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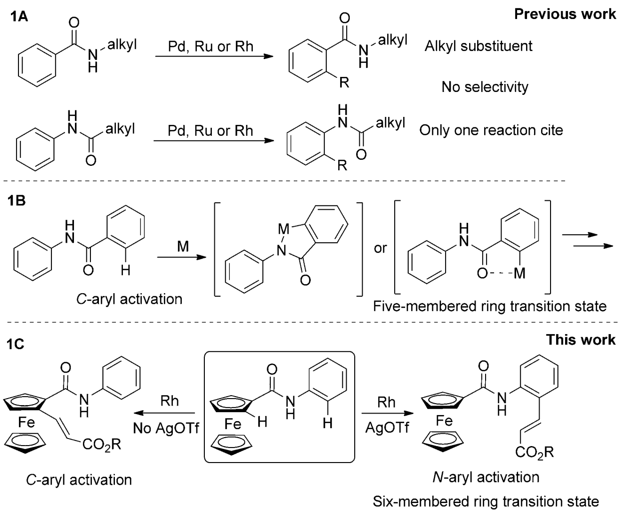
C–H Activation

Non-coordinating-Anion-Directed Reversal of Activation Site: Selective C–H Bond Activation of *N*-Aryl Rings

Dawei Wang,*[a] Xiaoli Yu,[a] Xiang Xu,[b] Bingyang Ge,[a] Xiaoli Wang,[a] and Yaxuan Zhang[a]

Abstract: An Rh-catalyzed selective C–H bond activation of diaryl-substituted anilides is described. In an attempt to achieve C–H activation of *C*-aryl rings, we unexpectedly obtained an *N*-aryl ring product under non-coordinating anion conditions, whereas the *C*-aryl ring product was obtained in the absence of a non-coordinating anion. This methodology has proved to be an excellent means of tuning and adjusting selective C–H bond activation of *C*-aryl and *N*-aryl rings. The approach has been rationalized by mechanistic studies and theoretical calculations. In addition, it has been found and verified that the catalytic activity of the rhodium catalyst is obviously improved by non-coordinating anions, which provides an efficient strategy for obtaining a highly chemoselective catalyst. Mechanistic experiments also unequivocally ruled out the possibility of a so-called “silver effect” in this transformation involving silver.

The motivation for chemists to develop new methods is to find effective solutions for challenging chemical transformations, particularly those with good chemo-, regio-, and stereoselectivities.[1] Among these selective transformations, C–H bond activation has attracted considerable attention due to its unique atom-economical properties and circumvention of the need for functionalized starting materials.[2] Anilides are effective as directing groups for C–H activation and therefore have been the focus of much attention in recent decades. In 2002, de Vries and van Leeuwen developed Pd-catalyzed *ortho* C–H bond activation of anilides with benzoquinone (BG) as an oxidant (Scheme 1).[3] Liu and Guo screened and improved the same reaction with oxygen as oxidant.[4] Shi demonstrated highly regioselective halogenation and arylation of acetanilide through palladium-mediated C–H functionalization.[5] Recently, Ackermann and co-workers reported Ru-catalyzed alkenylations of anilides and benzamides in water.[6] Related research has been reported by Yu,[7] Ma,[8] Chang,[9] Fagnou,[10] Glorius,[11] Cui,[12] Ackermann,[13] Shi,[14] Ge,[15] and many others[16] (Scheme 1 A). In 2010, the Rovis group developed Rh-catalyzed oxidative cycloaddition of benzamides and alkynes through *ortho* C–H activation in the absence of a silver salt. Their work provides a good example of functionalization of the *C*-aryl ring rather than the *N*-aryl ring of anilides.[17] Li and co-workers described activation of the *ortho* C–H bonds of *C*-aryl rings to give the vinylation products.[18] Chatani et al. reported Ni-catalyzed oxidative cycloaddition of aromatic amides with alkynes.[19] Tanaka and co-workers developed the oxidative annulation of Ac-protected anilides with internal alkynes using a dinuclear electron-deficient rhodium complex as catalyst. Later, they found that the same rhodium complex could be applied to alkene substrates, giving the desired products in moderated yields at mild temperatures.[20] These examples typically involved five- or six-membered ring transition states (Scheme 1 B), which led to *N*-aryl or *C*-aryl ring activation products. However, to the best of our knowledge, there is no general method for obtaining one or other of the products in a controlled manner.[21]



Scheme 1. Non-coordinating-anion-directed selective C–H activation with anilide as a directing group.

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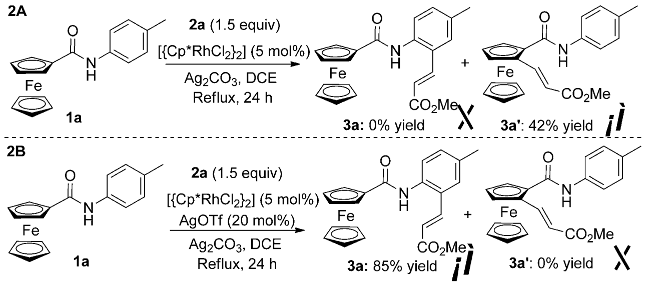
The chemistry of non-coordinating anions (NCAs) and very weakly coordinating anions (WCAs) is of fundamental importance in many areas, yet is often overlooked.[22] The application of NCAs and WCAs, such as in gold-catalyzed, silver-mediated, and hydrogen-bond related reactions, has attracted much attention. Indeed, many new chemical reactions rely on the assistance of NCAs and WCAs,[23] and furthering their application is a worthwhile goal. In the present work, we have found that NCAs play a key role in the selective C–H bond activation of anilides (Scheme 1 C).

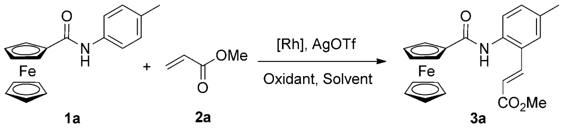
Our previous research was mainly focused on the competitive reactions of C–H bond activation and C–F activation.[24] Our results indicated that the selective C–H bond activation of ferrocenyl anilides[25] is an important issue (Scheme 2). When ferrocenyl anilide (**1 a**) was coupled with methyl acrylate (**2 a**), the *N*-aryl ring activation product **3 a** was obtained in 85 % yield in the presence of AgOTf, whereas the *C*-aryl ring activation product **3 a′** was obtained in 42 % yield in the absence of AgOTf (Scheme 2). Herein, we report oxidative coupling reactions of anilides with alkenes through Rh-catalyzed selective C–H bond activation. This methodology has proved to be an excellent means of selectively activating *N*-aryl rings rather than *C*-aryl rings, and has been supported by mechanistic studies and theoretical calculations.



Scheme 2. Selective C–H activation by a non-coordinating anion.

We first carried out the oxidative coupling reaction of ferrocenyl anilide (**1 a**) with methyl acrylate (**2 a**) in order to determine the C–H bond activation induced by the rhodium catalyst. The desired product was obtained in only 18 % yield, but this nevertheless implied the feasibility of the selective C–H bond activation of anilides. Next, the reaction conditions were screened to maximize the yield, and the results are shown in Table 1. The effects of different catalysts and oxidants on the reactivity were studied. With $[\{Cp^*RhCl_2\}_2]$ as catalyst and Ag_2CO_3 as oxidant in 1,2-dichloroethane (DCE), the product was obtained in 85% yield (Table 1, entry 9). The reaction proved to be highly dependent on the solvent, and the best results were achieved in DCE. A blank experiment showed that no reaction occurred in the absence of a rhodium catalyst (Table 1, entry 4). When the reaction was carried out with air as oxidant, only a low yield of the product was obtained (Table 1, entry 23).

Table 1. Screening of reaction conditions[a,b]

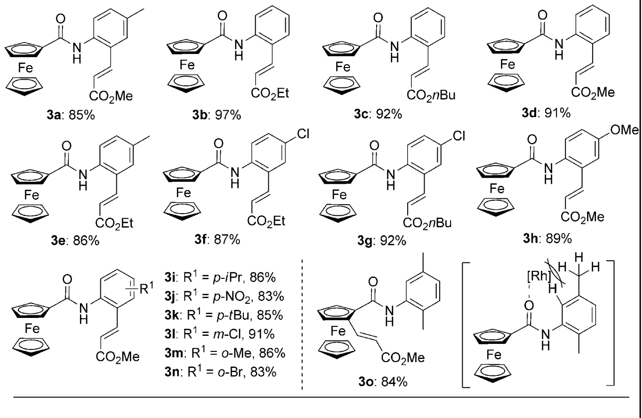


Entry	Catalyst	Oxidant	Solvent	Yield [%]
1	$[\{Rh(cod)Cl\}_2]$	$K_2S_2O_8$	DCE	18
2	$[\{Cp^*RhCl_2\}_2]$	$K_2S_2O_8$	DCE	35
3	$Pd(OAc)_2$	$K_2S_2O_8$	DCE	<5
4	none	$K_2S_2O_8$	DCE	<5
5	$[\{Cp^*RhCl_2\}_2]$	*p*-quinone	DCE	27
6	$[\{Cp^*RhCl_2\}_2]$	$Na_2Cr_2O_7$	DCE	11
7	$[\{Cp^*RhCl_2\}_2]$	Ag_2O	DCE	57
8	$[\{Cp^*RhCl_2\}_2]$	AgOAc	DCE	68
9	$[\{Cp^*RhCl_2\}_2]$	Ag_2CO_3	DCE	85
10	$[\{Cp^*RhCl_2\}_2]$	CuCl	DCE	30
11	$[\{Cp^*RhCl_2\}_2]$	$Cu(OAc)_2$	DCE	21
12	$[\{Cp^*RhCl_2\}_2]$	$CuSO_4$	DCE	8
13	$[\{Cp^*RhCl_2\}_2]$	Ag_2CO_3	THF	<5
14	$[\{Cp^*RhCl_2\}_2]$	Ag_2CO_3	dioxane	15
15	$[\{Cp^*RhCl_2\}_2]$	Ag_2CO_3	DMF	24
16	$[\{Cp^*RhCl_2\}_2]$	Ag_2CO_3	DME	9
17	$[\{Cp^*RhCl_2\}_2]$	Ag_2CO_3	H_2O	<5
18	$[\{Cp^*RhCl_2\}_2]$	Ag_2CO_3	toluene	<5
19	$[\{Cp^*RhCl_2\}_2]$	Ag_2CO_3	benzene	<5
20	$[\{Cp^*RhCl_2\}_2]$	Ag_2CO_3	DMSO	29
21	$[\{Cp^*RhCl_2\}_2]$	Ag_2CO_3	DMA	20
22	$[\{Cp^*RhCl_2\}_2]$	Ag_2CO_3	MeOH	<5
23	$[\{Cp^*RhCl_2\}_2]$	air	DCE	38

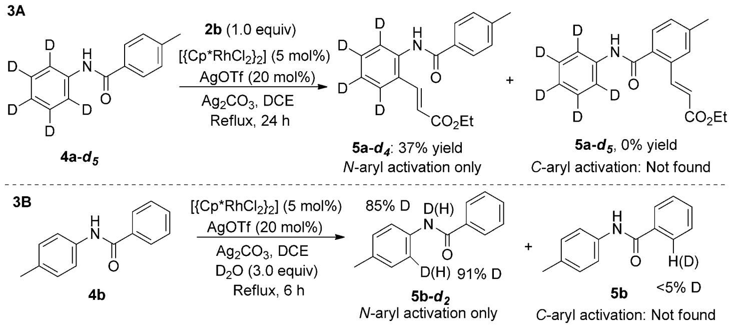
[a] Conditions: **1 a** (0.5 mmol, 1.0 equiv), **2 a** (0.75 mmol, 1.5 equiv), [Rh] (5 mol %), AgOTf (20 mol %), Ag_2CO_3 (1.5 equiv), DCE (3 mL), 24 h. [b] Isolated yields.

Having established the optimal conditions, we explored the scope of the Rh-catalyzed oxidative coupling reaction with AgOTf as an additive (Table 2). The reactions were carried out in DCE at 90 °C under air. As illustrated in Table 2, high yields were achieved with nearly all of the substrates. Very interestingly, reaction occurred at the *C*-aryl ring when there were two substituents on the *N*-aryl ring (**3 o**), which may be attributed to a steric effect. This suggested an alternative method for se-

Table 2. Substrate scope of ferrocenyl amides.[a]



[a] Conditions: **1** (0.5 mmol, 1.0 equiv), **2** (0.75 mmol, 1.5 equiv), $[\{Cp^*RhCl_2\}_2]$ (5 mol %), AgOTf (20 mol %), Ag_2CO_3 (1.5 equiv), DCE (3 mL), 12 h.



Scheme 3. Deuteration experiments.

lectively activating the *C*-aryl rings. Indeed, with this methodology in hand, both *C*-aryl ring products and *N*-aryl ring products were obtained in high yields.

To further test this result, deuterated anilide d_5-**4a** was subjected to the reaction, whereupon d_4-**5a** was obtained in 37% yield as the sole product, as determined by NMR (see the Supporting Information for details). It should be noted that the *C*-aryl ring activation product d_5-**5a** was not observed in this transformation (Scheme 3A). Furthermore, this cationic rhodium complex could lead to selective *ortho* H/D exchange on the *N*-aryl ring when D_2O was added to the reaction mixture instead of ethyl acrylate (Scheme 3B).

As illustrated by the reaction profiles (Figure 1), the reaction rate and yield were both strongly affected by the presence of silver salts. Higher yield and shorter reaction time were obtained when AgOTf was added to the mixture, whereas other silver salts, such as $AgBF_4$ and $AgSbF_6$, gave only moderate yields. It should be noted that the *C*-aryl ring activation product was obtained in the absence of a silver salt, which is consistent with the results of Li[18] and Glorius.[11] These experiments implied that the silver salt plays a decisive and crucial role in this transformation.

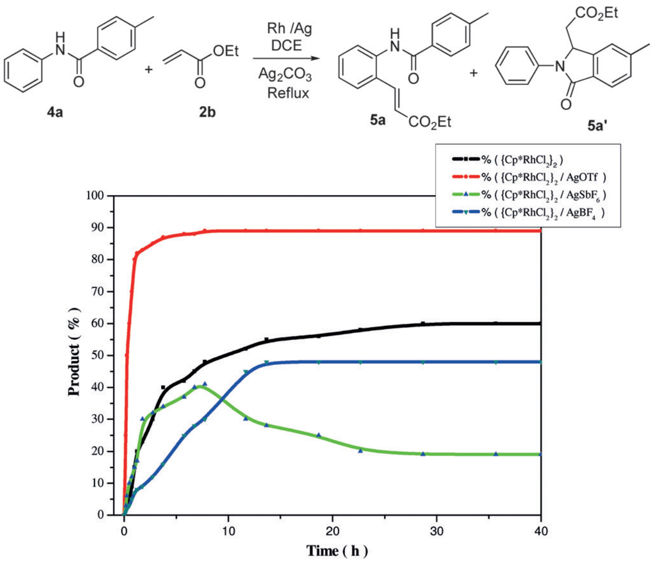


Figure 1. Reaction process profile.

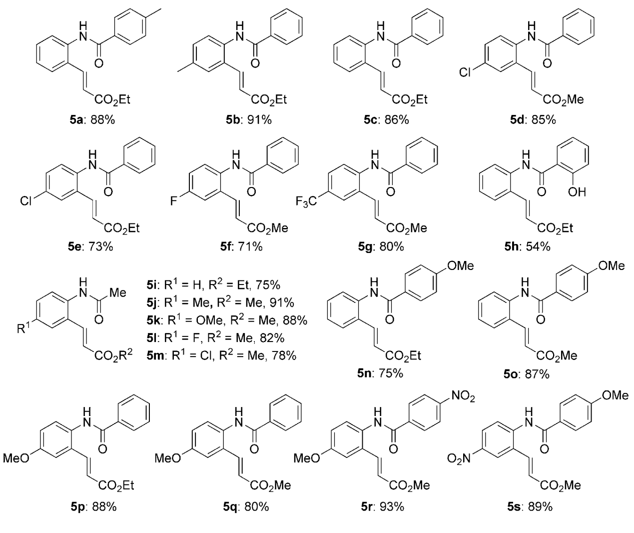
Next, we consider expansion of the reaction scope in terms of benzamide substrates (Table 3). Generally, all of the substrates were converted into the desired products. Moderate to good yields were obtained in most cases. Notably, a substrate bearing a hydroxyl group gave the desired product in 54% yield (**5h**, Table 3).

Moreover, we explored the Rh-catalyzed selective C–H bond activation of anilides in the absence of a silver salt (see the Supporting Information for details). Gratifyingly, the *C*-aryl ring activation products **5′** were obtained in good yields in most cases (Table 4). This methodology thus offers a convenient route to *C*-aryl ring products with excellent chemoselectivity and yields; it is supported by Li's results,[18a] albeit with different substrates.

Although NCA-directed reversal of the activation site has been overlooked in previous selective C–H bond activation reactions, we decided to seek evidence for this in the relevant literature reports. Tanaka developed the oxidative annulation of anilides with internal alkynes, and obtained both *C*-aryl and *N*-aryl ring activation with different catalysts, although one example with low yield was found,[20] which provides a power proof to support C–H activation of *N*-aryl ring. Li and co-workers reported the activation of *ortho* C–H bonds on *C*-aryl rings to give vinylation products,[18a] further demonstrating the preference for this process in the absence of non-coordinating anions. Other studies, such as those involving Ac-protected anilides,[6, 11a, 16b, i, 17] could give part of the supporting to C–H activation of *N*-aryl ring.[10]

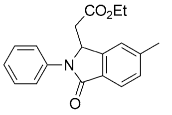
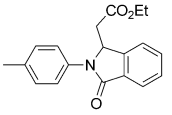
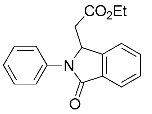
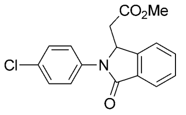
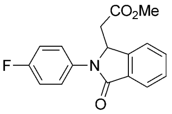
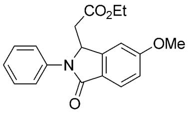
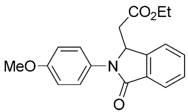
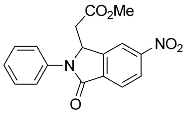
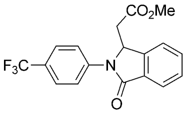
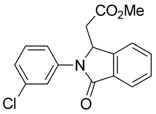
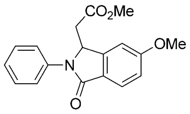
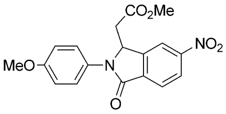
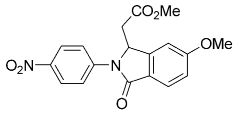
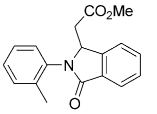
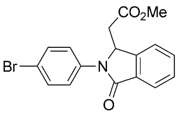
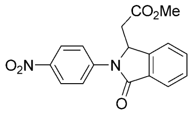
In order to gain a better understanding of this transformation, competition experiments to assess the electronic effect were conducted. It was found that an electron-rich amide was preferentially consumed, implying that substrates bearing an

Table 3. Substrate scope experiments of *N*-aryl ring activation.[a]



[a] Conditions: **4** (0.5 mmol, 1.0 equiv), **2** (0.75 mmol, 1.5 equiv), [{Cp*RhCl2}2] (5 mol%), AgOTf (20 mol%), Ag_2CO_3 (1.5 equiv), DCE (3 mL), 12 h.

Table 4. Substrate scope experiments of *C*-aryl ring activation.[a]

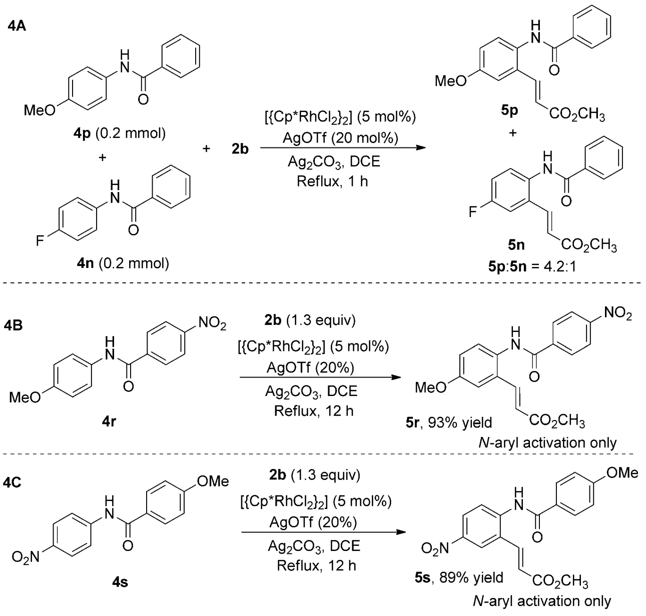
 **5a'**: 93%	 **5b'**: 90%	 **5c'**: 87%	 **5d'**: 88%
 **5e'**: 86%	 **5f'**: 93%	 **5g'**: 85%	 **5h'**: 82%
 **5i'**: 93%	 **5j'**: 89%	 **5k'**: 84%	 **5l'**: 48%
 **5m'**: 63%	 **5n'**: 94%	 **5o'**: 95%	 **5p'**: 82%

[a] Conditions: **4** (0.5 mmol, 1.0 equiv), **2** (0.75 mmol, 1.5 equiv), [{Cp*RhCl$_2$}$_2$] (5 mol %), Ag_2CO_3 (1.5 equiv), CH_3CN (3 mL), 12 h.

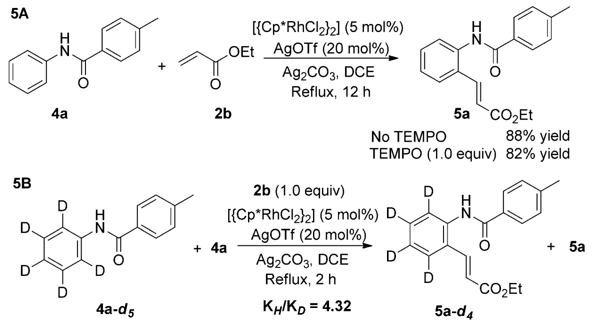
electron-donating group react more readily than those bearing an electron-withdrawing group (Scheme 4 A). Since the electronic effect has a great influence on the reaction, it may also govern the selectivity for reaction at the *N*-aryl ring. To test this hypothesis, two classical substrates were prepared (Scheme 4 B, C). However, only *N*-aryl ring products were obtained under the above conditions for both reactions, seemingly disfavoring the hypothesis.

2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) is widely used as a radical scavenger to probe reaction mechanisms. Therefore, a control reaction was performed in the presence of one equivalent of TEMPO. The corresponding product was obtained in almost the same yield, indicating that no radical intermediate was involved in the transformation (Scheme 5 A). Next, kinetic isotope effect (KIE) experiments were conducted to elucidate the mechanism (Scheme 5 B). When a 1:1 mixture of **4a** and d_5-**4a** was subjected to the reaction, an intermolecular KIE of $K_H/K_D = 4.32$ was determined. This indicated that C–H bond cleavage was involved in the rate-determining step and further confirmed that the reaction mechanism was a C–H activation process.

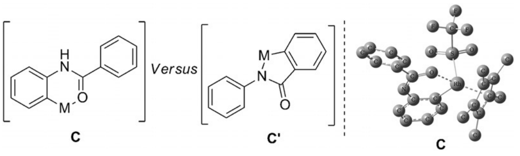
In addition, a computational study was performed (Scheme 6). Two structures were fully optimized using the B3LYP functional within the Gaussian 03 program,[26] and vibrational frequencies were calculated to confirm that they were stable minima on the potential energy surface. For C, O, N, and H, the 6-311++G(d, p) basis set was used; for Rh, the Lanl2DZ basis set with effective core potential (ECP) was used. Intermediate **C** was calculated to be lower in energy



Scheme 4. Intermolecular competition and electronic effect studies.



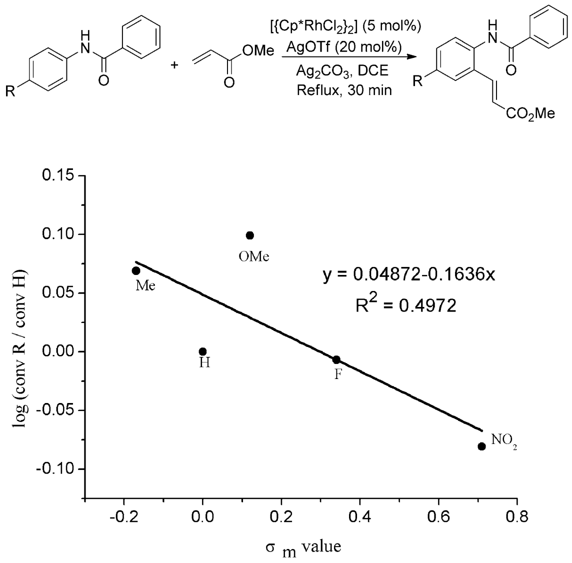
Scheme 5. Control experiment and isotope effect experiment.



Scheme 6. The two possible structures of intermediates.

(−1591.111355 hartree), and hence more stable, than intermediate **C**′ (−1590.531387 hartree). All energies were corrected for zero-point vibrational energies (ZPE), and the optimized structure of **C** is shown in Scheme 6. This clearly provided a direct corroboration of the observed selective C–H bond activation of *N*-aryl rings over *C*-aryl rings adjacent to an amide functional group in this system.

Furthermore, we determined the Hammett correlation for the process, which is a very useful method in mechanistic studies. We selected several typical substrates to build the equation, and the plot is shown in Scheme 7. The results showed that electron-rich substrates reacted more rapidly, indicating that the rate-determining transition state is more stabilized by electron-donating substituents.

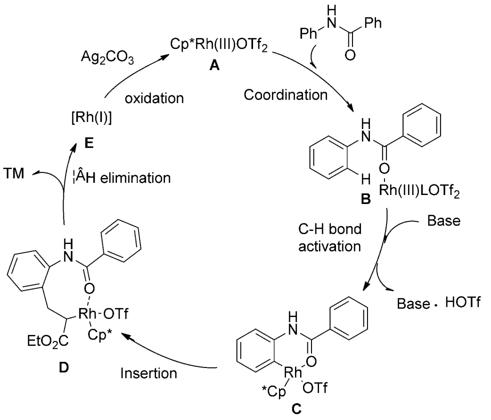


Scheme 7. Hammett plot for various anilides.

Taking together the above mechanistic evidence, a possible reaction pathway for this transformation may be proposed (Scheme 8). Initially, the substrate coordinates with Rh^{III} to give the complex **B**. Next, *ortho* electrophilic attack by the Rh^{III} cation with the assistance of the amide group forms complex **C** under basic conditions, and subsequent insertion leads to intermediate **D**. Through β-H elimination, intermediate **D** releases the coupling product. The Rh^{I} cation is oxidized back to Rh^{III} by Ag^{I} to complete the catalytic cycle and generate the catalyst **A**.

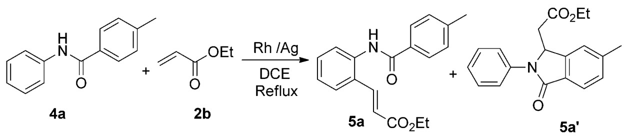
Recently, Shi et al. investigated the so-called "silver effect" in gold catalysis, which is another frequently overlooked important factor in transition metal catalysis.[27] Many reactions involving silver salts can actually be classified as bimetallic catalysis or silver-assisted metal catalysis. Silver nanoparticles or silver chloride are typically invoked in this context. To assess whether such an effect might be operative in the present case, a series of "silver effect" experiments was conducted. It was found that the *C*-aryl ring activation product was obtained with only [{Cp*RhCl$_2$}$_2$] as the catalyst, whereas the *N*-aryl ring activation product was obtained when a silver salt was added to the mixture. After removing silver chloride by filtration through Celite, the new catalyst [Cp*Rh^{III}OTf$_2$] showed almost the same catalytic effect and yield for this transformation (Table 5, entries 1, 6, and 7). These investigations indicated that: i) non-coordinating anions greatly improve the catalytic activity of a rhodium catalyst, effectively rendering it chemoselective; ii) silver does not play a role and the active catalyst is only rhodium in this transformation.

In summary, Rh-catalyzed chemoselective C–H bond activation of anilides with alkenes has been realized by introducing non-coordinating anions. This methodology provides an efficient means of selectively achieving *N*-aryl or *C*-aryl ring activation. Mechanistic studies and theoretical calculations have



Scheme 8. The proposed possible mechanism.

Table 5. "Silver effect" test experiments[a,b]



Entry	Catalyst	Conditions[b]	**5 a**:**5 a**′[%]
1	[{Cp*RhCl$_2$}$_2$]	–	0:58
2	[{Cp*RhCl$_2$}$_2$]	–	0:93[c]
3	none	–	0:0
4	AgOTf	–	0:0
5	Ag$_2$CO$_3$	–	0:0
6	[{Cp*RhCl$_2$}$_2$]/AgOTf	no filtration	88:0
7	[{Cp*RhCl$_2$}$_2$]/AgOTf	after filtration	85:0
8	[{Cp*RhCl$_2$}$_2$]/AgSbF$_6$	no filtration	35:0
9	[{Cp*RhCl$_2$}$_2$]/AgSbF$_6$	after filtration	31:0
10	[{Cp*RhCl$_2$}$_2$]/AgBF$_4$	no filtration	48:0
11	[{Cp*RhCl$_2$}$_2$]/AgBF$_4$	after filtration	45:0

[a] Optimal conditions. [b] AgCl was removed by filtration through Celite. [c] CH$_3$CN was used.

shown that lower energy is needed to activate *N*-aryl rings than *C*-aryl rings under non-coordinating anion conditions. Further mechanistic studies and experiments with silver salts have clearly indicated that the activity of the rhodium catalyst is obviously improved by non-coordinating anions, which rules out the possibility of a "silver effect" in this silver-mediated reaction.

Experimental Section

Typical procedure for the reaction of an anilide and an alkene

A mixture of ferrocenyl anilide (**1a**) (0.50 mmol), methyl acrylate (**2a**) (0.75 mmol), $[\{Cp^*RhCl_2\}_2]$ (5 mol%), AgOTf (20 mol%), and Ag_2CO_3 (1.5 equiv) in DCE (3.0 mL) was stirred at 90 °C under air for 12 h. Upon completion of the reaction, the mixture was concentrated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether, 1:5) to afford the corresponding product (**3a**) as a white solid.

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