

Highlight Review**Collaborative Interaction of Carbon–Carbon Unsaturated Bond Groups with Transition-metal Catalysts for C–H Bond Functionalization**

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Dr. Tamejiro Hiyama was appointed Assistant Professor at Kyoto University in 1972, completed his Ph.D. under the supervision of Professor Hitosi Nozaki at Kyoto University in 1975, and spent a postdoctoral year at Harvard University working with Professor Yoshito Kishi. In 1981 he started his research as a Principal Investigator at the Sagami Chemical Research Center. In 1992 he moved to Research Laboratory for Resources Utilization, Tokyo Institute of Technology, as a full professor and then to the Graduate School of Engineering, Kyoto University, in 1997. Since retirement from Kyoto University in 2010, he has been at Chuo University as a RDI Professor. His research stems from invention of synthetic methods for biologically active agents and materials like liquid crystalline and light emitting materials.

Abstract

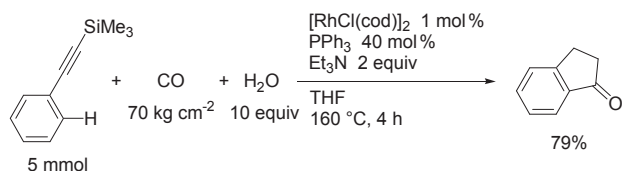
Alkynes, alkenes, and thiophenes are found to behave as a directing group for C–H bond activation by a transition-metal catalyst. This collaborative interaction led to the discovery of not only simple intramolecular cyclizations but also carbon–carbon bond formation or annulation reactions with other reactants involving such unsaturated bond-directing groups. This high-light review discusses the recent progress in this sort of novel synthetic tools.

Keywords: C–H bond activation | Metal catalyst | Carbon–carbon unsaturated bond

Introduction

As is obvious, alkenes and alkynes have been usually utilized as addition acceptors to form functionalized alkanes and alkenes, respectively, in synthetic organic chemistry. In the field of organometallic chemistry, these molecules can coordinate various metal centers to form η^2 -ligated metal complexes.¹ This elementary reaction is followed by various metal-mediated addition reactions or enhancement of selectivity and reactivity of metal centers. For example, the latter character is responsible for regioselective hydrosilylation² reaction and palladation of allenes.³

On the contrary, a wide variety of catalytic reactions involving selective C–H bond activation by a directing group have been the topic of recent research since *ortho*-alkylation of arenes directed by an acetyl group was disclosed as a path-breaking invention.⁴ At present, various lone pair electron-donating functional groups such as pyridyl, amide, and acetyl are utilized as a directing group due to effective and rigid ligation potential. With this respect, unsaturated bond groups also should have capability to act as the directing group. In 1988, Takahashi reported the reaction of diarylethyne with CO and H₂O in the presence of Co₂(CO)₈ and PPh₃ catalysts and Et₃N, giving 2-indanone derivatives.^{5,6} Later, Takeuchi demonstrated that silyl-ethynylarenes underwent a similar annulation reaction with CO and H₂O catalyzed by [RhCl(cod)]₂ and PPh₃ to give indanone derivatives via hydrosilylation (Scheme 1).⁷ Importantly, the key mechanistic step of this reaction is proposed to be *ortho*-C–H bond activation by the rhodium complex coordinated by the alkynyl group. Incidentally, Grotjahn reported that *ortho*-C–H bond in diphenyl ketene was activated by η^2 -C=O-coordinated chloroiridium complex to form aryliridium complexes.⁸ Thus, these reports strongly suggest that alkynes can work as a directing group in a manner similar to the α -ligand type functional groups. However, as mentioned above, the unsaturated bonds are normally reactive enough to undergo various addition reactions with nucleophiles, electrophiles, and radicals, thereby losing the role as the directing group. Therefore, unsaturated bond-directed



Scheme 1.

C–H bond activation has remained a challenging issue. Recently, carbon–carbon unsaturated bonds were gradually utilized as a directing group by effectively enhancing the coordination effect or/and by involving synthetic transformations.⁹

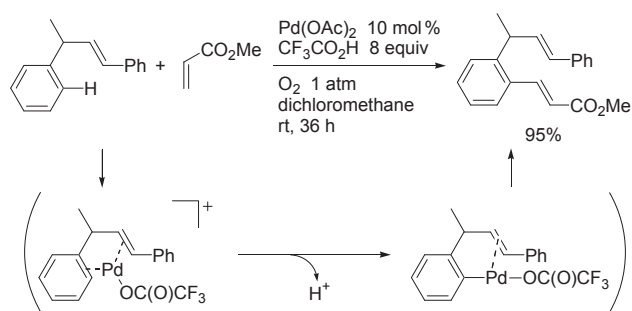
In this article, representative examples of carbon–carbon bond formation reactions and annulation reactions by carbon–carbon unsaturated bond-directed C–H bond activation are briefly summarized. Also, in this review, catalytic carbon–carbon bond functionalizations directed by a nitrile group are not included, since these reactions have been discussed previously.^{9a}

C–C Bond Formation Reaction

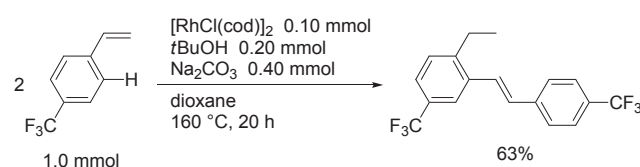
As alkynes and alkenes are highly reactive, it is difficult to maintain the structure of the original unsaturated bonds during the reaction course through C–H bond activation reactions. Suppression of oligomerization of unsaturated substrates is also required.

In 2012, Cheng reported that allyl-substituted arenes underwent *ortho*-alkenylation with electron-deficient alkenes under Pd(OAc)₂ catalyst with trifluoroacetic acid and O₂ (Scheme 2).¹⁰ Vinylic and homoallylic C=C bonds connected to arenes do not activate *ortho*-C–H bonds, suggesting that the location of the C=C bond is an important factor. The highly electrophilic [Pd(OC(O)CF₃)]⁺ is expected to be generated in the presence of trifluoroacetic acid, which is effectively coordinated by the C–C double bond and *ortho*- and *ipso*-aryl carbons and cleaves *ortho*-C–H bond electrophilically. Subsequent insertion of alkene and β -elimination afford alkenylation products.

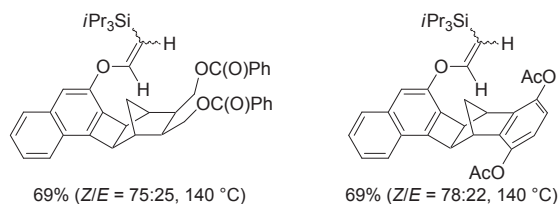
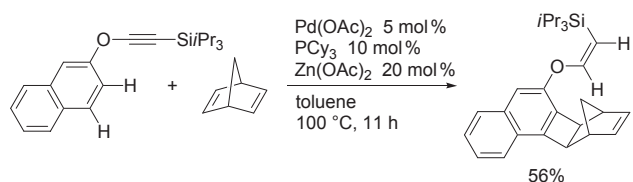
In light of the fact that alkynes and alkenes were often used as a dihydrogen acceptor, such unsaturated C–C bonds may be used as the directing group and dihydrogen acceptor to achieve dehydrogenative C–C bond forming reactions. In accord with this line, Tobisu and Chatani reported that styrene derivatives underwent rhodium-catalyzed homo-alkenylation of *ortho*-position with the hydration of a directing alkenyl group to give dimerization products (Scheme 3).¹¹ These authors proposed that the catalytic reaction starts with the oxidative cyclization of



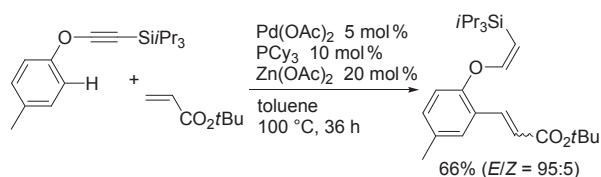
Scheme 2.



Scheme 3.



Scheme 4.

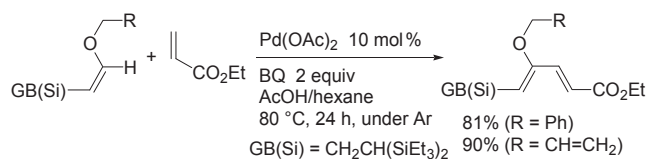


Scheme 5.

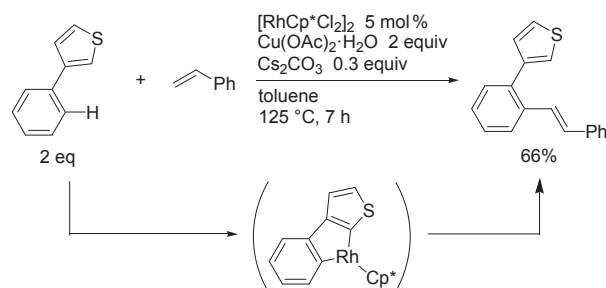
the π -Rh complex to which both vinyl C–C bond and *ortho*-*ipso*-aryl carbons participate to form a rhodacycle.

We have demonstrated that an alkyoxy group (–O–C≡C–) behaves as an electron-deficient alkyne group and thus is a highly reactive directing group for a palladium catalyst. For example, the reaction of alkyoxynaphthalenes with norbornadiene took place to form the corresponding naphthocyclobutene derivative with a vinyloxy group (Scheme 4).¹² This transformation is achieved by the cleavage of C3–H and C4–H bonds and the transfer of these two hydrogens to the silylethynyl group. Various bicyclic alkenes can be applied to this annulation reaction. Moreover, alkyoxyarenes react with an electron-deficient alkene in the presence of catalytic amounts of Pd(OAc)₂, PCy₃, and Zn(OAc)₂ to give an *ortho*-alkenylated product via hydrogenation of alkyoxy groups (Scheme 5). Of note, bulky silyl groups are usually introduced to the alkyoxy terminal carbon for successful transformation, which inhibit the nucleophilicity of this terminal carbon and the dimerization of alkyne ethers as an intrinsic side reaction due to steric repulsion. This factor is essential in the following reactions using alkyne ethers.

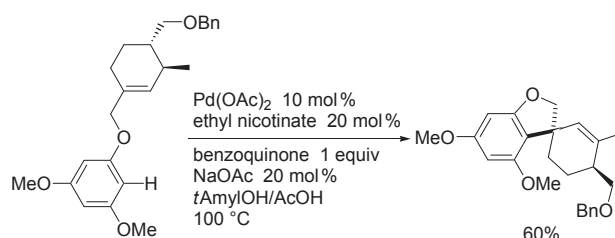
A combination of Pd(OAc)₂ with a benzyloxy group can activate C α –H bond of vinyl ethers, leading α -alkenylation to form a 1,3-diene product (Scheme 6).¹³ Both alkenyl and phenyl moieties might coordinate the palladium catalyst to activate the C α –H bond via the electrophilic attack of Pd(OAc)₂ to the enol double bond. Allyl vinyl ether can also undergo similar α -alkylation, whereas propargyl vinyl ethers remain intact. Thiophene ring is similarly used as a formal directing group. Satoh and Miura reported that 3-thienylbenzene underwent *ortho*-alkenylation with olefin in the presence of [RhCp*Cl₂]₂ (Cp*: pentamethylcyclopentadienyl) and Cs₂CO₃ catalyst, and Cu(II) as an oxidant (Scheme 7).¹⁴ A rhodacycle is proposed as an intermediate, which is generated via cleavage of *ortho*-C–H bond in benzene and C2–H bond in thiophene.



Scheme 6.



Scheme 7.



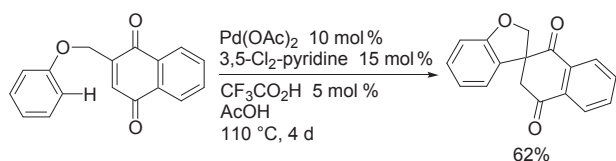
Scheme 8.

Cyclization Reactions

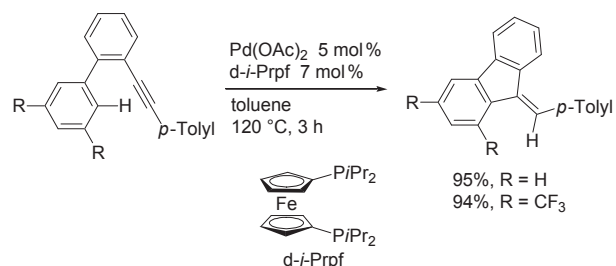
One of the most common behaviors of unsaturated bond-directing groups is an intramolecular insertion reaction to form cyclic products. Once a target C–H bond is cleaved and metalated, insertion of the directing unsaturated bond follows easily and smoothly without regeneration of C–H bond and undesired reaction.

Stolz reported that 3-pentenylindoles and electron-rich allylarenes underwent cyclization via C2–H bond activation by the Pd(OAc)₂/ethyl nicotinate catalytic system to form a corresponding cyclic product.¹⁵ For example, an optically active cyclohexenylmethyl aryl ether underwent cyclization in a diastereoselective manner to give a tricyclic product having a quaternary carbon center (Scheme 8).^{15b} Although Stolz did not propose alkenyl-directed C–H bond activation, these cyclizations seem to be promoted by the alkenyl group. Aryloxymethyl-1,4-naphthoquinones undergo intramolecular insertion of the C=C bond into *ortho*-C–H bond in the presence of Pd(OAc)₂, 3,5-Cl₂-pyridine, and trifluoroacetic acid catalysts (Scheme 9).¹⁶ The reaction is initiated by ligation of the electron-deficient C=C bond in 1,4-naphthoquinone to the palladium center, which enhances the electron deficiency for electrophilic C–H bond activation.

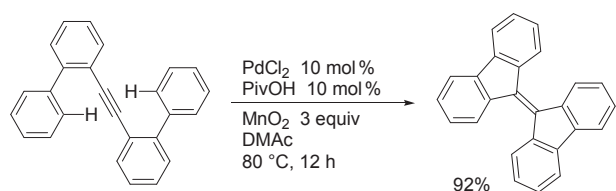
Alkyne moieties are a reactive directing group for intramolecular insertion reactions. 2-Alkyne biaryls undergo *exo-syn*-insertion reaction via C2'–H bond activation in the presence of Pd(OAc)₂ and bulky 1,1'-bis(diisopropylphosphino)ferrocene



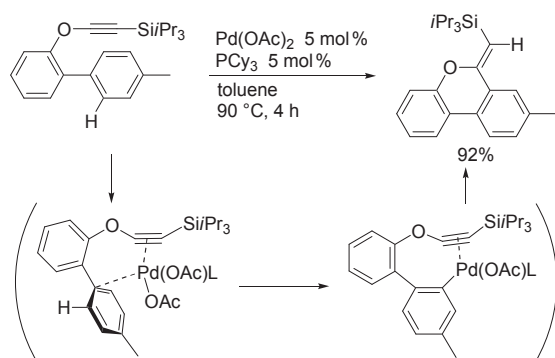
Scheme 9.



Scheme 10.



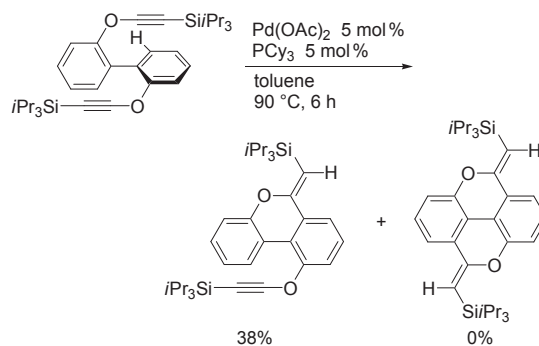
Scheme 11.



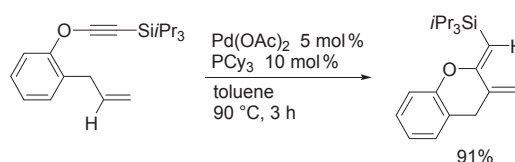
Scheme 12.

(*d-i-Prpf*) catalysts to form 9-methylene-fluorene derivatives (Scheme 10).¹⁷ Under the similar conditions, bis(biaryl)alkynes undergo double cyclization via both C2'-H bond activations in two biaryl moieties in the presence of catalytic amounts of PdCl₂ and pivalic acid and MnO₂ (3 equiv) in dimethylacetamide (DMAc) to form 9,9'-bifluorenylidene derivatives (Scheme 11).¹⁸

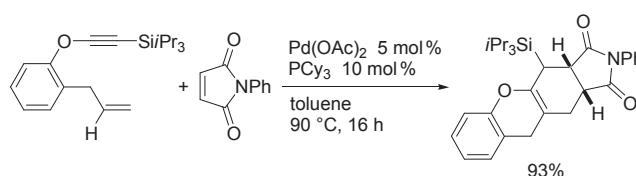
We showed that 2-silylethynoxy biaryls underwent intramolecular hydroarylation via C2'-H bond activation by a combination of Pd(OAc)₂/PCy₃ catalyst to give dibenzopyran derivatives (Scheme 12).¹⁹ In the case of the reaction using 2,2'-bis(alkynoxy)biphenyl, the monoannulation product is only provided without the generation of the double annulation product (Scheme 13). Based on these results, this reaction is considered to be triggered by the formation of both the



Scheme 13.



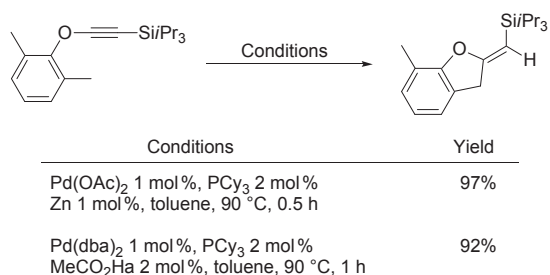
Scheme 14.



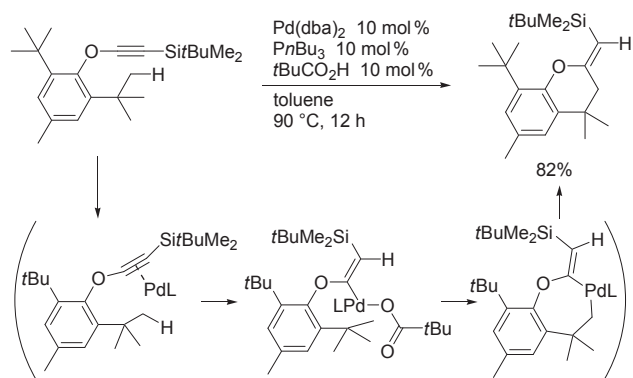
Scheme 15.

alkynoxy- and twisted aryl-ligated complexes, followed by C2'-H bond activation, leading to final products via intramolecular insertions. This concept is applicable to hydroalkenylation. 2-Allylphenyl silylethynyl ethers are converted into the corresponding 2,3-bismethylenechromanes (Scheme 14).²⁰ In particular, the same reaction in the presence of *N*-phenylmaleimide furnishes a condensed tetracycle, which is produced by sequential hydroalkenylation and a [4+2]-cycloaddition reaction (Scheme 15). Moreover, this C-H activation method can be applied to aliphatic C-H bond activation for straightforward intramolecular annulations. 2-Benzylic C-H bonds at the alkyoxyarenes are smoothly activated in the presence of Pd(OAc)₂, PCy₃, and Zn as a reductant to form Pd(0) and proceed hydrobenzylation to give 2-silylmethylene-2,3-dihydrobenzofurans (Scheme 16).²¹ The Pd(*dba*)₂, PCy₃, and acetic acid catalytic conditions also afford the same product, albeit in a slightly lower yield. Based on the latter catalytic conditions, the non-activated C(sp³)-H bond in the *tert*-butyl group can be activated in the presence of Pd(*dba*)₂, *Pn*Bu₃, and pivalic acid catalysts to form chromane derivatives (Scheme 17).²² This hydroalkylation is probably initiated by the formation of vinylpalladium pivalate from the reaction of η²-alkyne-coordinated palladium(0) complex with pivalic acid by reference to Yin and Han's mechanistic consideration.²³ Subsequent C-H activation proceeds via the CMD pathway.²⁴

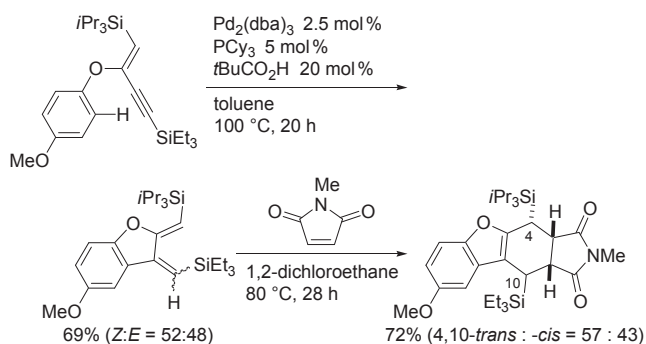
The mechanistic concept of the collaboration of Pd(0) and acid catalysts with alkynyl groups is applied to *exo*-



Scheme 16.



Scheme 17.

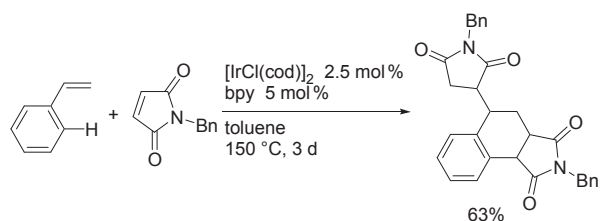


Scheme 18.

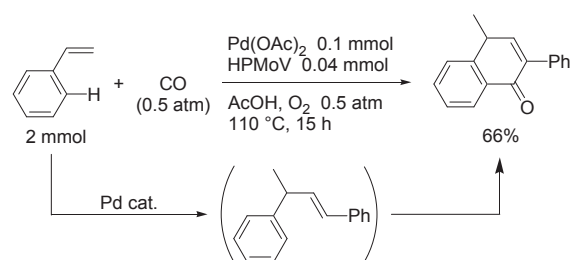
hydroarylation of C–C triple bond in enyne substrates, 2-aryloxy-1,4-disilylbut-1-en-3-yne, via *ortho*-C–H bond activation (Scheme 18).²⁵ The products, 2,3-bismethylene-2,3-dihydrobenzofurans, undergo [4+2]-cycloaddition with dienophiles to form condensed cyclic compounds. That is, this reaction system allows to construct condensed cycles from the enynes with 100% atom economy. The final condensed cyclic products can be obtained via the one-pot sequence involving *exo*-hydroarylation and [4+2]-cycloaddition.

Annulation Reactions

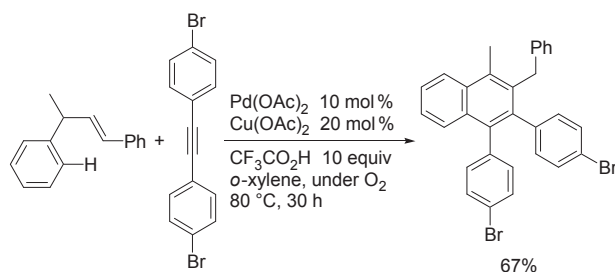
As shown in Scheme 1, the unsaturated bond-directed C–H bond activation for the insertion sequences is better suited for a combination with different alkynes and alkenes, and carbon monoxide, which undergo annulation reaction to produce multifunctionalized cyclic products.



Scheme 19.



Scheme 20.

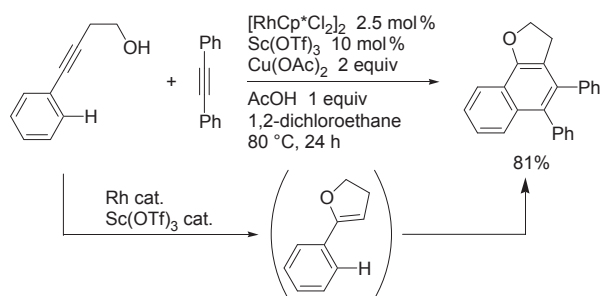


Scheme 21.

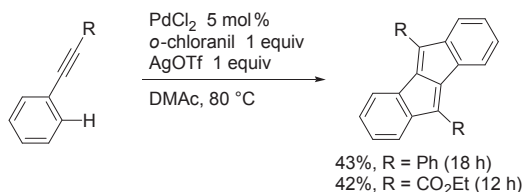
In 2005, Kiyooka reported that styrene and its derivatives undergo double incorporation/annulation reaction with two *N*-benzylmaleimides in the presence of catalytic amounts of [IrCl(cod)]₂ and 2,2'-bipyridyl (bpy) to give alkylated and annulated products (Scheme 19).²⁶ The transformation is proposed to be initiated by the generation of η^2 -alkene-coordinated iridium cation, which undergoes oxidative addition of the C–H bond.

Ishii showed that styrene or its derivatives transformed to naphthalen-1(4*H*)-one derivatives in the presence of Pd(OAc)₂ and molybdovanadophosphate (H₅PMo₁₀V₂O₄·26H₂O, HPMoV) under CO and O₂ atmosphere (Scheme 20).²⁷ In this reaction, α -methylallylbenzene is formed as an initial product, which undergoes carbonylation via *ortho*-C–H bond activation directed by the generated allyl group as is the case of Scheme 2. HPMoV acts as an oxidant with O₂ for the regeneration of Pd(II) from Pd(0) during both alkene dimerization and carbonylation reactions. Cheng reported that allylarenes underwent annulation reaction with internal alkynes instead of alkenes to form 1,2,3,4-tetrasubstituted naphthalenes (Scheme 21).²⁸ Of note, bis(*p*-bromophenyl)acetylene is applicable to this annulation, showing that *ortho*-C–H bond activation overrides the inherent reactivity of the aryl C–Br bond under this reaction system.

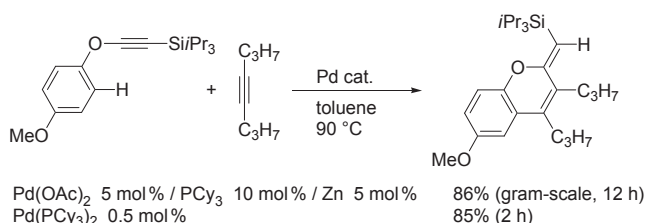
4-Arylbut-3-yn-1-ol and its derivatives undergo annulation with alkynes in the presence of [RhCp*Cl₂]₂, Sc(OTf)₃, and Cu(OAc)₂ as an oxidant for rhodium complex to give 2,3-



Scheme 22.



Scheme 23.

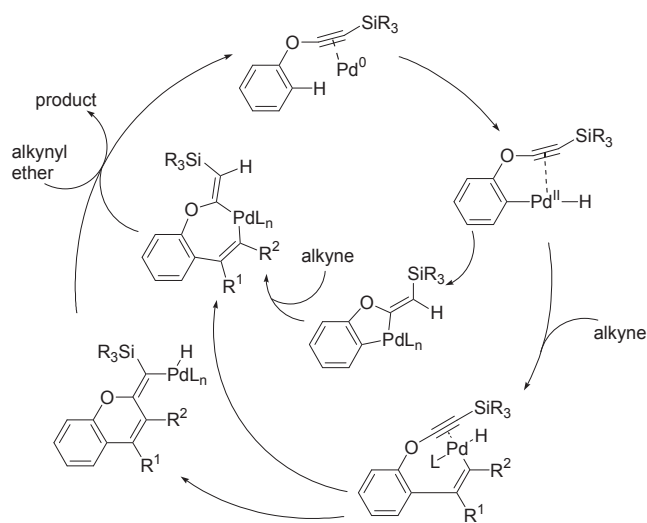


Scheme 24.

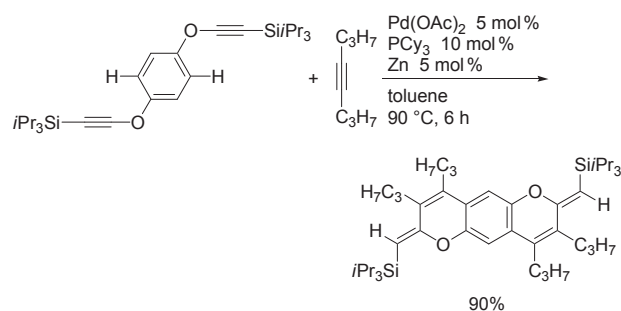
dihydronaphtho[1,2-*b*]furans (Scheme 22).²⁹ The reaction forms 4,5-dihydrofurylarenes as intermediates by the active rhodium catalyst [Cp**Rh*(III)] generated from [RhCp*Cl₂]₂ and Sc(OTf)₃. Subsequent *ortho*-C–H bond cleavage may occur directed by the vinyloxy group.

Diarylethynes undergo *ortho*-C–H bond cleaving annulation to give dibenzo[*a,e*]pentalenes in the presence of PdCl₂ catalyst, *o*-chloranil as an oxidant, and AgOTf (Scheme 23).³⁰ Ethyl phenylpropiolate also undergoes the similar annulation reaction regioselectively to give diethyl dibenzo[*a,e*]pentalene-5,10-dicarboxylate. The observed substrate reactivity and mechanistic studies support a scenario of alkyne-directed, *ortho*-selective, electrophilic C–H palladation, which triggers the transformation.

We have demonstrated that the C–H bond activation strategy by the collaboration of an alkynoxy group with a palladium catalyst allows to construct a variety of oxacyclic compounds by the annulative reaction using many alkynes and alkenes. Silylethynoxyarenes are transformed to 2-silylmethylene-2*H*-chromene derivatives through a double *ortho*-C–H bond activation/annulation with other alkynes in the presence of Pd(OAc)₂, PCy₃, and Zn (Scheme 24).³¹ The double annulation reaction is proposed to be initiated by the formation of a η²-alkynoxy-coordinated palladium(0) complex, which shows oxidative addition of the *ortho*-C–H bond (Scheme 25). Subsequent insertion of alkynes into the aryl–Pd bond and following intramolecular insertion lead to a vinylpalladium hydride or a 7-membered palladacycle. Finally, reductive elimination results in



Scheme 25.

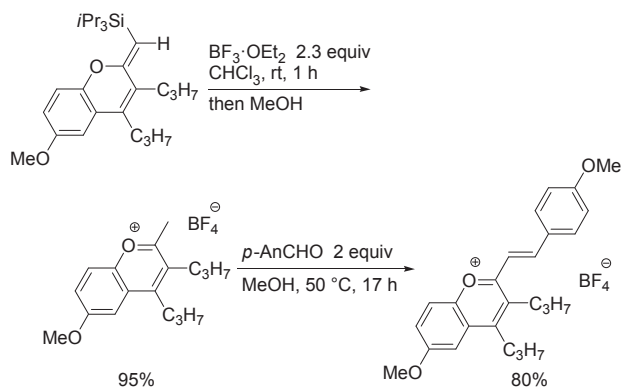


Scheme 26.

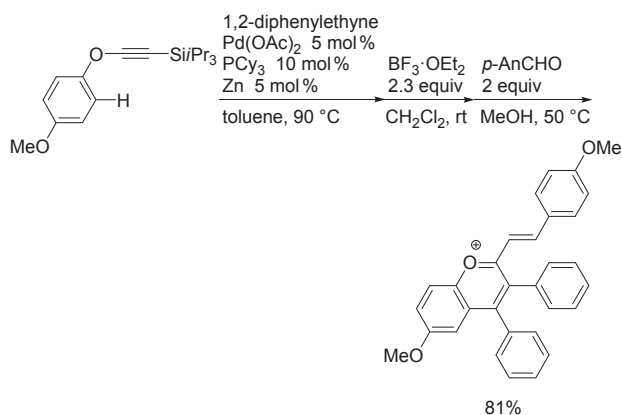
the formation of the product and regenerates the palladium(0) complex. Alternatively, once the oxidative addition occurs, it is also considered that intramolecular insertion generates a 5-membered palladacycle followed by insertion of alkynes to form the 7-membered palladacycle. The mechanism of the reaction was also examined by a theoretical study.³² The double insertion/annulation reaction is applicable to the double annulation of bis(alkynoxy)benzene with two alkynes, giving a condensed tricyclic product (Scheme 26).

Additionally, treatment of the products with boron trifluoride forms 2-methylbenzopyrylium tetrafluoroborates, which react with *p*-anisaldehyde to lead to 2-(*p*-anisylalkenyl)benzopyrylium tetrafluoroborates (Scheme 27).³³ Both the resulting pyrylium salts exhibit fluorescence at solid state under UV irradiation (365 nm). The effective solid-state emission is attributed mainly to tetrafluoroborate counter anion to interfere an interaction between the benzopyrylium planes. Of note, 2-(*p*-anisylalkenyl)benzopyrylium tetrafluoroborates can be formed via the one-pot sequential palladium-catalyzed double insertion annulation, treatment with boron trifluoride, and reaction with *p*-anisaldehyde (Scheme 28).

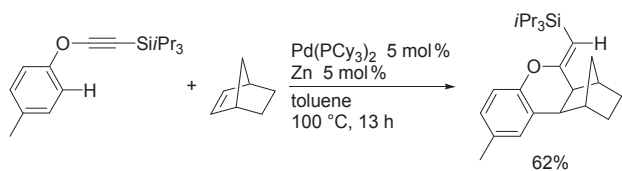
This palladium-catalyzed double intermolecular insertion/annulation system using aryl silylethynyl ethers is applicable to the production of various cyclic compounds. The reaction with norbornene proceeds in the presence of zero-valent palladium catalyst, Pd(PCy₃)₂ and Zn to form 2-silylmethylenechromene



Scheme 27.

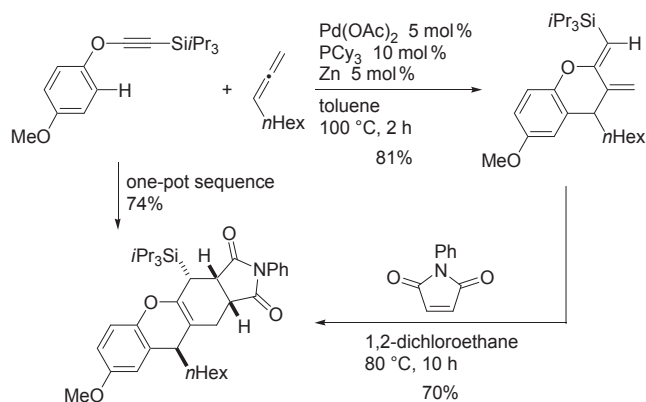


Scheme 28.

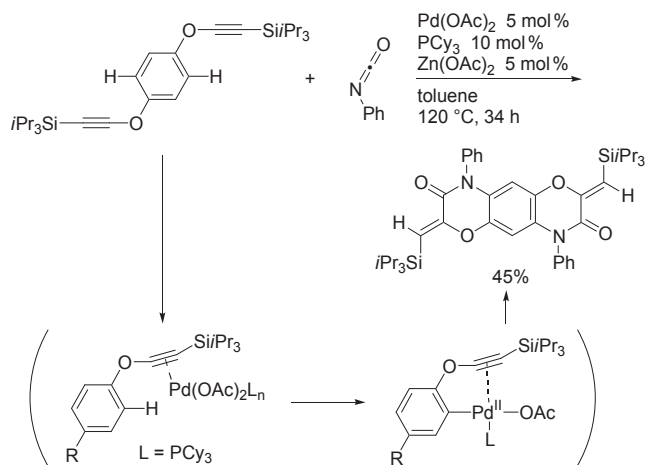


Scheme 29.

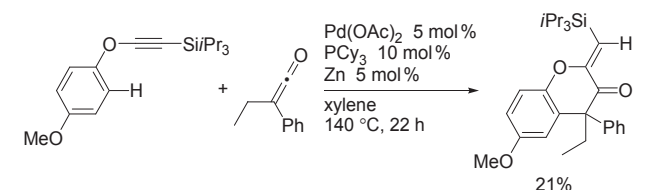
derivatives (Scheme 29).³⁴ Using allenes as the reaction partner, the annulation takes place selectively via the insertion of the internal C–C double bond in allene in the presence of Pd(OAc)₂, PCy₃, and Zn to provide 2,3-bismethylenechromane derivatives (Scheme 30).³⁵ This product can undergo [4+2]-cycloaddition with dienophiles to furnish the corresponding condensed cycle. The two-step, one-pot operation allows facile access to this condensed cycle. Arylisocyanates are applicable to this annulation with alkynyloxyarenes under Pd(OAc)₂, PCy₃, and Zn(OAc)₂ catalytic conditions. For example, the reaction of a bisalkynyloxybenzene with phenylisocyanate produced a benzo[1,2-*b*:4,5-*b'*]bis[1,4]oxazine-3,8-dione (Scheme 31).³⁶ In this case, *ortho*-C–H bonds are activated probably via a concerted metalation/deprotonation (CMD) pathway. These reaction conditions allow to use ketenes to form 2-methylene-chroman-3-ones (Scheme 32). The benzoxadione products from arylisocyanates also exhibit solid-state luminescence under UV irradiation. The electron-deficient acryl amide moiety in the product promotes



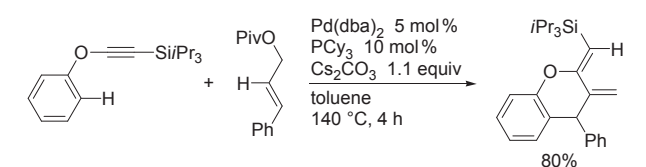
Scheme 30.



Scheme 31.



Scheme 32.



Scheme 33.

intramolecular CT transitions and bulky triisopropylsilyl group and an aryl group on nitrogen interfere with the intermolecular interaction, thereby contributing to solid-state emission.

Intermolecular annulation of aryl silyl ethynyl ethers with α - or γ -substituted allylpivalates takes place in the presence of Pd(dba)₂, PCy₃, and Cs₂CO₃ as a stoichiometric amount of base to give *exo*-bismethylene chromane derivatives (Scheme 33).²⁰

This reaction is achieved via activation of two C–H bonds: *ortho*-C–H bond in aryl silylethynyl ethers and β -C–H bond in allylpivalates, regarding a rare and environmentally benign annulation reaction. The annulation reaction takes place via a π -allylpalladium intermediate because both α - and γ -phenyl allyl pivalates provide the same annulation product having a phenyl group at C4.

Conclusion

Over the last decade, the synthetic strategy involving C–H bond activation by the use of a C–C unsaturated directing group and a suitable transition-metal catalyst has been studied by many researchers and novel methodologies were exploited for the easy construction of a variety of target molecules. In particular, this protocol provides readily cyclic products including solid-state emissive materials by annulation reactions. The key points for successful reaction are summarized as follows: (1) electron-deficient palladium catalysts with allyl, alkynyl, and benzyl directing groups, (2) electron-deficient unsaturated bond directing groups with a palladium catalyst, and (3) rhodium and iridium catalysts with vinyl, alkynyl, and thienyl directing groups. The reaction system using the alkynoxy group as the useful electron-deficient alkyne and palladium catalysts is particularly suited for various C–H bond activations and a variety of transformations. On the contrary, the transformations reviewed herein are mostly limited to the addition reactions. Simple substitution reactions such as cross-coupling are lacking. Thus, by overcoming the mechanistic problem, the unsaturated bond-directed C–H activation strategy will allow to synthesize a variety of useful organic compounds in straightforward manners without any limitations.

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