C–H Activation

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Ruthenium(II)-Catalyzed C–H Activation of Imidamides and Divergent Couplings with Diazo Compounds: Substrate-Controlled Synthesis of Indoles and 3*H*-Indoles

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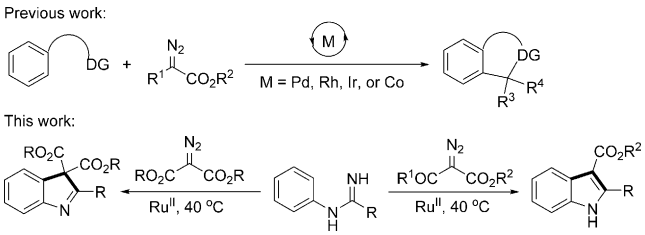
Abstract: *Indoles are an important structural motif that is commonly found in biologically active molecules. In this work, conditions for divergent couplings between imidamides and acceptor–acceptor diazo compounds were developed that afforded NH indoles and 3H-indoles under ruthenium catalysis. The coupling of α-diazoketoesters afforded NH indoles by cleavage of the C(N$_2$)–C(acyl) bond whereas α-diazomalonates gave 3H-indoles by C–N bond cleavage. This reaction constitutes the first intermolecular coupling of diazo substrates with arenes by ruthenium-catalyzed C–H activation.*



Scheme 1. Arene C–H activation and intermolecular coupling with diazo compounds.

Indoles are ubiquitously found in a diverse array of biologically active molecules.[1] Thus the synthesis of indoles[2] has attracted widespread interest. In particular, 3*H*-indoles exhibit excellent pharmacological properties, including antibacterial, antifungal, anti-inflammatory, and antiviral activity.[3] Their significance in pharmacology has called for the development of more efficient synthetic methods. However, most of the reported methods require highly functionalized starting materials and suffer from low atom economy and harsh reaction conditions.[4] It is thus highly desirable to develop cost-effective and efficient methods to access indoles and 3*H*-indoles.

Over the past decades, transition-metal-catalyzed C–H bond activation has emerged as a powerful synthetic strategy.[5] Recently, metal-catalyzed carbenoid functionalization has been increasingly employed for C–C bond formation, especially by Pd^{II}-, Rh^{III}-, Co^{III}-, and Ir^{III}-catalyzed C–H activation of arenes in the presence of a directing group (DG; Scheme 1).[6] In particular, Yu and co-workers disclosed the first Rh^{III}-catalyzed intermolecular insertion of C(aryl)–H bonds into diazo compounds.[6g] Following this report, the groups of Glorius,[7] Ackermann,[8] Wang,[9] Chang,[10] and others[11] have made significant progress in the construction of heterocycles by such approaches.

On the other hand, ruthenium(II) complexes have been shown to efficiently catalyze arene C–H activation with outstanding cost efficiency.[5c,12] However, the coupling partner is mostly limited to alkenes, alkynes, aryl/alkyl halides, isocyanates, allyl sources, and amidating reagents, among others.[13] Whereas Che, Yu, and co-workers have reported Ru^{II}-catalyzed intramolecular carbenoid insertion reactions into C–H bonds that proceeded by an outer-sphere mechanism,[14] to the best of our knowledge, the combination of Ru^{II}-catalyzed arene C–H activation and intermolecular coupling with diazo compounds has remained underexplored. We reasoned that the reactivity of a Ru^{II}–C bond towards an electrophile might also parallel and even exceed that of the Rh^{III} counterparts.[13k,l] We now report the facile construction of 2,3-disubstituted NH indoles and 3*H*-indoles by Ru^{II}-catalyzed C–H activation of imidamides and coupling with diazo compounds.

We initiated our studies by screening the reaction parameters of the coupling of *N*-phenylacetimidamide (**1a**) and ethyl α-diazoacetoacetate (**2a**; Table 1).[15] Using [Ru(*p*-cymene)Cl$_2$]$_2$/AgSbF$_6$ as the catalyst, indole **3aa** was isolated in 64% yield (80 °C, entry 1). The yield was slightly reduced in the absence of CsOAc (entry 3). When cobalt(III) catalysts were employed, the desired reaction did not occur (entries 4 and 5). With AcOH as an additive (2.0 equiv), the yield was significantly improved to 91% (entry 7) whereas other acid additives (PivOH and MesCO$_2$H) were less efficient (entries 8 and 9). Lowering the catalyst loading to 2 mol% resulted in diminished yield (entry 10). The effect of the reaction temperature was then explored, and coupling at 40 °C or higher temperatures gave comparable results (entries 11 and 12).

With optimized reaction conditions in hand (conditions A), we then explored the scope and generality of this coupling (Scheme 2). Acetimidamides bearing various electron-donating, -withdrawing, or halogen substituents at the *para* position of the *N*-aryl ring all reacted smoothly with **2a**, affording various NH indoles in 63–96% yield (**3ba**–**3ia**). Acetimidamides bearing *meta* halogen substituents also afforded the corresponding products in good yields with

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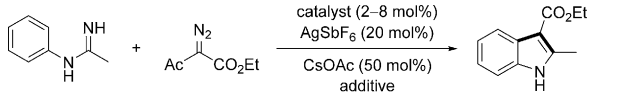
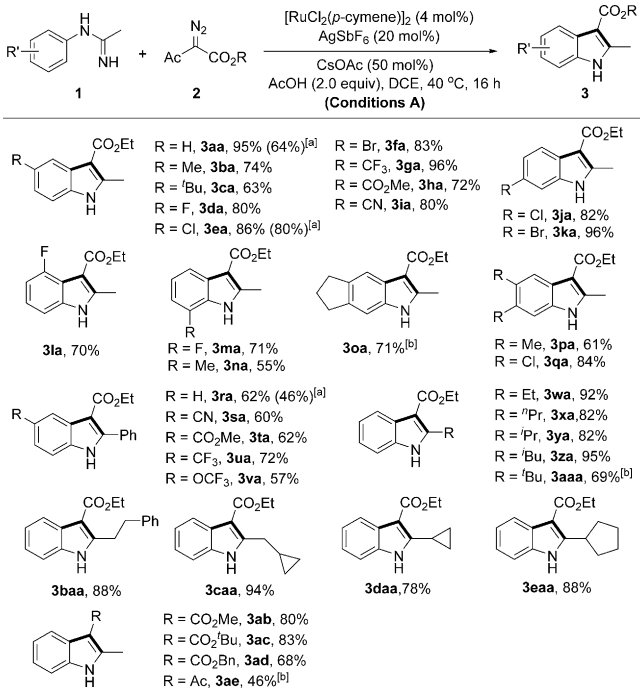
Table 1: Optimization studies.[a]



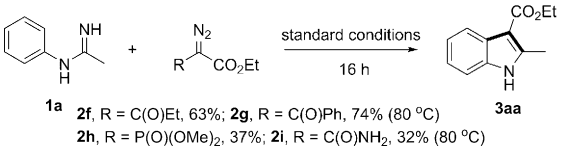
Entry	Catalyst (mol%)	Additive	*T* [°C]	Yield [%][b]
1	$[Ru(p\text{-cymene})Cl_2]_2$ (4)	–	80	64
2[c]	$[Ru(p\text{-cymene})Cl_2]_2$ (4)	–	80	37
3[d]	$[Ru(p\text{-cymene})Cl_2]_2$ (4)	–	80	55
4	$[Cp^*CoI_2CO]$ (8)	–	80	NR
5	$[Cp^*CoI_2]_2$ (4)	–	80	NR
6[e]	$[Ru(p\text{-cymene})Cl_2]_2$ (4)	–	80	35
7	$[Ru(p\text{-cymene})Cl_2]_2$ (4)	AcOH	80	91
8	$[Ru(p\text{-cymene})Cl_2]_2$ (4)	PivOH	80	65
9	$[Ru(p\text{-cymene})Cl_2]_2$ (4)	$MesCO_2H$	80	57
10[f]	$[Ru(p\text{-cymene})Cl_2]_2$ (2)	AcOH	80	64
11	$[Ru(p\text{-cymene})Cl_2]_2$ (4)	AcOH	40	95
12	$[Ru(p\text{-cymene})Cl_2]_2$ (4)	AcOH	30	70

[a] **1a** (0.2 mmol), **2a** (0.3 mmol), catalyst, $AgSbF_6$ (20 mol%), additive (0.4 mmol), CsOAc (50 mol%), DCE (2 mL), 16 h. [b] Yields of isolated products. [c] Without $AgSbF_6$. [d] Without CsOAc. [e] In EtOH. [f] $AgSbF_6$ (10 mol%). DCE = 1,2-dichloroethane, Mes = 2,4,6-trimethylphenyl, Piv = pivaloyl.



Scheme 2. Synthesis of N-unprotected indoles. Reaction conditions: **1** (0.2 mmol), **2** (0.3 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (4 mol%), $AgSbF_6$ (20 mol%), CsOAc (50 mol%), AcOH (0.4 mmol), DCE (2 mL), 40°C, 16 h. Yields of isolated products after column chromatography are given. [a] $[Ru(p\text{-cymene})Cl_2]_2$ (2 mol%). [b] 80°C.

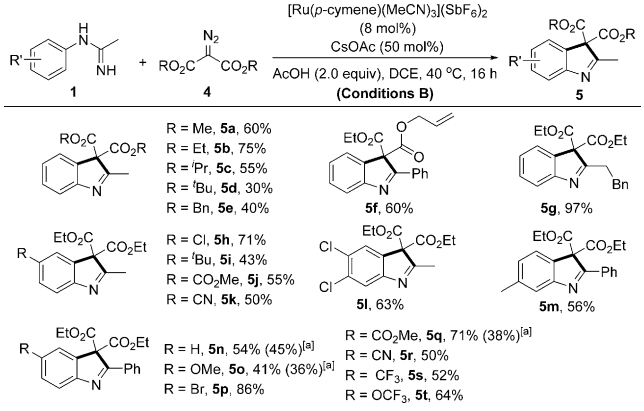
substituent-dependent site selectivity. The coupling occurred at the less hindered position for Cl and Br substituents (**3ja** and **3ka**), whereas C–H functionalization occurred at the more hindered site for the *meta*-fluoro substrate (**3l**). Furthermore, *ortho*-Me- and F-substituted and disubstituted acetimidamides were also viable substrates (**3ma**–**3qa**). *N*-Aryl benzimidamides with different substituents on the *N*-aryl ring were also coupled successfully, and C–H activation occurred exclusively at the *N*-aryl ring (**3ra**–**3va**). The C substituent of the imidamide was also extended to other primary, secondary, and tertiary (cyclo)alkyl substituents, and the corresponding products were obtained in consistently high yields (**3wa**–**3eaa**). The scope of α-diazoketoesters was examined with **1a**, and they were all converted into the desired products in good yields (**3ab**–**3ad**). Furthermore, symmetric α-diazoacetylacetone delivered indole **3ae** in 46% yield (80°C). Decreasing the catalyst loading to 2 mol% was attempted for several substrates (**3aa, 3ea**, and **3ra**), and the yields were not significantly affected. In line with previous reports on the Rh^{III}-catalyzed system,[15] coupling **1a** with different diazo esters **2f**–**2i** afforded the same product **3aa** [Eq. (1)], and $PhC(O)NH_2$ was detected as a byproduct for



(1)

the reaction of **2g** by GC-MS, indicating the rather rare cleavage of the C–C and C–P bonds in the diazo compound.[15,16]

To better define the scope of the diazo substrate, α-diazodiethylmalonate was employed. To our delight, 3*H*-indole **5b** was isolated in 50% yield under conditions A (Scheme 3). Switching to $[Ru(p\text{-cymene})(MeCN)_3](SbF_6)_2$ as the catalyst further increased the yield to 75%. Under these conditions (conditions B), we next investigated the generality of this coupling. A variety of α-diazomalonates, including an unsymmetric one, reacted with **1a** in moderate to good yields (**5a**–**5f**, 30–75%). The scope of the imidamide was then examined. Mono- and disubstituted imidamides as well as other *C*-alkyl imidamides were viable substrates for this transformation, furnishing the desired products **5g**–**5l** in moderate to high yields. In line with their efficient couplings with α-diazoacetoacetates, *N*-aryl benzimidamides also



Scheme 3. Synthesis of 3*H*-indoles (see the Supporting Information for details). [a] $[Ru(p\text{-cymene})(MeCN)_3](SbF_6)_2$ (4 mol%), 60°C.

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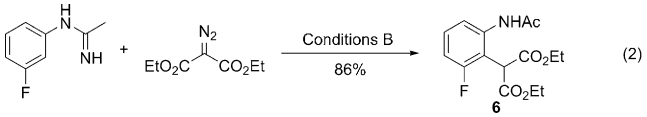
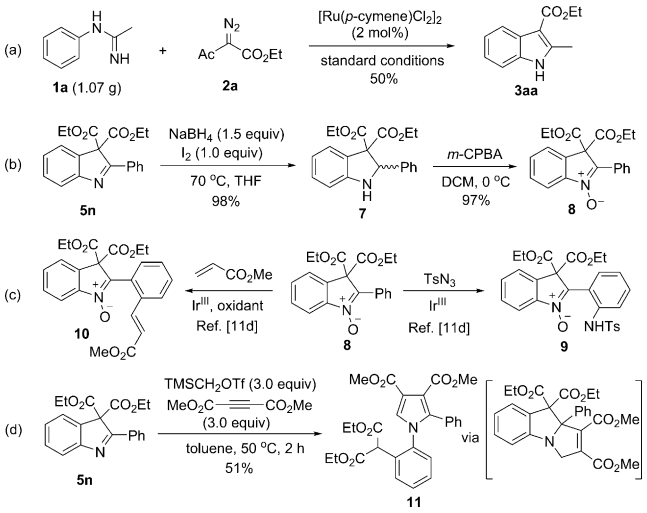
reacted with α-diazodiethylmalonate with high chemoselectivity; various electron-donating and -withdrawing groups were tolerated (**5m**–**5t**), and reducing the catalyst loading was also possible in some cases. A *meta*-fluoro-substituted imidamide also reacted with α-diazomalonate, but the reaction stopped at the alkylation stage [Eq. (2)]. Acetanilide **6** was



(2)

isolated in high yield after in situ hydrolysis of the imidamide moiety. The formation of product **6** indicates that the annulation reactions in Scheme 2 and Scheme 3 likely proceed by C–H activation and carbene insertion.

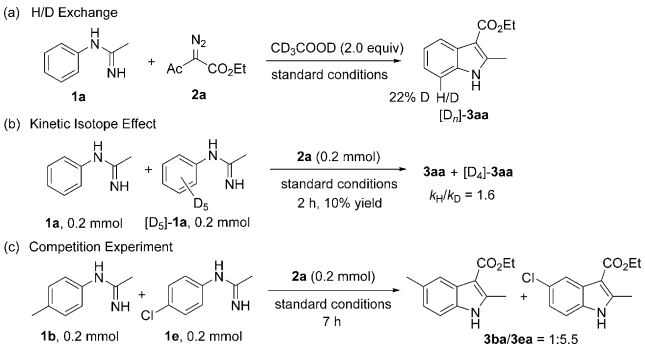
To demonstrate the synthetic utility of this transformation, a gram-scale synthesis of product **3aa** was carried out with reduced catalyst loading, and **3aa** was isolated in moderate yield (Scheme 4a). Derivatizations of 3*H*-indole



Scheme 4. Gram-scale synthesis of **3aa** and synthetic utility of 3*H*-indoles. *m*-CPBA = *meta*-chloroperbenzoic acid, Tf = trifluoromethanesulfonyl, TMS = trimethylsilyl.

5n were performed to further showcase the synthetic utility of these compounds. Reduction of the C=N bond of **5n** with $NaBH_4/I_2$ afforded indoline **7** in 98% yield (Scheme 4b).[17] Further treatment of **7** with *m*-CPBA afforded 3*H*-indole *N*-oxide **8** in 97% yield.[18] Synthetic applications of *N*-oxide **8** in C–H amidation and olefination have been reported by Zhou and co-workers (Scheme 4c).[11d] When treated with (trimethylsilyl)methyl triflate and dimethyl butynedioate, **5n** underwent a dipolar addition[17] followed by elimination and ring scission to afford pyrrole **11** in moderate yield (Scheme 4d).

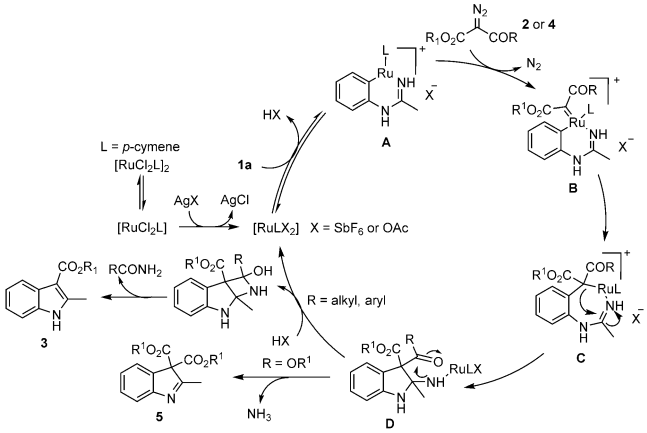
To gain insight into the mechanism of this cyclization process, a series of experiments were performed. H/D exchange of **1a** at the *ortho*′ position (the 7-position of the indole) was observed (with 22% D) in the presence of the



Scheme 5. Mechanistic studies.

coupling partner (Scheme 5a), suggesting reversible C–H activation. To further probe the C–H activation process, the kinetic isotope effect was determined by intermolecular competition experiments using an equimolar mixture of **1a** and [D_5]-**1a**. The small value of $k_H/k_D = 1.6$ suggests that C–H bond cleavage is likely not involved in the turnover-limiting step (Scheme 5b). Moreover, a competition experiment was conducted with an equimolar amount of **1b** and **1e**, which differ in their electronic properties; **3ba** and **3ea** were afforded in a ratio of 1:5.5, showing that the electron-poor arene reacted faster (Scheme 5c). This suggests that the C–H activation process might follow a concerted metalation deprotonation (CMD) mechanism.

On the basis of these observations and previous reports,[15] a plausible catalytic cycle is shown in Scheme 6. Cyclometalation of the imidamide affords a metallacyclic intermediate **A** by CMD. Subsequent coordination of diazo compound **2** or **4** to intermediate **A** is followed by denitrogenation to generate ruthenium carbene species **B**. The ruthenium–aryl bond in this intermediate will then undergo migratory insertion into the carbene unit to furnish seven-membered ruthenacyclic intermediate **C**. Intermediate **D** was then formed by Ru–C(alkyl) migratory insertion into the C=N bond. For diazoketoester substrates, product **3** is eventually released from **D** by protonolysis and intramolecular nucleophilic addition and subsequent elimination of one molecule of



Scheme 6. Proposed reaction mechanism.

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amide, together with regeneration of the active ruthenium(II) catalyst. In contrast, for diazomalonates, intermediate **D** undergoes elimination of ammonia with assistance of Ru^{II} or acetic acid, furnishing 3*H*-indole **5** as the final product. This change in selectivity is likely caused by the reduced electrophilicity of the ester carbonyl group.

In summary, we have developed the first ruthenium(II)-catalyzed intermolecular coupling between aryl imidamides and diazo compounds by C–H activation, which enabled the synthesis two classes of indole derivatives by [4+1] annulation under mild conditions. The coupling of α-diazoketoesters afforded NH indoles by cleavage of the $C(N_2)$–C(acyl) bond whereas α-diazomalonates gave 3,3-disubstituted 3*H*-indoles by C–N bond cleavage. These efficient synthetic methods may find application in the synthesis of bioactive compounds.

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Keywords: C–H activation · diazo compounds · indoles · ruthenium · transition-metal catalysis

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