Much effort has been devoted on controlling the regioselectivity and enantioselectivity in allylic substitution of substrates 1 or 2 (Scheme \(\PageIndex{1}\)). The palladium-catalyzed allylic substitution is versatile, however, the (E)-linear product 3 is often formed. Thus, the control of regioselectivity has been recently the main focus to provide product 4.

![Scheme \(\PageIndex{1}\)](image)

**4.1.1 Allylic Amination and Etherification of Allylic Alcohol Derivatives**

Chiral iridium complex having phosphoramidate 4a or 5a has been shown to catalyze the allylic amination of carbonate to give branched product with excellent enantioselectivity (Scheme \(\PageIndex{2}\)). An activated form of the iridium complex by *in situ* C-H activation at CH\(_3\) group of a hindered ligand 4a has been identified.

The direct reaction of allylic alcohols has been studied to give allylic amines in the presence of chiral iridium complex derived from [Ir(COD)Cl\(_2\)] and ligand 6 (Scheme \(\PageIndex{3}\)). In this reaction, sulfamic acid serves not only as a nitrogen source but also as an *in situ* activator of the hydroxyl group of the allylic alcohol.

![Scheme \(\PageIndex{2}\)](image)

![Scheme \(\PageIndex{3}\)](image)
Allylic amination is important for the construction of nitrogen-based heterocyclic compounds (Scheme \ref{Scheme:4}). The enantioselective intramolecular allylic amination has been accomplished using chiral iridium complex derived from \text{[Ir(CDD)Cl$_2$]} and ligand 7. Good enantioselectivity has been obtained upon activation using 1,5,7-triazabicyclo[4.4.0]undec-5-ene (TBD) as base. The catalytic system has also been used for the sequential aminations of \textit{bis} -allylic carbonate via an inter- followed by an intramolecular reactions.

Enantioselective allylic amination is also a powerful tool for the construction of natural products. For example, asymmetric desymmetrization of \textit{meso} -diol with \textit{p} -tosylisocyanate using chiral palladium complex gives easy access to chiral nitrogen-substituted heterocycles which are precursor for the synthesis of (-)-swainsonine (Scheme \ref{Scheme:5}).

The chiral palladium catalyzed enantioselective allylic amination has also been utilized for the total synthesis of (-)-tubifoline, (-)-dehydrotubifoline and (-)-strychnine (Scheme \ref{Scheme:6}).
The one-pot enantioselective synthesis of azacycle has been shown using a ruthenium-catalyzed ene-yne addition followed by a palladium-catalyzed asymmetric allylic amination (Scheme 7).

The regio- and enantioselective allylic etherification has been studied using chiral ruthenium complex. For example, planar-chiral cyclopentadienyl ruthenium complex 9 catalyzes efficiently the reaction of cinnamoyl chloride with 3-methylphenol with high enantioselectivity and yield (Scheme 8).

Enantioselective allylic substitutions of carbonates with a diboron using copper(I)-based catalysts has been demonstrated. For example, Cu(I)-phosphine complex generated in situ from Cu(O-t-Bu) with ligand 10 has been shown to catalyze the reaction of allyboronate with carbonate in excellent regioselectivity and enantioselectivity (Scheme 9). Addition-elimination mechanism having the generation of Cu-alkene π-complex and borylalkylcopper intermediate has been suggested.
4.1.2 Reaction of π -Allyl Intermediates

Nucleophilic attack of an amine to a π -allyl intermediate can afford an allylic amine derivative. For example, palladium complex derived from [Pd(C₃H₅)Cl]₂ and ligand 11 catalyzes the reaction of racemic vinyloxirane with phthalimide in nearly quantitative yield (Scheme 10). Involvement of the hydrogen bond of the nucleophile to the oxygen leaving group is proposed to deliver the nucleophile to the adjacent carbon to provide the target molecule. The process has been utilized for the synthesis of (+)-broussonetine G.

Palladium based systems has also been utilized for the cycloaddition reaction of epoxides and aziridines with heterocumulenes (Scheme 11).

Enantioselective copper(I)-catalyzed substitution reactions of propargylic acetates with amines has been explored. For examples, copper complexes derived from copper(I) salts and ligands 12 and 13 catalyze the reaction of propargylic amination with 85% ee (Scheme 12).
Scheme 1 (PageIndex{11})

Scheme 2 (PageIndex{12})