Video Article

Facile Preparation of (2*Z*,4*E*)-Dienamides by the Olefination of Electron-deficient Alkenes with Allyl Acetate

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Abstract

Direct cross-coupling between two alkenes *via* vinylic C-H bond activation represents an efficient strategy for the synthesis of butadienes with high atomic and step economy. However, this functionality-directed cross-coupling reaction has not been developed, as there are still limited directing groups in practical use. In particular, a stoichiometric amount of oxidant is usually required, producing a large amount of waste. Due to our interest in novel 1,3-butadiene synthesis, we describe the ruthenium-catalyzed olefination of electron-deficient alkenes using allyl acetate and without external oxidant. The reaction of 2-phenyl acrylamide and allyl acetate was chosen as a model reaction, and the desired diene product was obtained in 80% isolated yield with good stereoselectivity (*Z,E*/*Z,Z* = 88:12) under optimal conditions: $[Ru(p\text{-cymene})Cl_2]_2$ (3 mol %) and $AgSbF_6$ (20 mol %) in DCE at 110 ºC for 16 h. With the optimized catalytic conditions in hand, representative *α*- and/or *β*-substituted acrylamides were investigated, and all reacted smoothly, regardless of aliphatic or aromatic groups. Also, differently *N*-substituted acrylamides have proven to be good substrates. Moreover, we examined the reactivity of different allyl derivatives, suggesting that the chelation of acetate oxygen to the metal is crucial for the catalytic process. Deuterium-labeled experiments were also conducted to investigate the reaction mechanism. Only *Z*-selective H/D exchanges on acrylamide were observed, indicating a reversible cyclometalation event. In addition, a kinetic isotope effect (KIE) of 3.2 was observed in the intermolecular isotopic study, suggesting that the olefinic C-H metalation step is probably involved in the rate-determining step.

Video Link

The video component of this article can be found at https://www.jove.com/video/55766/

Introduction

Butadienes are widely occurring and are commonly found in many natural products, drugs, and bioactive molecules[1]. Chemists have made intense efforts to develop an efficient, selective, and practical synthetic methodology for the synthesis of 1,3-butadienes[2,3]. Recently, direct cross-couplings between two alkenes *via* double vinylic C-H bond activation was developed, representing an efficient strategy for the synthesis of butadienes, with high atomic and step economy. Among them, the palladium-catalyzed cross-coupling of two alkenes has attracted much attention, providing (*E,E*)-configured butadienes *via* alkenyl-Pd species[4,5]. For example, Liu's group developed a Pd-catalyzed butadiene synthesis by the direct cross-coupling of alkenes and allyl acetate (**Figure 1** and **Equation 3**)[4]. Meanwhile, the functional group-directed cross-coupling between alkenes provided butadienes with excellent (*Z,E*)-stereoselectivity due to the olefinic C-H cyclometalation event, representing a complementary method[6]. To date, some directing groups, such as enolates, amides, esters, and phosphates, have been successfully introduced to the cross-coupling between alkenes, providing a series of valuable and functionalized 1,3-butadienes. However, the directed cross-coupling reaction has not been developed, as there are still limited directing groups in practical use. In particular, a stoichiometric amount of oxidant is usually required to maintain the catalytic cycle, which produces a large amount of organic and inorganic wastes. There are very limited examples using electron-rich alkenes as the coupling partner.

Allyl acetate and its derivatives have been deeply investigated in organic transformations as powerful allylation and olefination reagents, including catalyzed cross-coupling, Friedel-Crafts allylation of electron-rich arenes, and catalytic C-H activation of electron-deficient arenes (**Figure 1** and **Equation 1**)[7]. More recently, the Loh group developed a rhodium(III)-catalyzed C-H allylation of electron-deficient alkenes with allyl acetates, creating 1,4-dienes (**Figure 1** and **Equation 2**)[8]. Meanwhile, the Kanai group reported a dehydrative direct C-H allylation with allylic alcohols by using a Co(III) catalyst[9]. Interestingly, Snaddon and co-workers disclosed a novel cooperative catalysis-based method for the direct asymmetric *α*-allylation of acyclic esters[10]. Very recently, the Ackermann group reported several novel allylation examples using inexpensive Fe, Co, and Mn catalysts[11]. These reports have made breakthroughs in allylation and olefination reactions, but double-bond migration and poor regioselectivity are usually inevitable and are not easily controlled. Hence, developing more efficient and selective reaction patterns of allyl acetates to construct valuable molecules is still highly desirable. With our interest in novel 1,3-butadiene synthesis *via* C-H olefination, we assumed that allyl acetate could be introduced to the directed allylation of electron-deficient alkenes, first delivering 1,4-diene. Then, the more thermodynamically stable 1,3-butadiene could be formed after the migratory isomerization of the C-C double bond[7], forming the diene product that cannot be obtained by cross-coupling using electron-rich alkenes, such as propene, as coupling partner[6]. Here, we report an

inexpensive Ru(III)-catalyzed olefinic C-H bond olefination of acrylamides with allyl acetates in the absence of any oxidant, which opens a novel synthetic route for the creation of (*Z,E*)-butadienes (**Figure 1** and **Equation 4**)[13].

Protocol

Caution: Please consult all relevant material safety data sheets (MSDS) before use. All cross-coupling reactions should be performed in vials under a sealed argon atmosphere (1 atm).

1. Preparation of Butadienes by the Olefination of Acrylamides with Allyl Acetate

1. Dry a screw-cap vial (8 mL) with a compatible magnetic stir bar in an oven at 120 °C for over 2 h. Cool the hot vial to room temperature by blowing on it with inert gas before use.
2. Use an analytical balance and weigh 3.7 mg (~3 mol %, ~0.005 mmol) of [Ru(*p*-cymene)Cl_2]$_2$ (brown powder) and 13.7 mg (20 mol%, 0.04 mmol) of $AgSbF_6$ (white solid) into the above reaction vial.
   NOTE: Since this is a new methodology, the cross-coupling reactions have been performed on a small scale for proof of concept to reduce waste formation. $AgSbF_6$ is used as an additive that may abstract chloride to generate a cationic ruthenium complex for electrophilic C-H bond activation[13]. Other silver salts, such as Ag_2CO_3, have also been tested, but no product was detected. The weight of the catalyst ([Ru(*p*-cymene)Cl_2]$_2$) is not very accurate and is in the range of 3.4-3.9 mg.
3. Add 1 mL of dry 1,2-dichloroethane to the reaction vial.
   NOTE: The amount of solvent is flexible-1 mL of 1,2-dichloroethane is just about enough to meet the minimal requirement of volume for the cross-coupling reaction. However, a little more (~0.1 mL) solvent is also permissible for a reaction of this scale. 1,2-dichloroethane was dried over a 3-Å molecular sieve before its use.
4. Use an analytical balance and add acrylamide (0.2 mmol, 1.0 equiv; solid or oil) to the above reaction vial.
5. Use a micro-syringe to add 43 µL (0.4 mmol, 2.0 equiv) of allyl acetate (a colorless liquid) to the above reaction vial.
   NOTE: Here, an excess amount of allyl acetate is required to inhibit the homo-coupling of acrylamide and to ensure that the acrylamide is fully converted. The product yield decreases if less allyl acetate (1.5 equiv) is added. The addition of more allyl acetate (3.0 equiv) cannot further improve the yield. In practice, there is no observed homo-coupling of allyl acetate, and the residual allyl acetate could be recovered.
6. Gently blow on the reaction vial with argon gas and cover the vial with a compatible screw-cap as quickly as possible.
   NOTE: The vial should be covered with a screw-cap as quickly as possible because an inert atmosphere is crucial for the cross-coupling reaction. It is better to perform the above protocol in a glove box.
7. Stir the reaction mixture at room temperature for an additional 5 min.
8. Heat the reaction vial to 110 °C in an oil bath with stirring for 16-18 h.
   NOTE: Generally, a color change to dark red is an indication that the reaction is taking place.
9. After cooling the vial down, use ethyl acetate:petroleum ether (2:1 or 1:3) mixtures as the solvent to develop the thin layer chromatography (TLC) plates to monitor the progress of the reaction by comparing the mixture to an acrylamide standard.
   NOTE: Depending upon the nature of the starting materials, the reaction may not go to completion. Typical R_f values of the products and starting materials are in the range of 0.3 - 0.7. The acrylamide starting material has been observed as a lower running spot than the butadiene product.
10. **Dissolve the crude product in a minimum of DCM and load it onto a silica column wet with petroleum ether. Separate the cross-coupling product *via* column chromatography using a mixture of ethyl acetate:petroleum ether (1:100 to 1:4) as the eluent.**
    1. Collect the eluent in a separate flask, evaporate the solvent on a rotatory evaporator, and place it under a high vacuum for a minimum of 2 h.
    2. Obtain approximately 20-50 mg of product for characterization by NMR spectroscopy.
       NOTE: The reaction mixture should be applied to column chromatography for purification directly after reaction completion.

2. Characterization of Dienamides

1. .Characterize and assess the purity of the final product using ^{1}H and ^{13}C NMR spectroscopy[14]. Typically, the chemical shift of the carbonyl carbon appears near 170 ppm on the ^{13}C NMR spectrum. The three sp^2 protons of the butadiene functional group are represented by characteristic peaks near 6.0 and 5.6 ppm.
2. Use infrared spectroscopy[14] to identify the characteristic carbonyl and C-C double-bond peak of the diene product.
3. Determine the molecular mass of the product and further validate the identity using high-resolution mass spectrometry (HRMS)[14].
4. Determine the melting point of the solid products[14].

Representative Results

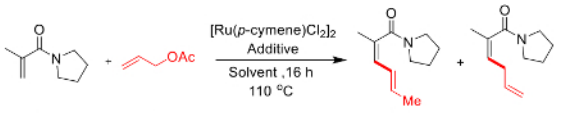
Our efforts were focused on the preparation of 1,3-butadiene from acrylamide and allyl acetate.

Table 1 illustrates the optimization of conditions, including the screening of various additives and solvents, using [Ru(*p*-cymene)Cl_2]$_2$ as the catalyst. After screening a series of representative solvents, we were pleased to find that the product yield dramatically improved to 80%, with good selectivity (*Z,E*/*Z,Z* = 88:12). The *cis*-structure was confirmed by the NOESY NMR analysis, indicating that the amido group directed the C-C bond formation step in the catalytic cycle. The *Z,E*/*Z,Z* ratio was determined by the integration of ^{1}H NMR. When the reaction was performed in 1,2-dichloroethane, only trace amounts of allylation product **4a** (**3a**/**4a** = 95:5) were obtained (**Table 1**, entry 6). However, other solvents, such as tetrahydrofuran and *t*-amyl alcohol, greatly hindered the reaction, while strong polar solvents, such as acetonitrile and *N,N*-dimethylformamide, provided no product (**Table 1**, entries 1 - 5). Moreover, a lower temperature (90 °C) resulted in decreased yield but facilitated the allylation process, while elevating the temperature (130 °C) enhanced the olefination process but caused a decreased yield, presumably due to degradation (**Table 1**, entries 7 and 8). The [Ru(*p*-cymene)Cl_2]$_2$ complex itself could not result in the corresponding butadiene **3a** (**Table 1**, entry 9). Other additives, such as Ag_2CO_3, KPF_6, and $Cu(OAc)_2$, were also screened, but all of them failed to assist the ruthenium complex in forming the product (**Table 1**, entries 10-12).

In **Table 2**, the scope of the reaction was explored by submitting various acrylamides to the optimized conditions in the presence of allyl acetate **2a**. Modest to excellent yields were obtained, with good regioselectivity and (*Z,E*/*Z,Z*) selectivity. As shown in **Table 2**, the differently *N*-substituted acrylamide **1** also reacted well with allyl acetate, providing the desired 1,3-butadienes with good stereoselectivity (*Z,E*/*Z,Z* up to 88:12) (**3a-3f**). This cross-coupling reaction also proceeded smoothly when performed on the gram-scale, as described in the synthesis of **3a**, showing the robustness of this method. Secondary and primary amides were also tested, but none of them delivered the olefination or allylation product. Installation of the phenyl ring in the *α*-position of acrylamide showed limited influence on the reaction. The desired product was isolated in 67% yield, with excellent regioselectivity (**3g**/**4g** = 97:3), but the stereoselectivity decreased slightly (*Z,E*/*Z,Z* = 83:17). Valuable functional groups, such as Br, F, or Me, could be well tolerated, although the product yields decreased when an electron-withdrawing group was introduced (**Table 2**, **3h-j**). Larger aromatic rings, such as naphthalene-substituted acrylamide, also provided good results (**Table 2**, **3k**). Other alkyl groups, such as benzyl and hexyl tethering substrates, were also reacted well, with good regioselectivity and *Z*/*E* selectivity (**Table 2**, **3l-o**). The reactivity of *α*,*β*-disubstituted acrylamides **1** were also examined. Acrylamide **1**, bearing a cyclopentenyl unit, reacted well, but the allylation product **4p** increased remarkably. Interestingly, acrylamide embedded with a cyclohexenyl moiety exhibited excellent regio- and stereoselectivity, forming trace amount of 1,4-diene **4q**.

In **Table 3**, the reactivity of different allyl derivatives was examined. Branched allyl acetates were also examined. *α*- or *β*-substituted allyl acetates were completely inert for cross-coupling, while *γ*-substituted allyl acetate afforded only trace product. Other allyl carboxylic esters, such as allyl hexanoate **2b**, allyl methacrylate **2c**, allyl phenoxyacetate **2d**, and allyl 3,3,3-trifluoropropanoate **2e**, were also tested, showing decreased reactivity comparing to allyl acetate **2a**. In contrast, allyl methyl carbonate **2f** was more inactive for olefination and allylation, forming product with only 24% yield. It is worth noting that allyl iodide **2g** did not exhibit any reactivity towards acrylamide, suggesting that the chelation of acetate oxygen to the metal is crucial in the catalytic process.

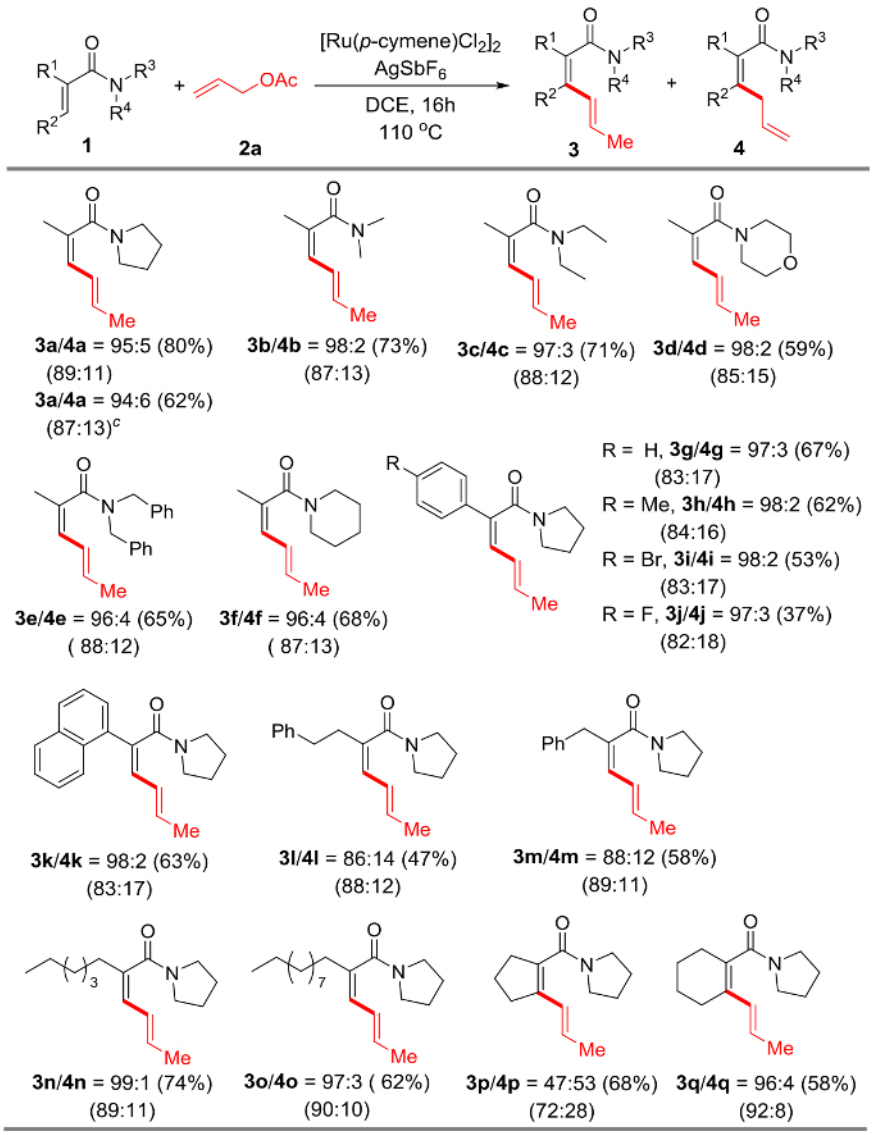
Moreover, to investigate the reaction mechanism, two deuterium-labeled experiments were conducted (**Figure 2**). If the acrylamide **1g** was subjected to a standard catalytic system in the presence of acetic acid-d_4 (10.0 equiv) without allyl acetate, the cationic ruthenium species led to a *Z*-selective H/D exchange on acrylamide; an *E*-selective H/D exchange was not observed, thereby indicating a reversible cyclometallation event[6,7,8]. Moreover, a kinetic isotope effect (KIE) of k_H/k_D = 3.2 was observed in the intermolecular isotopic study, suggesting that the olefinic C-H bond metalation step is probably involved in the rate-determining step[6].



entry	additive	solvent	yield (%)	*Z,E*/*Z,Z*	**3a**/**4a**
1	$AgSbF_6$	*t*-AmOH	10	86:14	68:32
2	$AgSbF_6$	DMF	0	-	-
3	$AgSbF_6$	dioxane	8	89:11	> 99:1
4	$AgSbF_6$	THF	21	> 99:1	77:23
5	$AgSbF_6$	MeCN	0	-	-
6	**$AgSbF_6$**	**DCE**	**80**	**88:12**	**95:5**
7[c]	$AgSbF_6$	DCE	45	> 99:1	46:54
8[d]	$AgSbF_6$	DCE	33	98:2	92:8
9	-	DCE	0	-	-
10	Ag_2CO_3	DCE	0	-	-
11	KPF_6	DCE	0	-	-
12	$Cu(OAc)_2$	DCE	0	-	-

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), [Ru(*p*-cymene) Cl_2]$_2$ (3 mol %), and an additive (20 mol %) at 110 °C in a specific solvent (1 mL), under argon, 16 h.

Table 1: Optimization of Catalytic Conditions.



[a]Reactions conditions: **1** (0.2 mmol), **2a** (0.4 mmol), [Ru(*p*-cymene) Cl_2]$_2$ (3 mol %), $AgSbF_6$ (20 mol %) in DCE (1.0 mL) at 110 °C, 16 h. [b]The yields indicated are of isolated products **3** and **4**; *Z,E*/*Z,Z* ratios of the **3** isomers given in parentheses and the regioisomeric ratio **3**/**4** were calculated by ^{1}H NMR spectroscopy. [c]The reaction was performed in 0.5 g scale.

Table 2: Scope of Differently Substituted Acrylamides.

2a, R = Me	80%, *Z*,*E*/*Z*,*Z* = 88:12	5%
2b, R = *n*-Hex	64%, *Z*,*E*/*Z*,*Z* = 86:14	10%
2c, R = $CH_3C{=}CH_2$	56%, *Z*,*E*/*Z*,*Z* = 83:17	< 5%
2d, R = CH_2OPh	61%, *Z*,*E*/*Z*,*Z* = 86:14	8%
2e, R = CH_2CF_3	35%, *Z*,*E*/*Z*,*Z* = 77:23	ND
2f, R = OCH_3	24%, *Z*,*E*/*Z*,*Z* = 86:14	< 5%
2g, allyl iodide	NR	

[a]Reactions conditions: **1a** (0.2 mmol), **2** (0.4 mmol), [Ru(*p*-cymene) Cl_2]$_2$ (3 mol %), $AgSbF_6$ (20 mol %) in DCE (1.0 mL) at 110 ºC, 16 h. [b] The yields indicated are isolated and total yields of **3a** and **4a**; *Z*/*E* ratio of **3a** and the yield of **4a** were determined by ^{1}H NMR.

Table 3: Scope of Different Allyl Derivatives.

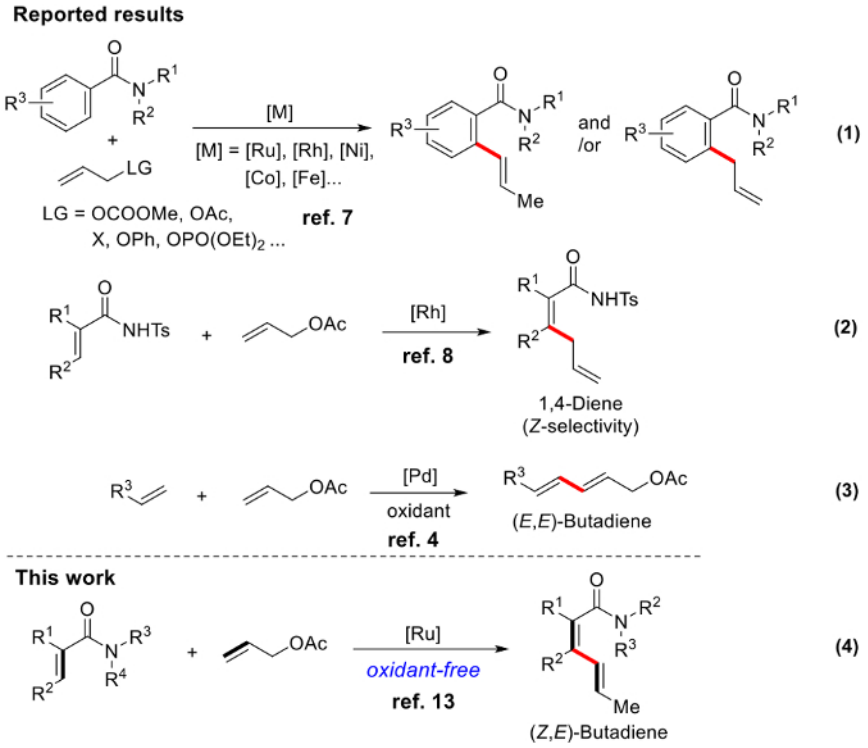


Figure 1: Transition Metal-catalyzed Olefination and Allylation by C-H Activation with Allyl Derivatives. Please click here to view a larger version of this figure.

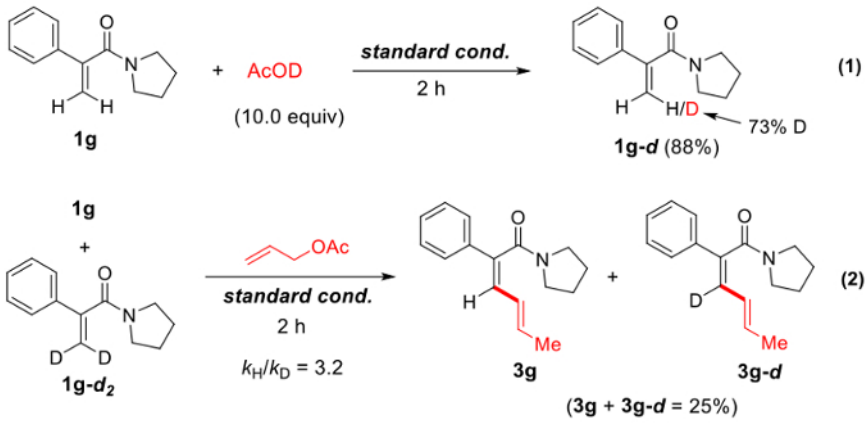


Figure 2: Deuterium-labeled Experiments. Please click here to view a larger version of this figure.

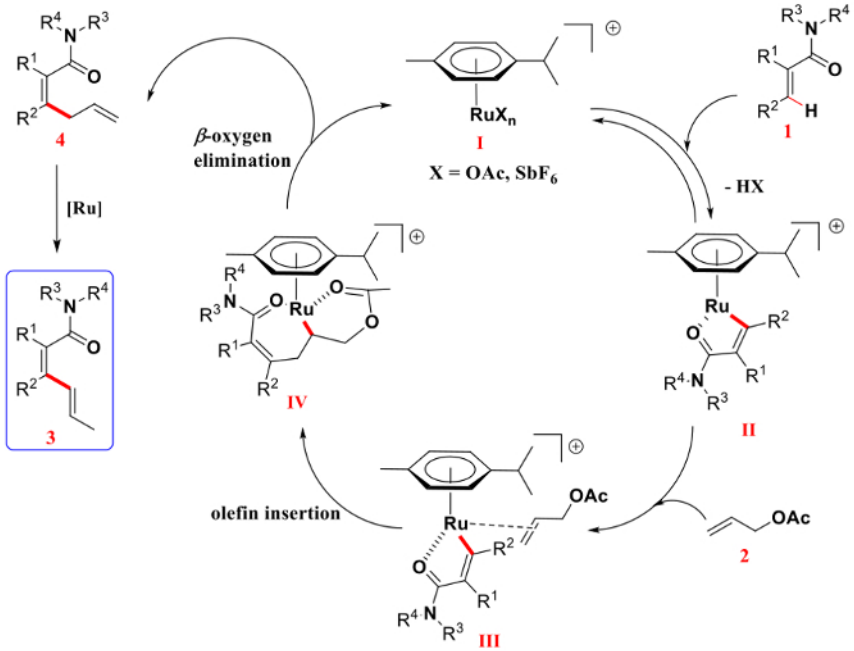


Figure 3: Proposed Mechanism for this Catalytic Olefination. Please click here to view a larger version of this figure.

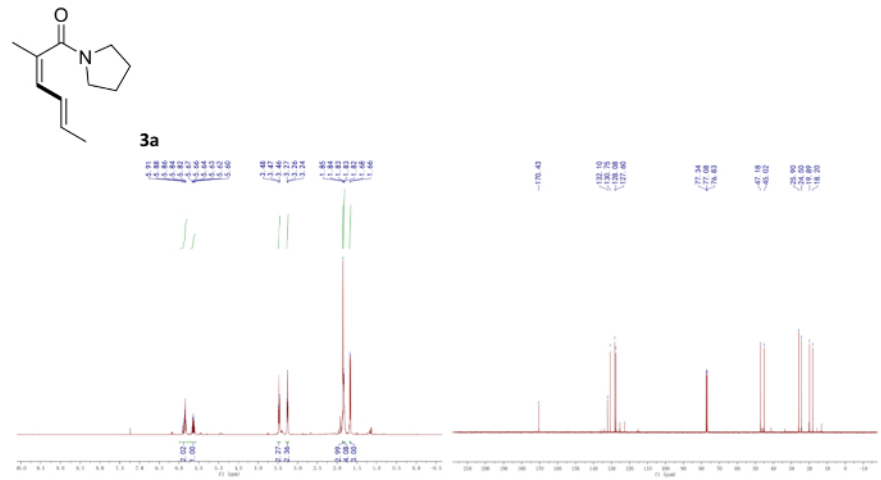


Figure 4: **^{1}H NMR and ^{13}C NMR Spectra for (2*Z*,4*E*)-2-methyl-1-(pyrrolidin-1-yl) hexa-2,4-dien-1-one (3a).** This compound was prepared by the general procedure described above and was obtained as a yellow oil (28.6 mg, yield = 80%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.00 - 5.87 (m, 2H), 5.76 - 5.66 (m, 1H), 3.54 (t, *J* = 7.0, 2H), 3.33 (t, *J* = 6.5 Hz, 2H), 1.93 (s, 3H), 1.92 -1.88 (m, 4H), 1.74 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.46, 132.11, 130.79, 128.11, 127.62, 47.21, 45.05, 25.92, 24.52, 19.92, 18.22. HR-MS (ESI): m/z calculated for $C_{11}H_{17}NO$: $[M+H]^+$180.1383, found: 180.1388. FTIR (KBr, cm^{-1}): v 3819, 3709, 3627, 3565, 2924, 1733, 1652, 1615, 1558, 1455. The *Z*/*E* ratio of the final products can be calculated from ^{1}H NMR by the integration of olefinic protons on isomers. Please click here to view a larger version of this figure.

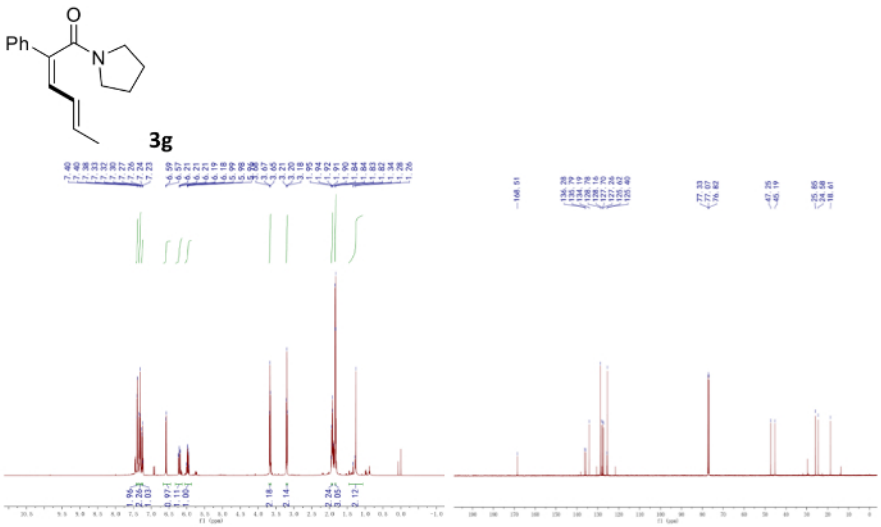


Figure 5: ^{1}H NMR and ^{13}C NMR Spectra for (2*Z*,4*E*)-2-phenyl-1-(pyrrolidin-1-yl) hexa-2,4-dien-1-one (3g). This compound was prepared by the general procedure described above and was obtained as a yellow solid (32.3 mg, yield = 67%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41-7.21 (m, 5H), 6.58 (d, *J* = 11.0 Hz, 1H), 6.26-6.17 (m, 1H), 6.02-5.93 (m, 1H), 3.67 (t, *J* = 7.0 Hz, 2H), 3.20 (t, *J* = 7.0 Hz, 2H), 1.82-1.95 (m, 7H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.48, 136.28, 135.83, 134.19, 128.78, 128.16, 127.70, 127.26, 125.40, 47.23, 45.18, 25.85, 24.58, 18.61. HR-MS (ESI): m/z calculated for $C_{16}H_{19}NO$ $[M+H]^+$ 242.1539, found: 242.1531. FTIR (KBr, cm^{-1}): v 3851, 3647, 3627, 3565, 2924, 1732, 1633, 1429, 966, 694. Melting point: 82-83 °C. The *Z*/*E* ratio of the final products can be calculated from ^{1}H NMR by the integration of olefinic protons on isomers. Please click here to view a larger version of this figure.

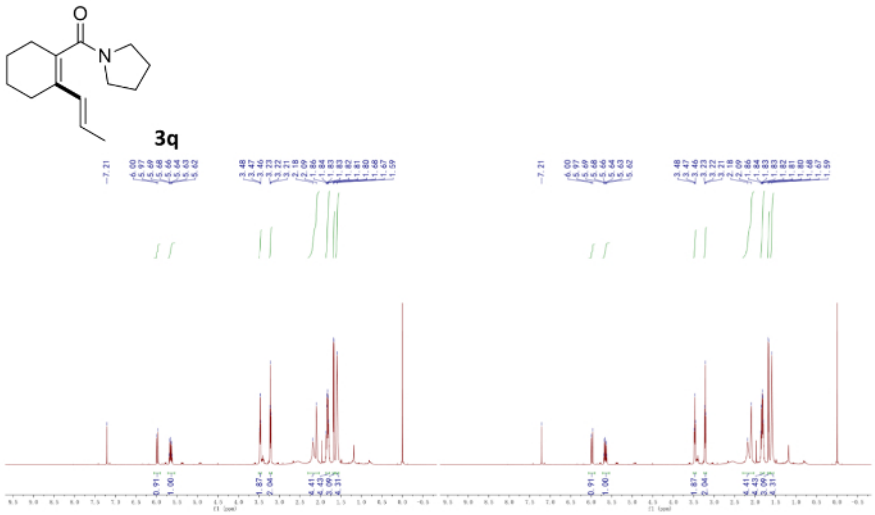


Figure 6: ^{1}H NMR and ^{13}C NMR Spectra for (*E*)-(2-(prop-1-en-1-yl)cyclohex-1-en-1-yl)(pyrrolidin-1-yl)methanone (3q). This compound was prepared by the general procedure described above and was obtained as a yellow oil (25.4 mg, yield = 58%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.98 (d, *J* = 15.5 Hz, 1H), 5.72 - 5.58 (m, 1H), 3.47 (t, *J* = 6.5 Hz, 2H), 3.22 (t, *J* = 6.5 Hz, 2H), 2.18-2.09 (m, 4H), 1.86-1.79 (m, 4H), 1.67 (d, *J* = 6.5 Hz, 3H), 1.59 (brs, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.53, 131.25, 129.92, 128.58, 124.04, 46.18, 43.99, 25.76, 24.89, 23.58, 23.37, 21.20, 21.17, 17.53. HR-MS (ESI): m/z calculated for $C_{14}H_{21}NO$ $[M+H]^+$: 220.1696, found: 220.1694. FTIR (KBr, cm^{-1}): v 3742, 3674, 3646, 3565, 2933, 1683, 1634, 1557, 1505, 1435. The *Z/E* ratio of the final products can be calculated from ^{1}H NMR by the integration of olefinic protons on isomers. Please click here to view a larger version of this figure.

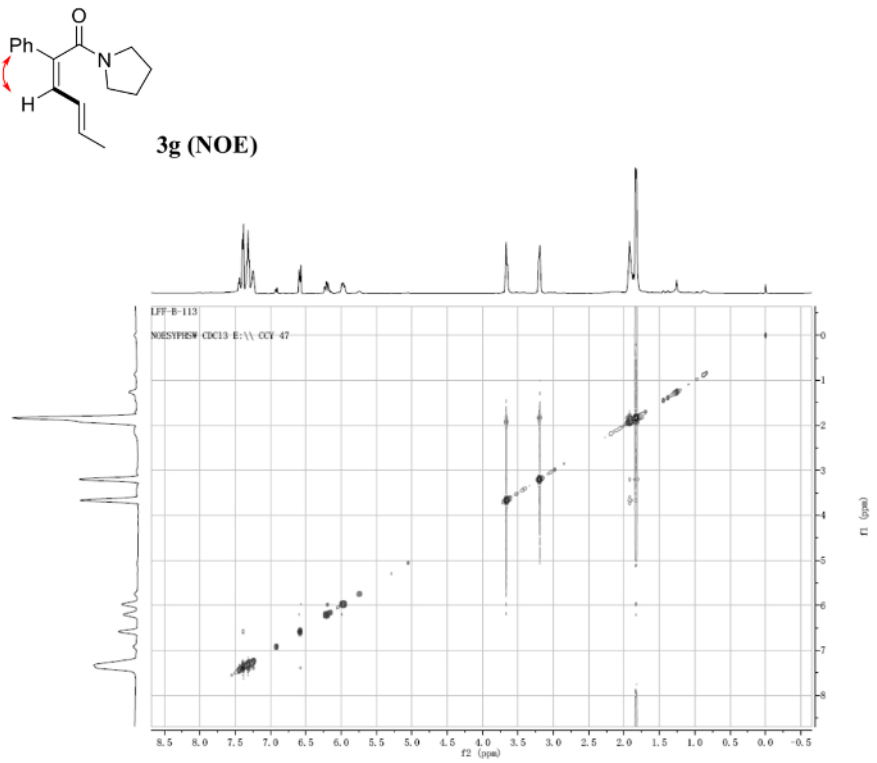


Figure 7: NOESY NMR Analysis for (2*Z*,4*E*)-2-phenyl-1-(pyrrolidin-1-yl) hexa-2,4-dien-1-one (3g).

Discussion

$[Ru(p\text{-cymene})Cl_2]_2$ is a cheap, easily accessible, air-stable, and highly active Ru-based catalyst with excellent functional group tolerance that efficiently operates under mild reaction conditions to give C-H/C-H coupling butadiene products. Silver salt $AgSbF_6$ was used as an additive that may abstract the chloride of $[Ru(p\text{-cymene})Cl_2]_2$ to generate a cationic ruthenium complex for the following C-H bond activation. However, only *α*-substituted and *α,β*-disubstituted acrylamides are suitable for this cross-coupling reaction. We also tested some other acrylamides, such as primary methacrylamide and *N*-benzyl methacrylamide, but both of them delivered no product. Also, *β*-substituted acrylamide, such

as crotonamide, and plain acrylamide without any substituent did not exhibit any reactivity, even at an elevated temperature. Moreover, allyl acetate proved to be the best coupling partner. We only demonstrated that the reaction can be scaled up to the gram-scale (0.5 g of **1a**), with 62% isolated yield and good stereoselectivity (*Z,Z/Z,E* = 87/13). The reactions may be performed on a larger scale.

On the basis of these mechanistic studies and previous reports, we propose a possible mechanism (**Figure 3**). First, an active cationic ruthenium complex **I** was generated from $[RuCl_2(p\text{-cymene})]_2$. Then, an acetic acid-assisted reversible C-H bond activation occurred by an electrophilic-type cycloruthenation, forming intermediate **II**. Subsequent coordination and the migratory insertion of allyl acetate delivered a seven-membered Ru (II) species **IV**. As coordination of the amide group may have prevented the *synβ*-hydride elimination of the benzylic hydrogen atom by conformational restriction, the following *β*-oxygen elimination was facile, producing allylation product **4** and regenerating the active Ru(II) complex **I**. The final butadiene **3** of the thermodynamically more stable product was formed *via* the migratory isomerization of the double bond with the help of the active [Ru] species.

Even though the described syntheses, as well as the coupling reaction protocols, are straightforward, some of the critical steps are listed here. Use newly purchased or properly stored $AgSbF_6$, as it is hygroscopic. Store $[Ru(p\text{-cymene})Cl_2]_2$ under an inert atmosphere. Use freshly distilled allyl acetate and store it under an inert atmosphere. Prepare the acrylamide freshly and store it under an inert atmosphere. Use dry 1,2-dichloroethane with high purity and store it over a 3-Å molecular sieve under an inert atmosphere. Dry all glassware in an oven at 120 °C for more than 2 h and cooling them under an inert atmosphere before use. Perform the cross-coupling under an inert atmosphere; argon is the best choice.

Disclosures

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