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REVIEW

Recent Developments of Palladium-Catalyzed C(sp^3)/C(sp^2)-H Bond Functionalizations Assisted by 8-Aminoquinoline Bidentate Directing Group

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Recently growing demand for cleaner, direct even more regioselective reaction sequences, the formation of carbon-carbon or carbon-heteroatom bonds through C-H activation has developed as a unique methodology. Since the pioneering work of Daugulis on the use of the 8-aminoquinoline auxiliaries as removable bidentate directing groups in palladium-catalyzed C-H bond activations has emerged as a ground breaking strategy for the construction of carbon-carbon or carbon-heteroatom bonds. Hence, this review intends to cover most of the recent advances on 8-aminoquinoline directed palladium-catalyzed C(sp^3)/C(sp^2)–H bonds functionalizations and highlighted the synthesis of C-branched glycosides.

Keywords: 8-Aminoquinoline, Palladium, C-H activation, Bidentate directing group.

INTRODUCTION

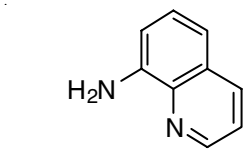
The field of transition metal-catalyzed or -mediated direct C-H functionalization has grown rapidly and powerful protocol in organic synthesis due to its efficiency in converting the ubiquitous inert C–H bonds to valuable carbon-carbon bonds as well as carbon–heteroatom bonds [1-3]. At the current stage, to make the C–H functionalization more convenient, chemists have been keen to develop a single synthetic operation that avoids the tedious prefunctionalization [4-6].

In the context of a growing demand for cleaner, shorter and even more regioselective reaction sequences, the direct formation of carbon-carbon or carbon-heteroatom bonds through C-H activation has emerged as a unique methodology [7-9]. Even a moderately simple organic molecule incorporates several types of unique C-H bonds. So, the fundamental challenge in this chemistry consists of the mild and selective activation of such robust C–H bonds (particularly unactivated C(sp^3)–H and C(sp^2)–H bonds).

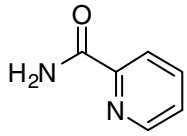
Recently, one powerful and robust strategy to improve the efficiency and control the selectivity of C-H activation is to introduce a directing group [10] Lewis basic motif present in the substrate that can form a relatively stable metallacycle intermediate, which can promote both the C-H activation and the subsequent functionalization.

In addition, Daugulis and co-workers [11] first reported palladium-catalyzed C-H bond functionalization by 8-aminoquinoline and picolinamide directing groups in 2005. After that, this specific field has been developed N, O- or N, N- and N,S-based bidentate groups, which provided good regioselectivities and greatly enriched the scope of C–H activation reactions (**Scheme-I**) [12,13]. These directing groups are readily attachable to the substrate and easily removable from the C-H functionalized products, which greatly enhance the synthetic value of the developed methodologies.

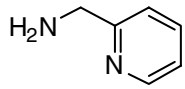
Over the past decades, extensive research efforts have been devoted to these bidentate auxiliaries-assisted metal-catalyzed functionalization of C(sp^3)–H/C(sp^2)–H bonds using like Pd [14-17], Co [18-20], Ni [21-24], Cu [25-27], Rh [28-30], Ru [31] and Fe [32-34]. Many transition-metal catalysis used to promote C–H functionalization, palladium catalyst showed outstanding for the functionalization of organic molecules due to strong coordination, especially with bidentate amide directing groups. Herein, this review highlights the recent developments



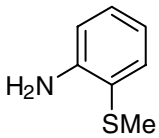
8-Aminoquinoline (AQ)



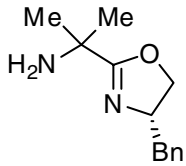
Daugulis *et al.* [11]



Chatani *et al.* [12]



Daugulis *et al.* [15]

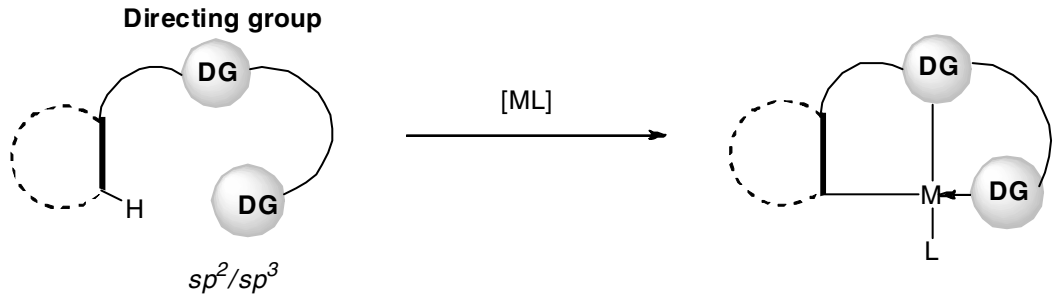


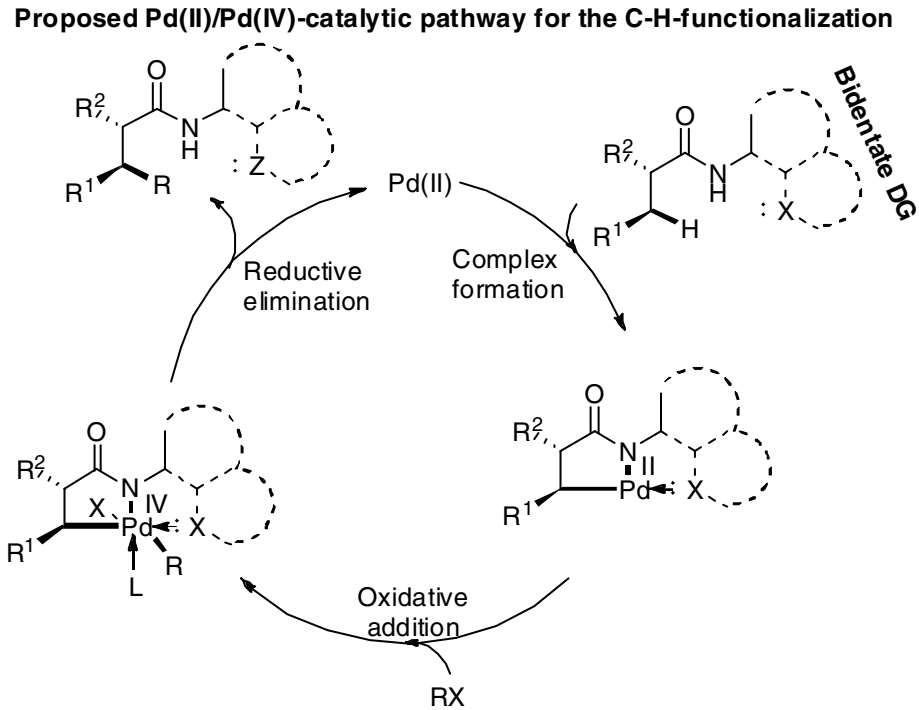
Shi *et al.* [44]

Scheme-I: Some important nitrogen-based bidentate directing groups

of palladium-catalyzed direct C(sp^3)/C(sp^2)–H bond functionalizations promoted by only an 8-aminoquinoline bidentate directing group.

A general mechanism proposed in **Scheme-II** followed by numerous bidentate directing groups mediated Pd catalyzed Csp^3/sp^2-H bond functionalization. Initially, palladacycle intermediate formed *via* the C-H activation process. After that, functionalization occurs through oxidative addition. Finally, reductive elimination generate desired product and released Pd catalyst into a catalytic path.





Scheme-II: Proposed palladacycle in bidentate auxiliary directed C-H bond activation

C(sp^3)-H functionalization: Chen *et al*. [35] employed the bidentate auxilliary 8-aminoquinoline coupled phthaloyl alanine which underwent β-Csp^3-H functionalization *via* Pd catalyst with α-iodoacetate. The same group in 2014, using PhI38 with *N*-phthaloyl-protected alanine, undergoes β-Csp^3-H arylation [36,37]. After that, the same group introduced olefination at the same moiety *N*-phthaloyl-protected alanine, leading to the formation of β-olefinated amino acids [38]. Next, Shi *et al.* [39], used *N*-phthaloyl-protected alanine for the stereoselective formation of β-silyl-α-amino acids (**Scheme-III**).

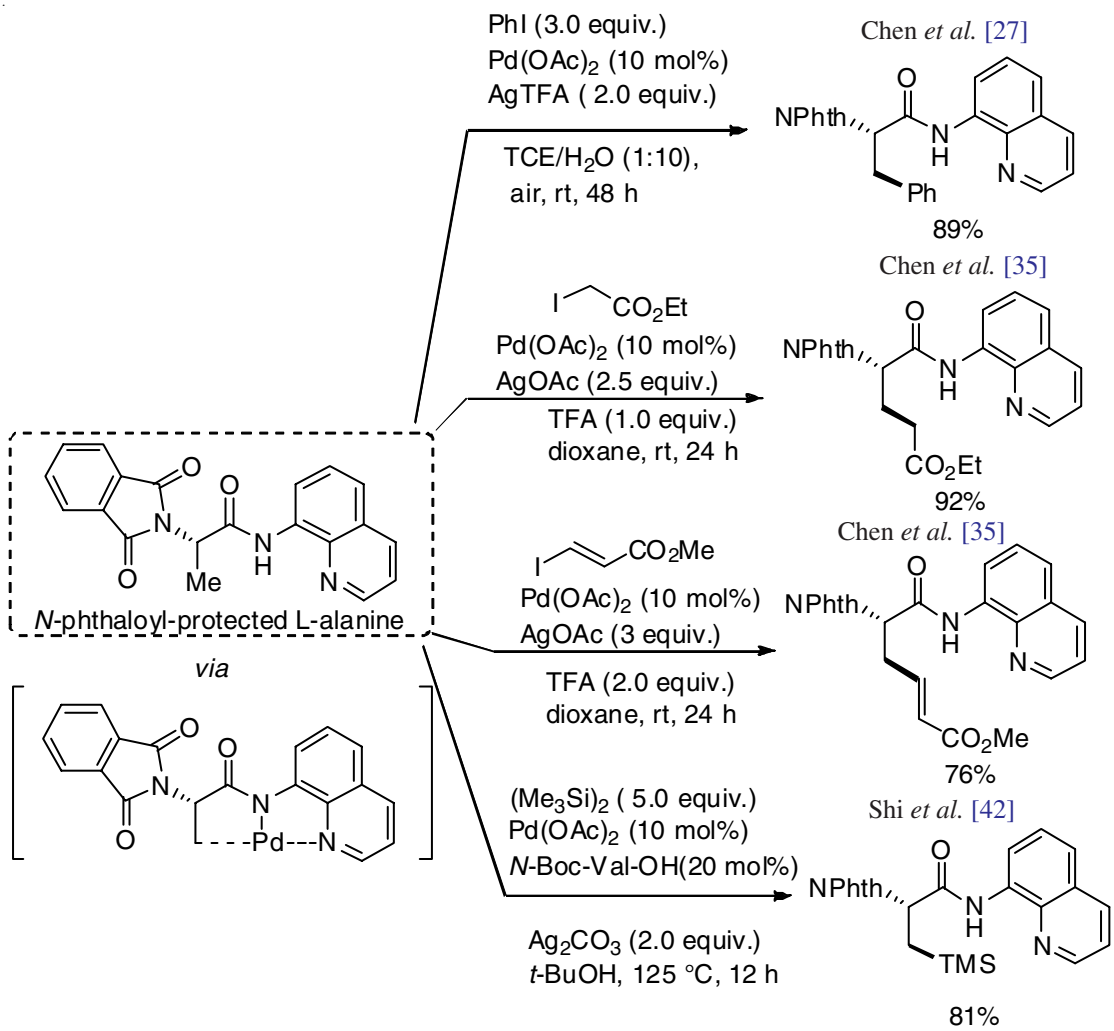
A flexible route to β-Csp^3-H arylation of *N*-protected β-alanine precursors at unactivated β-methylene position to furnished β-aryl-β-amino acids was described by Haq *et al.* [40] in 2019. Herein, 8-aminoquinoline plays a vital role in the regioselectivity of synthesized products in good to excellent yields. Furthermore, they proposed that the mechanistic path followed Pd(II)/Pd(IV) catalytic cycle (**Scheme-IV**).

By using same approach, a stereoselective β-C-H functionalization was achieved in *N*-protected amine and peptides by using 8-aminoquinoline as a directing group in presence of Pd catalysis was described in 2018 by Kazmaier *et al.* [41]. The protocol is also suitable to modify *C*-terminal alanines of dipeptides (**Scheme-V**).

Shi *et al.* [42] demonstrated that diarylhyperiodinium salts can be effectively used for Csp^3-H bond arylation in different 8-aminoquinoline amides in DCE at 120 ºC for 24 h. Based on KIE they suggested a mechanistic path. Initially, the formation of palladacycle intermediate was achieved by coordination of **A** with Pd catalyst. After that, C-H bond activation followed by oxidative addition gave C. Later on, reductive elimination released the desired arylated product and Pd catalyst back into the catalytic cycle (**Scheme-VI**).

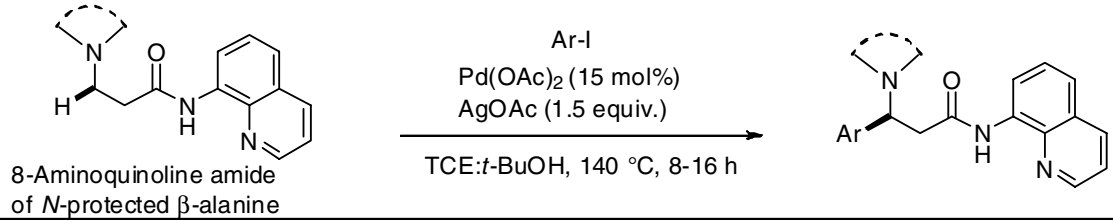
Afterwards, a practical approach to $Pd(OAc)_2$-catalyzed arylation of β-C(sp^3)–H bonds in α-cyano-α-methyl aliphatic amides was reported by Watkins & Reddy [43] in the presence of 8-aminoquinoline, as a removable directing group, using Na_2CO_3 and $Mn(OAc)_2$ (**Scheme-VII**). This protocol appears to be compatible with electron-donating as well as withdrawing group and heteroaromatic substituents on aryl iodide. This method was applied to synthesized α,α-dialkylated acid.

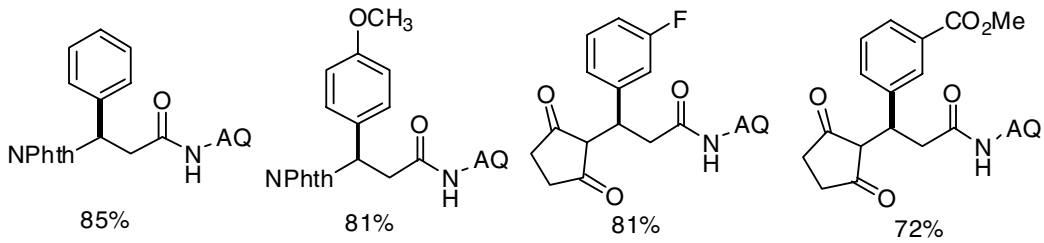
In 2015, Shi *et al*. [44] first reported 8-aminoquinoline directed synthesis of aryl alkyl sulfones through sulfonylation of unactivated Csp^3-H bond of alanine substrate. Optimal reaction conditions involved the use of $Pd(OAc)_2$ (10 mol%), $MesCO_2H$ (20 mol%) as an additive with Ag_2CO_3 in DCM at 90 ºC (**Scheme-VIII**). This methodology synthesized a wide range of aryl alkyl

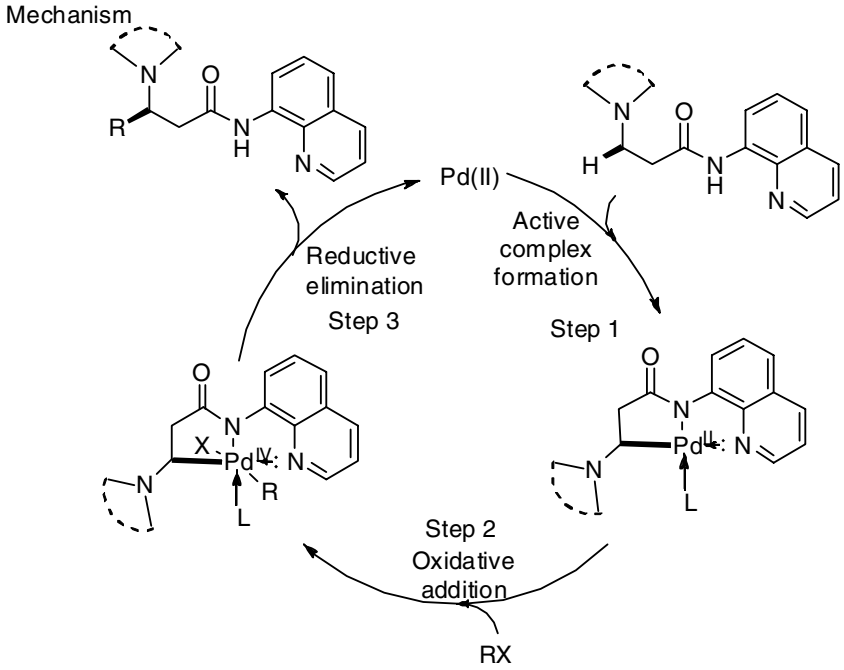


Scheme-III: C(sp^3)-H functionalization of protected L-alanine

Chowdhury *et al.* [40]

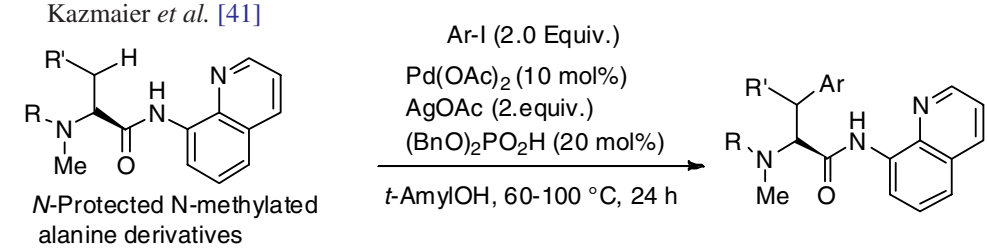


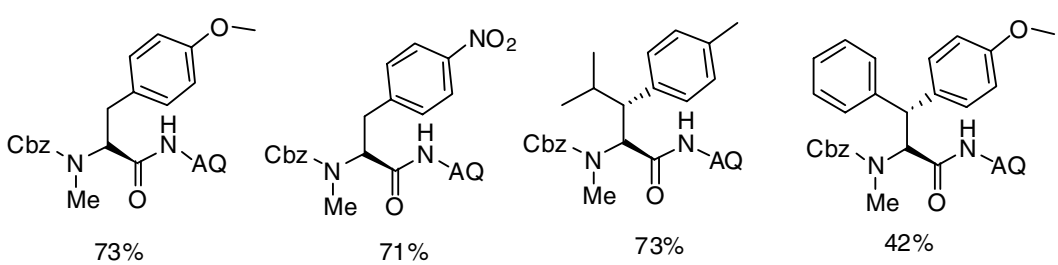




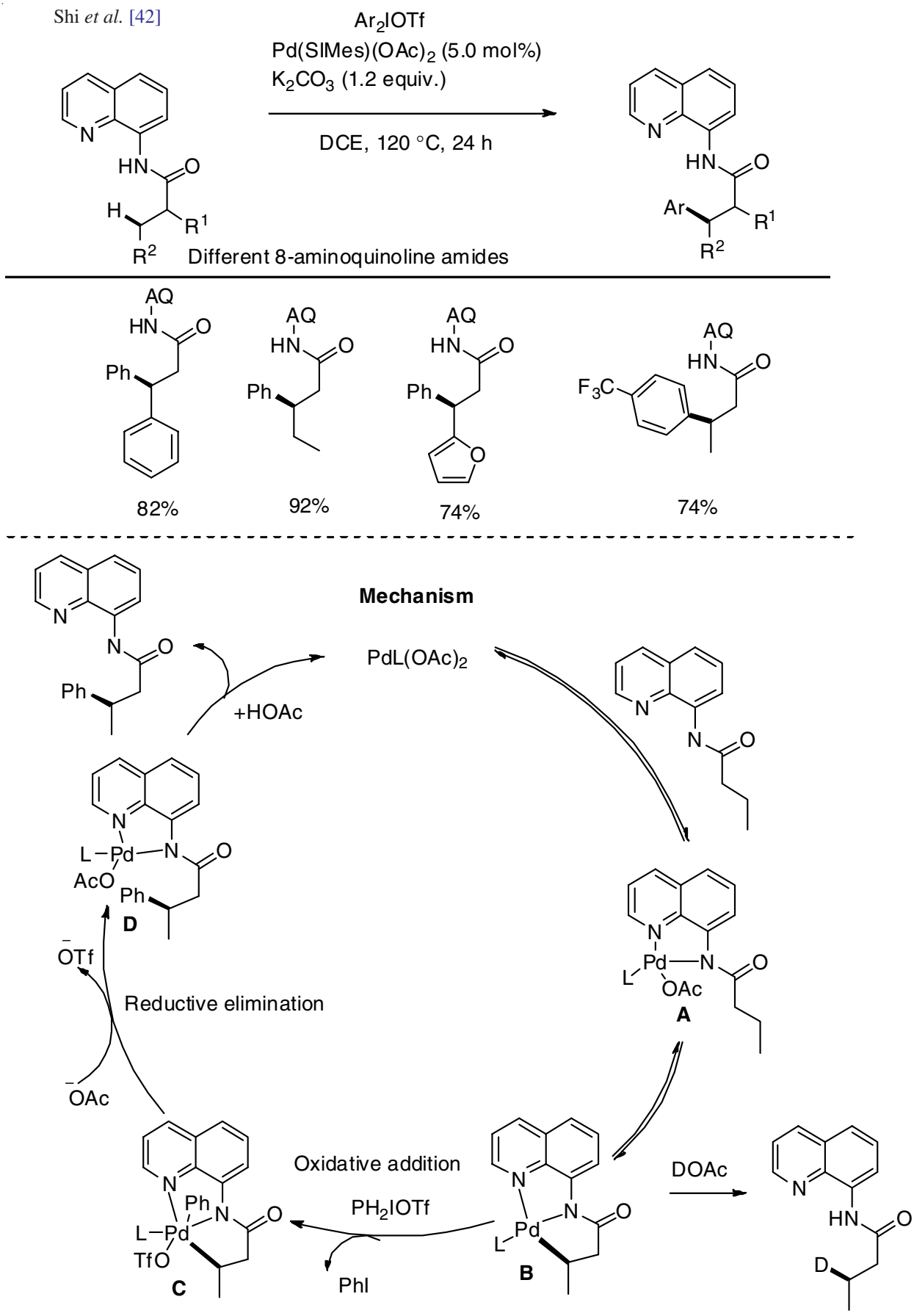
Scheme-IV: C(sp^3)-H functionalization of β-alanine

Kazmaier *et al.* [41]

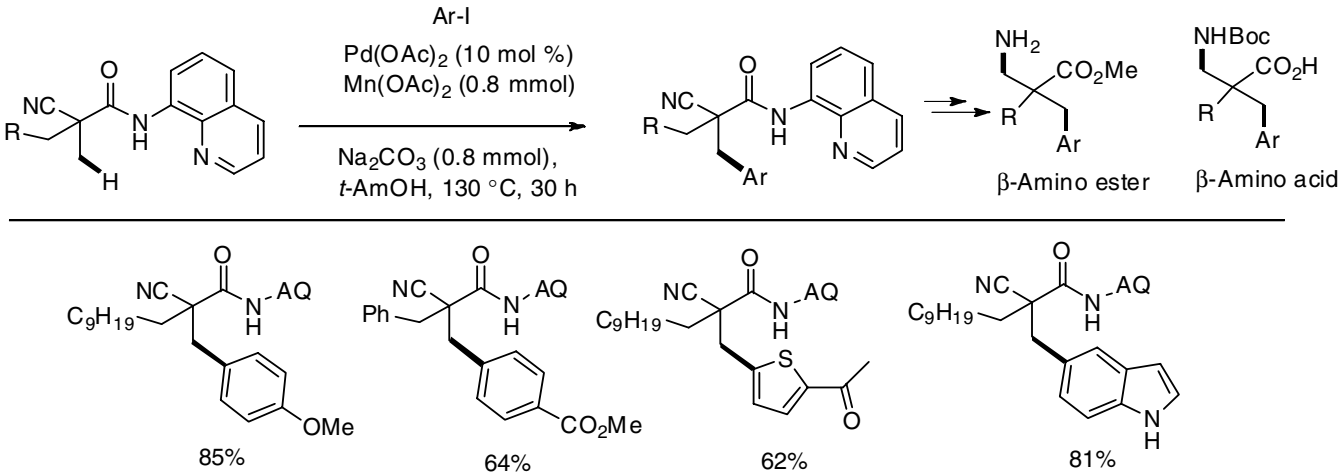




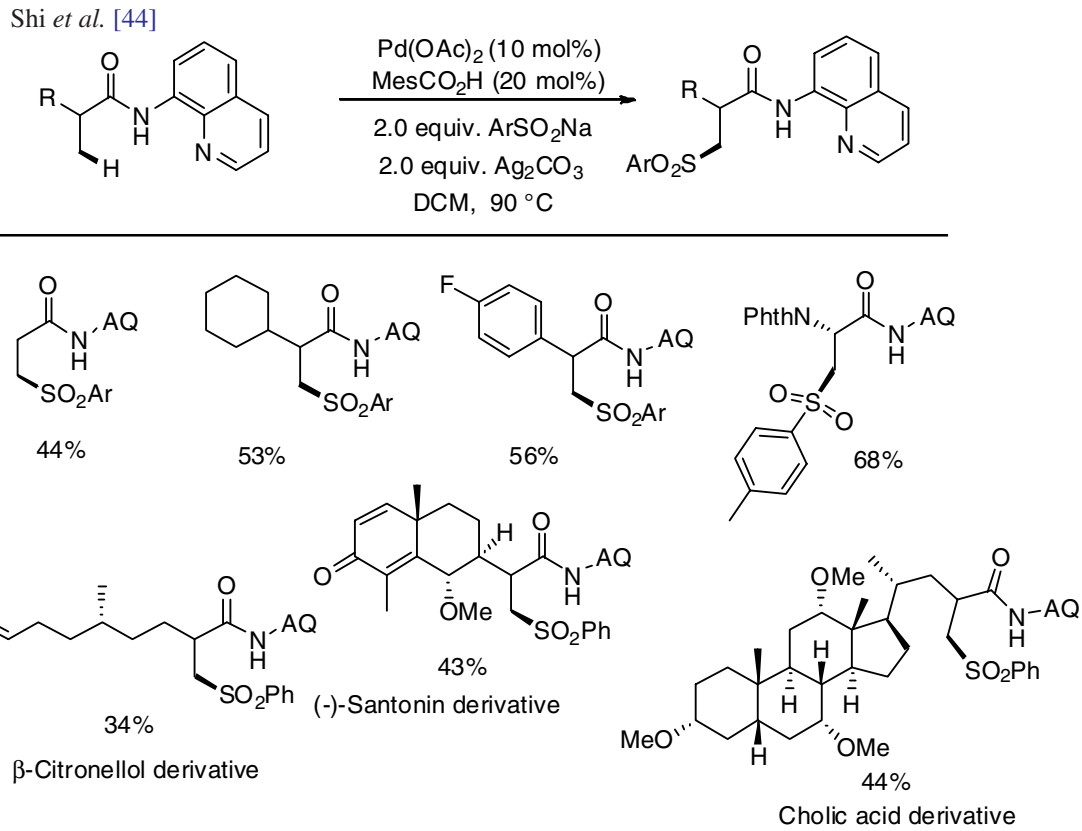
Scheme-V: C(sp^3)-H functionalization α-amino acids



Scheme-VI: Direct arylation of C(sp^3)–H bonds with diarylhyperiodonium salts



Scheme-VII: Pd-Catalyzed direct arylation of unactivated C(sp^3)–H bonds of aliphatic amides



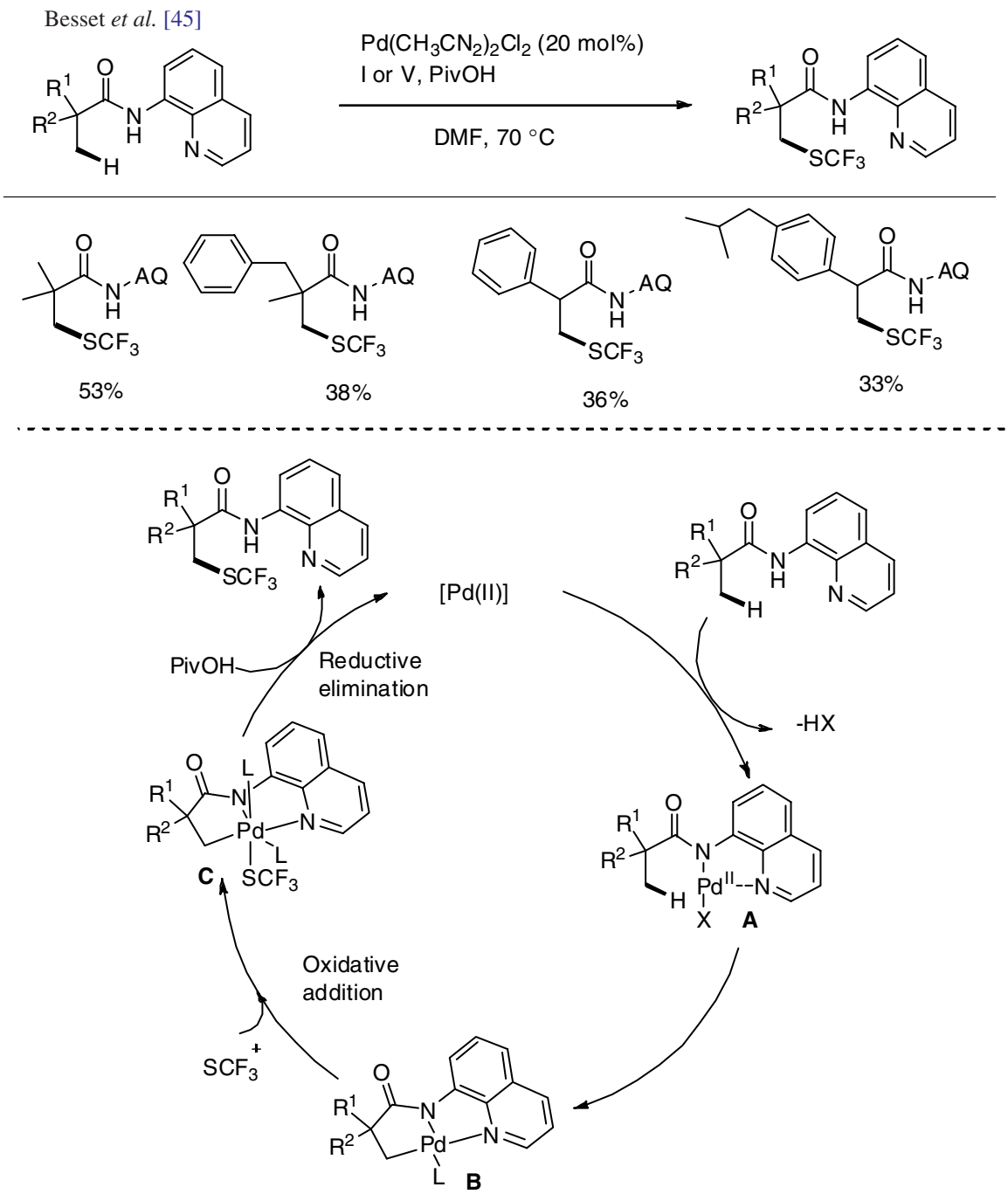
Scheme-VIII: Pd(II)-Catalyzed direct sulfonylation with sodium sulfinates

sulfone derivatives in good yields. This sulfonylation method was applied in late-stage modification of natural product derivatives such as β-citronellol, (–)-santonin and cholic acid.

At the same time, in 2015, Besset *et al*. [45] described a palladium catalyzed C-H process for trifluoromethylthiolation of 8-AQ directed α,α-dialkylamides in presence of Brønsted acid and an electrophilic –SCF_3 reagent. The synthetic utility of this method was demonstrated by the formation of –SCF_3 containing the derivative of biologically active Ibuprofen and naproxen. Moreover, a reasonable mechanism was proposed in **Scheme-IX**. Initially, palladacycle intermediate **A** forms *via* β-Csp^3-H-bond activation through the CMD process. After that, oxidative addition is followed by reductive elimination, leading to form the trifluoromethylthiolation products.

In 2015, Xu *et al.* [46] reported the C-H fluorination of 8-aminoquinoline butyramide derivatives in presence of Pd catalyst to form β-fluorinated carboxylic acid derivatives in good yields. They proposed a plausible mechanism of reaction, at the outset [5,5] fused bicyclic palladated intermediate, followed by oxidative addition. Finally, reductive elimination form β-fluorinated product (**Scheme-X**).

By compare, enantioselective CH activation has not expected many reports probably because of the absence of proper ligands to control the stereoselectivity in the CH activation reaction.

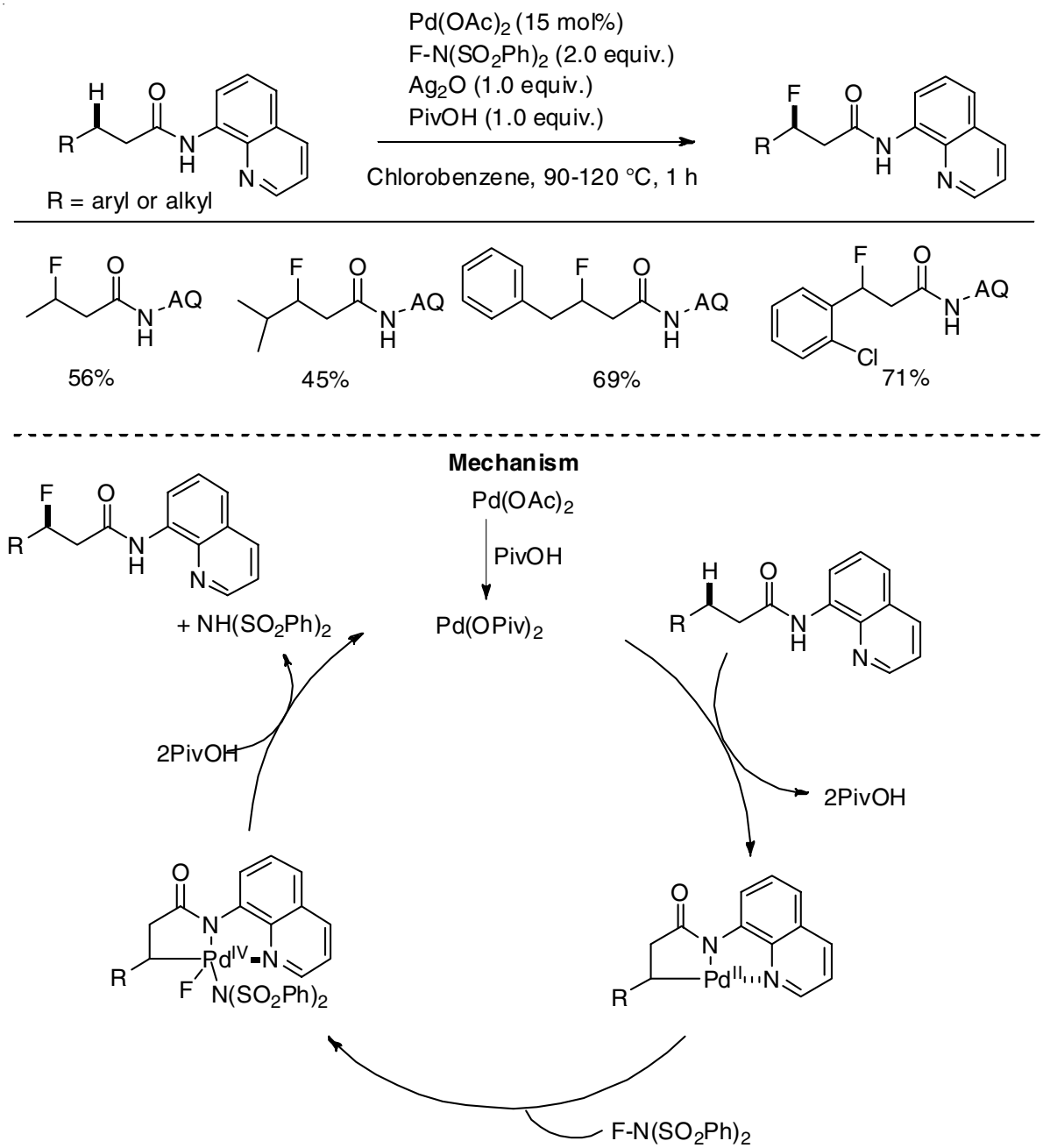


Scheme-IX: Directed trifluoromethylthiolation of unactivated C(sp^3)–H bonds

Duan *et al*. [47] reported Pd-catalyzed enantioselective asymmetric arylation of 8-aminoquinoline (8-AQ) amides to synthe-size β,β-diaryl carboxylic derivatives (**Scheme-XI**). A plausible mechanism starts with the ligand substitution followed by oxidative addition to form intermediate **C**. Finally, reductive elimination synthesized product. The reaction probably follows a $Pd^{II/IV}$ manifold, which has been most widely accepted for Pd-catalyzed AQ-directed C–H functionalization reactions.

Chen *et al*. [48] found that 8-aminoquinoline directed 3-arylpropanamides underwent coupling with aryl iodide *via* Pd(0) catalyst by using BINOL-phosphoramidite (P^{III}) ligand to form desired product in good to excellent yield with enantioselectivity up to 95% (**Scheme-XII**). Supported by DFT calculations, a feasible mechanism was proposed that followed $Pd^{0/II}$ catalytic path which is unprecedented for bidentate directing group-mediated C–H functionalization reactions.

A new approach to synthesize *cis*-2,3-disubstituted proline *via* palladium-catalyzed C(sp^3)–H functionalization of unactivated C3 position of proline derivative by using 8-aminoquinoline as a directing group was described by Bull *et al.* [49,50]. Further, another elegant protocol was reported by Zhang [51] *via* Pd catalyzed coupling of proline derivative with diversely substituted aryl iodide in toluene at 110 ºC, leading to the formation of C-3-substituted proline (**Scheme-XIII**).

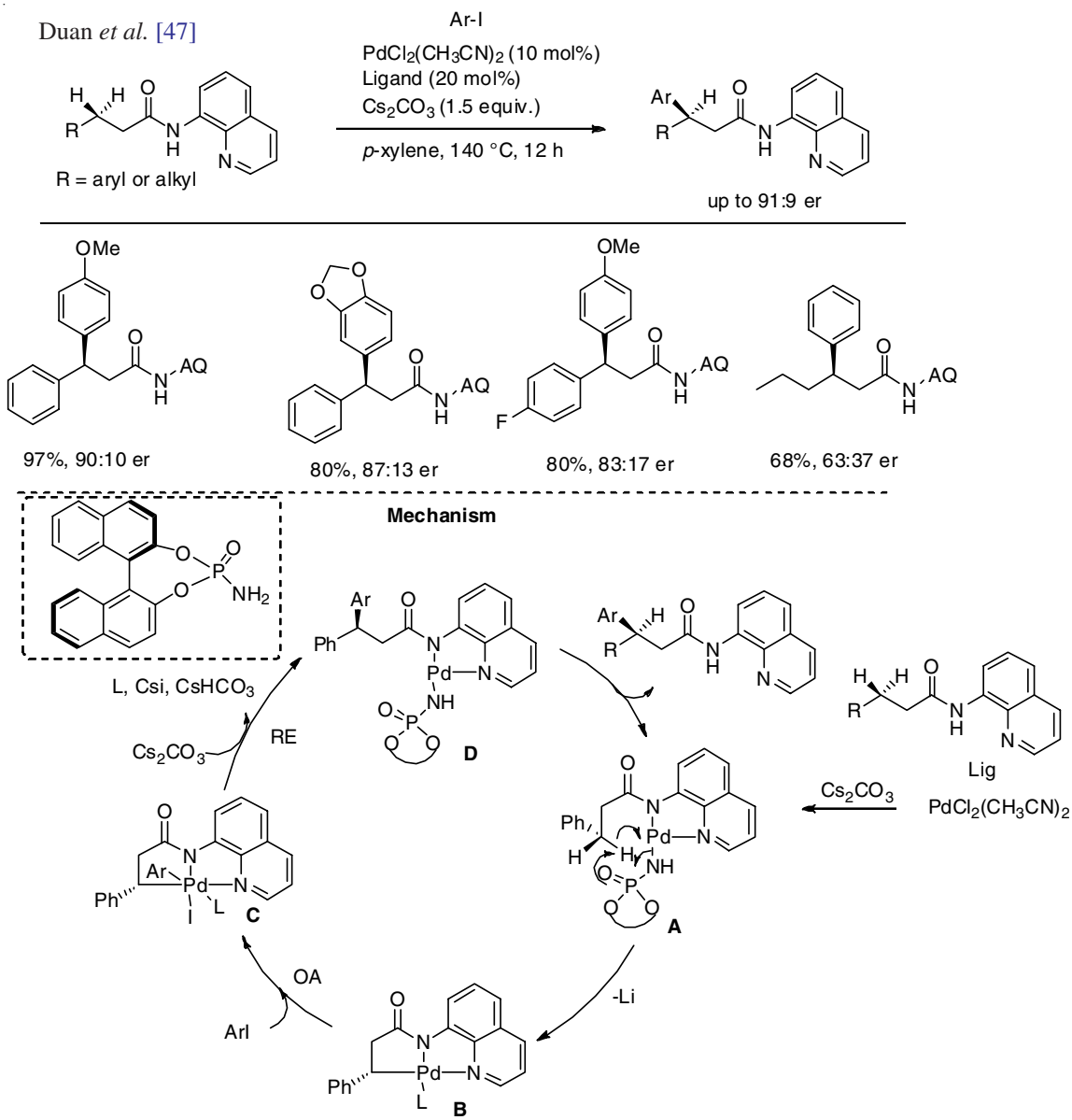


Scheme-X: β-Csp^3-H fluorination of butyramide derivatives

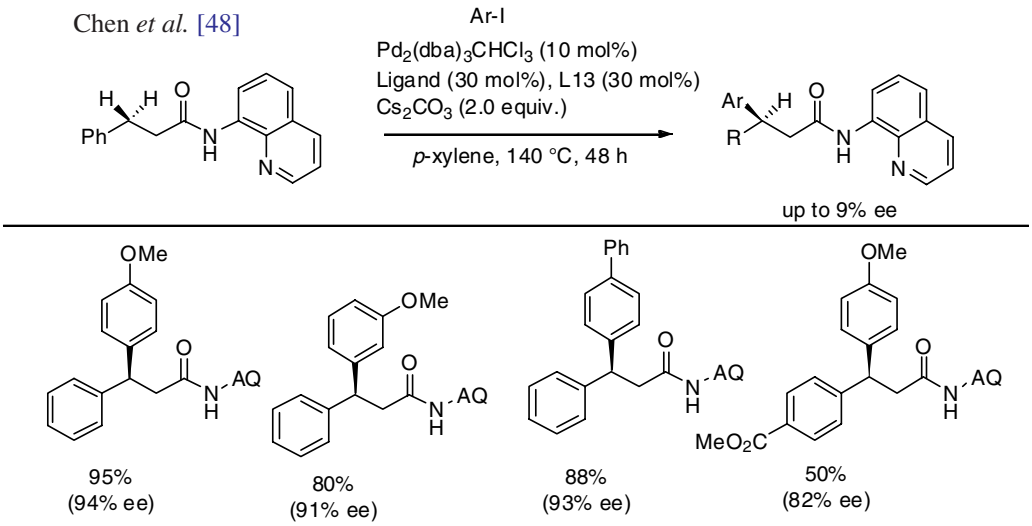
The synthetic importance of this methodology is the formation of pharmaceutically important monoamine reuptake inhibitor. Then, Schreiber *et al*. [52-54] described to access bicyclic azetidine by Pd catalyzed 8-aminoquinoline mediated C(sp^3)-H arylation of proline- and piperidine-based 8-aminoquinoline amide derivatives. This method proceeds in a one-pot manner and is effectively applied in pyroglutamic acid substituents.

Recently, a facile alkenylation and alkynylation at the C3 position of proline derivative with aliphatic, aromatic and heteroaromatic substituted vinyl iodide in presence of Pd catalyst was introduced by Verho *et al*. [55] (**Scheme-XIV**). A wide range of C3 alkenylated products formed in good to high yield. Moreover, this method was also applicable on TIPS protected alkynyl bromide to install an alkynyl group into the pyrrolidine scaffold.

One of the approaches to build C-C glycosidic bonds is established by 8-aminoquinoline directing group-equipped C-H functionalization of a sugar C-H bond. In this contest, Messaoudi *et al*. [56] reported Pd catalyzed Csp^3-H functionalization of β- and α-amidosugar substrates to give 2,3-*trans*-diastereoselective C3-arylglycosylamides in good to excellent yields with diastereoselectivity (**Scheme-XV**). Aryl iodide showed high functional group tolerance in this protocol. Based on the DFT study reasonable mechanistic path is suggested. Begin with concerted metalation-deprotonation followed by oxidative addition, then reductive elimination gave palladacycle intermediate **IV**. Finally, ligand substitution furnished the desired product and Pd catalyst regenerated into catalytic path.

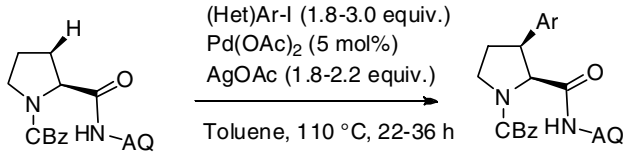


Scheme-XI: Pd-catalyzed enantioselective asymmetric arylation

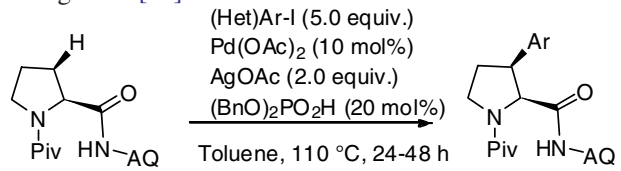


Scheme-XII: Bidentate 8-aminoquinoline auxiliary directed enantioselective benzylic C–H arylation

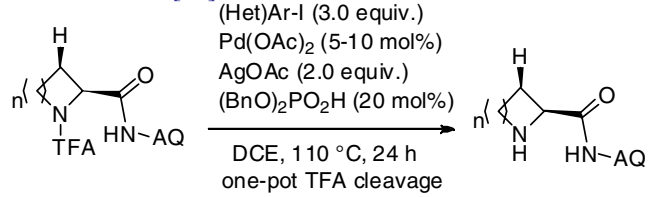
Bull *et al.* [49]



Zhang *et al.* [51]

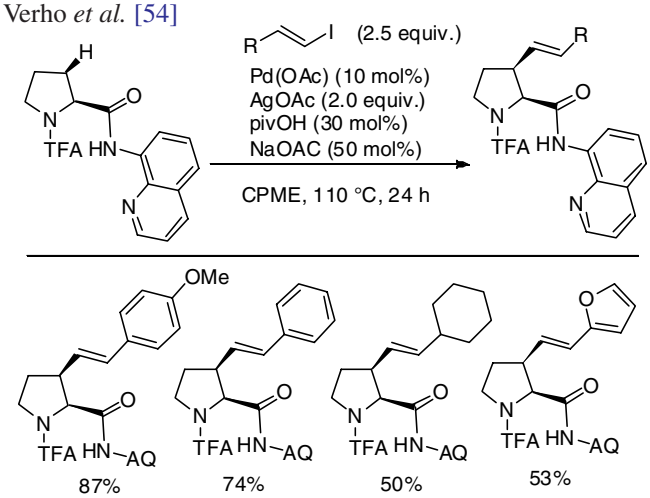


Schreiber *et al.* [54]



Scheme-XIII: Pd catalyzed 8-AQ mediated C(sp^3)-H arylation with aryl iodide

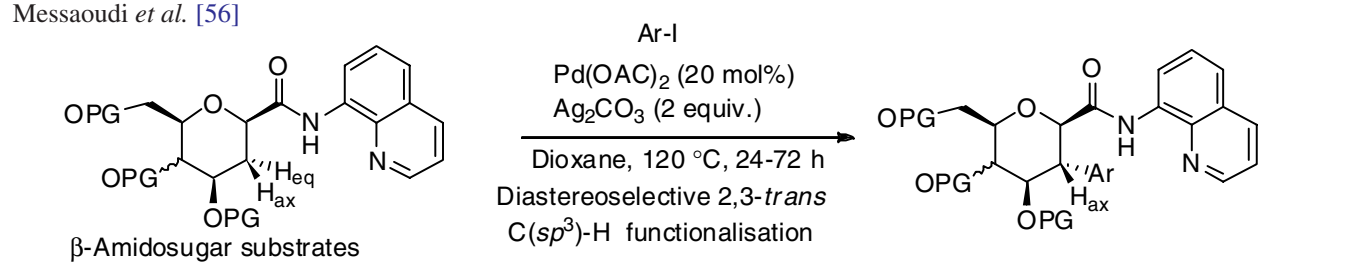
Verho *et al.* [54]

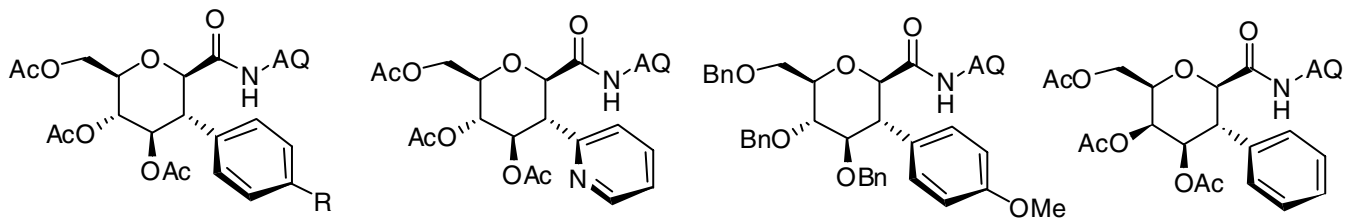


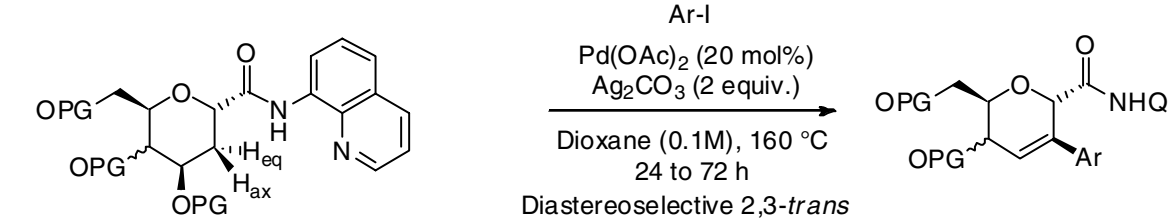
Scheme-XIV: C(sp^3)-H cross coupling of 8-AQ directed proline derivative with vinyl iodides

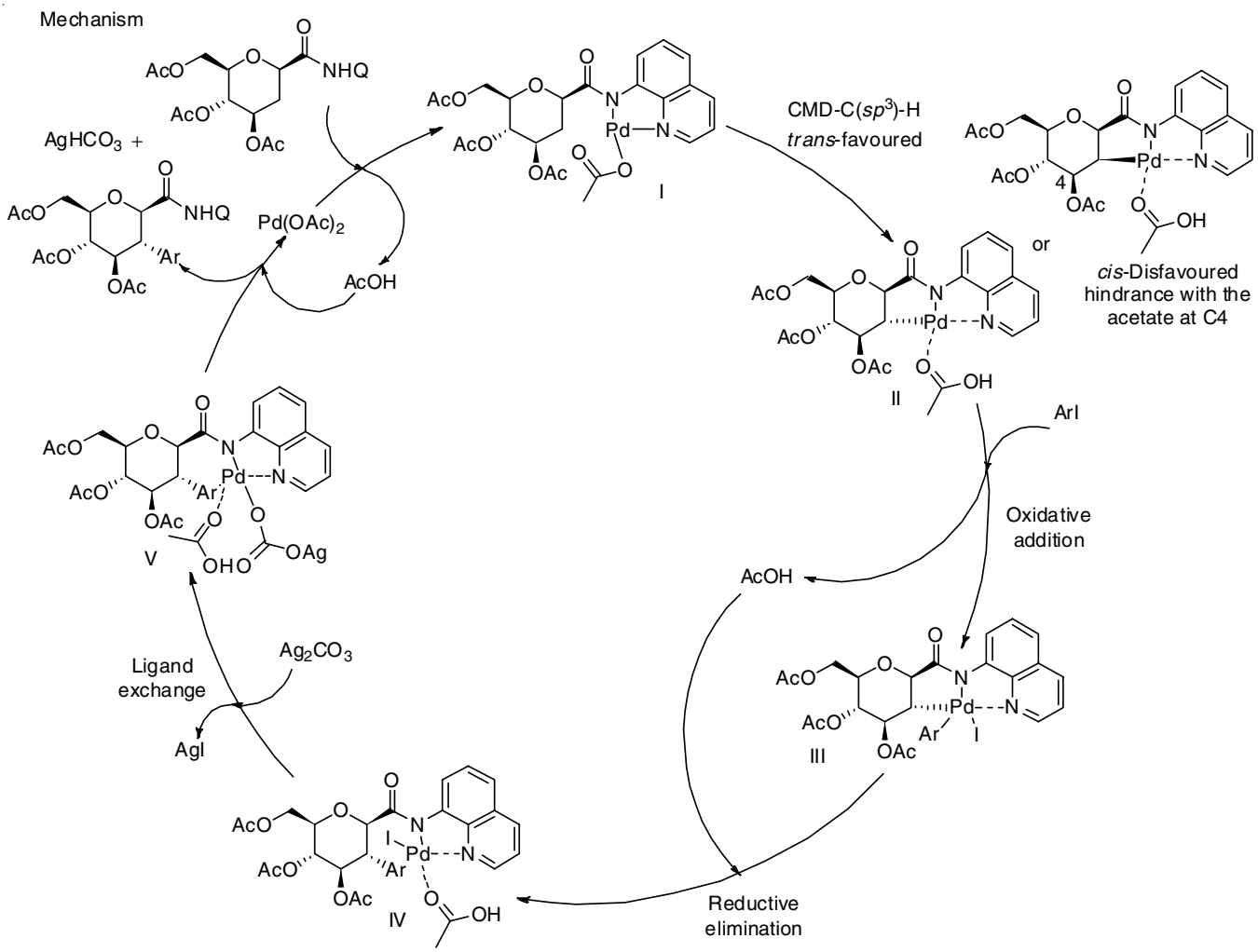
C(sp^2)-H functionalization: Now move our attention to β-Csp^2-H functionalization. In 2016, Ye *et al*. [57] described ligand controlled monoselective formation of aryl-C-$\Delta^{1,2}$-glycosides. *Ortho* C-H activated coupling occurs between varieties of TIPS protected glycal with diversely substituted

Messaoudi *et al.* [56]









Scheme-XV: C(sp^3)–H arylation of glycosides

8-aminoquinoline amides by utilizing L-proline as a ligand (**Scheme-XVI**). Based on experimental results authors proposed a mechanistic path, starting with the formation of palladacycle intermediate **A**. After that, oxidative addition followed by reductive elimination furnished product.

Recently, a remarkable work was reported by Chen *et al.* [58] in 2019, by using glycosyl chloride donors in presence of $Pd(OAc)_2$ catalyst underwent *ortho*-directed C(sp^2)-H glycosylation of aryls and heteroaryls equipped *N,N*-bidentate 8-aminoquinoline (AQ) directing group to synthesize *C*-aryl glycosides. Various directing groups were tested in the C(sp^2)–H functionalization process, showing that the presence of a bidentate moiety, as well as an unsubstituted *N*-amide atom, were crucial in this reaction, leading to the desired products (**Scheme-XVII**).

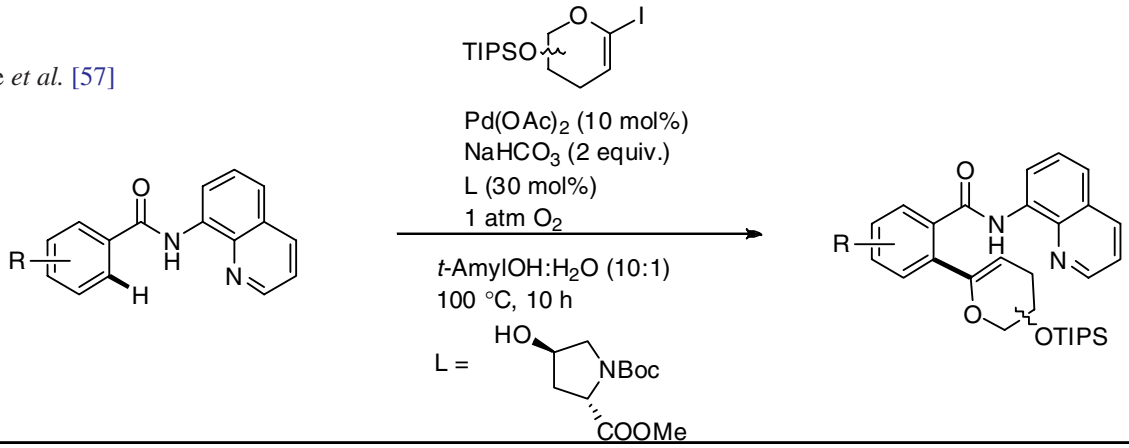
Recently, in 2021, Chen *et al.* [59] accessed *ortho*-directed C-H glycosylation of urea-and amide-linked bidentate auxiliaries equipped aryl amine with glycosyl donors (**Scheme-XVIII**). A wide variety of pyranose and furanose worked efficiently in this methodology, synthesizing products in excellent yield and with regio- and diastereoselectively.

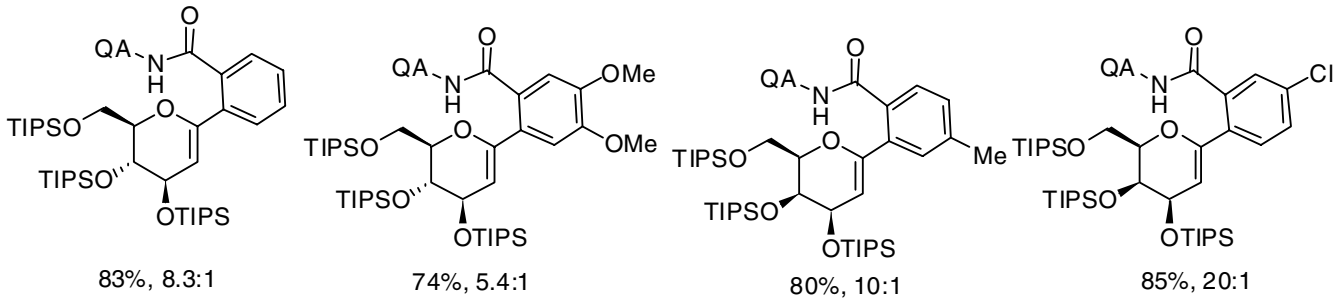
Same group in the same year described the synthesis of C-vinyl glycoside *via* C-H glycosylation of unactivated alkene in presence of Pd catalyst [60] (**Scheme-XIX**). The γ-C-H allylamines and δ-C-H homoallylamine derivative coupled with glycosyl donor, leading to the formation of regio- and stereoselective products. In 2015, Chen *et al.* [61] utilized 8-aminoquinoline mediated benzamide in presence of a Pd catalyst, which underwent mono-selective *ortho*-β-Csp^2-H alkylation with alkyl iodide, leading to alkylated product. Also in 2018, *N*-(8-quinolinyl) benzamide precursor treated under an electrochemical environment with I_2 *via* palladium catalyzed β-Csp^2-H iodination, generate corresponding product [62,63] (**Scheme-XX**).

In 2017, an efficient and generalized strategy for diastereoselective trifluoromethylthiolation of acrylamides *via* Pd catalysis by using 8-aminoquinoline as a directing group was accomplished by Basset *et al.* [64]. A wide variety of substituted acrylamide transformed into trifluromethylthiolated olefins with Z-selectivity (**Scheme-XXI**). Based on KIE the authors proposed the mechanism, which begins with the coordination of the catalyst with an auxilliary followed by C-H bond activation. Subsequently, oxidative addition then reductive elimination released desired product.

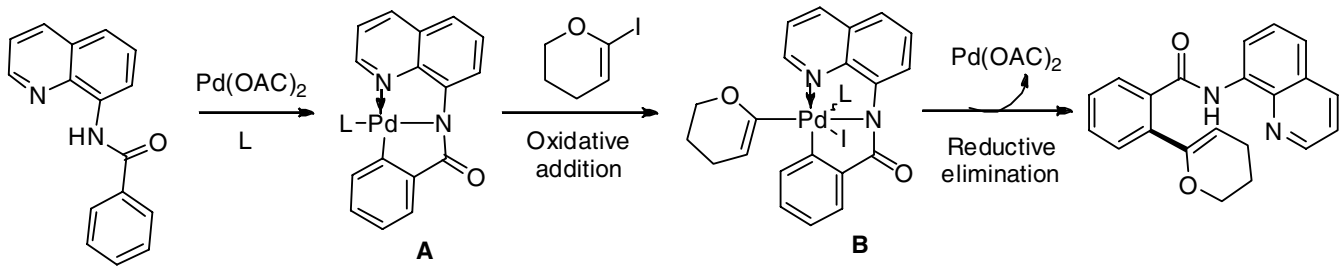
An additive free approach to form a variety of isothiazolones has been developed *via* Pd catalyzed C-H bond activation

Ye *et al.* [57]



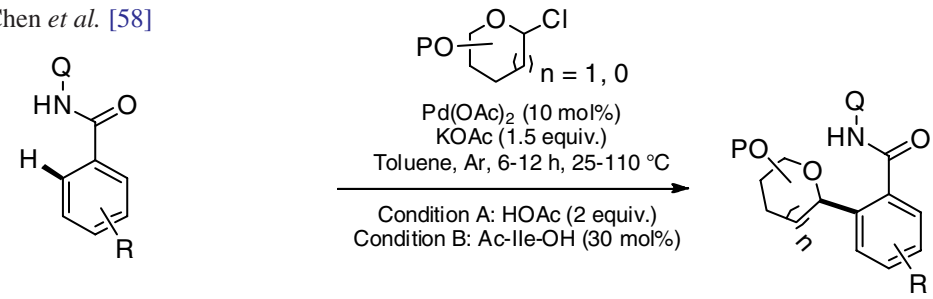


83%, 8.3:1 | 74%, 5.4:1 | 80%, 10:1 | 85%, 20:1

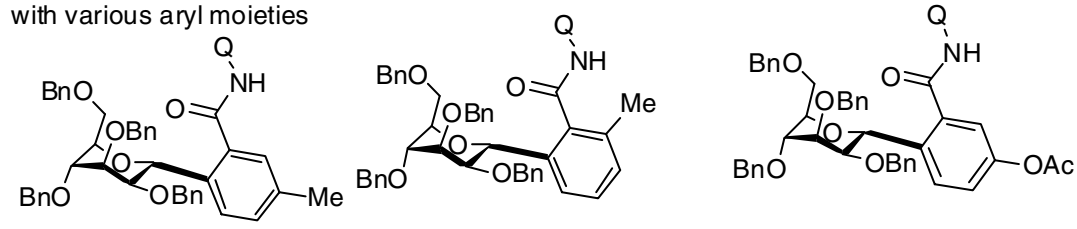


Scheme-XVI: Ligand controlled monoselective C-arylation

Chen *et al.* [58]



with various aryl moieties



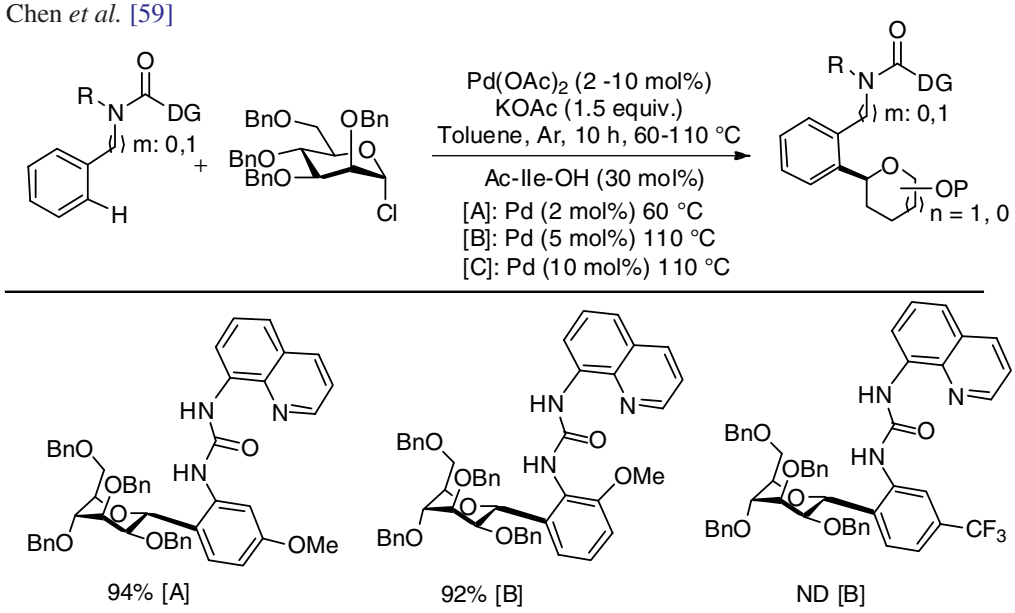
95%, A, 45 °C
90%, B, 45 °C

87%, B, 60 °C

40%, A, 110 °C
78%, B, 110 °C

Scheme-XVII: DG mediated C(sp^2)-H functionalization with glycosyl donors

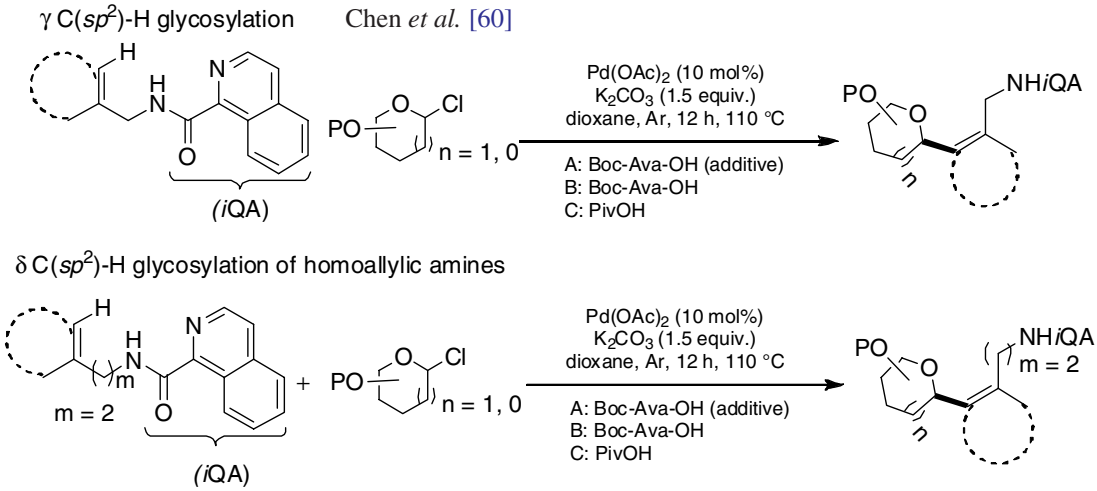
Chen *et al.* [59]



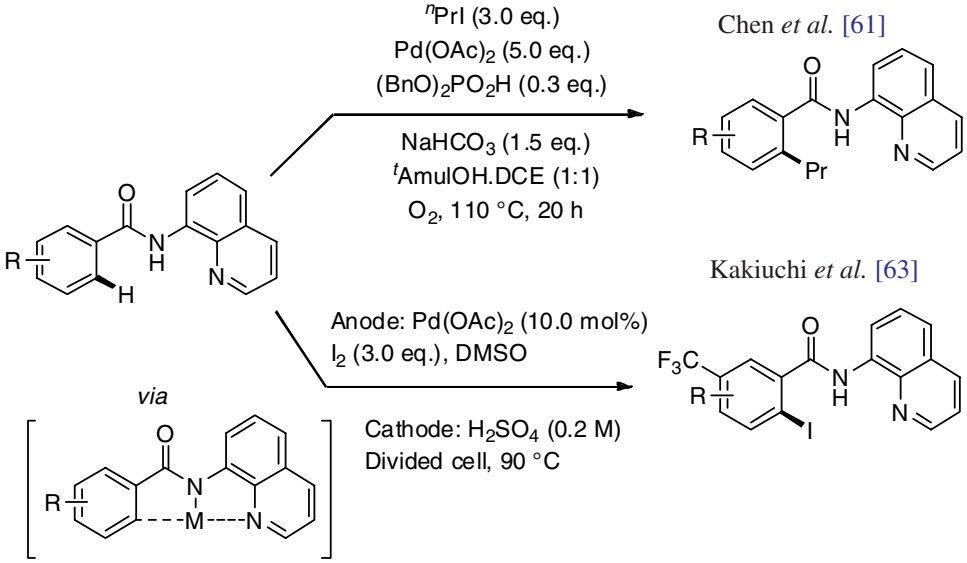
Scheme-XVIII: C-H glycosylation of bidentate auxiliaries equipped aryl amine with glycosyl donors

γ C(sp^2)-H glycosylation Chen *et al.* [60]

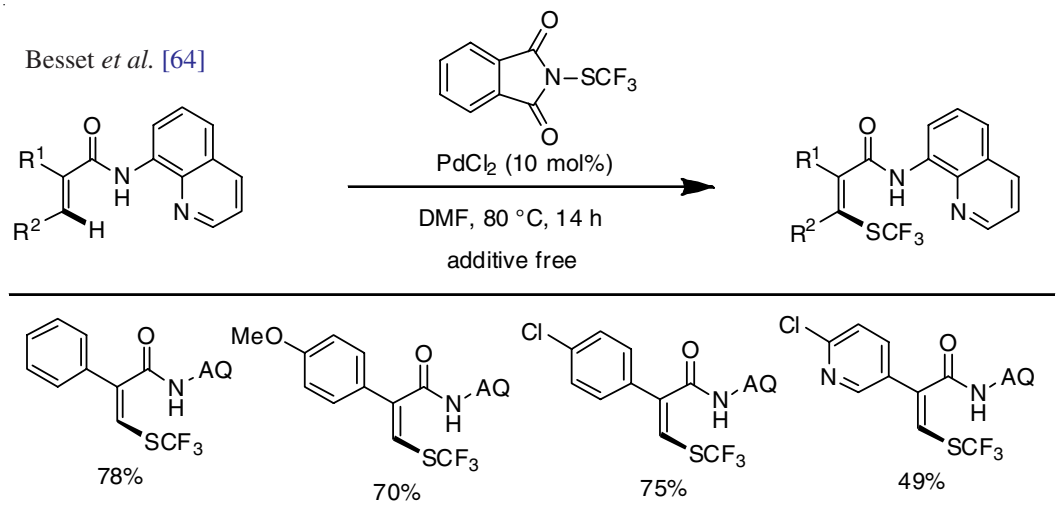
δ C(sp^2)-H glycosylation of homoallylic amines



Scheme-XIX: C–H glycosylation of unactivated alkene



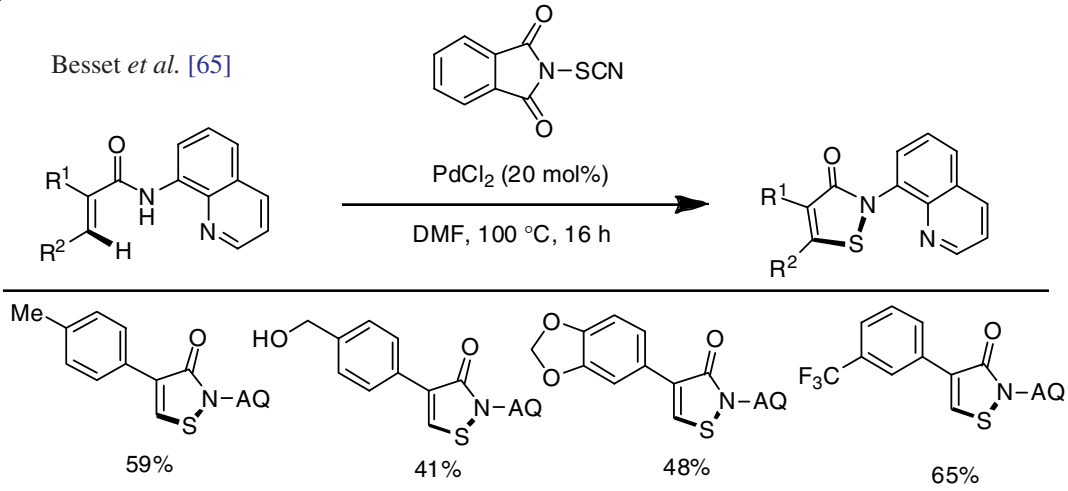
Scheme-XX: 8-Aminoquinoline auxiliary in diverse Csp^2-H functionalization



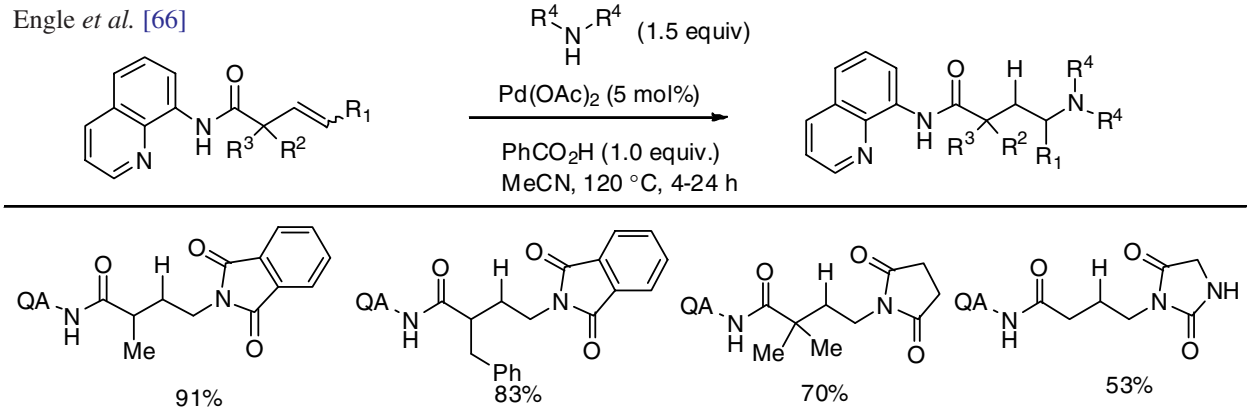
Scheme-XXI: Additive free diastereoselective trifluoromethylthiolation

of acrylamides by using 8-aminoquinoline as a directing group and an electrophilic SCF_3 reagent in 2019 by Besset *et al.* [65] (**Scheme-XXII**). In this, mild reaction conditions require $PdCl_2$ (20 mol%) in DMF at 100 ºC for 16 h. A reaction tolerates a wide variety of substrate scope including EWG, EDG and hetero-aromatic substituents on acrylamides to synthesize corresponding products up to 71% yield.

A generalized method by Engle *et al.* [66] in which 8-amino-quinoline serves as a directing group for regiocontrolled proto-palladation. Under mild reaction conditions. directing group mediated alkene amide treated with a variety of nitrogen nucleo-philes in presence of Pd catalyst undergoes hydroamination in MeCN at 120 ºC to afford corresponding products in good to excellent yield (**Scheme-XXIII**).



Scheme-XXII: Pd catalyzed C-H bond activation with acrylamides

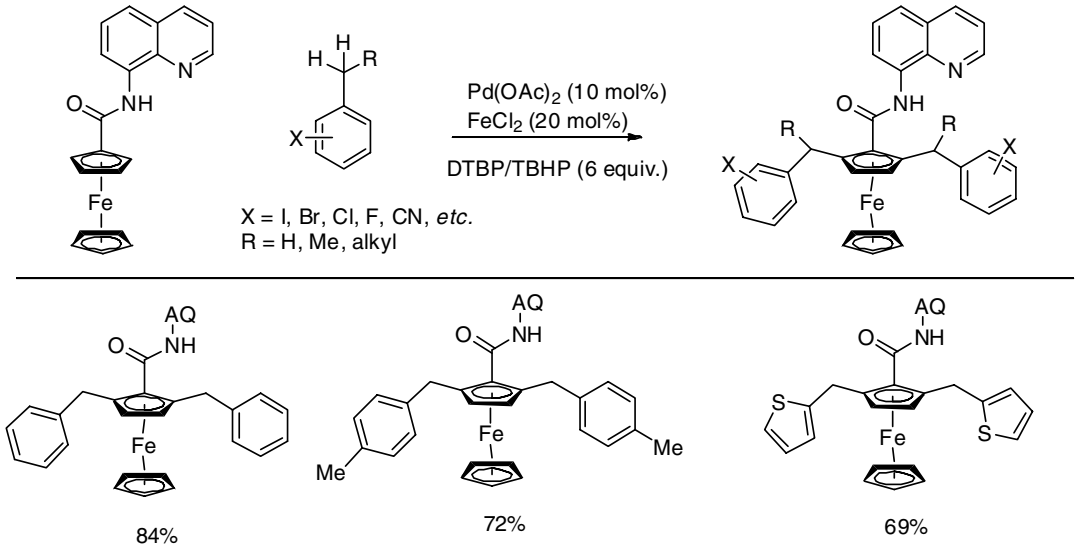


Scheme-XXIII: Synthesis of hydroaminated products

In 2017, a facile dual catalysis approach has been developed by Kumar & Sattar [67] in which 8-aminoquinoline mediated ferrocene coupled with substituted toluene, underwent Csp^2/Csp^3-H functionalization (**Scheme-XXIV**). This protocol affords highly functionalized products in good to excellent yield with chemo- and regio-selectively.

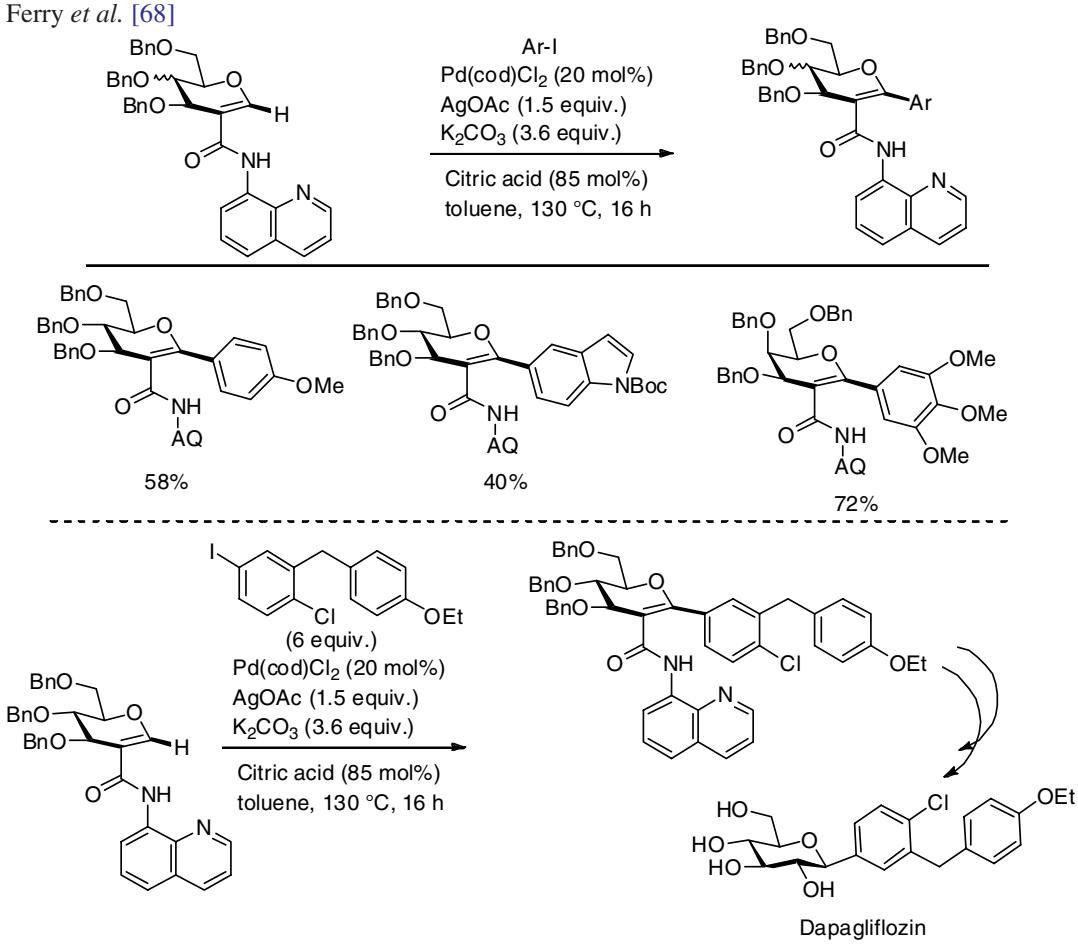
Ferry *et al.* [68] reported a palladium catalyzed efficient method for the synthesis of C-aryl/alkenyl glycosides (**Scheme-XXV**). In this method, Csp^2-H glycosylation occurs at anomeric position of glycal substrate in presence of Pd catalyst (20 mol%), AgOAc (1.5 equiv.), K_2CO_3 (3.6 equiv.) in toluene at 130 ºC for 16 h. It is noteworthy that this protocol gave access to a dapagliflozin analogue, which is used to treat type-2 diabetes.

Kumar *et al.* [67]



Scheme-XXIV: Palladium catalyzed regioselective coupling of 8-AQ assisted ferrocene

Ferry *et al.* [68]



Scheme-XXV: C-H Bond activation access to C-aryl/alkenyl glycosides

Conclusion

In this review, *N,N*-bidentate 8-aminoquinoline auxilliary proved to be facile for numerous metal-catalyzed C-H bond transformations. This auxilliary plays a crucial role in metal-catalyzed β-Csp^3/Csp^2-functionalization, owing to its versatility. Importantly, 8-aminoquinoline assists the regioselectivity in functionalized products. However, after using 8-aminoquinoline the removal of directing group required additional steps and late-stage modification needed a long template. So, these pitfalls need to be solved by a chemist with future developments.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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