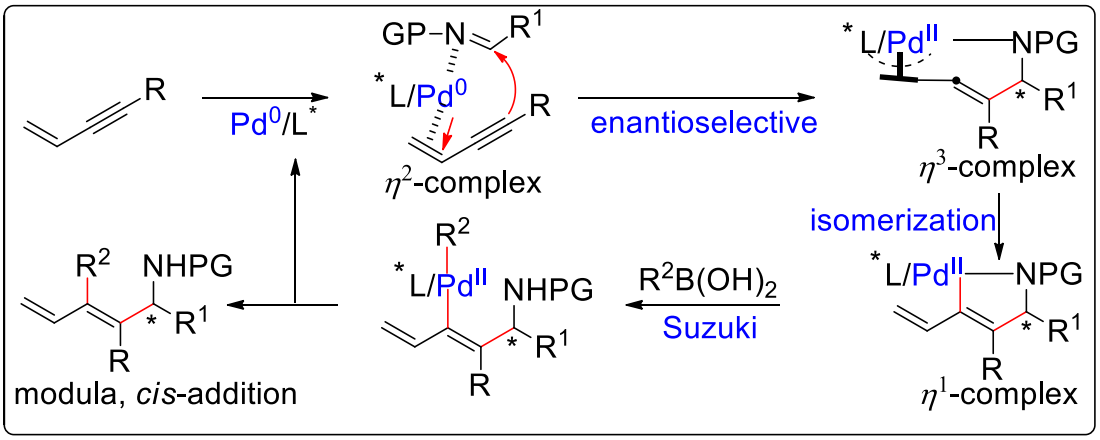


Scheme 30. Formation of precatalyst **56**.

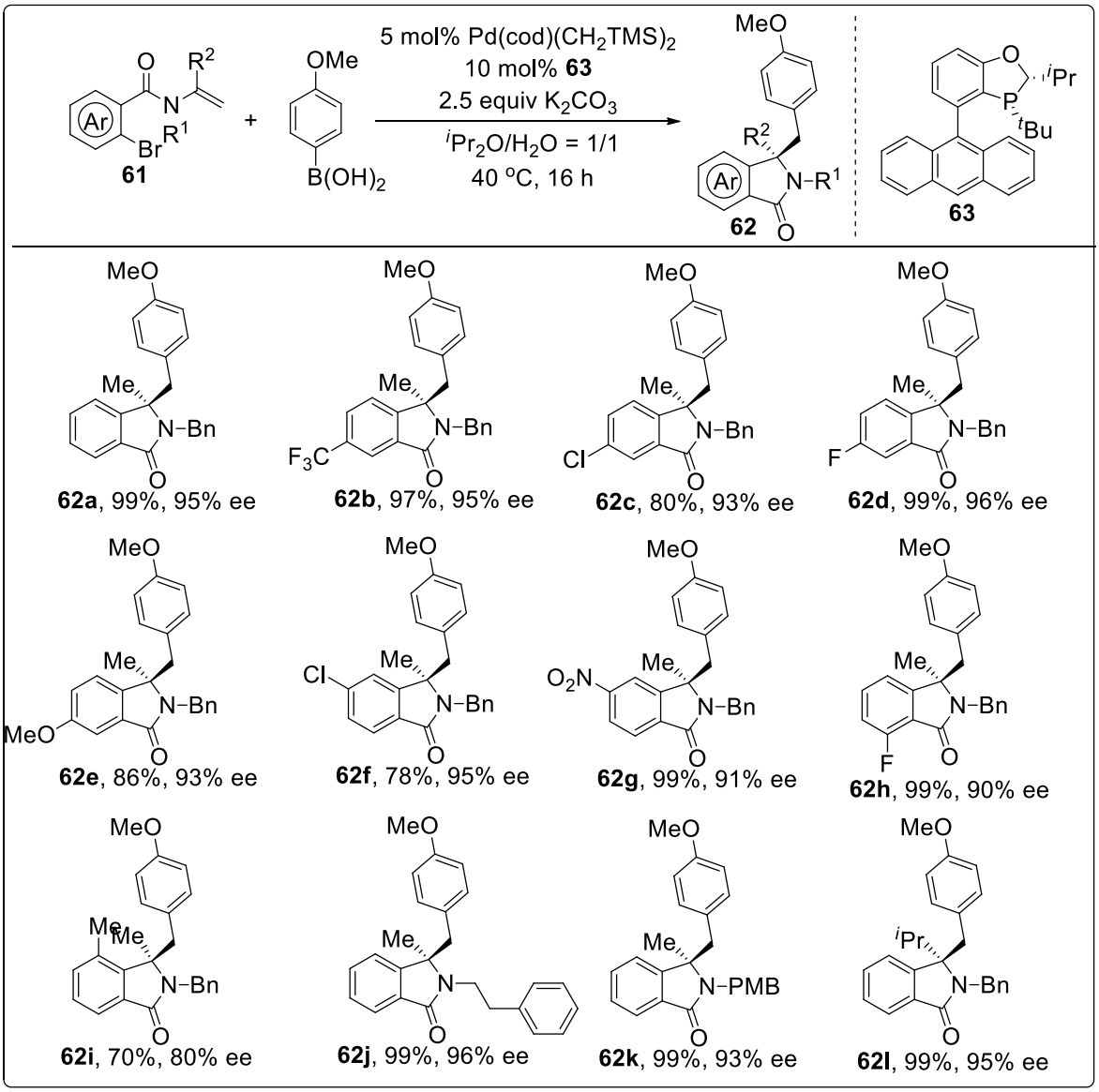


Scheme 31. Asymmetric cis-disubstitution of 1,3-enynes.

Then, η^1-aza-palladacyclopetene is produced as the intermediate which upon Suzuki coupling with organoboronic species delivers cis-1,2-disubstitution **59** of the alkyne moiety (Scheme 32). Moreover, phosphoramidite ligand **60** derived from BINOL was employed in the enantioselective synthesis of structurally diverse molecules by assembling three components.

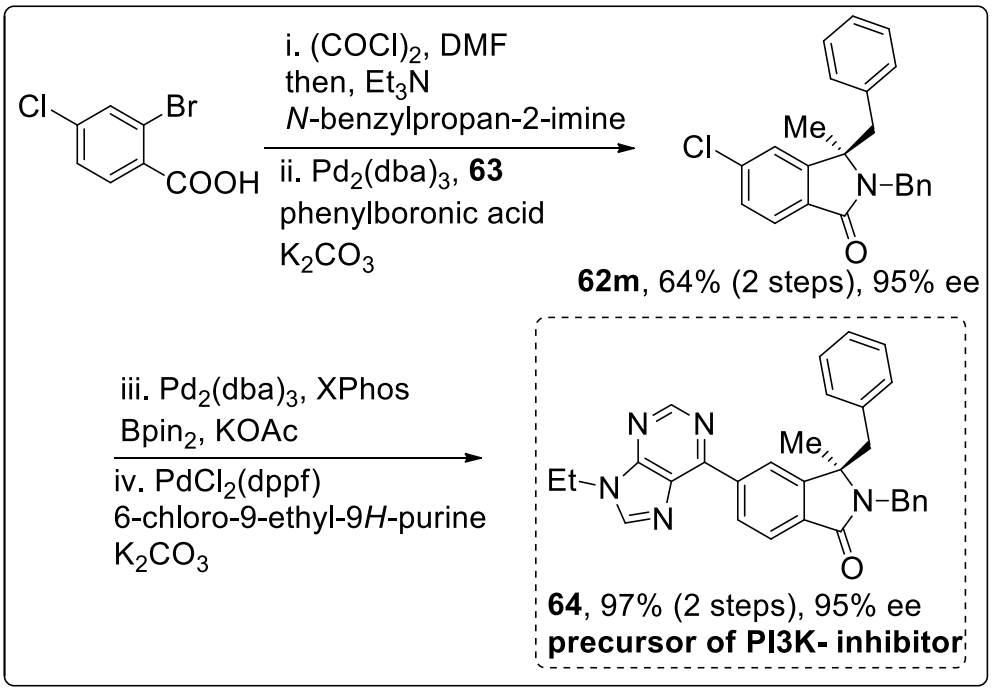


Scheme 32. Tentative pathway for the c*is*-addition of 1,3-enynes.



Scheme 33. Pd-catalyzed dicarbofunctionalization of enamides.

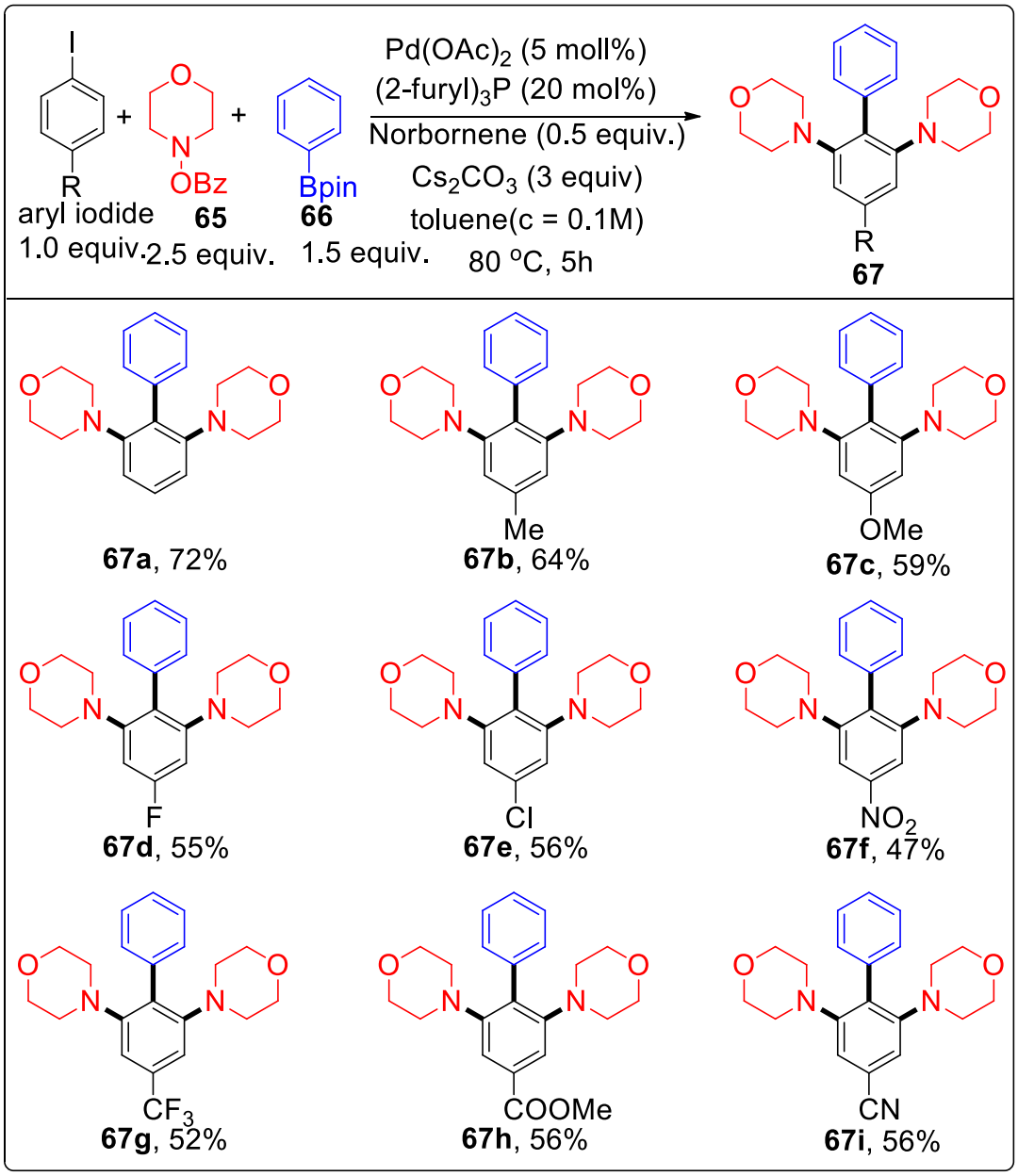
Also in 2021, the Huang group[46] have reported an asymmetric preparation of 3,3-difunctionalized isoindolinones **62** from enamides **61** via a sequence of Heck-Suzuki reaction (Scheme 33). It is a dicarbofunctionalization of enamides **61** with organoboronic acids in the presence of palladium catalyst and **63**. The great success of this strategy is that the reaction shows high enantioselectivity in the production of the final compounds **62** generating a quaternary center. Moreover, the synthetic usefulness of this approach was displayed by producing **64**, the precursor of a PI3K-inhibitor (Scheme 34).



Scheme 34. Preparation of a precursor of a PI3K- inhibitor.

2.7. Norbornene mediated Catellani reaction/Suzuki coupling

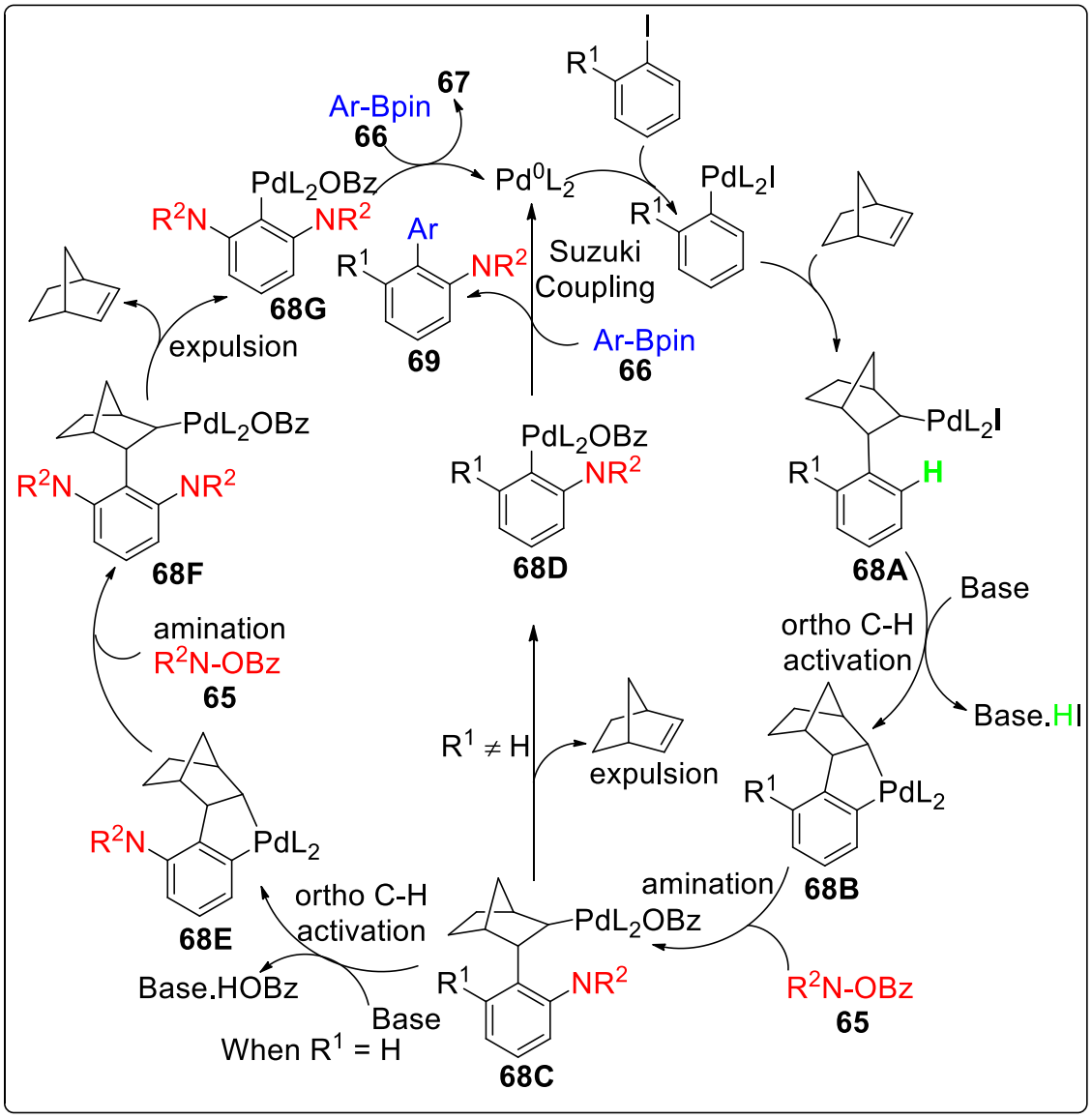
In Catellani reaction, a remote C-H bond of an aromatic motif can be activated and functionalized directly employing the combination of palladium and norbornene system as an efficient catalyst.[47-48] As a result, two groups are introduced from various halides at a time, giving polysubstituted molecules as well as fused rings. The progress of this area was exploited by the Ye group[49] in 2014 in which they discovered an efficient method to produce various 2,6-dimorpholino-1,1'-biphenyl **67**. Herein, a mixture of morpholino benzoate **65**, aryl halide and pinacol boronate **66** are reacted in the presence of palladium/norbornene (Scheme 35). This protocol gives an opportunity for the novel preparation of biarylamines **67** with partly high yields and excellent tolerance of diverse functional groups.



Scheme 35. Preparation of 2,6-dimorpholino-1,1'-biphenyl **67.**

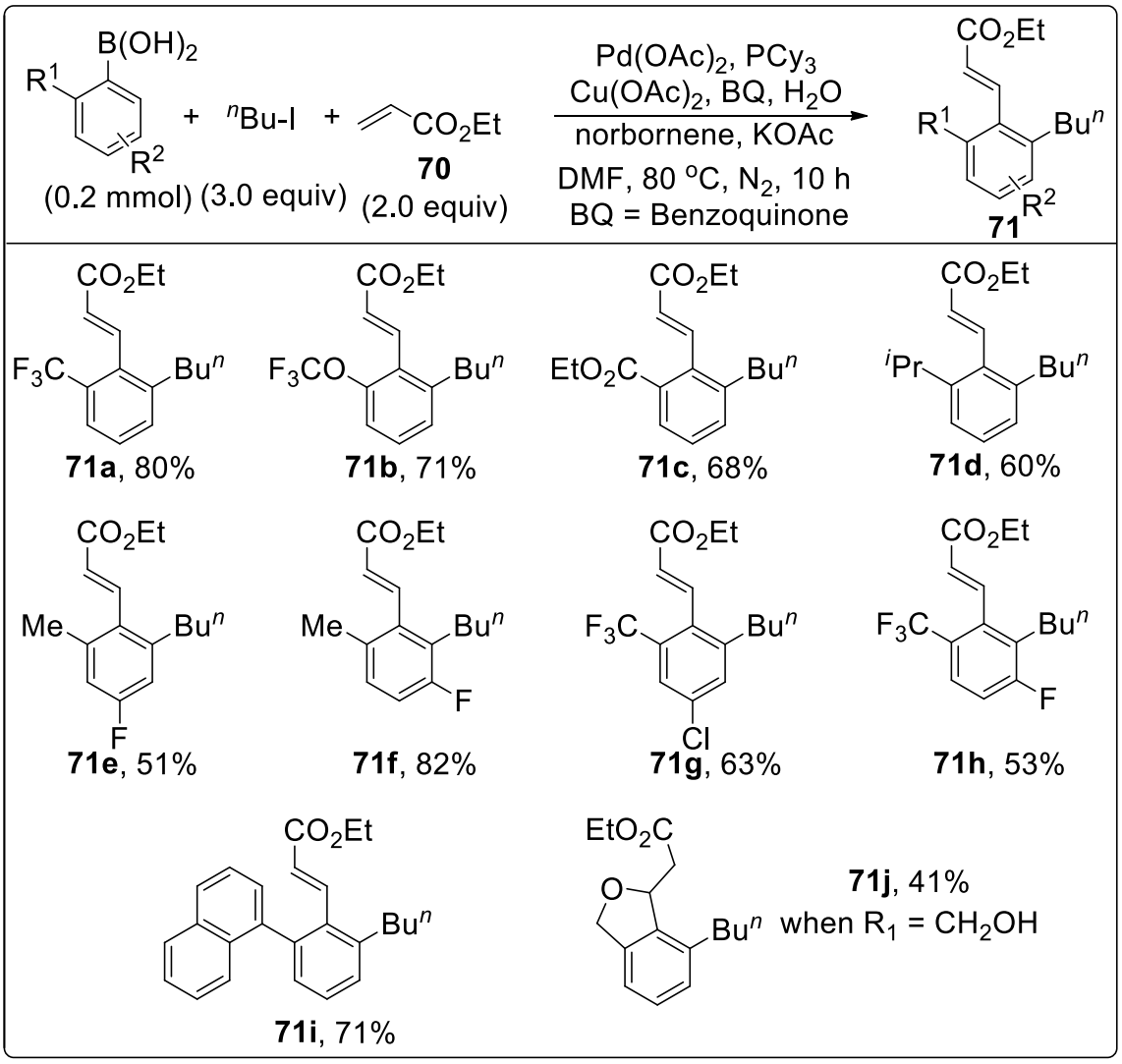
Then, they proposed the mechanistic course for this cascade reaction based on their previous report as well as the established Catellani reaction (Scheme 36). The reaction starts with the oxidative addition of the aryl iodide with Pd(0). Next, the species **68A** is produced from norbornene by the *syn*-carbopalladation. The activation of *ortho* C-H bond and followed by HI elimination generates the palladacycle **68B**. The reaction proceeds through another oxidative addition between R_2N-OBz **65** and Pd-center of species **68B** leading to the formation of a Pd(IV) complex, which on reductive elimination gives the arene **68C**. The alternate course, in which direct reaction of R_2N-OBz**65** with palladacycle **68B** as well asN-O bond breaking to deliver **68C** might also be considered. Next, the decarbopalladation and the removal of norbornene produces the intermediate **68D** for *ortho*-substituted systems (**$R_1 \neq H$**) which on Suzuki-type coupling with **66** gives the final compound **69** and the completion of the catalytic cycle is obtained by the reproduction of Pd(0). On the other hand, when the complex **68C** does not have ortho-substitution ($R_1 = H$), the other *ortho*-C-H activation givesa new palladacycle **68E** along

with the complex **68F**. Finally, the diaminated compound **67** is prepared by the elimination of norbornene to give the intermediate **68G** and subsequent Suzuki-type reaction with **66**.



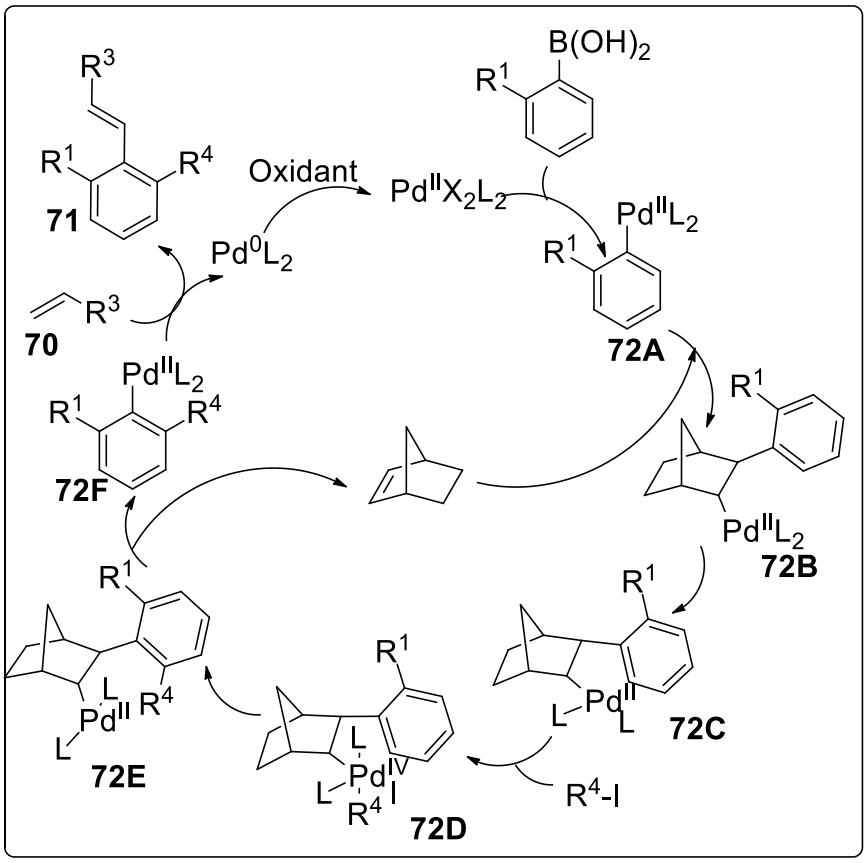
Scheme 36. Proposed mechanistic pathway.

In 2018, an efficient approach was discovered by Shi and co-workers[50] for the synthesis of multifunctionalized arenes **71** by the cascade reaction of alkyl iodides with olefins **70** (Scheme 37). This is the first report in which mono or dialkylation can be obtained at the *ortho* locations of an arylboronic acid by Pd(II)-catalyst. The advantage of the use of Pd(II) as catalyst instead of Pd(0) is that it avoids the possibility of the formation of unwanted products during the coupling reaction with new electrophiles. As a result, this protocol offers a new avenue to develop various Catellani-type syntheses.



Scheme 37. Pd(II)-catalyzed Catellani reaction.

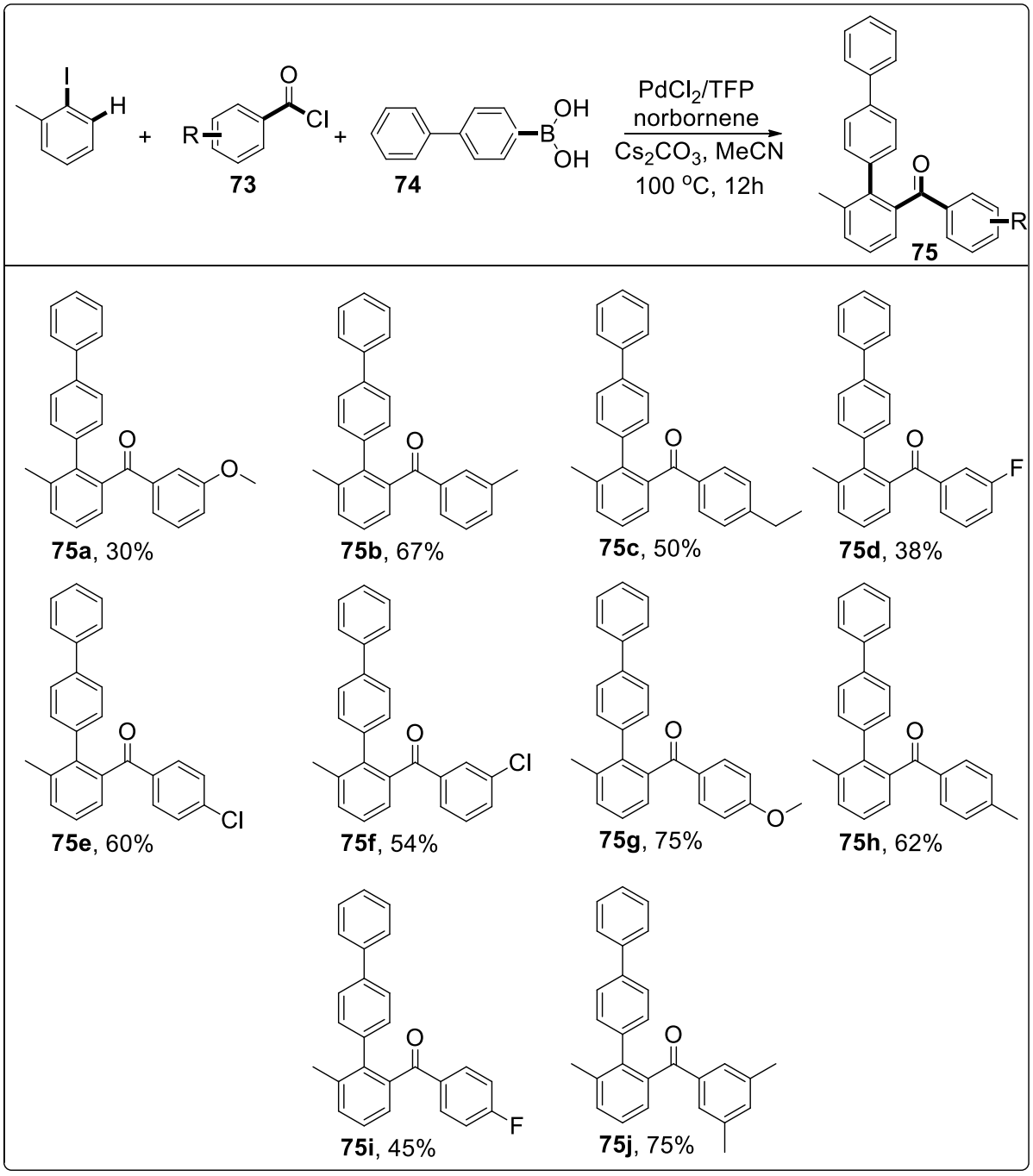
The role of the norbornene can easily be understood from the mechanism proposed for the newly established Catellani reaction (Scheme 38). The cycle started with the making of aryl-Pd(II) complex **72A** by the involvement of Pd(II) and arylboronic acids. Then, a palladacycle, species **72C**, is formed by norbornene's migratory insertion generating **72B** as well as activation of the *ortho*-C-H bond. An oxidative addition occurs between alkyl iodides and **72C** to give palladacycle **72D**. Subsequent reductive elimination giving the species **72E** which on releasing norbornene yields Pd(II) species **72F**. Finally, **72F** is trapped by alkenes**70** to afford the desired products **71** with the liberation of Pd(0) species, which on oxidation regenerates Pd(II) catalyst.



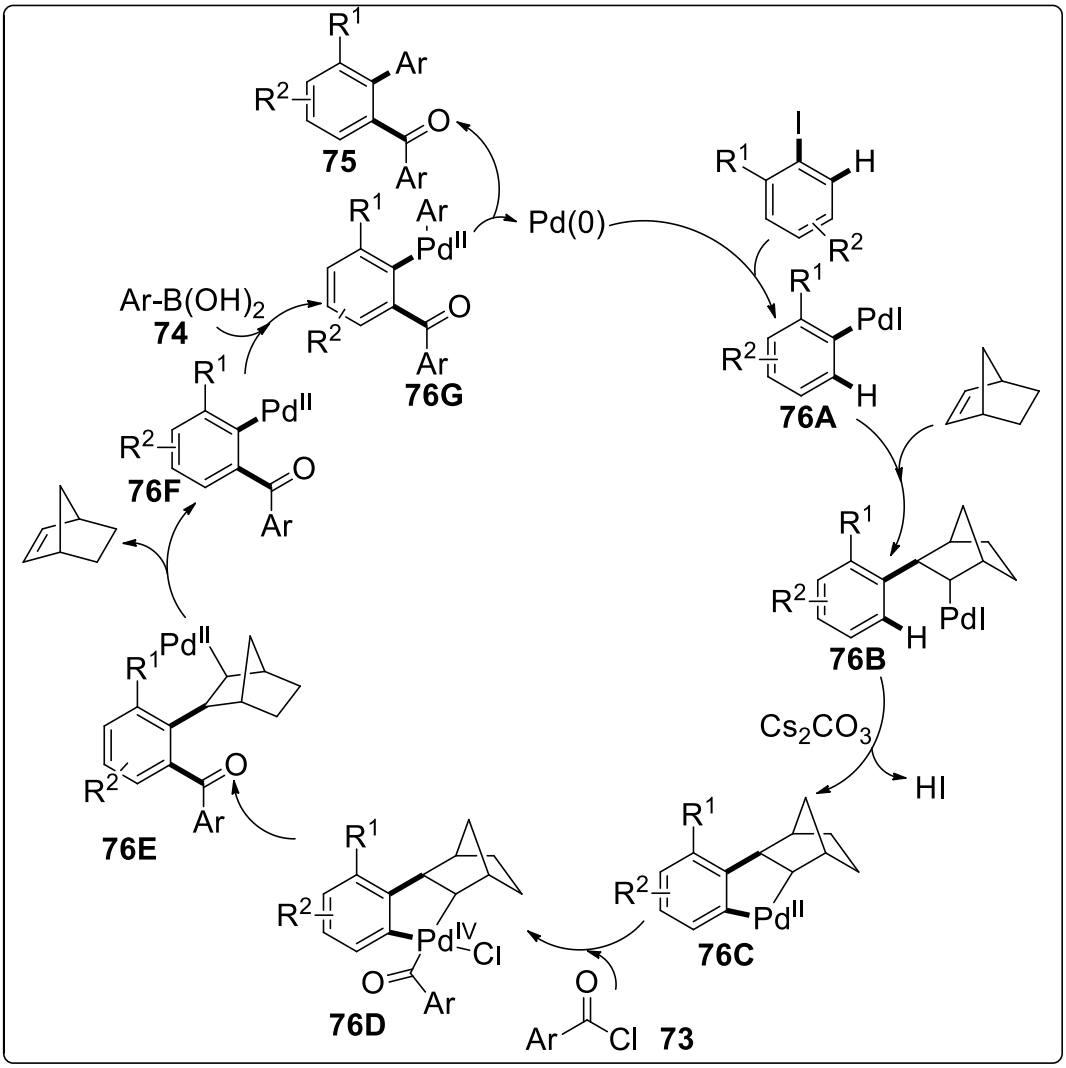
Scheme 38. Tentative mechanism.

Based on the norbornene-promoted Catellani Reaction, an efficient Pd-catalyzed protocol was reported by the Wu group,[51] in which a regiospecific domino reaction of *ortho*-acylation and *ipso*-Suzuki reaction occurs with aryl iodides (Scheme 39). Here, acyl chlorides **73** and arylboronic acids **74** are employed for the acylation and quenching the reactions respectively to deliver the final product **75**. Utilizing this approach, few uncommon acylated products **75** were obtained, which cannot be easily prepared by the regular acylation strategy.

Based on the previous discussions, the plausible reaction pathway for the catalytic cycle was provided as depicted in Scheme 40. Initially, aryl iodide participates in oxidative addition giving aryl-Pd(II) species **76A**, which on subsequent norbornene incorporation generates **76B**. Then, the activation of *ortho*-C-H bond yields an intermediate **76C**. The palladium(IV) complex **76D** is produced by the oxidative addition between acyl chloride **73** and **76C**, which on subsequent reductive elimination delivers the intermediate **76E**. Next, the immediate elimination of the norbornene from **76E** affords a new Pd(II) complex **76F**. The classical Suzuki coupling of species **76F** with arylboronic acids **74** generates the intermediate **76G**, which on reductive elimination produces the final acylated compounds **75** along with the regeneration of the Pd(0) catalyst.

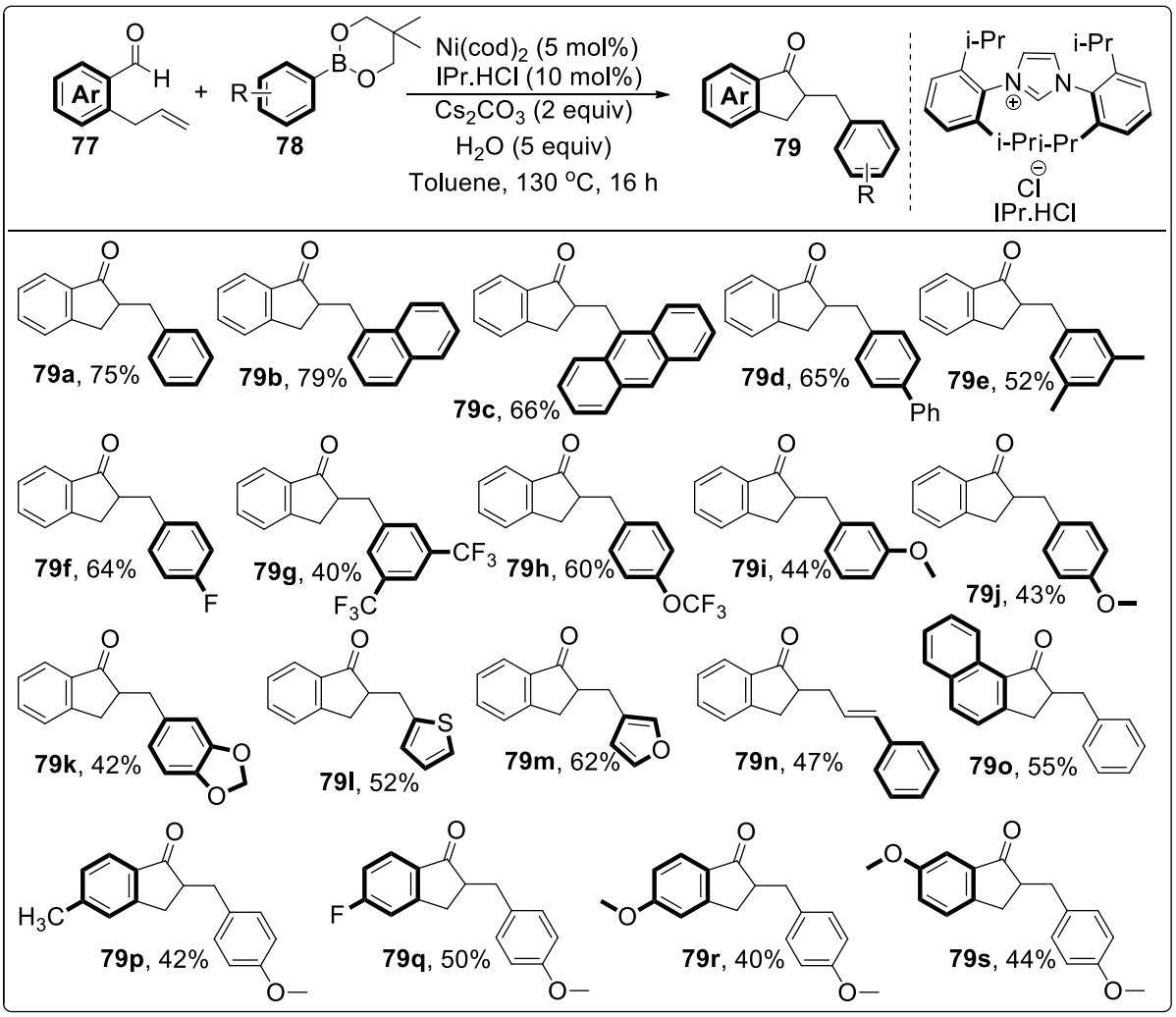


Scheme 39. Palladium and norbornene-catalyzed cascade of acylation/Suzuki reaction.



Scheme 40. Plausible mechanism.

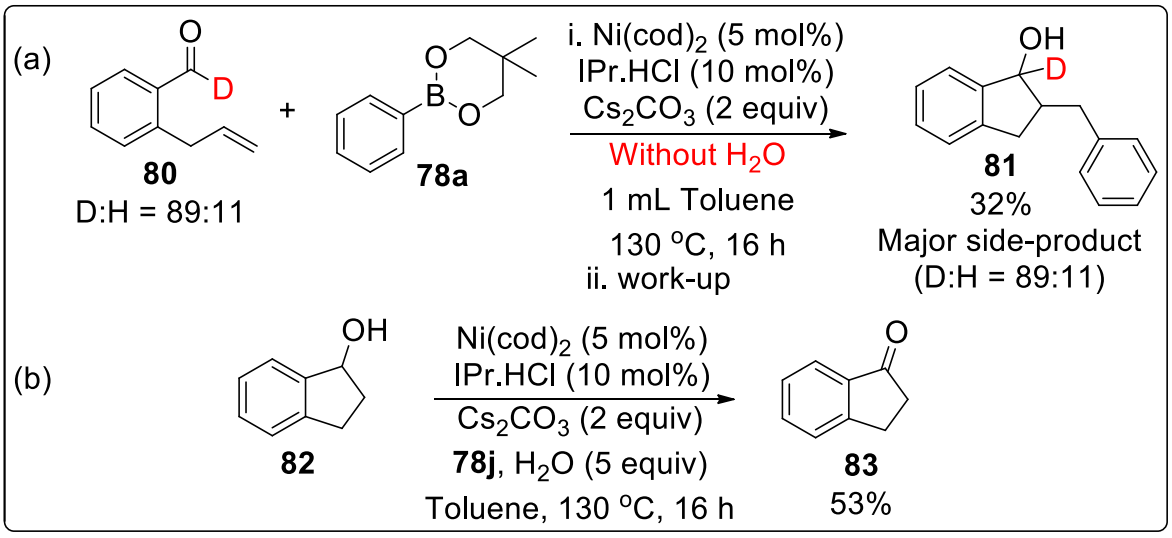
Now the cascade of hydroacylation/Suzuki reaction by Lee group[52] can be considered. Hydroacylation is referred to be a reaction leading to the formation of two new C-C bonds by the activation of formyl C-H bonds with olefinic C-C bonds.[53-54] It provides the efficient synthesis of variety of ketone compounds as well as hetero- and macrocycles in a simple manner. Alkenes or alkynes are found to be more effective in the hydroacylation by the presence of transition metals like Rh, Ru, Co and Ni. In this regard, the protocol developed by the Lee group[52] can be represented as an illustration in which Ni-catalyst has been employed in the *exo*-selection for intramolecular cascade of hydroacylation/ Suzuki reaction. Herein, the reaction of diverse *o*-allyl benzaldehydes **77** with glycol esters of arylboronic acid **78** gives indanones **79** effectively (Scheme 41).



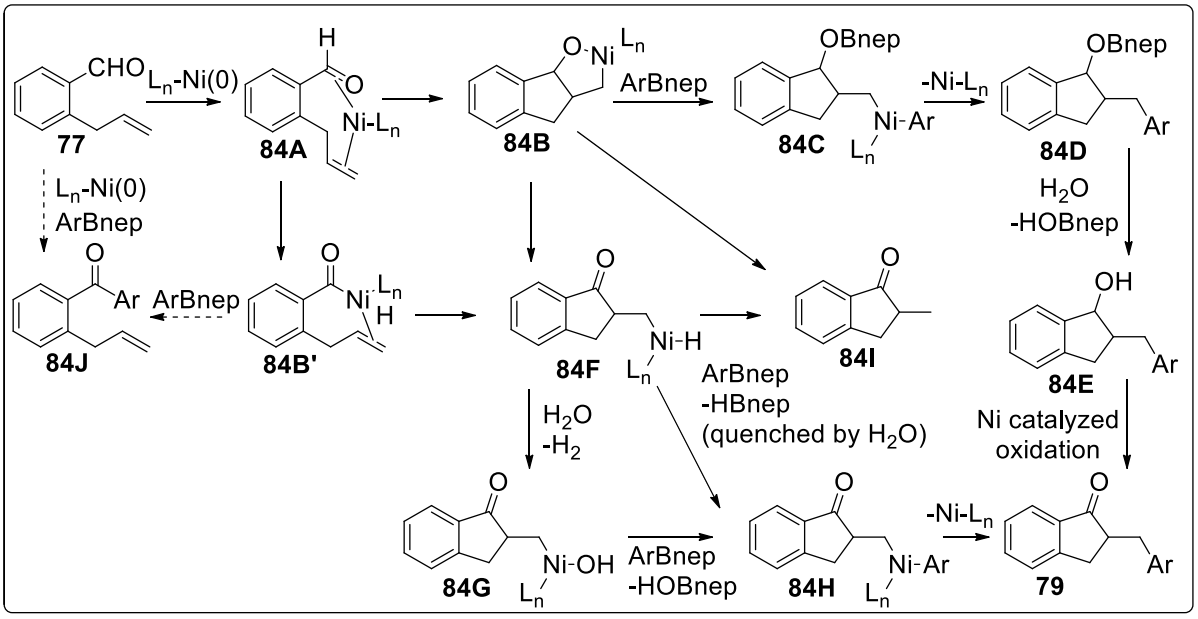
Scheme 41. Hydroacylation/Suzuki domino reaction.

Next, two different investigations were done to determine the plausible mechanism for the above domino reaction (Scheme 42). The reaction of deuterated compound **80** with **78a** gives the deuterated product **81** without water (Scheme 42a). On other hand, indenol **82** gives the oxidized product **83** under optimal conditions (Scheme 42b). These two observations suggested that the domino reaction completes in a number of possible pathways.

The above observations and other reports helped them to depict a plausible mechanism for this cascade reaction as shown in Scheme 43. Initially, the coordination between IPr and Ni(0) gives IPr-Ni(0) species **84A**, which on oxidative addition generates oxanickelacycle complex **84B**. Transmetalation between arylboronic acid neopentyl glycol esters, ArBnep **78** and **84B** yields **84C**, which undergoes reductive elimination to afford 1-indanol **84D**. Subsequent hydrolysis as well as oxidation produces the final compound **79** via indenol **84E**. Again, **84B** can undergo elimination ofβ-hydride alternately to form intermediate **84F**, which on transmetalation or hydrolysis and followed by transmetalation delivers **84H**. Finally, reductive elimination occurs to give **79**. Moreover, acyl nickel(II) complex **84B'** is also likely to be formed which can participate inhydroacylation to yield intermediate **84F**. Then, the final product **79** is obtained by the course as already mentioned above.



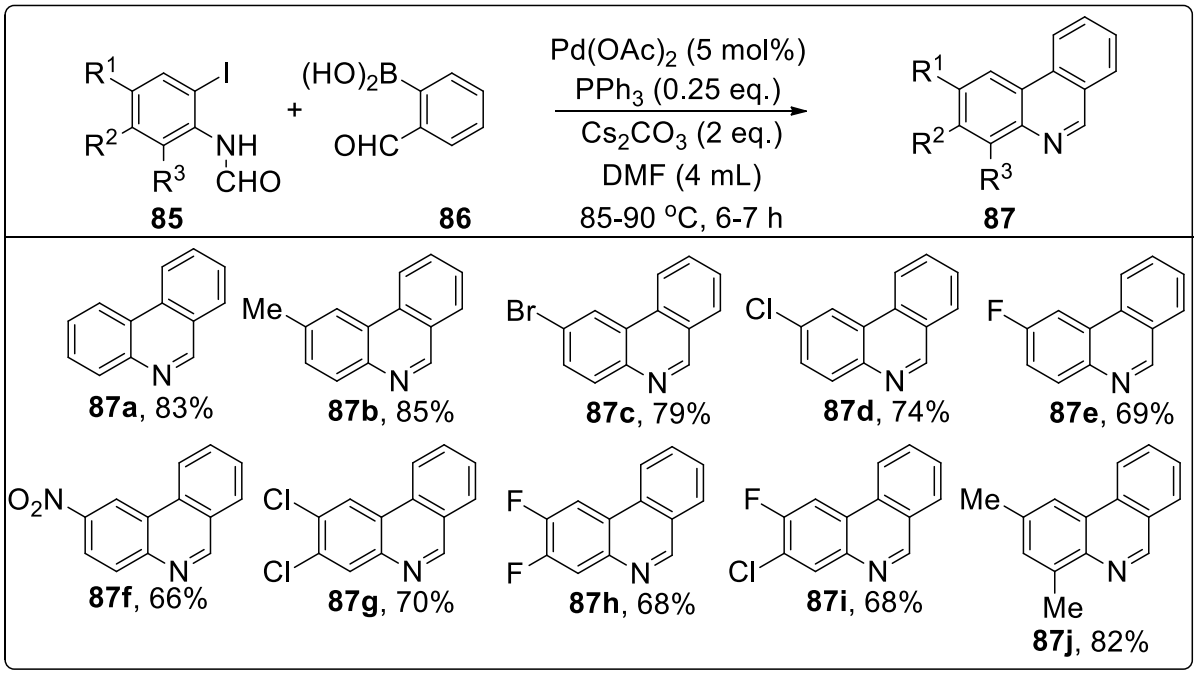
Scheme 42. Investigation of course of the reaction.



Scheme 43. Tentative mechanism for the cascade of hydroacylation/Suzuki reaction.

2.8. Suzuki coupling/cyclocondensation reaction

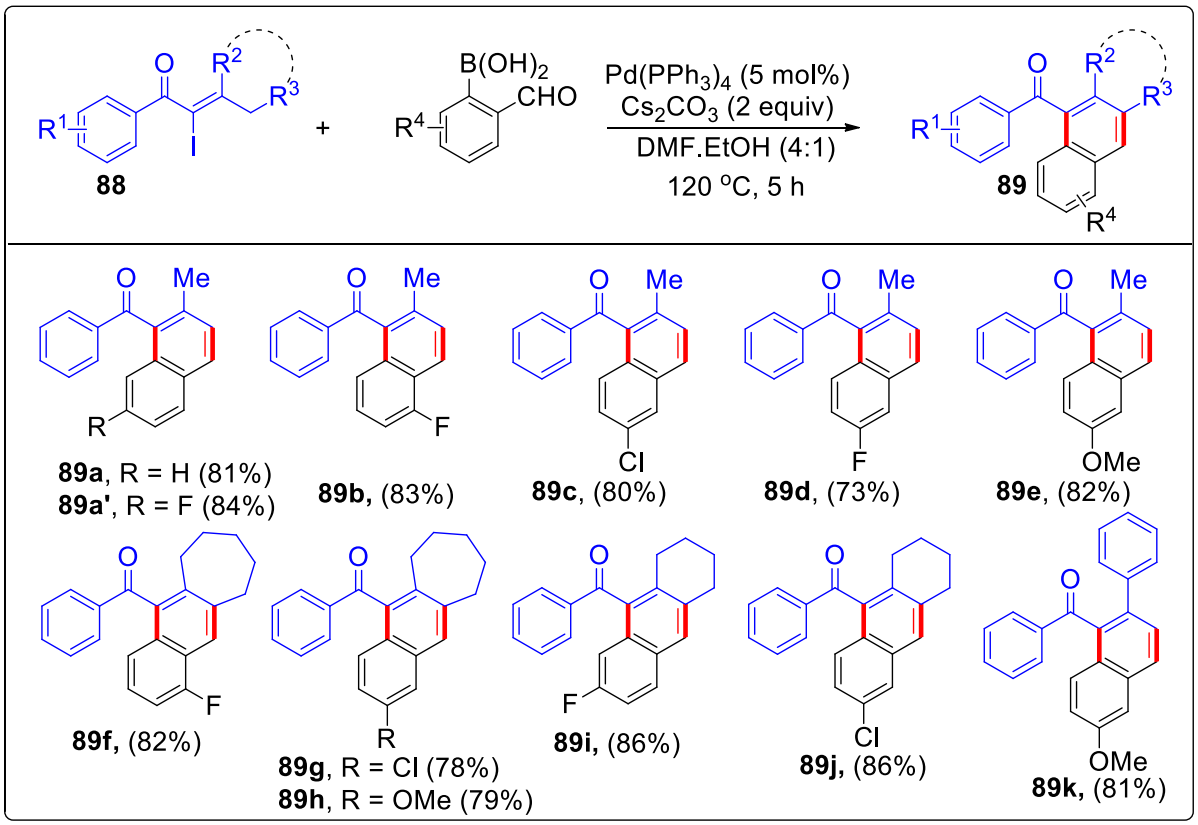
The cascade of Suzuki reaction and cyclocondensation has been employed in the synthesis of various heterocycles like phenanthridines and naphthalenes. Phenanthridine scaffolds are found in compounds having diverse biological as well as therapeutic activities like antiviral and anticancer properties.[55]On the other hand, naphthalenes as well as naphthyl ketones are present in various natural products having medicinal properties including antimicrobial and anticancer.[56-57] In 2014, Ghosh and co-workers have established a short and convenient strategy for the preparation of phenanthridines **87** by the reaction of *N*-(2-iodo-aryl)formamides **85** and 2-formyl-phenylboronic acid **86** (Scheme 44).[58] The substrate *N*-(2-iodo-aryl)formamides **85**[58] was produced simply from *o*-iodoanilines by Vilsmeier-Haack reagent. Hence, this protocol serves an easy transformation of aryl amino group to aryl-NHCHO as well as automatic deprotection of the protecting group leading to efficient synthesis of phenanthridines **87**.



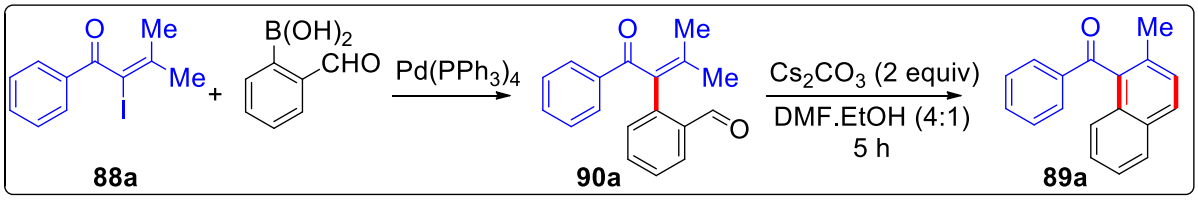
Scheme 44. Preparation of phenanthridines by Suzuki reaction/cyclocondensation.

In 2023, the Waghmare group[59] have developed a novel strategy for one-pot preparation of various naphthyl ketones from easily accessible starting materials. The reaction of *α*-iodoenones **88** with 2-formylphenylboronic acids or ester affords the desired naphthyl ketones **89** through a sequence of intermolecular Suzuki coupling, and subsequent *γ*-aldol condensation in intramolecular manner (Scheme 45). Herein, a different type of condensation instead of regular aldol condensation makes this method synthetically important.

Then, the mechanism was confirmed by isolating the intermediate product **90a** of a Suzuki-Miyaura reaction. When the isolated product **90a** was allowed for cyclization separately employing Cs_2CO_3 (2 equiv) and DMF:EtOH (2 mL) as solvent at 120 °C for 5 h, the desired ketone **89a** was produced in 85% yield (Scheme 46).

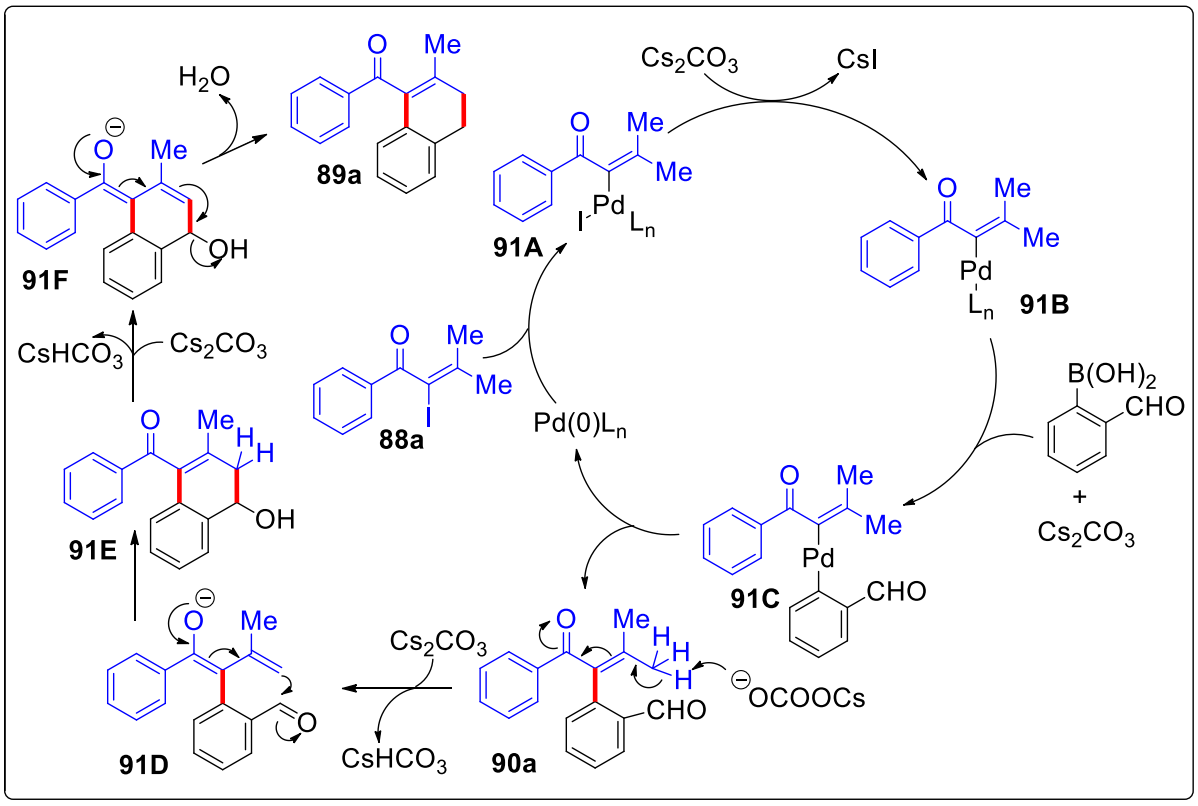


Scheme 45. Synthesis of naphthyl ketones bySuzuki coupling/*γ*-aldol condensation cascade.



Scheme 46. Control Experiments.

Based on the above observations, a possible mechanism was depicted for the formation of **89a** (Scheme 47). At first, Pd(0) undergoes oxidative addition with *α*-iodoenone **88a** generating Pd(II) complex **91A**, which is then transformed to **91B**. Then, transmetalation converts **91B** to **91C** which on subsequent reductive elimination delivers the Suzuki product **90a** as well as Pd(0) is regenerated to complete the catalytic cycle. Then, the *γ*-methyl group of **90a** engages in an intramolecular base promoted condensation to give the final product **89a** via **91D, 91E** and **91F**.

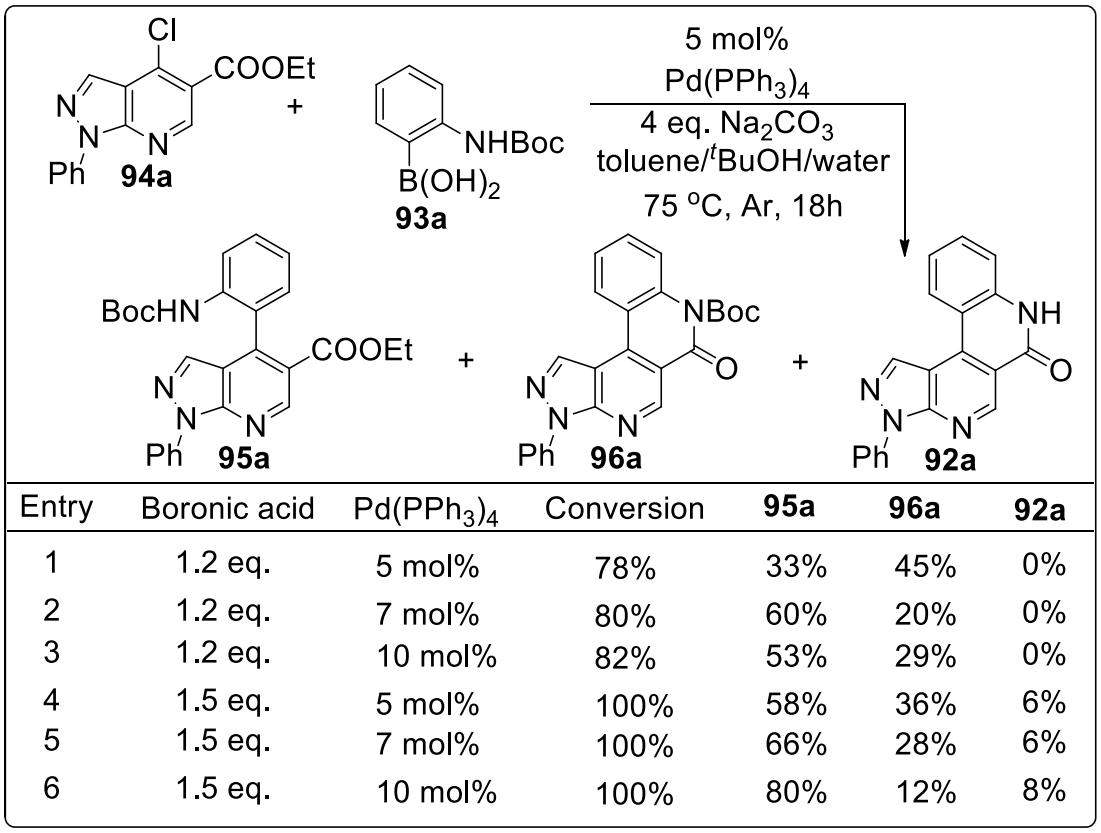


Scheme 47. Proposed mechanism of the formation of**89a**.

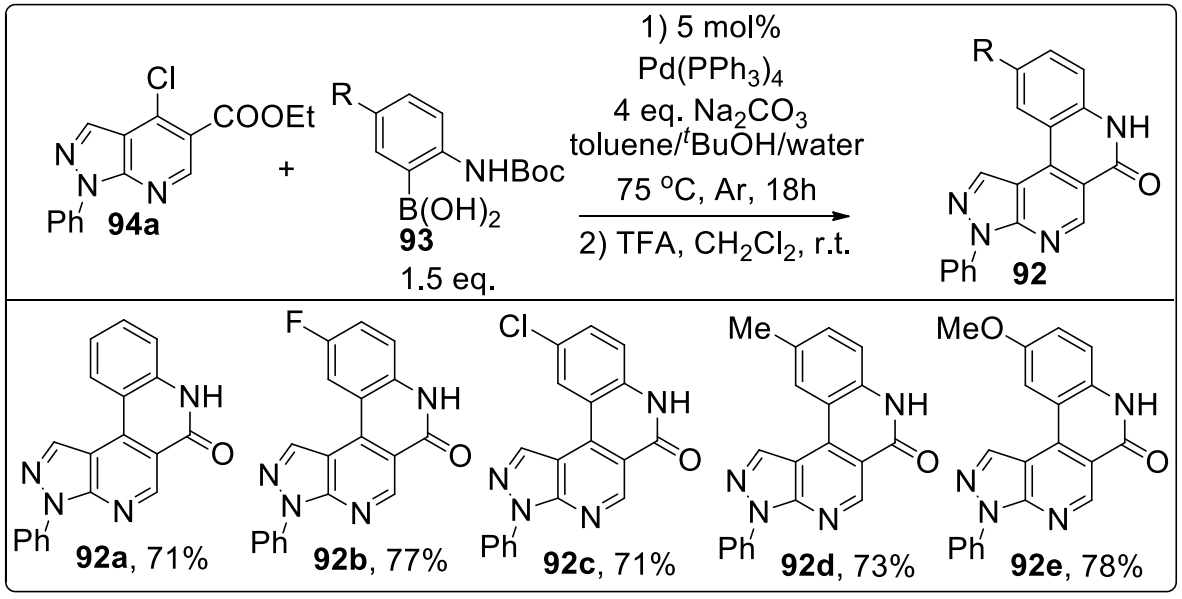
2.9. Suzuki/cyclization reactions

Compound **92a** has been established as a potent antineoplastic agent which was prepared by Lavrard group[60] in 2017 employing the cascade of Suzuki reaction-cyclization. Primarily, the synthesis of **92a** was tried with boronic acids protected by *N*-Boc **93a** with pyrazolo[3,4-b]pyridine **94a**. The lack of availability of 2-aminophenylboronic acids forced them to utilize the compound **93a** to produce **92**. However, the reaction was found to give a mixture of unconverted pyridine **94a** (22%), Suzuki product **95a** (33%) and Suzuki/cyclization cascade product **96a** (45%) rather than the direct formation of **92a**. The highest yield of compound **92a** was achieved up to 8% with the use of 1.5 equiv of boronic acid **93a** (Table 1). Then, they avoided the isolation of these products to make the protocol simple by treating with TFA which transformed **95a** and **96a** to the desired product **92a** efficiently (Scheme 48).

Table 1. Finding optimal reaction conditions



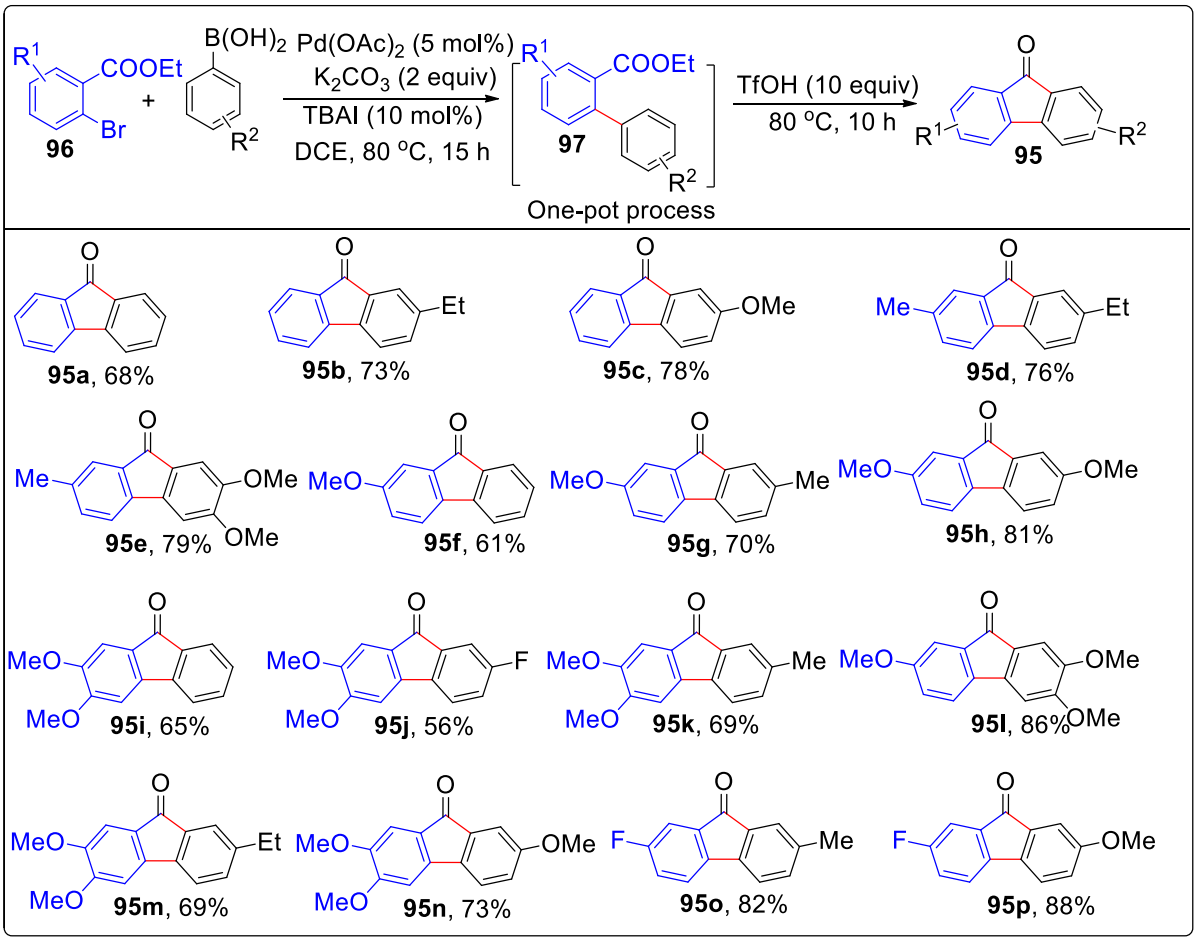
Entry	Boronic acid	$Pd(PPh_3)_4$	Conversion	**95a**	**96a**	**92a**
1	1.2 eq.	5 mol%	78%	33%	45%	0%
2	1.2 eq.	7 mol%	80%	60%	20%	0%
3	1.2 eq.	10 mol%	82%	53%	29%	0%
4	1.5 eq.	5 mol%	100%	58%	36%	6%
5	1.5 eq.	7 mol%	100%	66%	28%	6%
6	1.5 eq.	10 mol%	100%	80%	12%	8%



Scheme 48. Suzuki/cyclization cascade.

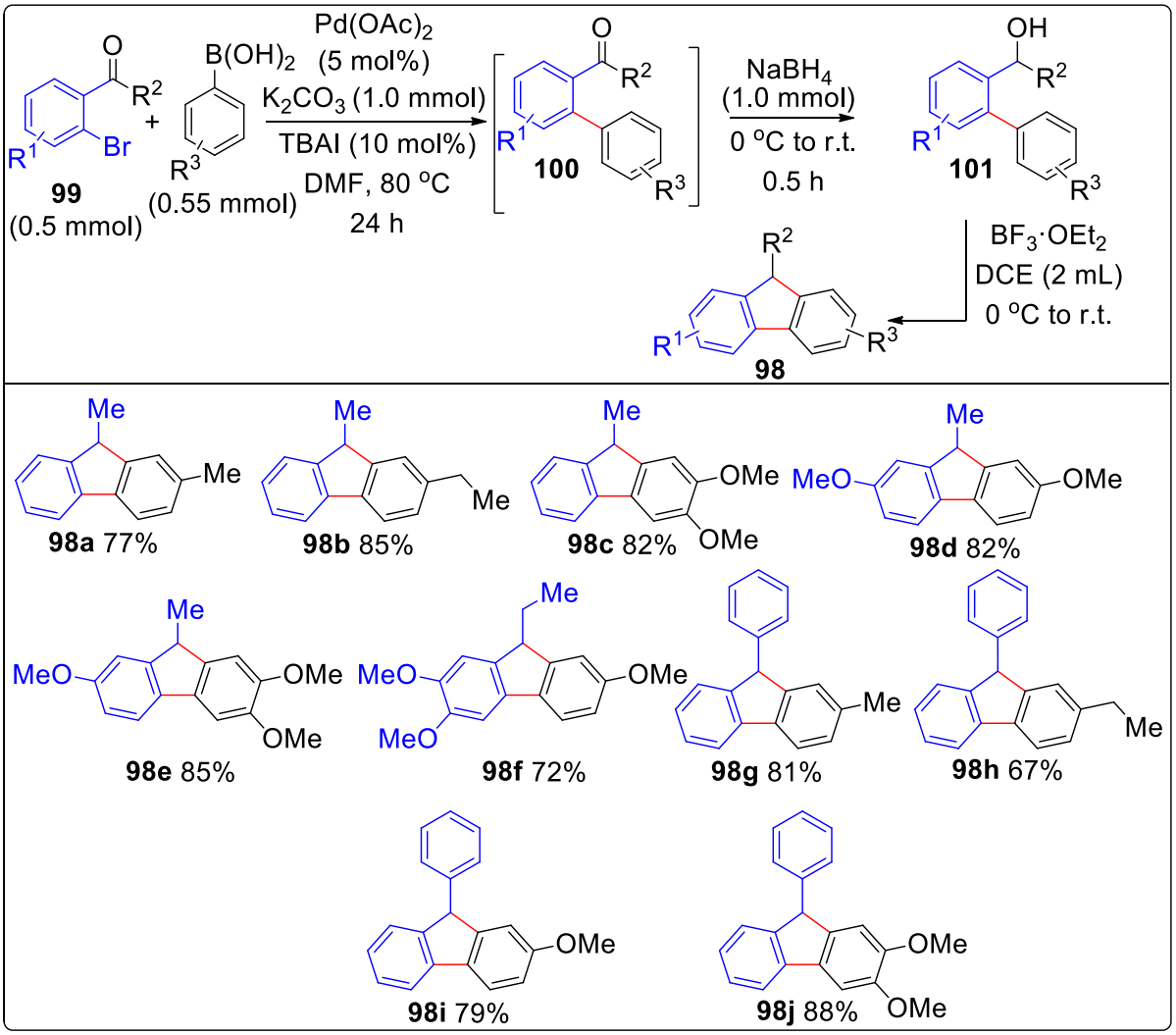
Fluorenones are tricyclic molecules which are found to be present as a building block in various biologically and pharmaceutically active compounds. In 2018, the Ravi Kumar group[61] developed a simple strategy to produce fluorenones **95**. The synthesis of **95** involved the sequential reaction of aryl ester **96** with boronic acid

giving the Suzuki product **97** and subsequent acid-promoted Friedel-Crafts acylation in intramolecular manner (Scheme 49). In addition, they have also provided a protocol for the preparation of fluorenes **98** by a sequence of Suzuki coupling between aryl ketone **99** and aryl boronic acid to give **100**-reduction by $NaBH_4$ affording **101** and followed by Friedel-Crafts alkylation intramolecular manner (Scheme 50).



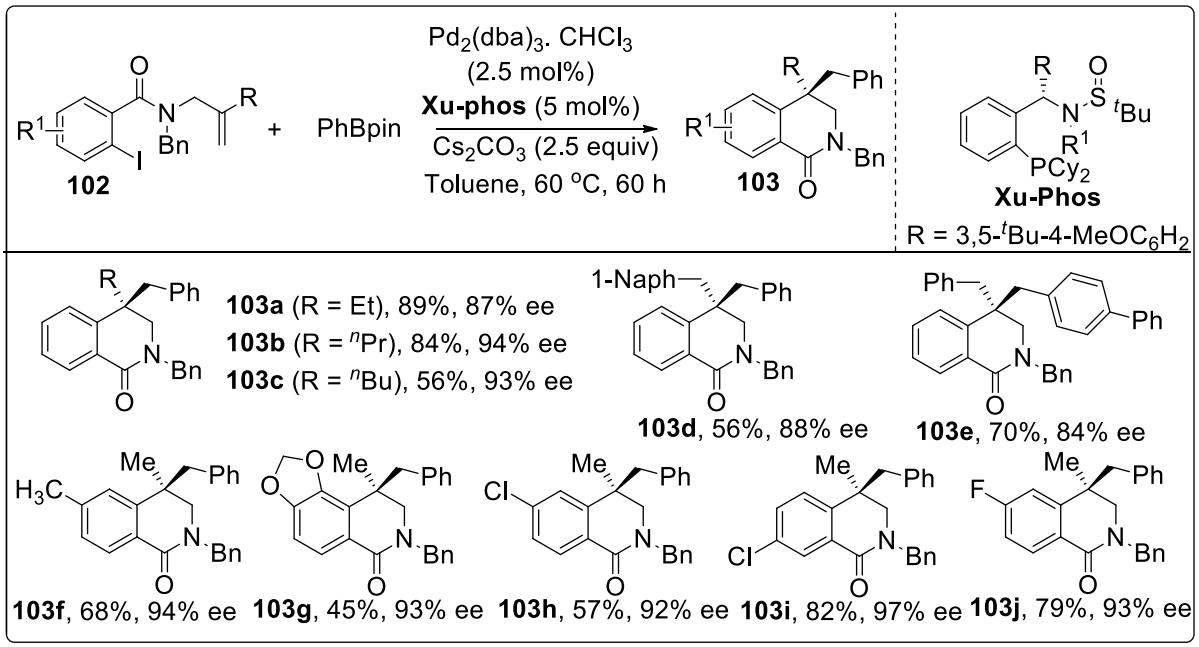
Scheme 49. Preparation of fluorenones.

Disubstituted dihydroisoquinolinone are present as prominent structural scaffold in naturally occurring products as well as compounds having biological activities. Compounds bearing this core structure are found to have cytotoxicity and anti-inflammatory properties. The construction of the backbone is challenging, particularly in the preparation of the quaternary stereocenters at C-4 of dihydroisoquinolinone. Hence, the synthesis of this structural motif by the Chen group[62] is synthetically important. They have established a protocol introducing palladium/Xu-Phos catalyst in the enantioselective Heck/Suzuki cascade. The reaction of variety of pinacol esters of alkenyl- and arylboronic acids (RBpin) with 2-iodobenzamides **102** gives the production of dihydroisoquinolinones **103** (Scheme 51). The enantioselective construction of a chiral quaternary center in single step with up to high yield made this approach superior over existing conventional strategies.

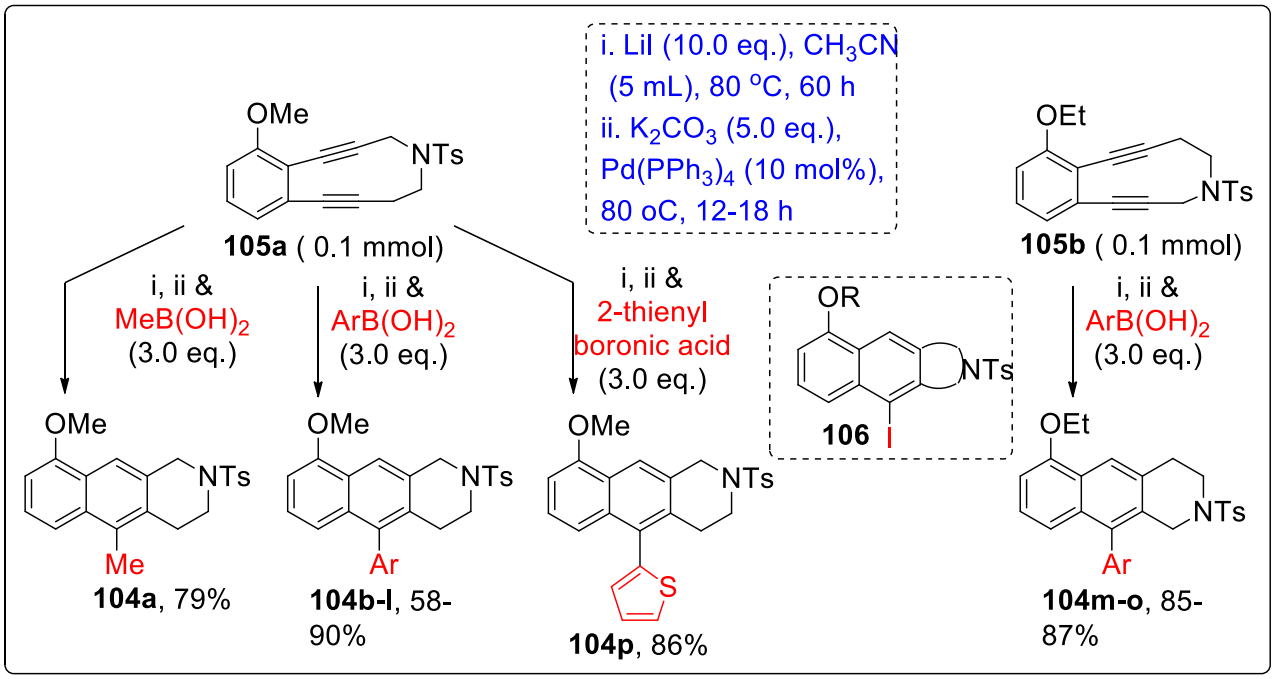


Scheme 50. Synthesis of fluorenes.

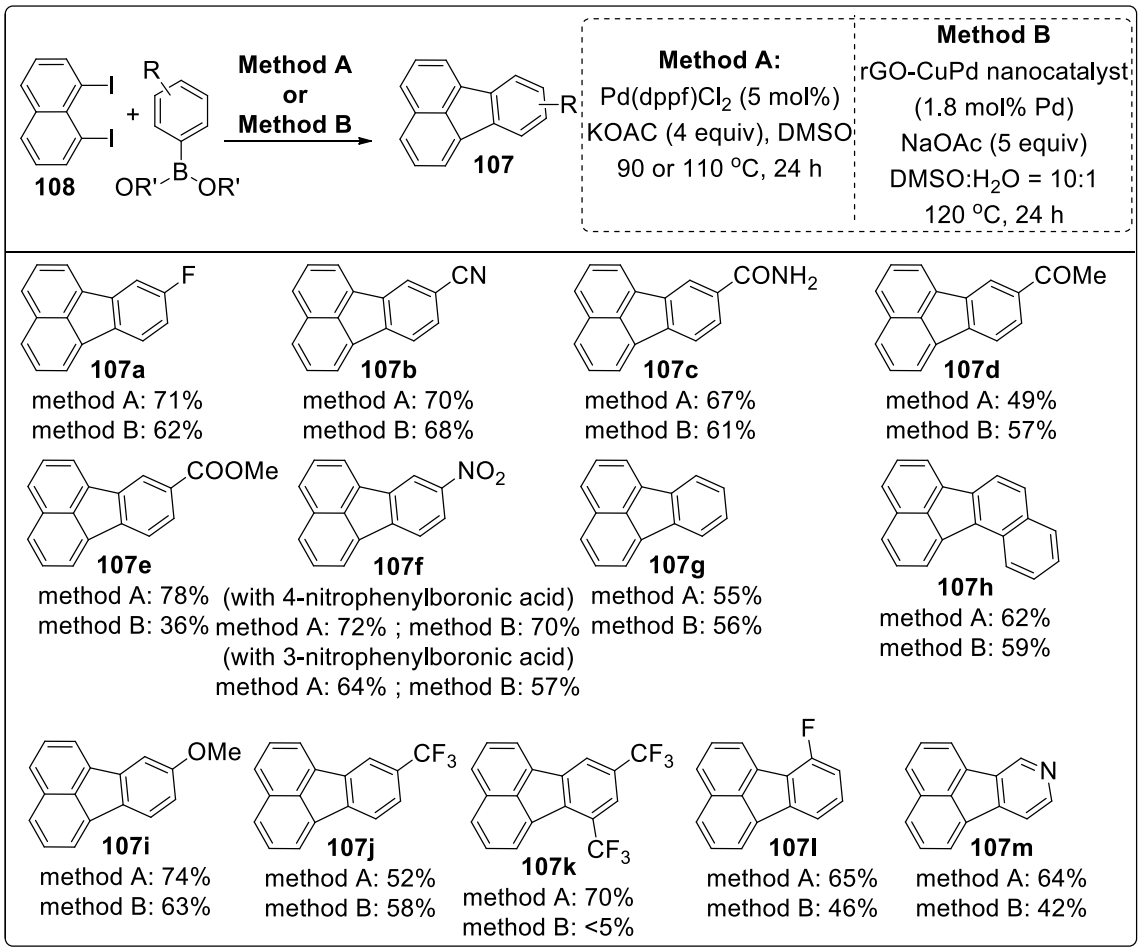
In this context, the protocol demonstrated by the Das group[63] can be represented for the preparation of tetrahydroisoquinoline motif **104**. In this synthesis, enediynes **105** undergo regioselective halogenation producing non-isolated intermediate **106** via *p*-benzyne and subsequent Suzuki coupling (Scheme 52). The advantages like two reactions in one-pot with up to excellent yields as well as the successful utilization of the various boronic acids such as aromatic, aliphatic and heteroaryl as the coupling partner make this protocol novel. Again, this type of tetrahydroisoquinoline-based scaffold is biologically important because they can act as the inhibitor to cyclic GMP phosphodiesterase.



Scheme 51. Synthesis of dihydroisoquinolinones.



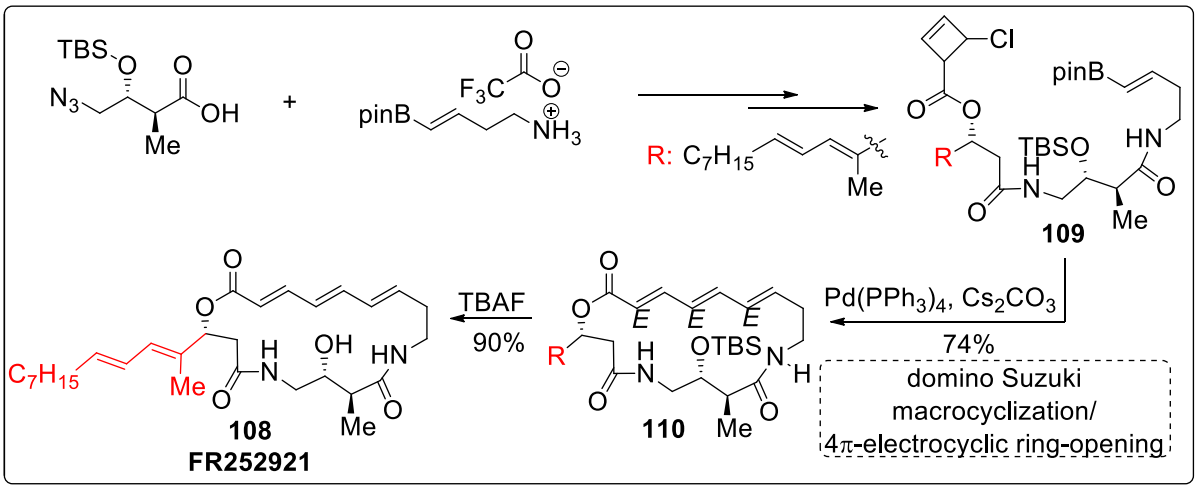
Scheme 52. One-pot synthesis of tetrahydroisoquinoline motif.



Scheme 53. Synthesis of fluoranthenes.

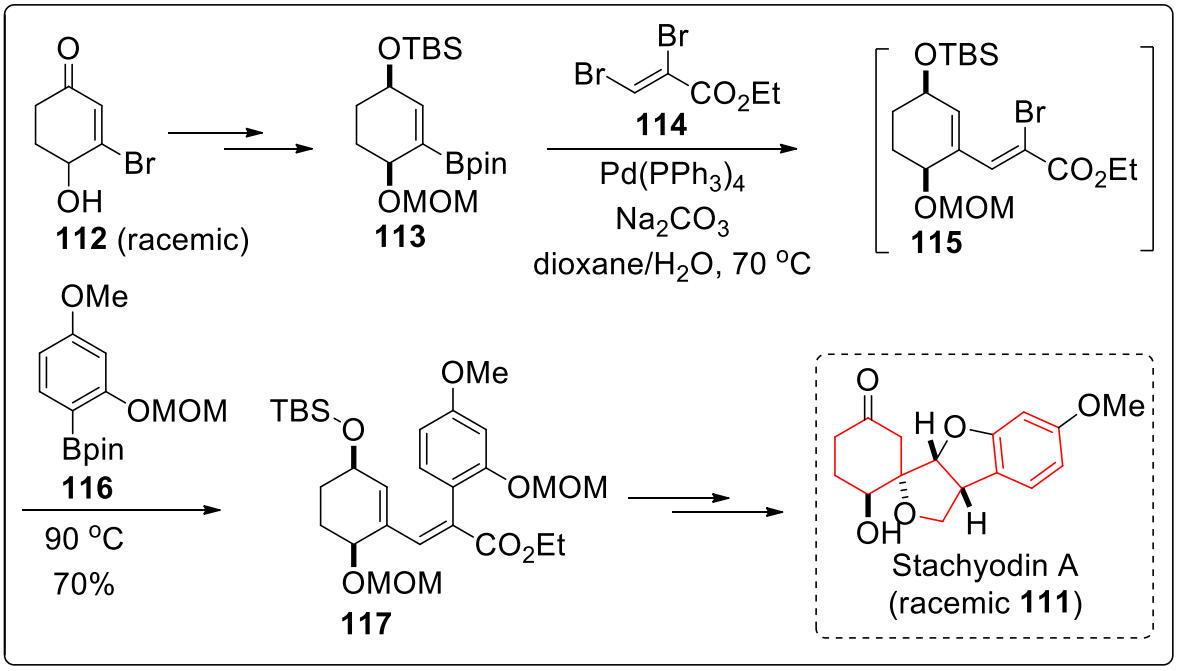
Fluoranthenes are prominent polycyclic aromatic compounds having a wide range of applications. Fluoranthene is present as a core structure in numerous natural products like daldinone E and hortein.Fluoranthenes are also applied in the field of materials sciences to develop organic electronics. In this regard, new approaches are developed regularly to afford this motif. Among these, the protocol discovered by the Pal group[64] is simple and hence, synthetically important. This is a straightforward preparation of various fluoranthenes **107** starting from 1,8-diiodonaphthalene **108** by the cascade of Suzuki coupling/C-H arylaton in intramolecular manner (Scheme 53). The great success of this approach is that both the homogenous catalyst, $Pd(dppf)Cl_2$ as well as the heterogenous rGO-CuPd nanocatalysts were much effective in the production of fluoranthenes **107**. The reaction was found to tolerate a wide range of functional groups with both electron-withdrawing and donating groups. The advantage of the use of the nanocatalysts is that it can be reusable in this method.

In 2019, Chen and co-workers[65] developed a unique approach for the efficient construction of immunosuppressive naturally isolated products FR252921 **108**. The key step of the synthesis comprises a sequence of Suzuki macrocyclization of **109** as well as 4π-electrocyclic ring-opening in conrotatory torquoselective manner to deliver **110** in 74% yield. Then, the reaction of **110** with TBAF produces FR252921 **108** in 90% yield (Scheme 54). The superiority of this method over conventional approach is that herein, the possibility of isomerization of C=C bond is overcome. These drugs are regularly consumed to cure from autoimmune-related diseases and allograft repulsions.



Scheme 54. Synthesis of immunosuppressive naturally occurred products FR252921.

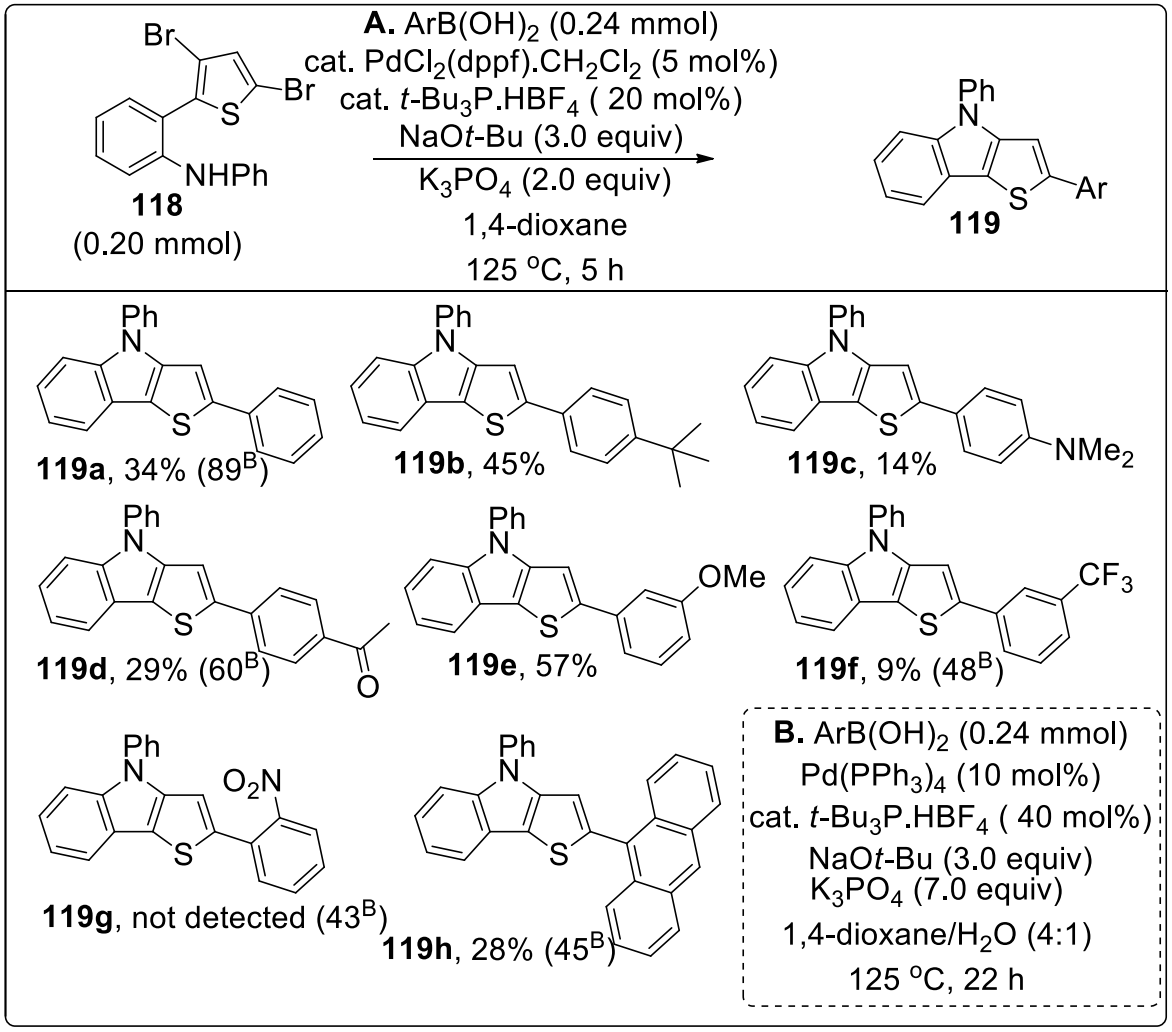
In continuation of the application of domino Suzuki coupling in the production of natural products, the first report by the Kawamoto group [66] on the preparation of racemic Stachyodin A **111** can be mentioned. This natural product isolatedfrom *Indigofera stachyodes* shows anti-inflammatory properties and hence, chemists became interested in the synthesis of**111**. The Kawamoto synthesis involved 14 steps starting from accessible compound **112**. Among these, one of the key steps is a one-pot reaction where *Z*-2,3-dibromopropenoate **114** underwent Suzuki coupling with **113** obtained from **112** giving **115**which on subsequent second Suzuki coupling with **116** yielding **117** (Scheme 55). Then, other important reactions like stereoselective epoxide formation, reductive epoxide opening and followed by spirocyclization delivered the target compound **111** from **117**.



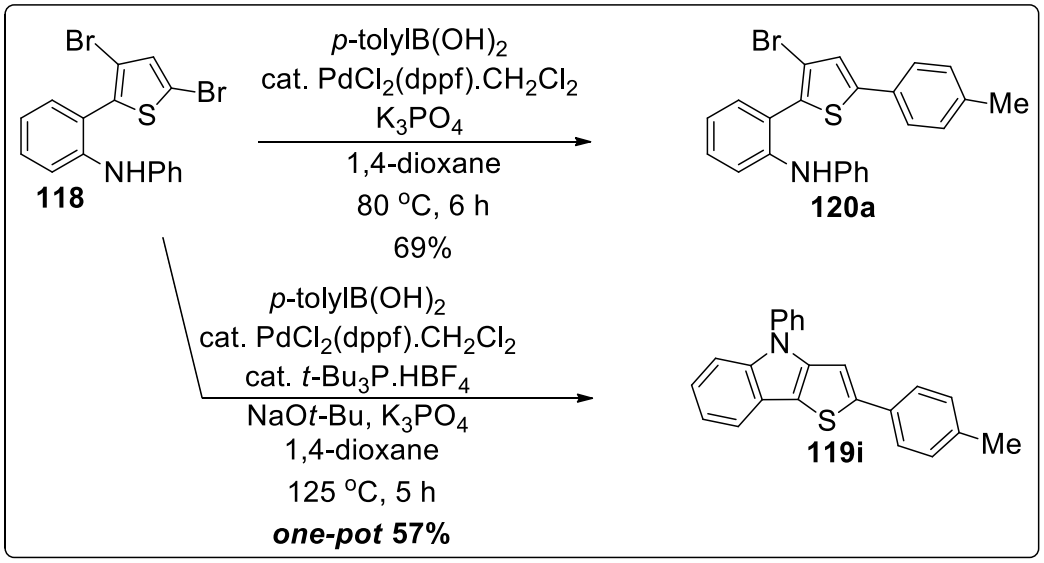
Scheme 55. Double Suzuki couplings in the synthesis of Stachyodin A.

2.10. Domino Suzuki coupling in the construction of indole scaffolds

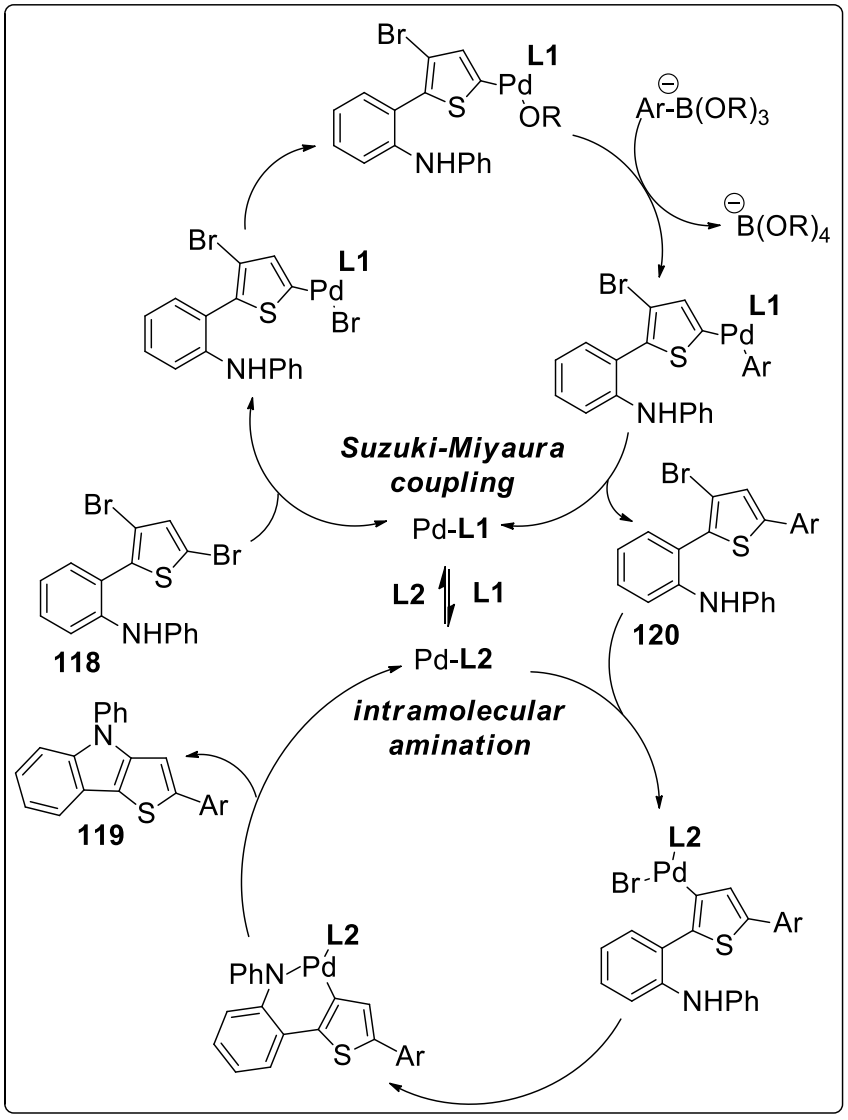
Domino Suzuki coupling strategies have been widely employed in the formation of indole scaffolds. This motif is present as a core structure in numerous biologically active molecules. For example, thiophene-based indoles are prominent type of π-extended compounds and medicinal molecules. Hence, the approach discovered by Hayashi and co-workers[67] in 2017 shall be mentioned, in which thieno[3,2-*b*]indoles **119** are produced from arylthiophenes **118** (Scheme 56) in one pot. The conversion is associated with a halogen dance in which a ligand is found to control the cascade couplings towards the preparation of **119**. On the other hand, the incomplete product **120a** was isolated in the absence of the ligand (Scheme 57). Then, the role of the ligand was understood from the plausible mechanism as depicted in Scheme 58. At the beginning, Pd(0) along with DPPF (**L1**) serves as catalyst towards the coupling reaction to afford Suzuki product **120**. Next, in situ generated Pd(0)-*t*-Bu_3P (**L2**) promotes the intramolecular amination reaction. The experiment shows that both **L1** and **L2** are essential to achieve the desired cascade product and assists the catalytic cycle.



Scheme 56. Suzuki coupling/intramolecular amination cascade.



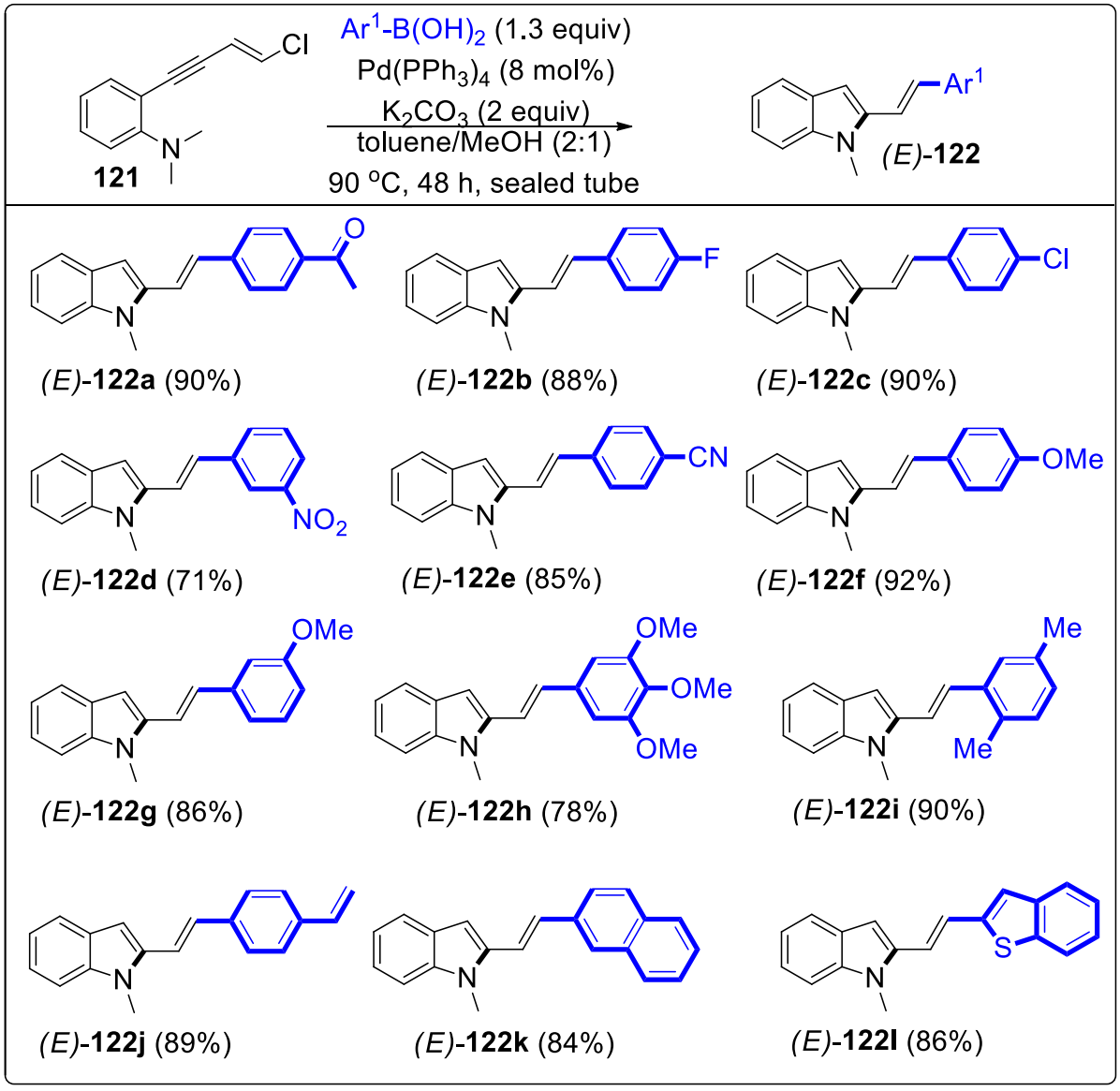
Scheme 57. Ligand-controlled cascade reaction.



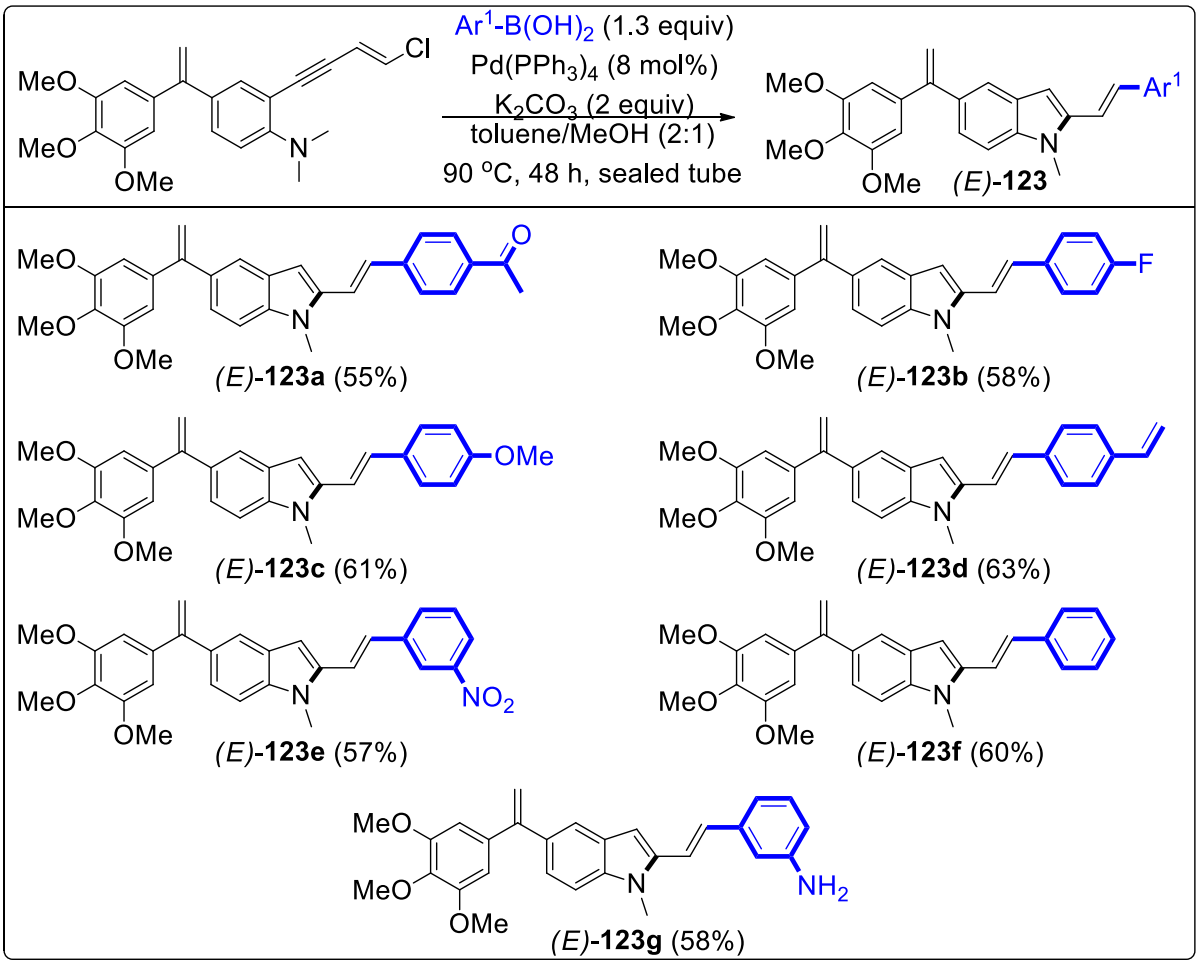
Scheme 58. Plausible catalytic cycle.

In 2018, the Zhao group[68] reported an efficient one-pot production of 2-styrylindoles **122** starting from (*E*)-2-(4-chlorobut-3-en-1-yn-1-yl)-*N*,*N*-dimethylanilines **121** (Scheme 59). The synthesis involves a 3-step cascade of Suzuki arylation-cyclization and *N*-demethylation giving **122** partly in excellent yields. Moreover, this protocol was successfully employed in the preparation of 1,1-diarylethylenes **123** (Scheme 60) and diarylmethylamines **124** (Scheme 61) containing a 3,4,5-trimethoxyphenyl motif and diverse substituted 2-styrylindoles. Initial results showed indoles **123c** and **123e** to be the most active compounds having nanomolar GI_{50}values against HCT116, a human colon carcinoma cell line.

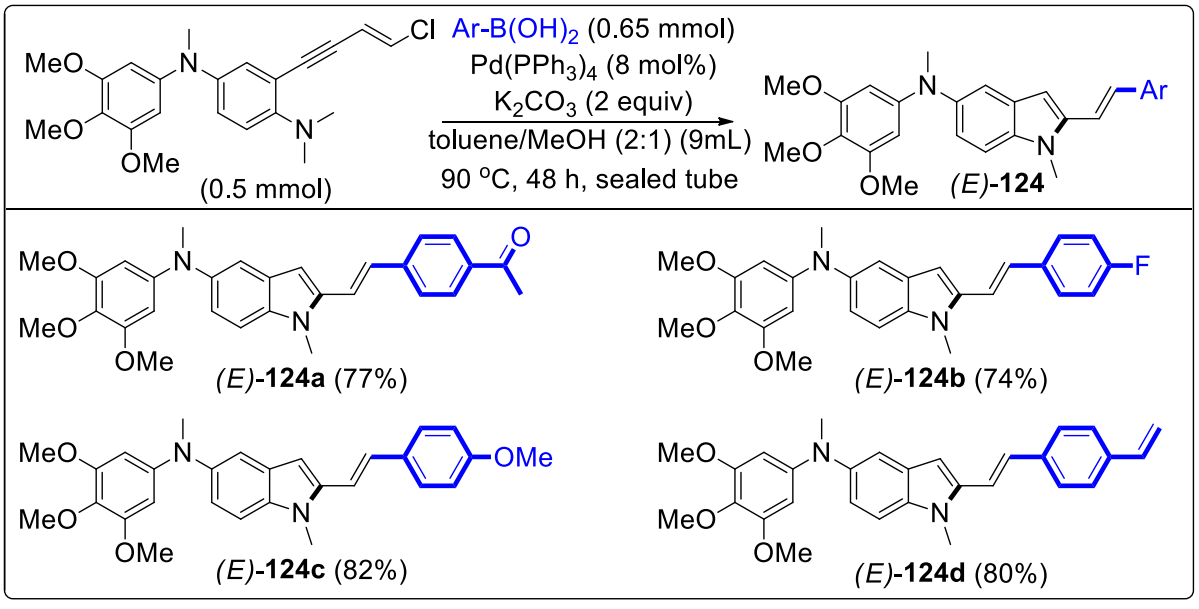
A plausible reaction course is represented in Scheme 62 involving the generation of an indolinium salt **126** obeying 5-*endo-dig* cyclization of **125**. Then, MeOH leads the N-demethylation of **126** to styrylindole **122**.



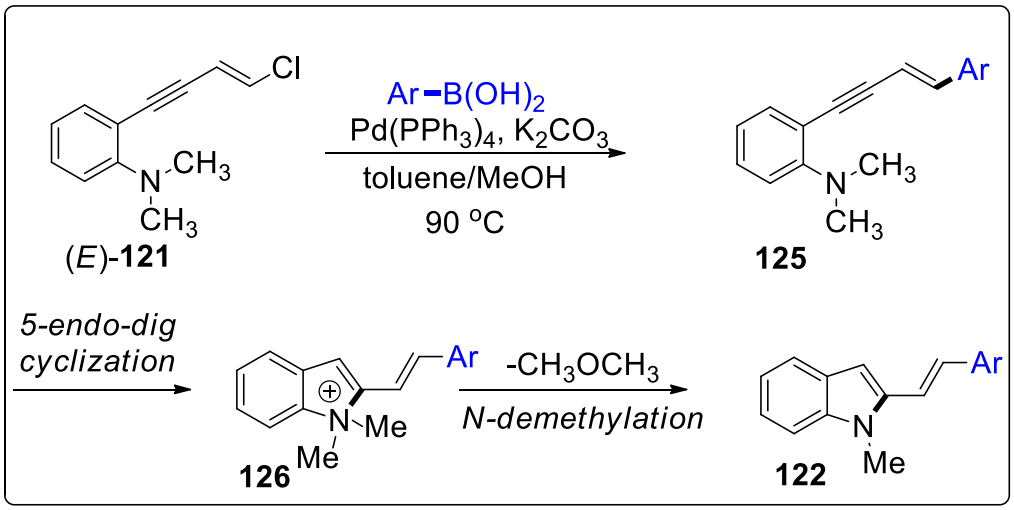
Scheme 59. Synthesisof 2-styrylindoles.



Scheme 60. Synthesis of 1,1-diarylethylenes.



Scheme 61. Synthesis diarylmethylamines.



Scheme 62. Plausible reaction course for the production of styrylindoles.

3. Conclusions

In conclusion, this review is mainly focused on those cascade reactions involving one Suzuki-Miyaura (SM) cross-coupling as a prominent tool to generate C-C bonds which have appeared in reports since 2014. Herein, the combination of a variety of reactions like Heck, aza- Michael, amination, carbopalladation, C-H functionalization, Catellani or cyclocondensation with SM cross-coupling are explored in detail. In addition, the synthetic applications of this domino protocol towards the preparation of naturally found molecules and indole core structure are also discussed. Again, several plausible mechanisms are depicted to understand the course of few crucial transformations. In the future, the emergence of new domino Suzuki-Miyaura coupling reactions will prompt the synthesis of diverse organic compounds under eco-friendly conditions. Furthermore, microwave or ultrasound-assisted domino SM coupling reactions should be examined to get higher yields in shorter reaction time. In addition, transition metals other than Pd and Ni could be tested for this protocol. It is expected that this methodology can be designed in such a way that it will become more benign. Hopefully, this review will help the organic synthetic chemists and researchers working in the area of SM coupling-based synthesis of diverse pharmaceuticals and molecules having biological activities.

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