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Allylic C–H Activation

Recent Advancements in Allylic C(sp^3)–H Functionalization of Olefins Catalyzed by Rh(III) or Ir(III) Complexes

Ramasamy Manoharan[a] and Masilamani Jeganmohan*[b]

Dedicated to Prof. Pierre H. Dixneuf for his outstanding contribution to organometallic chemistry and catalysis.

Abstract: Olefins are widely available feedstocks and can be readily functionalized into complex organic molecules. In particular, the regioselective allylic C–H functionalization of olefins can provide highly valuable allylic functionalized organic molecules in a highly atom- and step-economical manner. This present review describes the recent advancement on allylic C(sp^3)–H functionalization of olefins catalyzed by Rh(III) or Ir(III) complexes. This review covers the advancement in the allylic C–H amination, arylation and etherification of olefins catalyzed by Rh(III) or Ir(III) complexes.

1. Introduction

Over the past few decades, the transition-metal-catalyzed functionalization of C–H bond has emerged as an inevitable tool in organic synthesis.[1] By employing this strategy, various chemical bonds such as C–C and C–hetero bonds can be achieved in a highly atom- and step-economical manner. Various natural products and biologically active molecules are prepared by using the C–H bond activation as a key step.[2] In particular, the allylic C–H bond functionalization reaction has evolved as a potential alternative to the corresponding allylic substitution reaction having the leaving group (Figure 1, Path A).[3]

In general, a substrate having a leaving group at the allylic position is required to attain allylic substitution (Figure 1, Path A). Interestingly, the allylic C–H bond functionalization method provides a direct access to allylic functionalized products by using unsaturated hydrocarbons (Figure 1 Path B).[3] Thus, the later method is considerably more atom- and step-economical. Allylic functionalization of unsaturated hydrocarbons can be attained by two distinct mechanistic pathways. A) A nucleophilic metalation followed by β-hydride elimination of unsaturated hydrocarbons can provide desired allylic functionalized molecules (Figure 2, Path A).

Meanwhile, the C–H bond activation followed by reductive elimination can also provide the desired allylic functionalized

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Masilmani Jeganmohan was born in Vazhapattampalayam, Tamilnadu, India, in 1978. He received his master's degree in organic chemistry from the University of Madras in 2001. He earned his PhD from the National Tsing Hua University, Taiwan, under the guidance of Prof. Chien-Hong Cheng in 2005 and pursued postdoctoral work in the same laboratory (2005–2009). Then, he moved to the Ludwig-Maximilians-Universität, Munich, Germany, for a postdoctoral study with Prof. Paul Knochel supported by Alexander von Humboldt foundation (2009 to 2010). He started his independent research carrier in November 2010 at IISER Pune as an assistant professor. In April 2016, he was promoted to associate professor at IISER Pune. At present, he is working as an associate professor at Indian Institute of Technology Madras (October 2016–till now). He is the recipient of DAE Young Scientist Research Award (2011), Science Academy Medal for a young associate, Indian Academy of Sciences (2012–2015), Science Academy Medal for Young Scientists, Indian National Science Academy (2013), Alkyl Amines – ICT Young Scientist Award by Institute of Chemical Technology Mumbai (2013), ISCB Award of Appreciation for Chemical Science, CSIR-CDRI (2014), India and Fellow Royal Society of Chemistry (2019). His research interest includes the development of new synthetic methods using metal complexes as catalysts, asymmetric synthesis and natural product synthesis.

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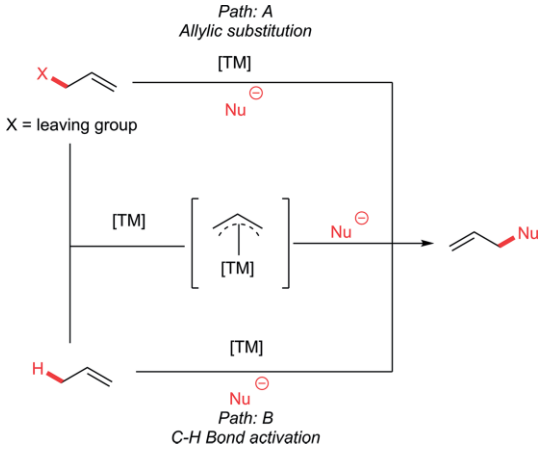


Figure 1. Allylic substitution vs. C–H functionalization.

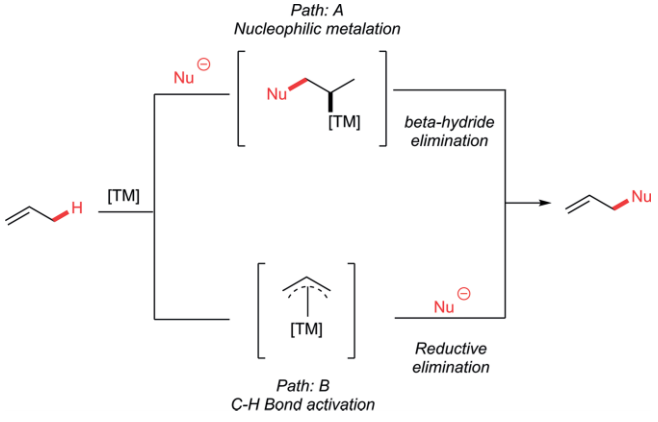


Figure 2. Nucleophilic metalation vs. C–H activation.

products (Figure 2, Path B). It is important to note that a linear type selective functionalization of terminal alkenes can be achieved efficiently via π-allyl-palladium intermediate (Figure 3a).[4] However, the functionalization of allylic C–H bond present in the internal alkenes is hard to achieve due to the high thermodynamic stability of the internal olefins. On the other hand, the branch selective C–H functionalization of terminal alkenes is very difficult to achieve due to the formation of thermodynamically more stable linear selective products.

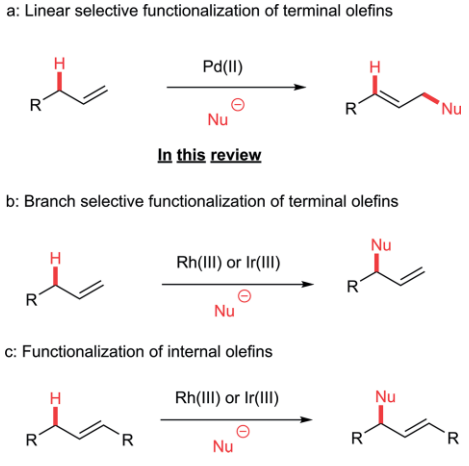


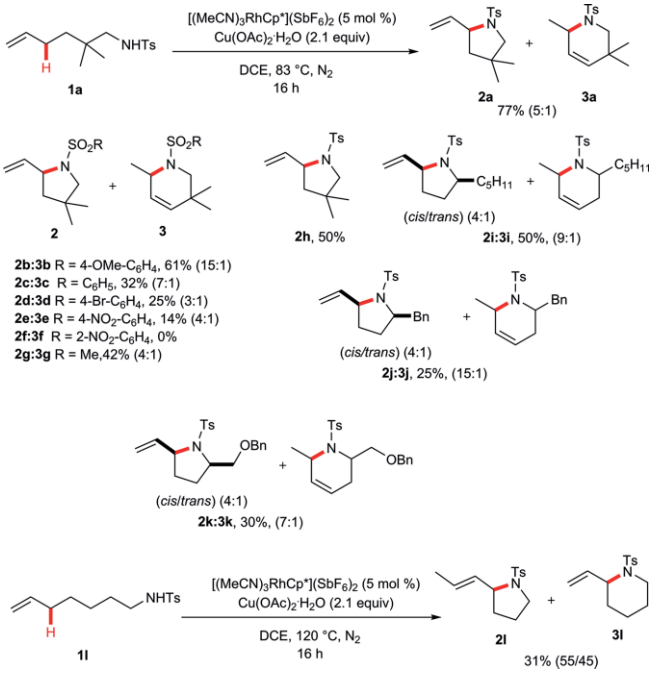
Figure 3. Linear and branch selective C–H functionalization of olefins.

Despite of significant progress made in the linear selective C–H bond functionalization of olefins, the complementary branch selective C–H bond functionalization reaction remains underexplored. Recently, Rh(III) and Ir(III) complexes were found suitable catalysts to achieve branch selective C–H bond functionalization of terminal olefins. In addition, it has been realized that the allylic C–H bond functionalization of internal olefins was also achieved efficiently by using these complexes. This review describes the recent advancements on the allylic C–H bond functionalization of olefins with nucleophiles by using Rh(III) and Ir(III) complexes (Figure 3b and Figure 3c).

2. Allylic C–H Bond Amination

2.1. Rh(III)-Catalyzed Intramolecular C(sp^3)–H Amination of ω-Unsaturated *N*-Tosylamide Derivatives

In 2015, Cossy's group has reported the intramolecular C(sp^3)–H amination using activated amines providing cyclic amine derivatives catalyzed by a rhodium(III)complex.[5] It is important to note that the amine employed in this reaction was protected by the tosyl group. When ω-unsaturated *N*-tosylamide (**1a**) was treated in the presence of cationic complex [(MeCN)$_3$RhCp*](SbF$_6$)$_2$ (5 mol%), and Cu(OAc)$_2$·H$_2$O (2.1 equiv.) at 83 °C in DCE, *N*-tosylpyrrolidine **2a** and *N*-tosyltetrahydropyridine **3a** were isolated in 77 % combined yields in a 5:1 ratio (Scheme 1). This methodology was compatible with various substituted sulfonamides and ω-unsaturated *N*-tosylamides. In the reaction, mixture of cyclized products **2b**/**3b** to **2k**/**3k** were observed in good to moderate yields. *N*-Hept-6-en-tosylamide produced

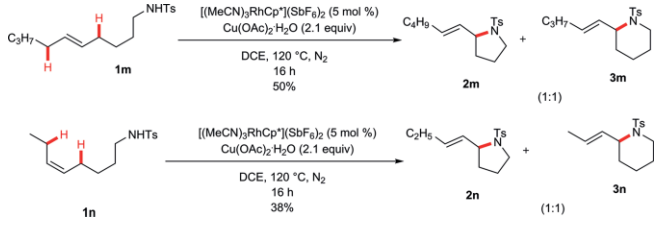


Scheme 1. Synthesis of *N*-tosylpyrrolidine and *N*-tosyltetrahydropyridine derivatives.

mixtures of corresponding 2-crotylpyrrolidine **2l** and 2-vinylpiperidine **3l** in 31 % combined yields under optimized reaction conditions.

Cossy's group has proposed a plausible mechanism for the present catalytic reaction which involves the formation of π-allylic rhodium intermediate followed by *N*-metalation and reductive elimination sequence. Finally, the active Rh(III) complex can be regenerated by external oxidant $Cu(OAc)_2$. But, Blakey's group has recently revealed that the present amination reaction might proceed through the formation of energetically feasible allyl acetate intermediate which undergoes a Lewis acid catalyzed S_N1 type substitution with amine to deliver allylic C(sp^3)–H amination product (Section 2.8).[14]

To examine the formation of π-allyl rhodium species, tosyl amides contains *E* and *Z* double bonds **1m** and **1n** were examined under the optimized reaction conditions. In these reactions, 1:1 ratio of cyclized products **2m**/**3m** and **2n**/**3n** were observed in 50 % and 38 % yields, respectively. It is important to note that in both reactions, products **2m**/**3m** and **2n**/**3n** possessing *E*-double bond were observed. This result clearly supports the formation of π-allyl rhodium intermediate during the reaction process (Scheme 2).

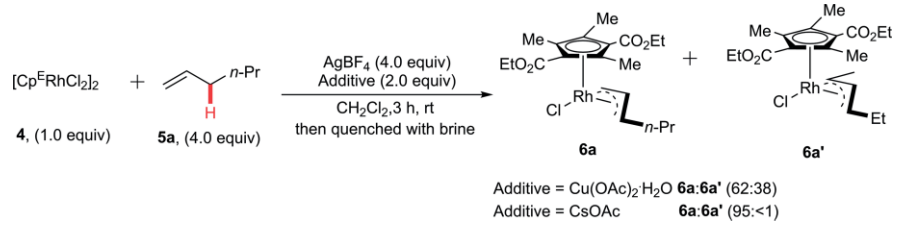


Scheme 2. Reaction of *E* and *Z* tosylamides.

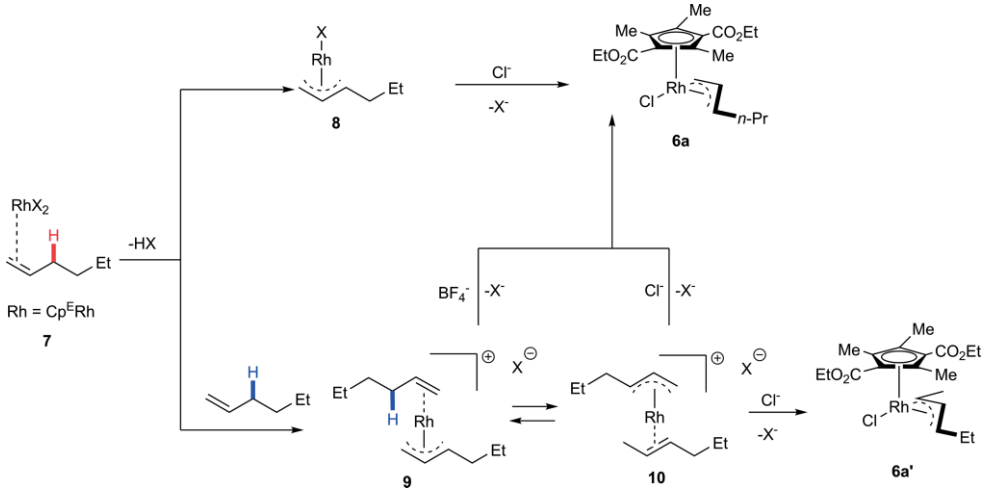
2.2. Electrophilic Rh(III)-Mediated Intramolecular C(sp^3)–H Amination

In 2016, Tanaka's group has reported a strongly electrophilic η^5-cyclopentadienyl rhodium complex, $[Cp^ERhCl_2]_2$, is capable for activating allylic C–H bond of terminal olefins at room temperature.[6] When electron deficient rhodium complex $[Cp^ERhCl_2]_2$ **4** was treated with aliphatic alkene **5a** (4.0 equiv.) in the presence of $AgBF_4$ (4.0 equiv.) and CsOAc (2.0 equiv.), π-allyl rhodium (III) complex **6a** was isolated in 95 % yield (Scheme 3). During the optimization studies, it was found that the non-coordinating anion BF_4 significantly increased the yield of the complexes **6a** and **6a′** as compared with SbF_6. The more ionic CsOAc was also crucial to increase the yield of the complex.

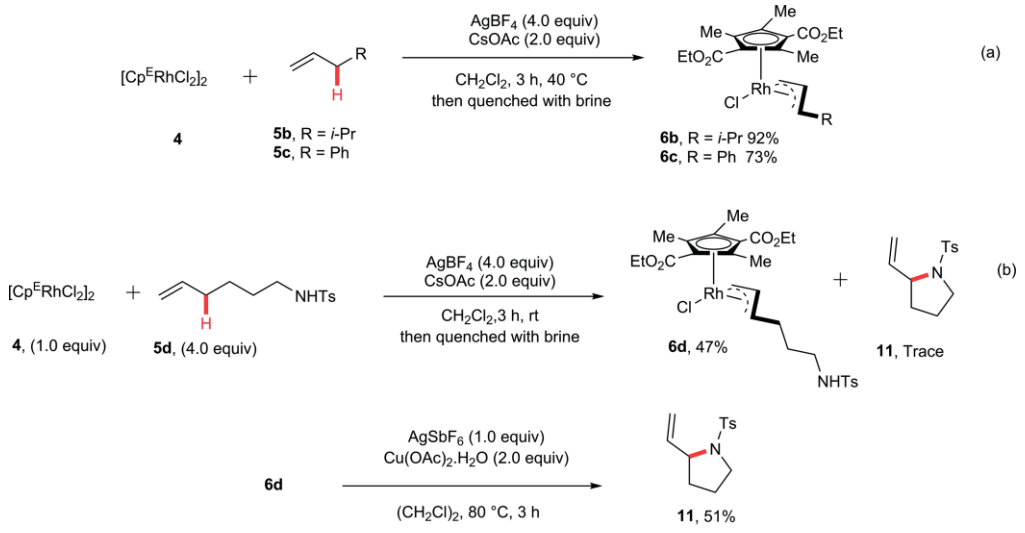
A possible mechanism for the formation of complexes **6a** and **6a′** was proposed in Scheme 4. An active alkene rhodium complex **7** was formed from electron deficient rhodium complex **4** and silver additive. In the presence of coordinating counter anions (OTf, NTf_2 and OAc), complex **7** undergoes allylic deprotonation and ligand exchange with chloride anion leads to the formation of π-allyl rhodium complex **6a**. On the other hand, the association of non-coordinating counter anions such as BF_4 or SbF_6 with complex **7** provides more reactive cationic complex **9** after the allylic deprotonation. Then, a series of hydrogen transfer reactions leads to the formation of complex **6a′**.



Scheme 3. Isolation of π-allyl rhodium (III) complex.



Scheme 4. Possible mechanism.

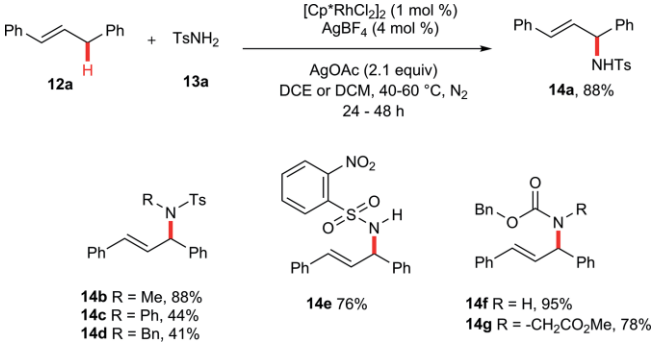


Scheme 5. Scope of alkenes and intramolecular oxidative cyclization.

The sterically hindered terminal alkenes **5b** and **5c** were also compatible for the reaction producing corresponding π-allyl rhodium complexes **6b** and **6c** in good yields (Scheme 5a). *N*-tosylamine substituted alkene **5d** produced alkene complex **6d**, which further converts into pyrrolidine derivative **11** under the oxidative conditions (Scheme 5b).

2.3. Rh(III)-Catalyzed Oxidative Intermolecular C(sp^3)–H Amination Reaction

In 2017, Blakey's group reported the intermolecular C(sp^3)–H amination of internal alkenes with activated amides catalyzed by a rhodium(III) complex in the presence of external oxidant.[7] When *trans*-1,3-diphenylpropene (**12a**) was treated with *N*-tosylamide (**13a**) (2.5 equiv.) in the presence of $[Cp^*RhCl_2]_2$ (1.0 mol-%), $AgBF_4$ (4.0 mol-%) and AgOAc (2.1 equiv.) at 40 °C in DCM for 24 h, an allylic C–H amination product **14a** was observed in 88 % yield (Scheme 6). Tosylamine derivatives containing *N*-substituent such as Me, Ph and Bn produced allylic C–H amination products **14b-d** in 88–41 % yields, respectively. *o*-Nosyl amide **13e** yielded the corresponding C–H amination product **14e** in 76 % yield. Activated amide having Cbz group **13f–g** produced the corresponding C–H amination products **14f–g** in 95–78 % yields, respectively.



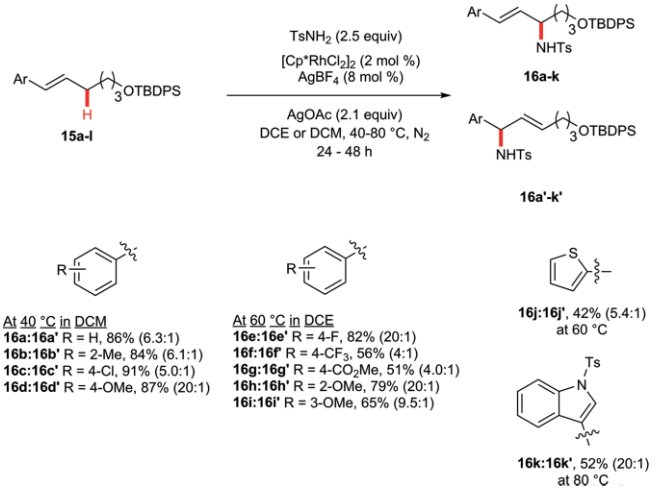
Scheme 6. Scope of activated amides.

The scope of amination reaction was examined with unsymmetrical olefin **15a**. In the reaction, regioisomeric products **16a** and **16a′** were observed in 86 % yields in 6.3:1 ratio (Scheme 7). A similar type of reactivity and selectivity was also observed with other unsymmetrical olefins **16b–k** in 91–42 % yields, respectively (Scheme 7).

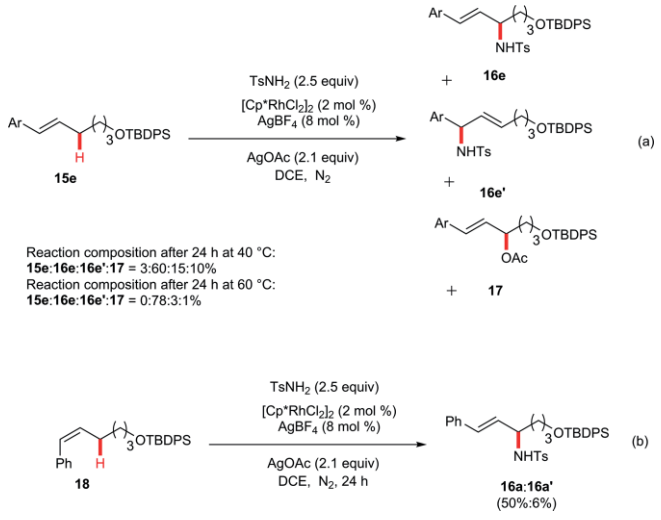
In the present reaction, a thermodynamically more stable product formation was observed at elevated temperatures (Scheme 8a). An olefin containing *Z*-type double bond **18** was examined for the present amination reaction. In the reaction, products **16a**/**16a′** were observed in 50 % and 6 % yields, respectively. It is important to note that no *Z*-type amination product was formed in the reaction. This result clearly supports that the formation of π-allyl rhodium species in the reaction during the course of the reaction (Scheme 8b).

2.4. Cp*Ir(III)-Catalyzed Oxidative Intermolecular C(sp^3)–H Amination Reaction

In 2019, our group has reported an intermolecular C(sp^3)–H amination of internal alkenes with substituted sulfonamides under the oxidative conditions catalyzed by Cp*Ir complex.[8]

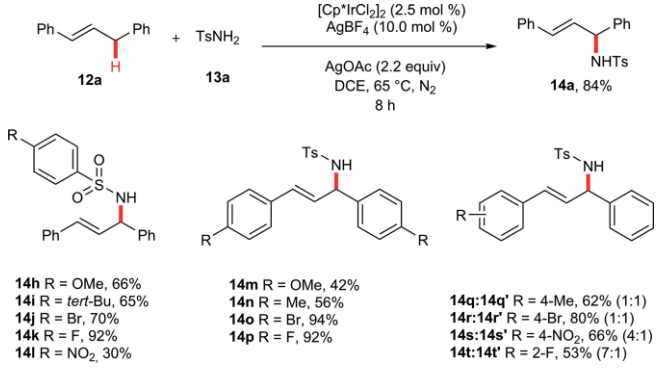


Scheme 7. Scope of unsymmetrical olefins.

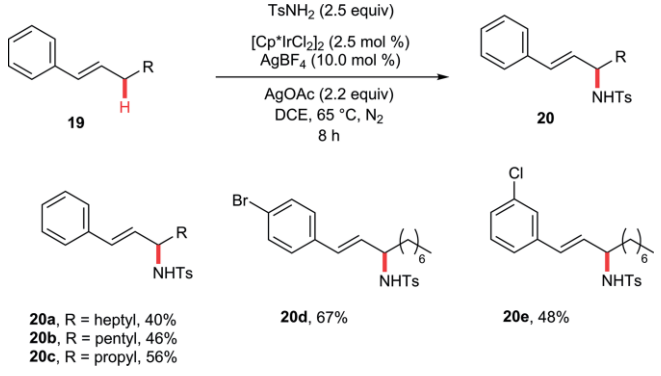


Scheme 8. Preliminary mechanistic studies.

Treatment of *trans*-1,3-diphenylpropene (**12a**) with tosylamide **13a** (2.5 equiv.) in the presence of $[Cp^*IrCl_2]_2$ (2.5 mol-%), $AgBF_4$ (10 mol-%) and AgOAc (2.2 equiv.) at 65 °C in DCE for 8 h provided allylic C–H amination product **14a** in 84 % yield (Scheme 9). The present oxidative amination reaction was examined with various substituted aryl sulfonamides **14h-l**, symmetrical *trans*-1,3-diarylpropenes **14m–p** and unsymmetrical *trans*-1,3-diarylpropene derivatives. In the reaction, the expected amination products were observed in good to excellent yields. It is important to note that in the case of unsymmetrical alkenes, the C–N bond formation majorly take place at the allylic carbon of phenyl ring rather than the phenyl ring having an electron-withdrawing substituent **14s–t**.



Scheme 9. Scope of alkenes and activated amides.



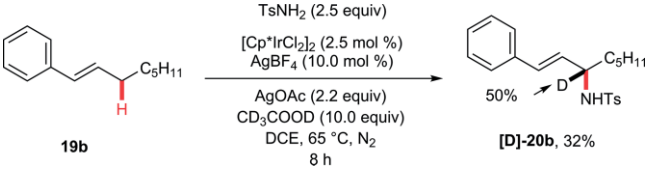
Scheme 10. Scope of activated amides.

The amination reaction was examined with unsymmetrical aryl-alkyl alkenes **19a–e**. In the reaction, amination selectively takes place at the alkyl-substituted allylic carbon of internal alkenes (Scheme 10). The reaction of aryl-alkene **19b** with tosylamide **13a** in the presence of CD_3COOD under the optimized reaction conditions was examined. In the reaction, the deuterium incorporation was observed at the alkyl-substituted allylic carbon of product **20b** (Scheme 11).

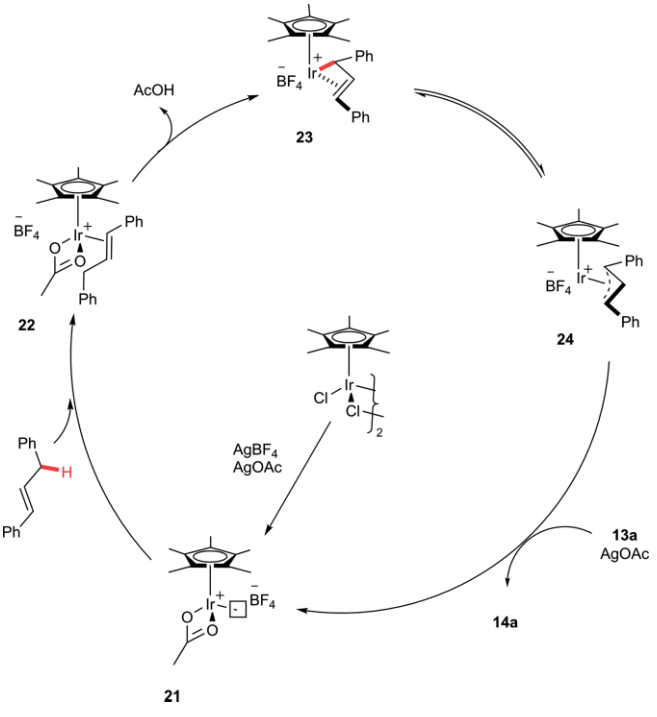
A possible mechanism was proposed in Scheme 12. The catalytic cycle likely commences by the formation of cationic Ir complex **21** from $[Cp^*IrCl_2]_2$, $AgBF_4$ and AgOAc. Coordination of alkene, C–H cleavage and isomerization sequence leads to the formation of intermediate **24**. Nucleophilic addition of tosyl amide with intermediate **24** followed by reductive elimination provides product **14a**. An active catalyst **21** was regenerated in the presence of AgOAc for the next cycle.

2.5 Cp*Ir(III)-Catalyzed Intermolecular Redox-Neutral C(sp³)–H Amination Reaction

In 2019, Rovis's group has reported an Iridium(III)-catalyzed intermolecular C(sp^3)–H amination of alkenes with dioxazolones



Scheme 11. Deuterium scrambling studies.

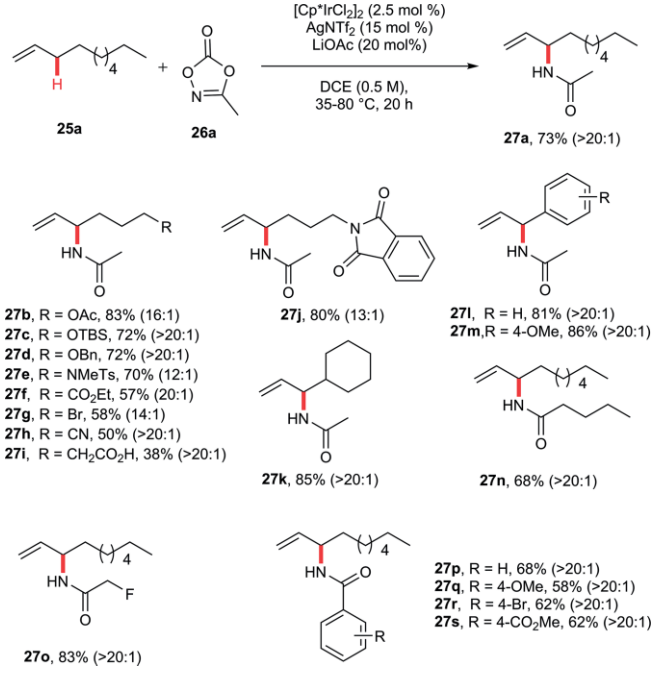


Scheme 12. Plausible mechanism.

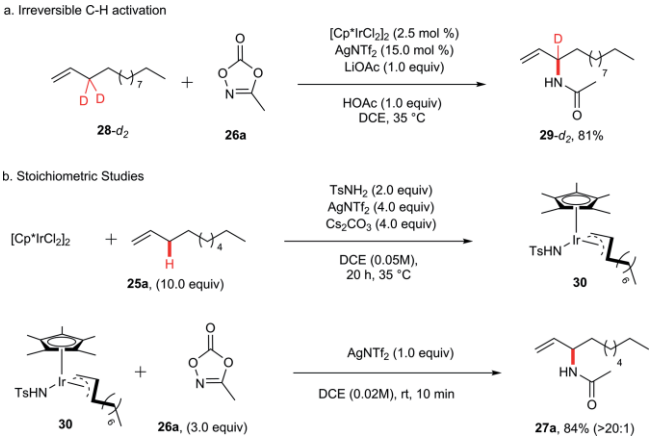
as nitrenoid precursors under the redox-neutral conditions.[9] The reaction of alkene **25a** with dioxazolone **26a** (1.5 equiv.) in the presence of $[Cp^*IrCl_2]_2$ (2.5 mol-%), $AgNTf_2$ (15 mol-%) and LiOAc (20 mol-%) at 35 °C in DCE for 20 h provided allylic C–H amination product **27a** in 70 % yield (Scheme 13). Terminal alkenes containing various substituents such as OAc, OTBS, CO_2Et, Br, CN, COOH and phthalimide **25b**–**25j** were compatible for the amination reaction. In the reaction, the C(sp^3)–H amination products **27b**–**27j** were observed in good to excellent yields. Substituted allylarenes were also compatible for the reaction. The dioxazolones having alkyl and aryl substituents were also effectively involved in the reaction, producing amination products **27o**–**27s** in good yields. When **28**-d_2 was subjected for the reaction with AcOH as a proton source, amination product **29**-d_2 was obtained in 81 % yield without any loss of deuterium. This result clearly reveals that the C–H activation process might be irreversible in nature (Scheme 14a).

An allyl Ir(III) complex **30** was isolated when *p*-toluenesulfonamide employed as a stabilizing agent in the reaction of terminal alkene with a stoichiometric amount of rhodium complex. Treatment of complex **30** with **26a** in the presence of $AgNTf_2$ produced amination product in 84 % yield (Scheme 14b). A possible mechanism for the formation of amination product **27** was proposed in Scheme 15. The catalytic cycle like commences by the formation of coordinatively unsaturated Ir complex **31** from $[Cp^*IrCl_2]_2$, $AgNTf_2$ and LiOAc. Coordination of alkene to the complex **31** followed by irreversible metalation leads to the formation of species **33**. The N–O bond cleavage followed by CO_2 extrusion of **26** furnishes nitrenoid intermediate **34**. Migratory insertion followed by proto-demetalation of intermediate **34** produces amination product **27** and regenerates the active catalyst **31** for the next cycle.

In the meantime, a similar type of transformation was observed by Glorius's group.[10] When alkene **35** was treated with

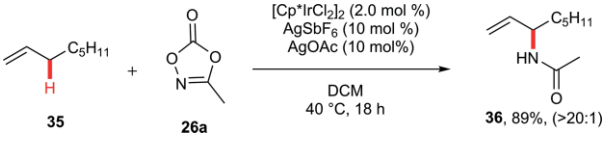


Scheme 13. Iridium-catalyzed redox-neutral C(sp^3)–H amination reaction.



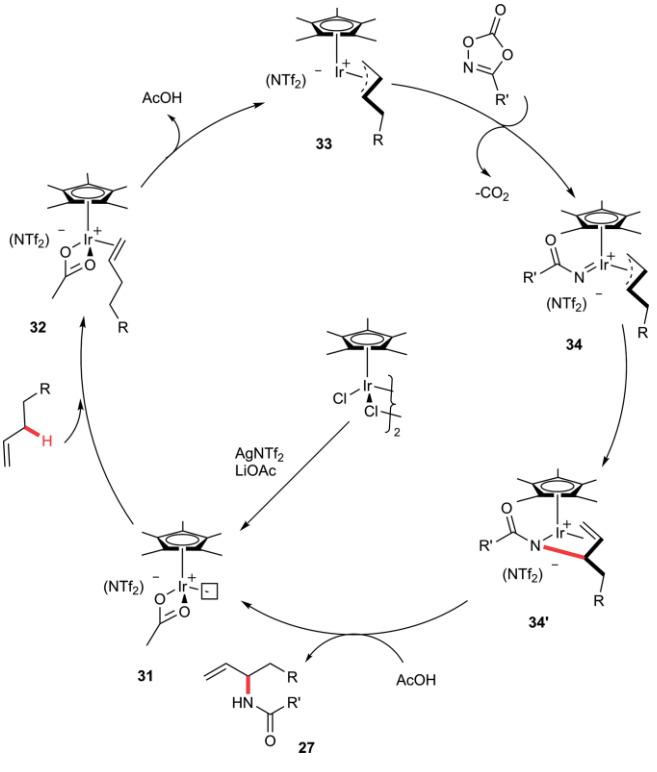
Scheme 14. Preliminary mechanistic studies.

dioxazolone **26a** (1.2 equiv.) in the presence of $[Cp^*IrCl_2]_2$ (2.0 mol-%), $AgSbF_6$ (10 mol-%) and AgOAc (20 mol-%) at 40 °C in DCM for 18 h, an allylic C–H amination product **36** was observed in 90 % yield (Scheme 16). The reaction was also compatible with various substituted alkenes and dioxazolones.



Scheme 16. Iridium-catalyzed C(sp^3)–H amination reaction.

Later, Blakey's group has reported redox-neutral C(sp^3)–H amination of terminal and *trans*-disubstituted olefins catalyzed by Cp*Rh(III) and Cp*Ir(III) complexes.[11] Interestingly, it was

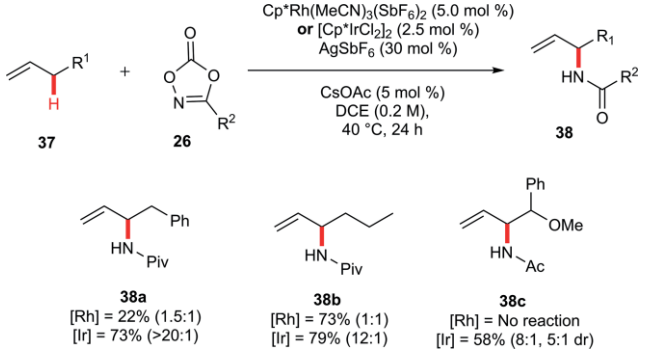


Scheme 15. Plausible mechanism.

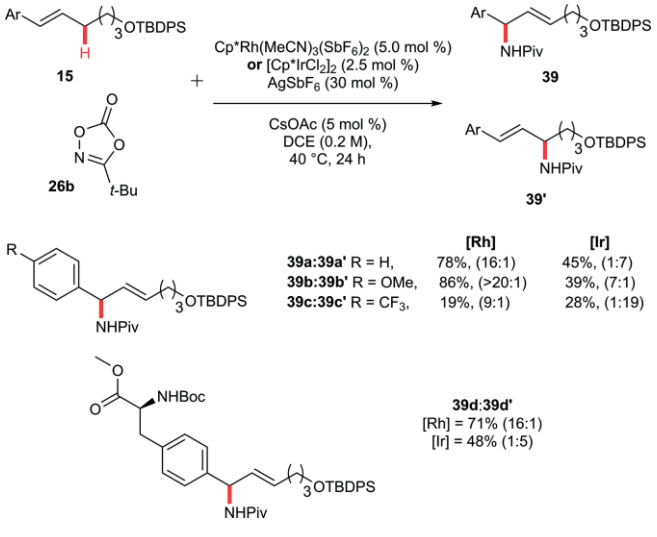
demonstrated that the Cp*Ir complex provides a high branch selective products in terminal olefins as compared with a rhodium complex (Scheme 17). Meanwhile, Cp*Rh complex was efficient for the regioselective benzylic amination of *trans*-disubstituted olefins (Scheme 18).

2.6 Cp*Ir(III)-Catalyzed Regioselective C(sp^3)–H Amination Reaction

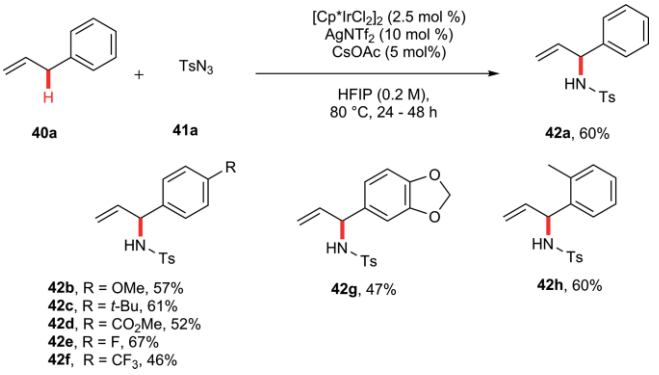
In 2019, Blakey's group has reported the redox-neutral C(sp^3)–H amination of allylarene derivatives with sulfonyl azides as nitrenoid precursors catalyzed by an Iridium (III) complex.[12] When allylarene (**40a**) was treated with *p*-toluenesulfonyl azide (**41a)** (2.0 equiv.) in the presence of $[Cp^*IrCl_2]_2$ (2.5 mol-%), $AgNTf_2$ (10.0 mol-%) and CsOAc (5.0 mol-%) at 80 °C in HFIP for 24 h, benzylic C–H amination product **42a** was observed in 60 % yield with exclusive benzyl selectivity (Scheme 19). The present reaction was compatible with various substituted allylarenes having substituents such as 4-OMe, 4-*t*Bu, 4-CO_2Me, 4-F and 4-CF_3 **40b–h**. In the reaction, desired products **42b–f** with exclusive benzyl selectivity was observed in 67–46 % yields, respectively.



Scheme 17. Ir-catalyzed branch selective amination.

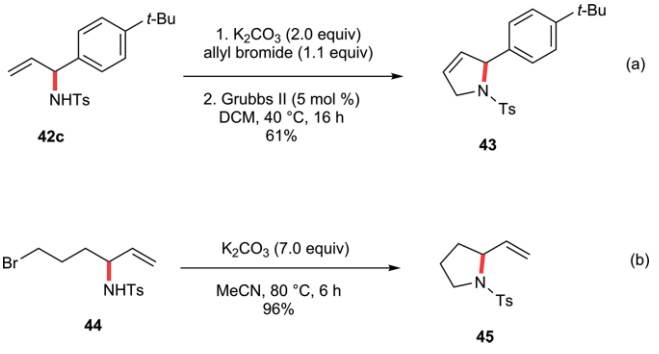


Scheme 18. Rh-catalyzed branch selectivity.



Scheme 19. Iridium-catalyzed redox-neutral C(sp^3)–H amination with azides.

The amination products were utilized to synthesize pharmaceutically relevant nitrogen-containing heterocyclic molecules (Scheme 20). The allylation of **42c** followed by ring-closing metathesis (RCM) provides dihydropyrrole in 61 % yield (Scheme 20a). The tosylamide **44** was cyclized under the basic conditions providing 2-vinyl pyrrolidine in 96 % yield (Scheme 20b).

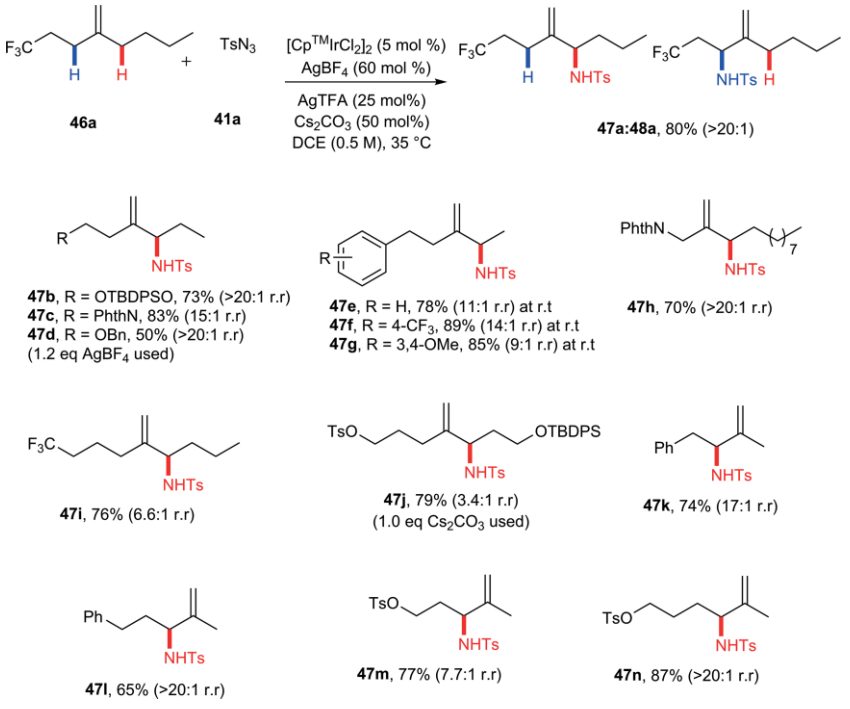


Scheme 20. Diversification of amination products.

2.7 Ir-Catalyzed Site Selective Amination Reaction

In 2020, Rovis's group has reported a site selective amination of unsymmetrical disubstituted alkenes catalyzed by Cp^{TM}Ir complex (Cp^{TM}, tetramethylcyclopentadienyl).[13] Treatment of 1,1-disubstituted alkene **46a** with *p*-toluenesulfonyl azide (**41a)** in the presence of $[Cp^{TM}IrCl_2]_2$ (5.0 mol-%), $AgBF_4$ (60.0 mol-%), AgTFA (25.0 mol-%) and Cs_2CO_3 (50.0 mol-%) at 35 °C in DCE provided δ C–H amination product **47a** along with a minor amount of β C–H amination product **48a** in 80 % yield with 20:1 ratio (Scheme 21).

Initially, the catalytic reaction was examined with metal complexes such as $[Cp^*RhCl_2]_2$, $[Cp^*CoCl_2]_2$ and $[Cp^*IrCl_2]_2$. Among them, Ir complex was active for the reaction providing the expected amination product. However, Rh and Co complexes were completely ineffective. The present selective δ C–H amination reaction was examined with various 1,1-disubsitituted alkenes **46b–m**. The reaction was tolerated with electron withdrawing and aryl-substituted alkenes. In these reactions, the expected δ C–H amination products **47b–j** were observed in good yields. It is important to note that the ratio of the regio-

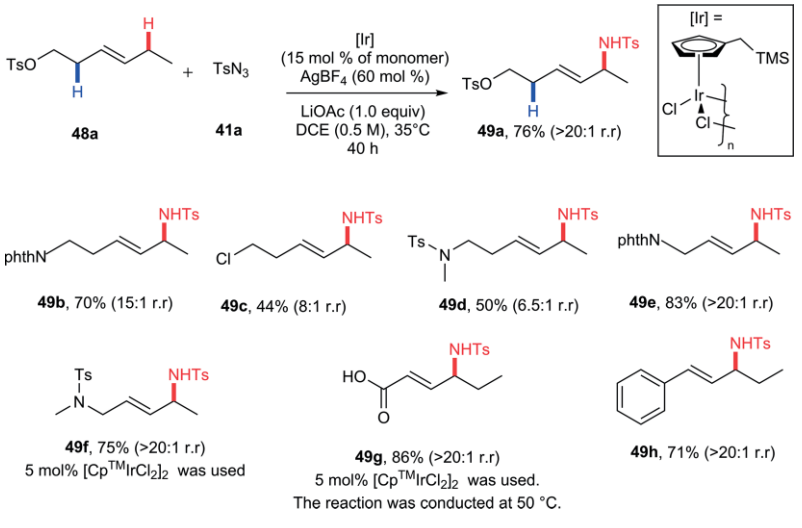


Scheme 21. Scope of unsymmetrical 1,1-disubstituted alkenes.

selectivity was increased while increasing the number of methylene group between 1,1-disubstituted double bond and electron withdrawing group of the alkene **46**. Meanwhile, the C–H amination was observed selectively at the methylene position in products **47k–n**.

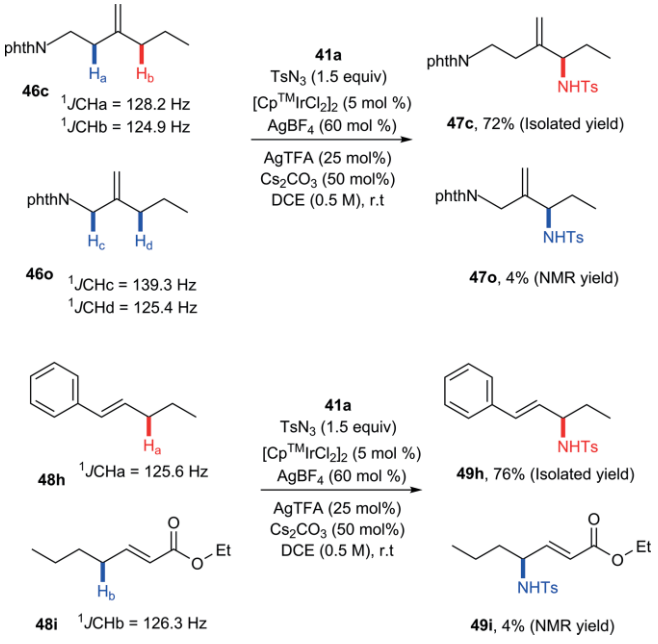
After the successful selective C–H activation of 1,1-disubstituted alkenes, the *trans*-1,2-disubstituted alkenes were examined. The reaction of *trans*-1,2-disubstituted alkene **48a** (1.0 equiv.) with *p*-toluenesulfonyl azide (**41a)** (1.5 equiv.) in the presence of TMS substituted Cp based [Ir] complex (15 mol-% of monomer), $AgBF_4$ (60 mol-%) and LiOAc (1.0 equiv.) at 35 °C in DCE for 40 h yielded the distal allylic C–H amination product **49a** along with a minor amount of other regioisomeric product combinedly in 76 % yields with >20:1 ratio (Scheme 22).

Initially, the reaction was examined with various CpIr complexes having sterically hindered electronically variable aryl substituents such as pentafluoro phenyl and *p*-trifluoromethyl phenyl group. In addition, Cp ligand having less substituent was also examined. Among them, sterically hindered electronically variable ligands show little effect on the outcome of the selectivity of the reaction. Interestingly, the Cp ligands having less substituent show improved regioselectivity. Various alkenes having electron withdrawing groups, conjugated carbonyl group and aryl substituents yielded the desired amination



Scheme 22. Scope of unsymmetrical *trans*-1,2-disubstituted alkenes.

products in good to moderate yields **49b–h**. Meanwhile, it was found that in a competition between intramolecular or intermolecular allylic C–H bonds, the one which having lowest $^1J_{CH}$ constant preferably get functionalized (Scheme 23).



Scheme 23. $^1J_{CH}$ Coupling constants and regioselectivity.

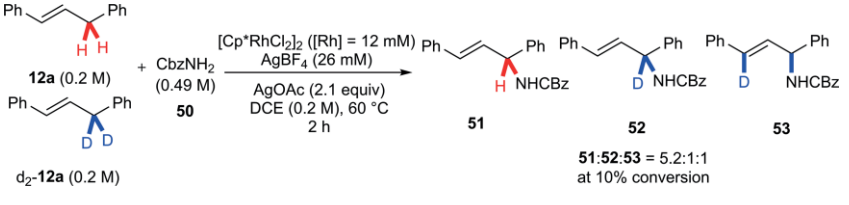
2.8. Detailed Mechanistic Analysis of Rhodium-Catalyzed Allylic C–H Oxidative Amination Reaction

In 2020, Blakey's group has reported a detailed investigation of the course of allylic C(sp^3)–H oxidative amination process by using kinetics experiments, mechanistic investigation, DFT calculations and cyclic voltammetry experiments.[14] This report states that the desired amination product was formed through a S_N1 ligand exchange mechanism of allylic acetate intermediate which was formed by an oxidatively induced reductive elimination of allyl fragment with acetate ligand via Rh(IV) intermediate.

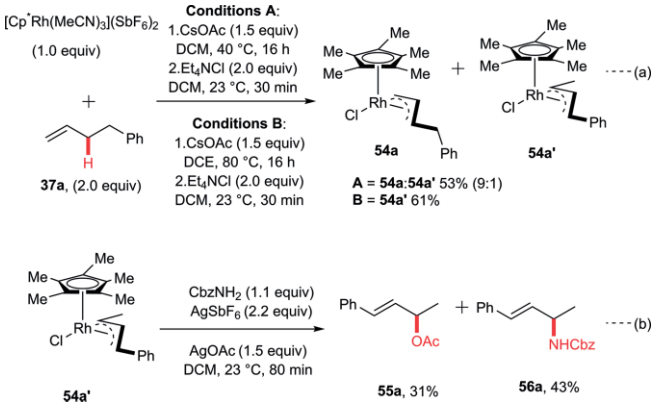
It was found that the coordination of alkene with a rhodium follows the first order kinetics. The inverse rate constant was observed in the amine concentration. The inverse rate constant observed in amine concentration could be due to the nucleophilic binding to the rhodium metal in an off cycle equilibrium. The KIE of k_H/k_D = 2.6 with equal distribution of deuterium at C1 and C3 carbons was observed (Scheme 24). This observation indicates the formation of π-allyl rhodium complex during the course of the reaction. In addition, Blakey's group has showed that the allylic C–H cleavage is an irreversible in nature. Aforementioned observation clearly indicates the irreversible allylic C–H activation could be the rate-limiting step for the allylic C(sp^3)–H oxidative amination process.

In addition, the synthesis of possible intermediates and their reactivity analysis provided more insight on the catalytic cycle. Treatment of $[Cp^*Rh(MeCN)_3](SbF_6)_2$ with 4-phenyl-1-butene **37a** (2.0 equiv.) in the presence of CsOAc (1.5 equiv.) at 40 °C in DCM for 16 h followed by the addition of tetraethylammonium chloride provided a mixture of π-allyl rhodium complexes **54a** and **54a′** in 53 % yield with 9:1 ratio (Scheme 25a conditions A). At slightly elevated temperature, thermodynamically stable complex **54a′** was observed in DCE solvent exclusively in 61 % yield (Scheme 25a conditions B). Complex **54a′** was isolated and characterized by ^1H and ^{13}C NMR spectroscopy and a single-crystal X-ray diffraction technique. Allylic acetate **55a** and expected allylic amine **56a** were isolated under the identical reactions conditions in 31 % and 43 % yields, respectively (Scheme 25b). But, the complex **54a′** was remain unreacted after 48 h with treatment of one equivalent of amine **50**. These experimental observations indicated that the active species **54a′** could be formed by the exchange of ligand between Cl into OAc in the presence of AgOAc. The required allylic C(sp^3)–H oxidative amination product could be formed via the formation of substituted allyl acetate **55a**. In addition, the expected allylic aminated product was not observed in the treatment of **57** with 5.0 equivalent of amine **50** at 40 °C in DCM for 14 h followed by the addition of tetraethylammonium chloride (Scheme 26a). Complex **58** produced only 10 % of expected amination products **56b** and **56c** under the oxidative conditions (Scheme 26b). In contrast, complex **59** yielded allyl acetate product **55a** quantitatively in the presence of $AgSbF_6$ (2.0 equiv.) (Scheme 26c). This result clearly reveals that the allylic amination process proceeds through the formation of substituted allylic acetate **55a** via an oxidatively induced reductive elimination pathway.

Further, allyl acetate **55a** was converted into amination product **56a** in the presence of Lewis acid. Notably, at 0 °C, in the presence of $AgSbF_6$, the expected allyl amination product **56a** was formed in 2.5 h in few seconds. DFT calculations revealed that the reductive elimination from Rh(III) to Rh(I) (38.4 kcal/mol) has higher activation barrier than the reductive elimination of oxidized metal center Rh(IV) to Rh(II) (17.6 kcal/mol). In addition, reductive elimination from Rh(V) to Rh(III) does not significantly enhance the reaction center (19.5 kcal/mol). Further, the cyclic voltammetry experiment showed that the formation of Rh(V) complex (≈ 0.85 V) is less likely in the reaction as



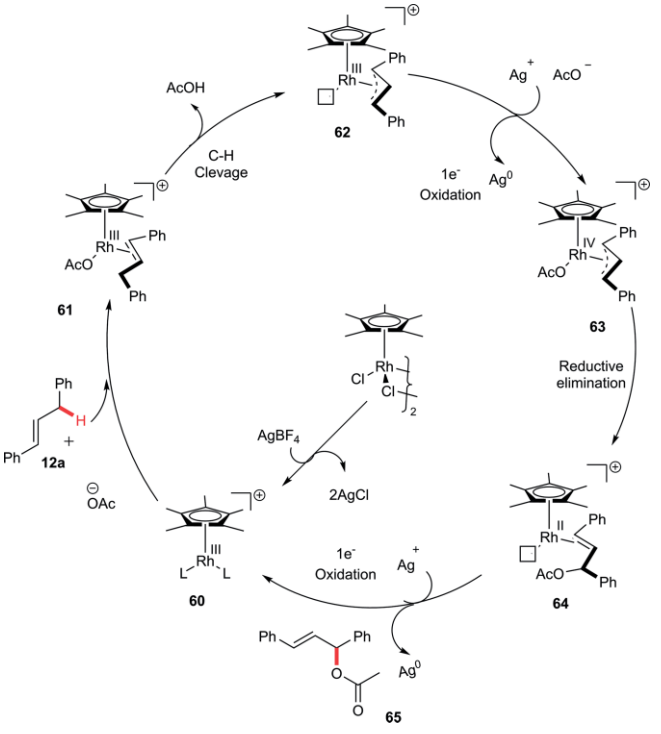
Scheme 24. Kinectic isotope experiments.



Scheme 25. Synthesis and reactivity of Cp*Rh(III)(π–allyl) complexes.

the redox potential of Ag^+ is ≈ 0.65 V. Based on the aforementioned studies, a possible reaction mechanism for the allylic acetoxylation was proposed in Scheme 27.

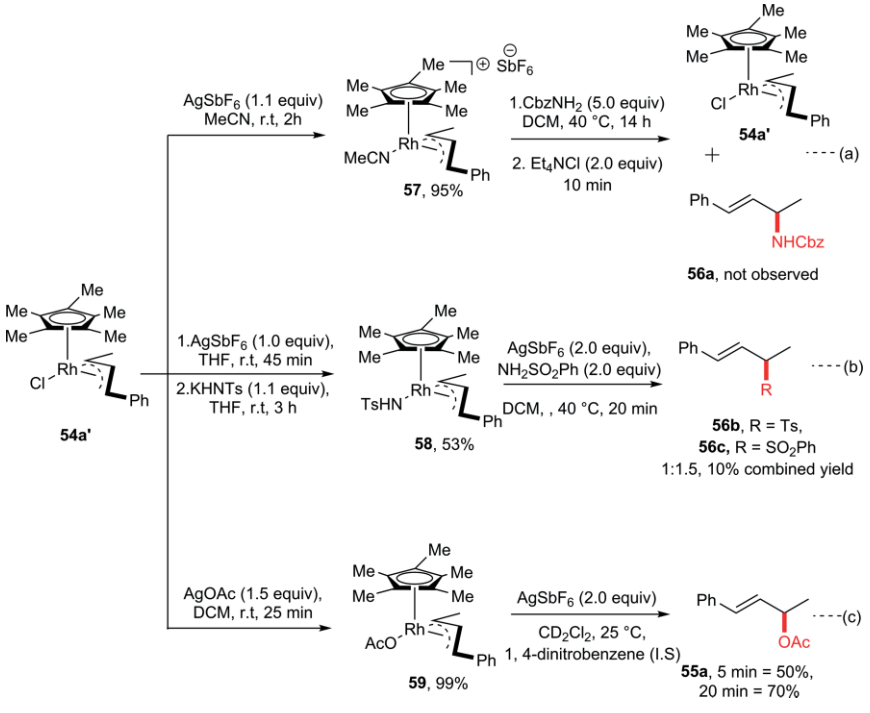
The catalytic cycle starts with the coordination of olefin **12a** and acetate ligand with complex **60** followed by concerted metalation deprotonation pathway (CMD) leads to the formation of complex **62** which requires mild elevated temperature (computed activation barrier 26.7 kcal/mol) (Scheme 3). The complex **63** was formed via ligand exchange and one electron oxidation of Rh(III) to Rh(IV). This one electron oxidation is required for the facile reductive elimination (computed activation barrier 17.6 kcal/mol). Finally, one electron oxidation of Rh(II) to Rh(III) releases product **65** via ligand exchange process. The allyl amination product **56** was obtained via allyl cation intermediate **67** catalyzed by Rh(III) or Ag(I) followed by S_N1 nucleophilic substitution of amine (Scheme 28).



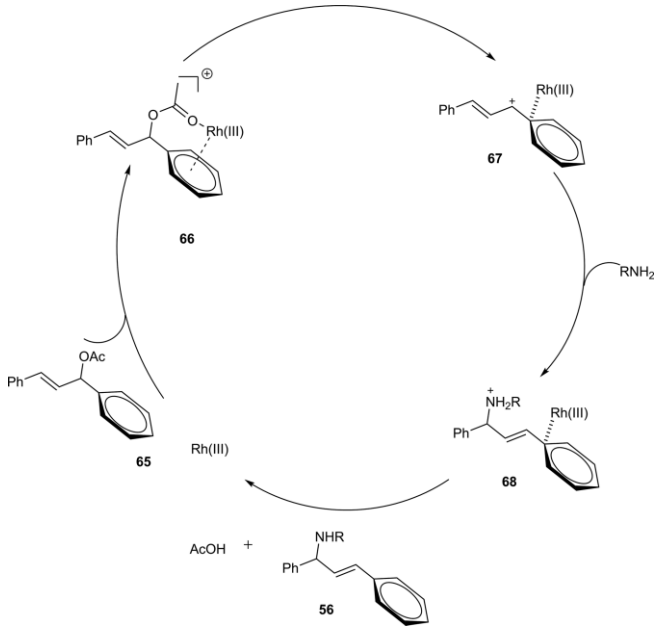
Scheme 27. Plausible mechanism.

2.9 Enantioselective Allylic C(sp^3)–H Amination Reaction

In 2020, Blakey's group has reported an enantioselective allylic C(sp^3)–H amination of terminal as well as *trans* disubstituted alkenes with dioxazolones catalyzed by a new planar chiral indenyl rhodium complex.[15] This method proceeds via a Rh^V



Scheme 26. Synthesis and reactivity of Cp*Rh(III)(π–allyl) complexes.

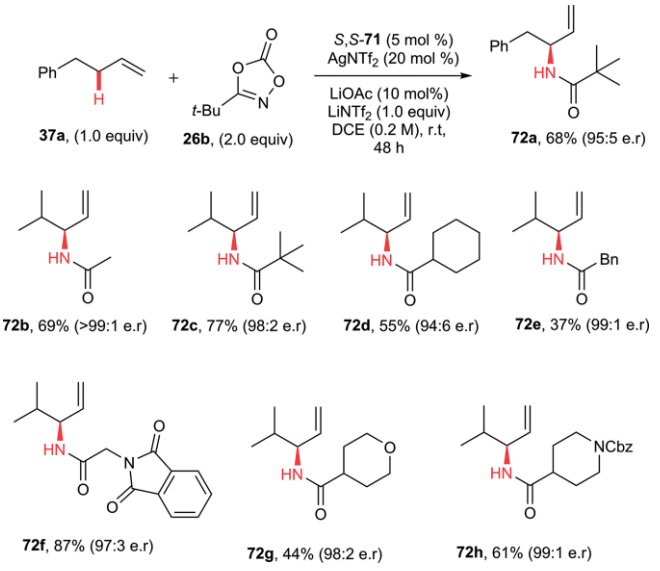


Scheme 28. Formation of allyl amination product.

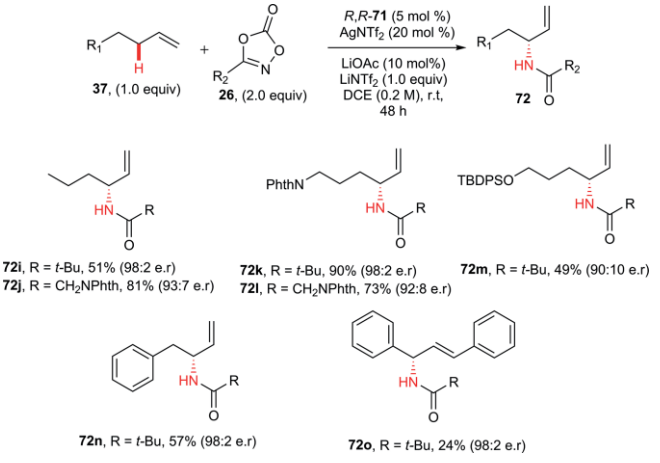
nitrenoid intermediate. The reaction provides highly valuable enantioenriched allylic amide products. Treatment of 2-methyl-3-phenylindene (**69**) with $[Rh(I)(COD)Cl]_2$ provided racemic mixtures of chiral Rh complexes **70** (Scheme 29). The corresponding enantiomers were resolved by chiral HPLC. Then, they were further oxidized into the corresponding Rh(III) complex **71** by the addition of I_2. When 4-phenylbut-1-ene (**37a**) was treated with *tert*-butyldioxazolone (**26b**) in the presence of (***S***,***S***)-71 (5.0 mol-%), $AgNTf_2$ (20.0 mol-%), LiOAc (10.0 mol-%) and $LiNTf_2$ (1.0 equiv.) at room temperature in DCE, the C–H amination product **72a** was observed in 68 % yield with 95:5 er (Scheme 30). The present regio- and enantioselective amination reaction was compatible with various substituted dioxazolones having substituents such as *t*Bu, cyclohexyl and benzyl group. In the reaction, the expected amination products were observed in moderate to good yields **72b–h**. (Scheme 31)**.**

The present amination reaction was also compatible with substituted linear terminal olefins. In the reaction also, the expected amination products were observed in good to moderate yields with excellent enantioselectivity **72i–n**. In addition, *trans*-disubstituted alkene such as 1,3-diphenylpropene (**12a**) was also involved in the reaction, affording corresponding amination product **72o** in 24 % yield with 98:2 er.

A possible reaction mechanism for the formation of regio- and enantioselective amination product was proposed in

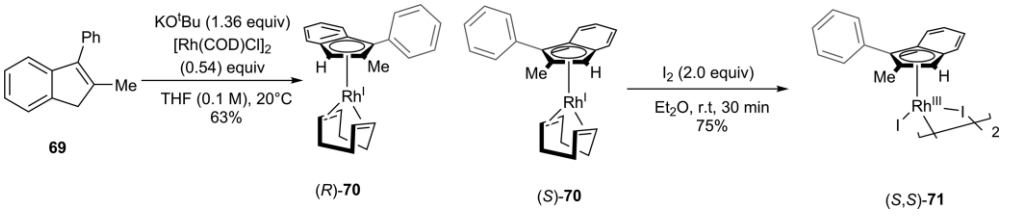


Scheme 30. Scope of dioxazolone substrates.

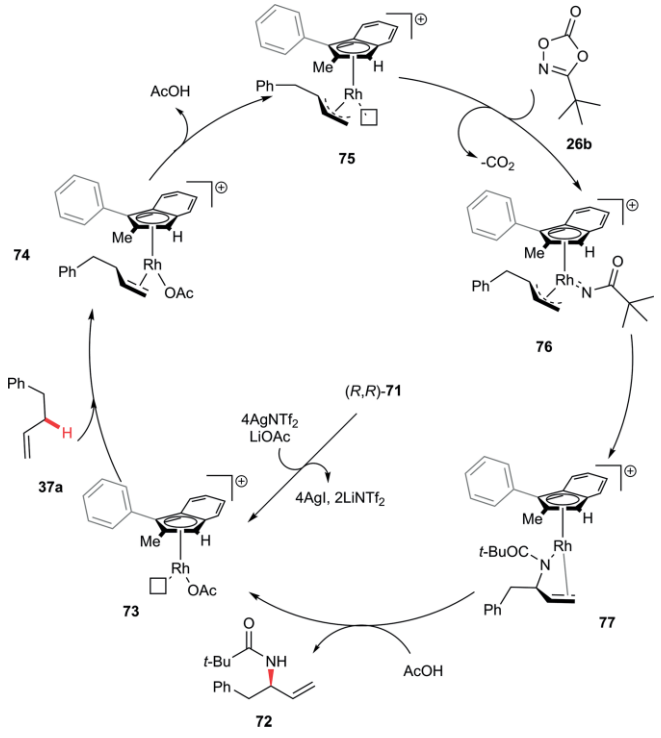


Scheme 31. Scope of dioxazolone and alkene substrates.

Scheme 32. The catalytic cycle like commences by the formation of coordinatively unsaturated Rh complex **73** from (*R*,*R*)-Rh **71**, $AgNTf_2$ and LiOAc. Coordination of alkene to the complex **73** followed by irreversible enantioselective metalation leads to the formation of species **75**. The N–O bond cleavage followed by CO_2 extrusion furnishes nitrenoid intermediate **76**. Migratory insertion followed by proto-demetalation of intermediate **76** produces amination product **72** and regenerates the active catalyst **73** for the next cycle. (Scheme 32).



Scheme 29. Synthesis of planar chiral Rh(III) complex.

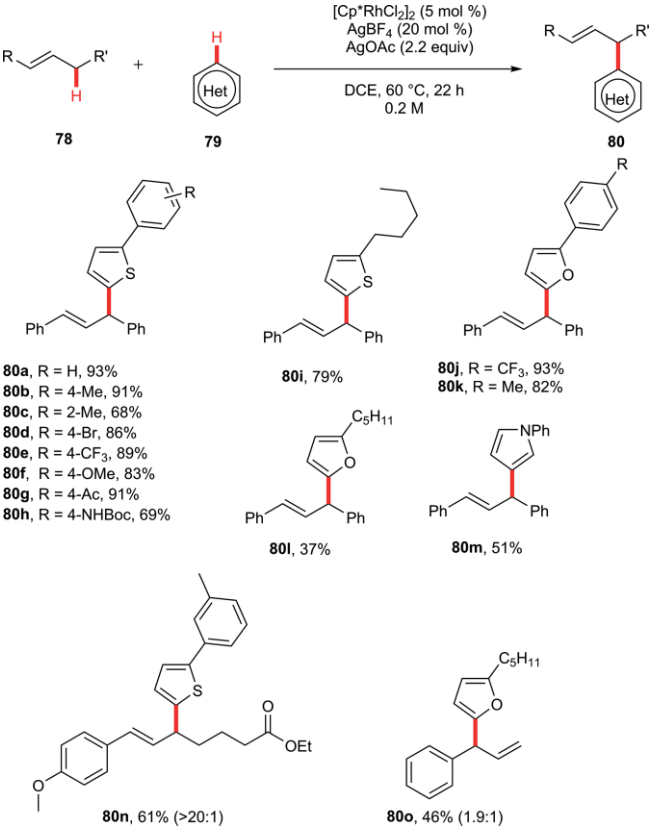


Scheme 32. Plausible mechanism.

3. Allylic C–H Bond Arylation

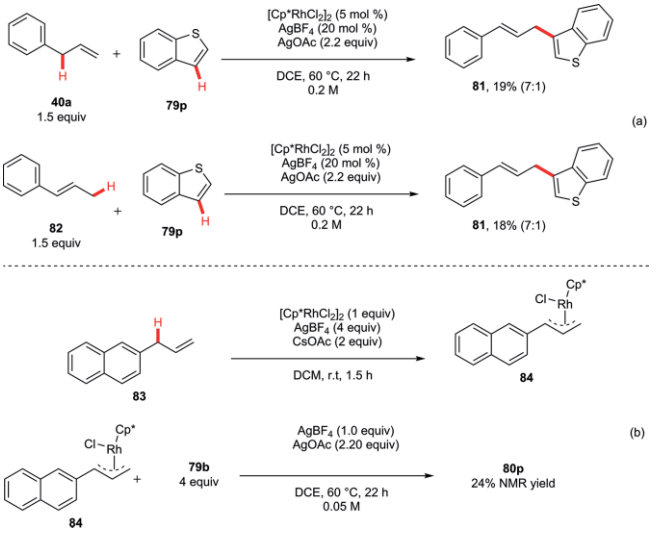
3.1 Cp*Rh(III)-Catalyzed Dehydrogenative C(sp^3)–H Arylation Reaction

In 2018, Glorius's group has reported the cross dehydrogenative coupling of allylic C(sp^3)–H bonds with heterocycles. The reaction of *trans*-1,3-diphenylpropene (**12a**) (7.5 equiv.) with 2-arylthiophene **79a** (1.0 equiv.) in the presence of $[Cp^*RhCl_2]_2$ (5.0 mol-%), $AgBF_4$ (20 mol-%) and AgOAc (2.2 equiv.) at 60 °C in DCE for 22 h gave the C–H arylated product **80a** in 93 % yield (Scheme 33).[16] The present arylation reaction was examined with various substituted 2-aryl thiophene derivatives **79b–i.** In the reaction, the expected C–H arylated products **80b–i** were observed in good to excellent yields. Arylated and alkylated furans **79j-l** and *N*-phenyl pyrrole (**79m**) were also compatible for the reaction.



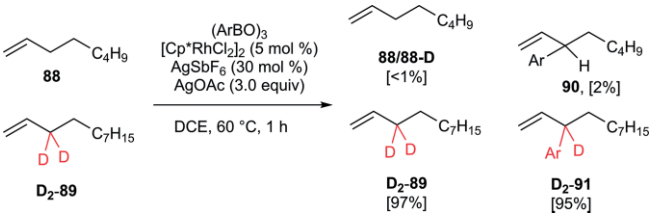
Scheme 33. Dehydrogenative C(sp^3)–H arylation.

When allylbenzene (**40a**) or *trans*-β-methylstyrene (**82**) was treated with thiophene **79p** under the optimized reaction conditions, the same type of allyl C–H arylated product **81** was observed with identical selectivity (Scheme 34a). This result



Scheme 34. Mechanistic investigations.

supports the possible formation of π-allyl Rh intermediate during the reaction progress. This hypothesis was further confirmed by the successful isolation of π-allyl Rh intermediate **84.** Later, intermediate **84** was converted into arylated product **80b** in 24 % NMR yield in the presence of **79b** (Scheme 34b).



Scheme 36. Deuterium scrambling studies.

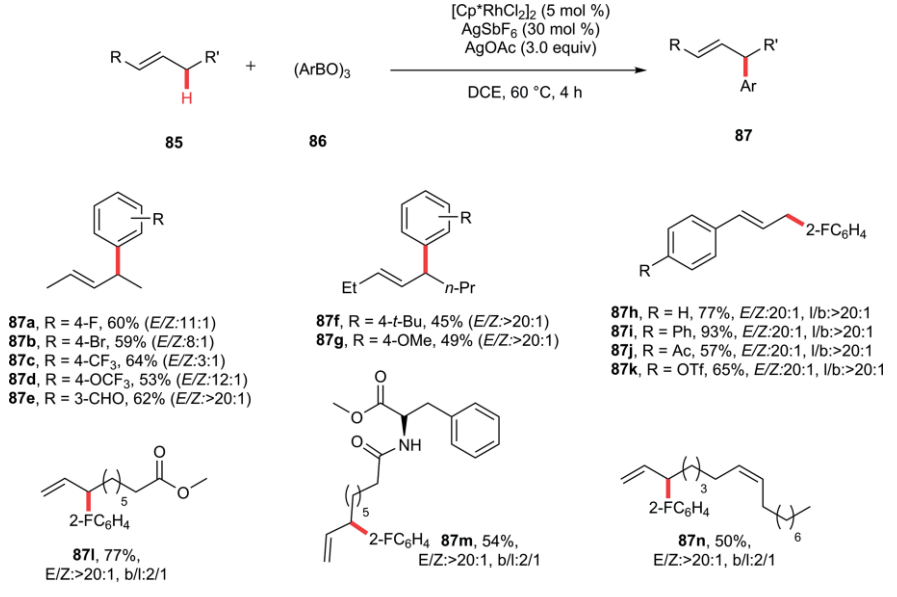
3.2 Cp*Rh(III)-Catalyzed C(sp^3)–H Arylation of Olefins with Boroxines

In 2019, Glorius's group reported a rhodium-catalyzed allylic C(sp^3)–H arylation of olefins with aryl boroxines.[17] When (*E*)-2-pentene (**85a**) was treated with tris(4-fluorophenyl)boroxine (**86a**) in the presence of $[Cp^*RhCl_2]_2$ (5 mol-%), $AgSbF_6$ (30 mol-%) and AgOAc (3.0 equiv.) at 60 °C in DCE for 4 h, the C–H arylated product **87a** was observed in 60 % yield (Scheme 35). During the optimization studies, it was found that the arylboronic acid provides traces of homocoupling arene product and the expected C–H arylated product was not observed. The aryl boroxine was effective for the reaction, providing the desired arylation product in the presence of a Rh(III) catalyst. The present reaction was compatible with various substituted aryl boroxines **86b–g**. It is interesting to note that the allylarenes produced arylation products **87h–k** with good diastereoselectivity. Phenylalanine derivative containing olefin and an alkene having internal double bond provided products **87m** and **87n** in 54 % and 50 % yields, respectively.

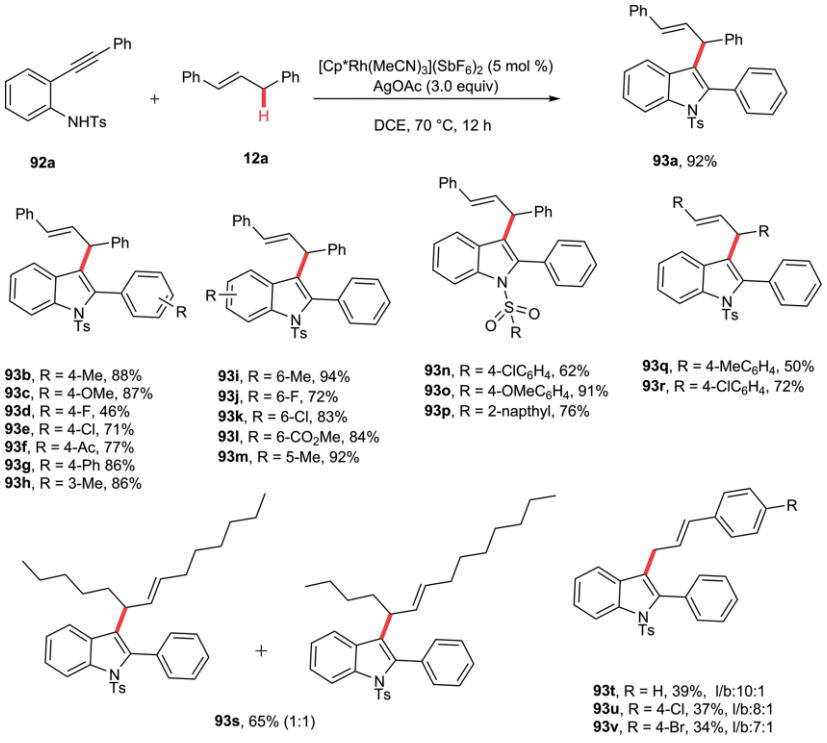
The deuterium scrambling studies between olefin **88** and deuterated olefin **D_2-89** under the optimized reaction conditions produced arylated products **90** and **D_2-91** without any significant amount of deuterium/hydrogen exchange (Scheme 36). This result indicated that the initial C–H activation or olefin coordination may not be reversible in the nature.

3.3 Cp*Rh(III)-Catalyzed Oxidative Allylic C–H Indolylation

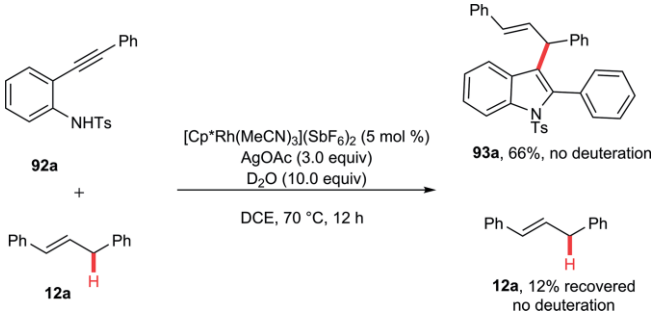
In 2019, Li's group reported a rhodium-catalyzed allylic C(sp^3)–H indolylation of *o*-alkynyl anilines with olefins.[18] When *o*-alkynyl aniline **92a** was treated with *trans*-1,3-diphenylpropene (**12a**) in the presence of $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (5 mol-%) and AgOAc (3.0 equiv.) at 70 °C in DCE for 12 h, the C–H indolylated product **93a** was observed in 92 % yield (Scheme 37). The present reaction was compatible with various substituted alkynes containing aryl substituents at the *para* and *meta* position **92b–h**. In addition, the present oxidative cyclization reaction produced the expected indolylated products **93i–m** in good to excellent yields. However, an internal alkene yielded 1:1 mixture of indolylated regioisomers **93s**. Under the optimized reaction conditions, substituted allyl benzene derivatives having halogen substitutents provided indolylated products **93t**, **93u** and **93v** in 39 %, 37 % and 34 % yields, respectively. There was no H/D exchange observed in indolylated product **93a** and the starting material *trans*-1,3-diphenylpropene (**12a**) was recovered when D_2O (10 equiv.) was employed under the optimized reaction conditions. It reveals that the C–H cleavage might be irreversible in nature (Scheme 38).



Scheme 35. C(sp3)–H arylation of alkenes with boroxines.



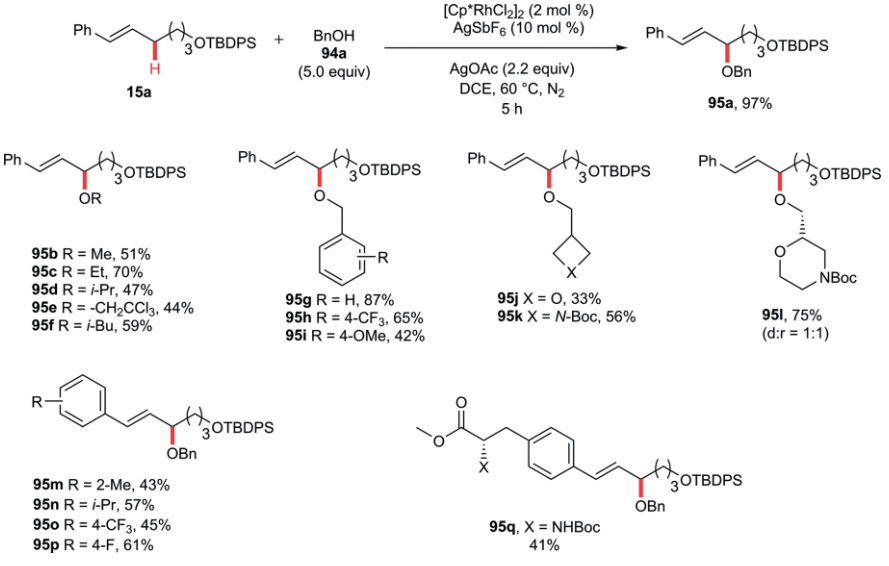
Scheme 37. Scope of alkenes and alkenes.



Scheme 38. Deuterium scrambling studies.

4. Cp*Rh(III) Catalyzed Allylic C–H Etherification

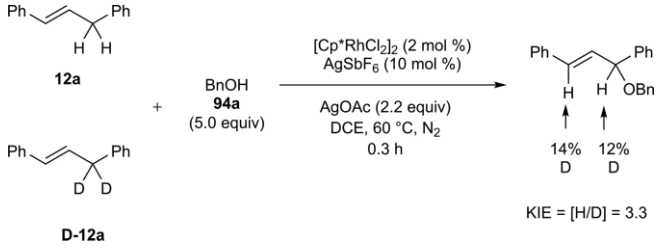
In 2018, Blakey's group reported a rhodium-catalyzed allylic C(sp^3)–H etherification of olefins with alcohols.[19] Treatment of **15a** with benzyl alcohol (**94a**) (5.0 equiv.) in the presence of $[Cp^*RhCl_2]_2$ (2 mol-%), $AgSbF_6$ (10 mol-%) and AgOAc (2.2 equiv.) at 60 °C in DCE for 5 h provided C–H etherification product **95a** in 97 % yield (Scheme 39). The present reaction was compatible with various substituted alcohols **94b-l**. In the reaction, the corresponding etherification products **95b-l** were observed in good to moderate yields. Various substituted un-



Scheme 39. Scope of alkenes and alcohols.

symmetrical alkenes produced the desired products **95m–q** in good yields in a highly regioselective manner.

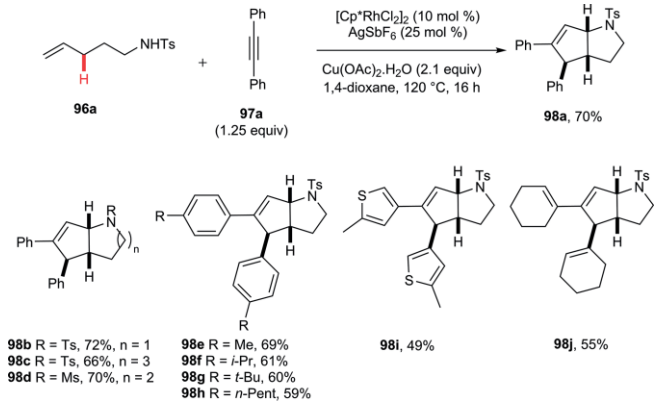
The primary kinetic isotope effect (KIE = 3.3) was observed in the reaction of 1:1 mixture of **12a** and **D-12a** under the optimized reaction conditions (Scheme 40).



Scheme 40. Deuterium labeling studies.

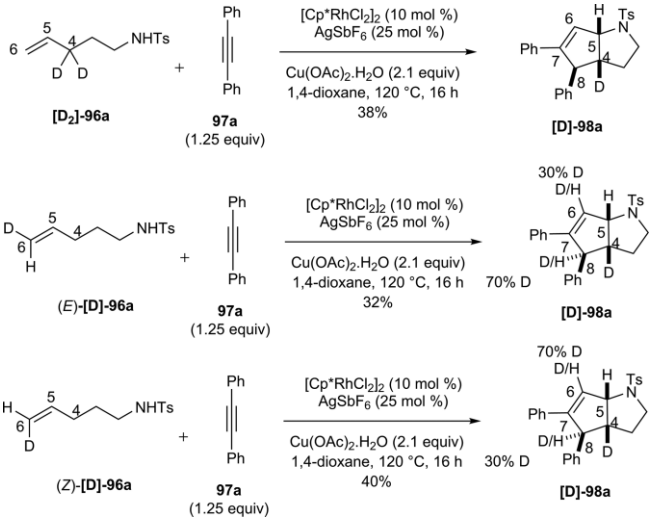
5. Miscellaneous Reaction

In 2015, Rovis's group reported the formation of azabicycles via a rhodium-catalyzed allylic C(sp^3)–H activation of olefins with alkynes.[20] When olefin **96a** was treated with diphenylacetylene (**97a**) (1.25 equiv.) in the presence of $[Cp^*RhCl_2]_2$ (10 mol-%), $AgSbF_6$ (25 mol-%) and $Cu(OAc)_2{\cdot}H_2O$ (2.1 equiv.) at 120 °C in 1,4-dioxane for 16 h, the cyclized product **98a** was observed in 70 % yield (Scheme 41). The present cyclization reaction provided various 6–7 membered ring systems with various substituents on the nitrogen atom. The present reaction was also compatible with various substituted diarylacetylene derivatives **97e–h**. In the reaction, the desired products **98e–h** were observed in good to moderate yields. The reaction of 2-methyl thiophene and vinyl cyclohexene substituted alkynes were also effective for the reaction, providing the cyclized products **98i–j** in good to moderate yields.

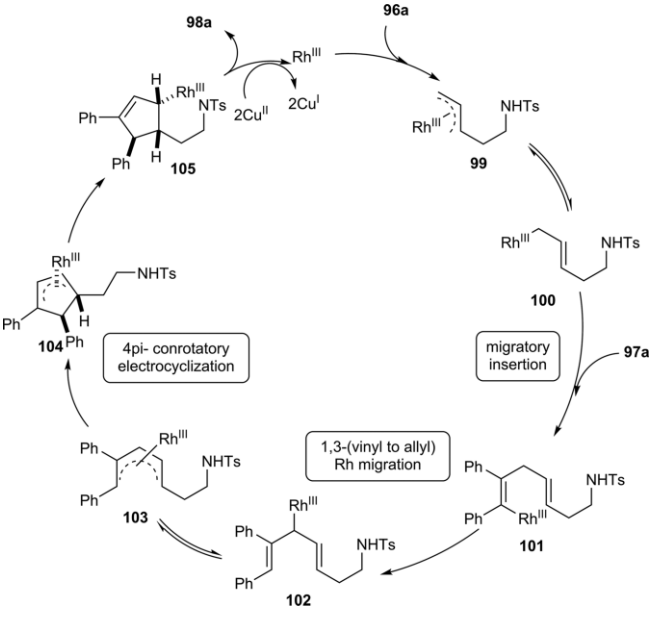


Scheme 41. Scope of alkenes and alkynes.

The deuterated olefin **[D_2]-96a** reacted with alkyne **97a** yielding product **[D_2]-98a**. In the product, the deuterium was retained at the position C4. In the reaction of olefins (*E*)-**[D]-96a** and (*Z*)-**[D]-96a**, product **[D]-98a** was observed with the deuteration at position 6 and 8. It reveals that the possibility of 1,3-shift during reaction process (Scheme 42). A possible mechanism for the formation of product azabicycle was proposed in Scheme 43. The catalytic cycle commences with C(sp^3)–H activation followed by the formation of π-allyl rhodium complex **99**. Insertion of alkyne **97a** with intermediate **100** followed 1,3-Rh migration leads to the formation of intermediate **102**. A sterically favorable 4π-conrotatory electrocyclization followed by reductive elimination produces product **98a** with the reduced form of Rh(I). The active Rh(III) catalyst was regenerated to the next cycle in the presence of $Cu(OAc)_2{\cdot}H_2O$.



Scheme 42. Deuterium labeling studies.



Scheme 43. Catalytic cycle.

6. Conclusion

In this present review, the recent advancement in allylic C(sp^3)–H activation of various substituted olefins catalyzed by Rh(III) or Ir(III) complexes has been discussed. This method provides highly valuable allylic functionalized molecules in a highly atom- and step-economical manner. It is important to note that the Rh(III) or Ir(III) complexes can be able to do the functionali-

zation of internal as well as terminal olefins efficiently in a highly regioselective manner. Apart from this significant advancement, there are still several challenges are in the field and it has to be explored. For instance, an enantioselective allylic C(sp^3)–H activation of olefins has to be explored. Very recently, Blakey's group has demonstrated an enantioselective allylic amination of olefins in the presence of a chiral rhodium complex.[15] This type of enantioselective reactions can be explored with various chiral ligands[21a] as well as chiral additives.[21b–21d] In addition, the catalytic reaction has to be explored with abundant first row transition metal complexes.

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