Asymmetric Coupling

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Rhodium-Catalyzed Enantioselective Oxidative [3+2] Annulation of Arenes and Azabicyclic Olefins through Twofold C–H Activation

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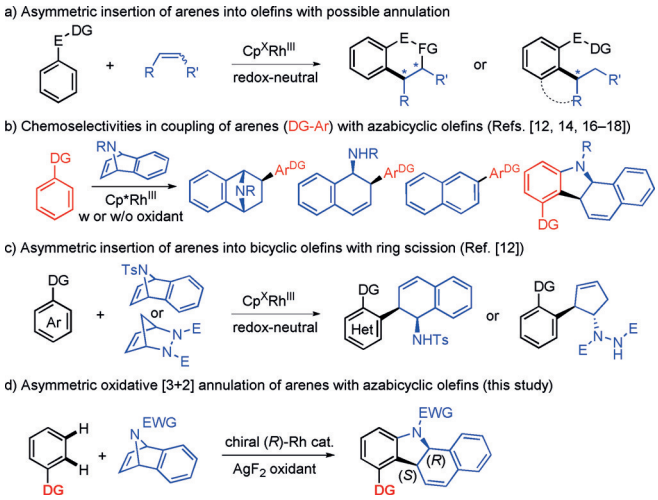
Abstract: *C–H bond activation is mostly limited to ortho selectivity. Activation of both ortho and meta C–H bonds constitutes a particularly important strategy for annulation, but has rarely been studied in enantioselective systems. Reported herein is rhodium(III)-catalyzed asymmetric [3+2] transannulation of arenes with 7-azabenzonorbornadienes. Two distinct classes of arenes have been identified as substrates, and the coupling proceeded with high enantioselectivity and excellent diastereoselectivity through sequential activation of ortho and meta C–H bonds.*

Metal-catalyzed C–H bond activation has allowed the development of various synthetic methods to access value-added organic compounds.[1] Given the covalent nature of M–C species in the catalytic cycle, enhanced metal–ligand and metal–substrate interactions occur when a high-valent metal is employed. In this regard, Rh^{III} catalysts stand out in C–H activation, allowing the functionalization of a plethora of arenes.[2] Despite tremendous progress, enantioselective C–H activation remains largely underdeveloped.[3] The research groups of Cramer,[4] Rovis,[5] You,[6] Antonchick/Waldmann,[7] and others[8,9] have made significant contributions. However, it remains necessary to develop novel asymmetric systems to increase the competitiveness of Rh^{III} catalysis in the synthesis of chiral functional molecules. Mechanistically, C–H cleavage, reductive elimination, and migratory insertion can be stereodetermining. Olefins are ubiquitous, and their insertion into M–C bonds represents a straightforward strategy to generate stereogenic centers. In previous rhodium(III)-catalyzed enantioselective C–H activation–olefin insertion systems, substrate activation strategies have been adopted to ensure high efficiency and enantioselectivity. By resorting to arenes bearing a strong or oxidizing directing group, Cramer,[4a,i,l] Rovis,[5] Antonchick/Waldmann,[7b] and Perekalin[9] realized asymmetric C–H activation using olefins, with [4+2] annulation being the dominant pattern (Scheme 1 a). By employing activated olefins, such as enones and nitroolefins, Matsunaga and co-workers[10a] and others achieved enantioselective Michael addition of arenes. In comparison, by taking advantage of ring strain,[11] we[12a] and Wang and Cramer[12b] realized asymmetric, redox-neutral coupling using (di)azabicyclic olefins (Scheme 1 c). Despite the progress, these systems are limited to *ortho* C–H activation. Recently, Wang and co-workers[13] developed [2+2+2] coupling of indolinones with two alkynes for the synthesis of axially chiral naphthalenes through twofold C–H activation.[13–15] However, twofold C–H activation has not been employed in the asymmetric generation of central chirality.



Scheme 1. (Asymmetric) coupling of olefins with arenes (DG = directing group).

In 2013, we[14] reported the rhodium(III)-catalyzed synthesis of dihydrocarbazoles through twofold C–H activation of 2-arylpyridines and coupling with 7-azabenzonorbornadienes. However, the harsh conditions (120 °C) and limited compatibility argue against the development of an enantioselective version of the reaction. The low reactivity of 2-arylpyridines can most likely be ascribed to a low tendency of directing-group dechelation en route to the second C–H activation. Thus, a successful system calls for a flexible directing effect to facilitate the first C–H activation step while accommodating the second C–H activation step by dechelation. Otherwise, pitfalls will emerge in the form of side reactions of the azabicyclic olefins, such as ring-retentive insertion,[16] insertion–ring opening,[12a,17] and olefin insertion–elimination/aromatization (naphthylation),[14,18] even in the presence of oxidants (Scheme 1 b).[12a] Moreover, the directing group and the arene ring should be sterically biased to allow for recognition by the chiral environment. We now report the enantioselective [3+2] annulation of two distinct classes of arenes with azabenzonorbornadienes with high enatioselectivity and excellent diastereoselectivity (Scheme 1 d).

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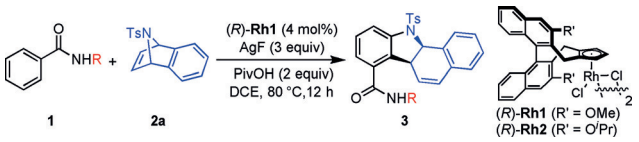
On the basis of the rationale, benzamides with dissociable directing groups drew our attention (Table 1). Despite the possibility of [4+2] annulation,[4,5,7b,9] simple benzamide underwent smooth [3+2] annulation with 7-azabenzonorbornadiene **2a** in good yield but with poor enantioselectivity when catalyzed by the Cramer-type[4k] (*R*)-**Rh1** catalyst.

Table 1: Optimization studies on the amide directing group.[a]



1 2a 3

R	H	Me	Et	^{n}Bu	^{i}Pr	^{t}Bu	Bn
Yield [%]	67	65	60	59	70	0	0
e.r.	55:45	74:27	73:27	71:29	75:25	–	–

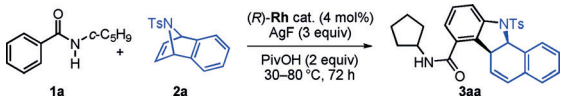
R	OMe	*c*-C_3H_5	*c*-C_4H_7	*c*-C_5H_9	*c*-C_6H_{11}	*c*-C_7H_{13}	*c*-C_8H_{15}
Yield [%]	0	75	79	86	71	40	26
e.r.	–	68:32	74:26	79:21	80:20	80:20	80.5:19.5

[a] Reactions were carried out using the amide (0.2 mmol), **2a** (0.1 mmol), (*R*)-**Rh1** (4 mol%), AgF (3.0 equiv), and PivOH (2.0 equiv) in DCE (2 mL) at 80°C for 12 h. Yields are for the isolated product. DCE = 1,2-dichloroethane, Piv = pivaloyl, Ts = *p*-toluenesulfonyl.

However, moving to a longer *N*-alkyl group only led to lower enantioselectivity. A secondary *N*-alkyl group seemed beneficial, and a series of *N*-cycloalkyl benzamides were then extensively explored. High yield and promising enantioselectivity (e.r. 79:21) were observed for *N*-cyclopentylbenzamide (**1a**).

We next conducted further optimization using **1a** (Table 2). Anisole was found to be superior to halogenated solvents (92:8 e.r., entries 1–5). Switching to methyl *tert*-butyl ether (MTBE) boosted the enantioselectivity but reduced the yield (entry 6). To our delight, use of a MTBE/PhOMe mixture allowed the isolation of **3aa** in high yield with high enantioselectivity (entry 7). Both AgF and AgF_2 seemed to be suitable oxidants (entries 7 and 8). However, our further studies confirmed that AgF_2 enabled a much broader substrate scope, and this reaction proceeded well at 30°C using AgF_2 (entry 9). Screening of acid additives revealed that AcOH and AdCOOH both gave lower enantioselectivity.

Table 2: Further optimization studies using amide **1a**.[a]

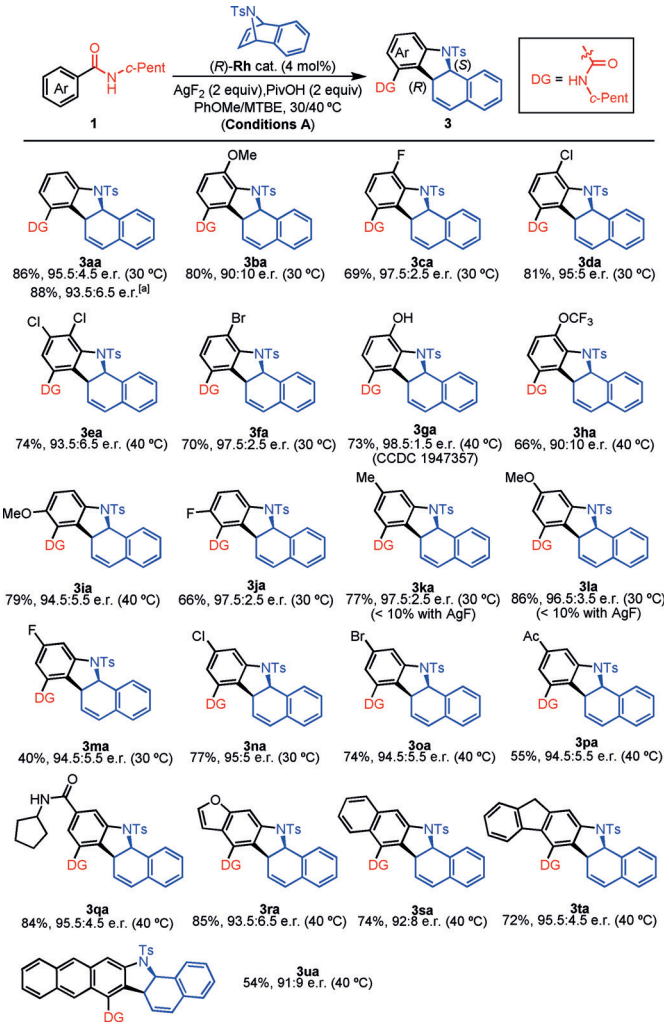


1a 2a 3aa

Entry	Solvent	*T* [°C]	Yield[b] [%]	e.r.
1	DCE	80	83	79:21
2	PhCl	80	81	81:19
3	1,4-dioxane	80	81	85:15
4	PhOMe	80	88	87:13
5	PhOMe	40	85	92:8
6	MTBE	40	26	94:6
7	MTBE/PhOMe (3:1)	40	82	94.5:5.5
8[c]	MTBE/PhOMe (3:1)	40	82	94.5:5.5
9[c]	MTBE/PhOMe (3:1)	30	86	95.5:4.5
10[d]	MTBE/PhOMe (3:1)	30	85	93.5:6.5
11[e]	MTBE/PhOMe (3:1)	30	84	93.5:6.5
12[f]	MTBE/PhOMe (3:1)	30	76	93:7

[a] Reactions were carried out using **1a** (0.2 mmol), **2a** (0.1 mmol), **Rh1** (4 mol%), AgF (3.0 equiv), and PivOH (2.0 equiv) in a solvent (2 mL) for 72 h under air. [b] Yield of the isolated product. [c] AgF_2 (2.0 equiv) was used instead of AgF. [d] Catalyst **Rh2** (4 mol%) was used. [e] AcOH was used instead of PivOH. [f] AdCOOH was used instead of PivOH. MTBE = ^{t}BuOMe.

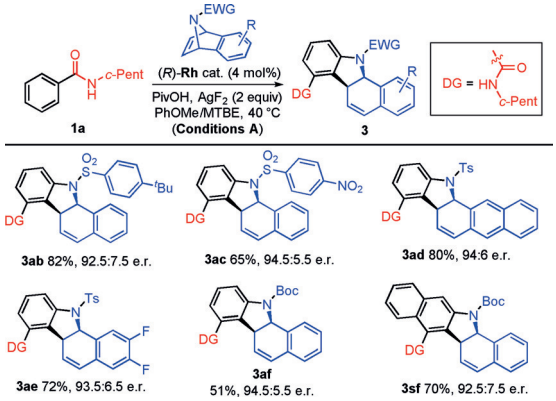
The scope of this coupling system was next examined (Scheme 2). *N*-Cyclopentylbenzamides bearing *para* OMe, halogen, OH, and OCF_3 groups all underwent smooth coupling to give **3ba–ha** with 90:10 to 97.5:2.5 e.r. The effectiveness of these substrates suggested tolerance of steric hindrance during C–N bond formation. High enantioselectivity was also observed for benzamides bearing *ortho* OMe and F groups (product **3ia** and **3ja**). The reaction proceeded well when various *meta* electron-donating, electron-with-



Scheme 2. Scope of the oxidative [3+2] annulation with respect to the benzamide substrate. Reactions were carried out with the amide (0.2 mmol), **2a** (0.1 mmol), **Rh1** (4 mol%), AgF_2 (2.0 equiv), and PivOH (2.0 equiv) in PhOMe/MTBE (0.5/1.5 mL) at 30 or 40°C for 72 h under air (conditions A). [a] The reaction was carried out on a 1 mmol scale at 50°C. *c*-Pent = cyclopentyl.

drawing, and halogen groups were installed (products **3ka–qa**, 94.5:5.5 to 97.5:2.5 e.r.). Different fused benzamides also underwent efficient coupling to afford the corresponding polycyclic products **3ra–ua** with ≥91:9 e.r. The synthesis of **3aa** was also scaled up with only slightly attenuated enantioselectivity. In all cases, only the *cis* product was detected, and the absolute configuration of product **3ga** was determined by X-ray crystallography.[19]

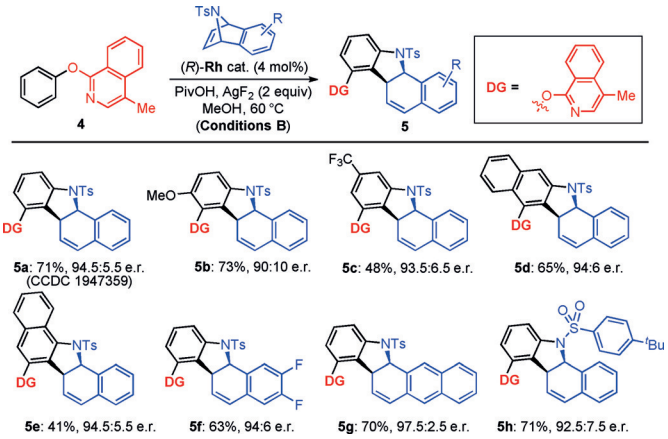
The scope of the reaction with respect to the olefin substrate was next examined. 7-Azabenzonorbornadienes bearing different *N*-sulfonyl groups reacted with similarly high efficiency and enantioselectivity (Scheme 3). Extension



Scheme 3. Scope of the oxidative [3+2] annulation with respect to the azabenzonorbornadiene substrate (see Scheme 2 for detailed reaction conditions).

to several ring-substituted 7-azabenzonorbornadienes was also successful (products **3ae** and **3af**). Importantly, *N*-(*tert*-butoxycarbonyl)azabenzonorbornadiene was also viable (product **3sf**), with no deterioration of the enantioselectivity. In contrast, no desired reaction occurred when 7-oxabenzonorbornadiene was used.

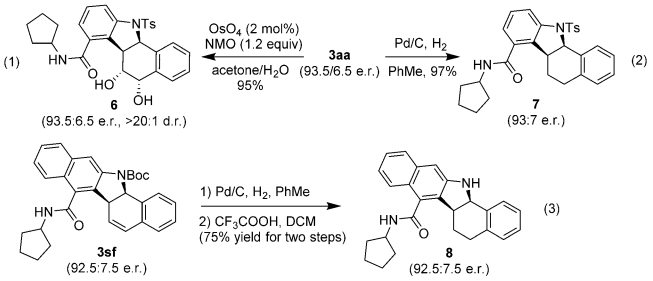
To better define the arene scope, we next moved to another class of arene (Scheme 4). We reasoned that a directing group that allows the formation of flexible six-membered



Scheme 4. Phenoxyisoquinolines in the oxidative [3+2] annulation (conditions B). Reactions were carried out using **4** (0.2 mmol), **2** (0.1 mmol), **Rh1** (4 mol%), AgF_2 (2.0 equiv), and PivOH (2.0 equiv) in MeOH (2.0 mL) at 60 °C for 72 h.

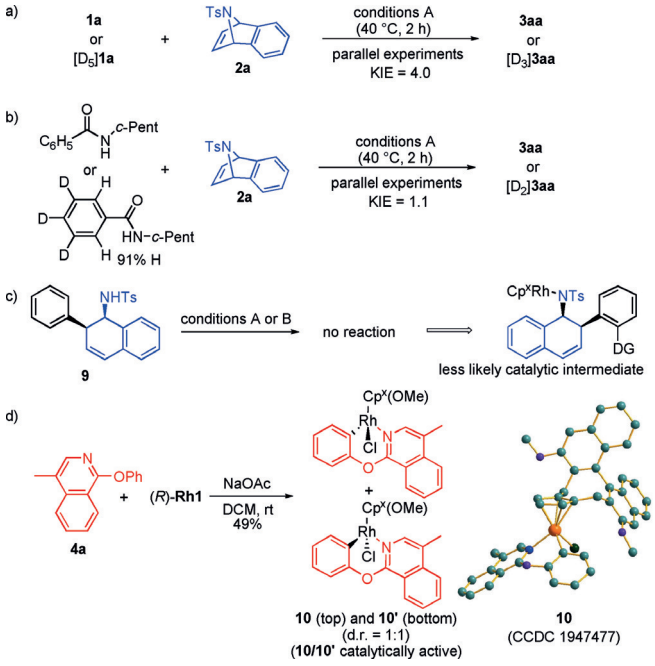
rhodacycles may suffice. Thus, phenol ethers bearing various O-tethered heterocycle directing groups were screened, and a (4-methyl)-1-isoquinolyl group outperformed others in terms of reactivity and selectivity. Under modified reaction conditions (MeOH, 60 °C, conditions B), phenyl ethers bearing an electron-donating group (product **5b**), an electron-withdrawing group (product **5c**), or a fused ring (products **5d** and **5e**) all coupled with substituted 7-azabenzonorbornadienes in generally good yield and with 90:10 to 97.5:2.5 e.r. The same absolute configuration of **5a** was confirmed by X-ray crystallography.[19]

Synthetic applications were briefly demonstrated in derivatization reactions. Osmium-catalyzed dihydroxylation of **3aa** afforded product **6** with high diastereoselectivity [Eq. (1)]. Hydrogenation of **3aa** provided product **7** in excellent yield [Eq. (2)]. Hydrogenation and deprotection of product **3sf** afforded indoline **8** [Eq. (3)]. In all cases, essentially no erosion of enantiopurity was detected.



The mechanism of this coupling system was next explored (Scheme 5). Coupling of **1a** and **2a** in the presence of CD_3CO_2D caused no deuterium incorporation into the product or the recovered **1a**, thus indicating the irreversibility of C–H activation. To further explore the C–H activation, we measured kinetic isotope effects (KIEs). Parallel couplings for benzamides **1a** and [D_5]**1a** allowed determination of the overall KIE to be 4.0 at a low conversion (Scheme 5a), which suggests that either the first (*ortho*) or the second (*meta*) C–H cleavage is turnover-limiting. Moreover, a KIE value of 1.1 was obtained from the parallel couplings using **1a** and [D_3]**1a** (Scheme 5b). Therefore, only the *ortho* C–H activation is turnover-limiting. Control experiments in which the NHTs-functionalized dihydronaphthalene **9** was subjected to both conditions A and B failed to give oxidative C–N coupling (Scheme 5c). Therefore, a reaction pathway of C–H activation, olefin insertion, and subsequent β-nitrogen elimination to deliver a dihydronaphthalene seems unlikely.[14]

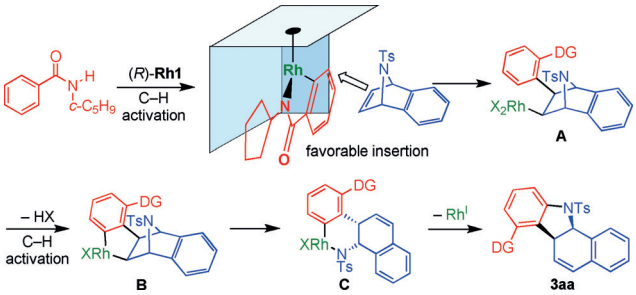
To further explore the mechanistic details, we conducted a stoichiometric reaction of arene **4a** and (*R*)-**Rh1** (Scheme 5d). Products **10** and **10′** were isolated as a diastereomeric mixture with 1:1 d.r. as a result of cyclometalation. Complex **10** crystallized from the mixture, and the dissolution of **10** gave back an equimolar **10**/**10′** mixture, thus indicating the existence of an equilibrium through reversible ligand dissociation. Product **10** was characterized by X-ray crystallography,[19] and it was found that the smallest chloride ligand was pointed toward the chiral binaphthyl backbone for



Scheme 5. Mechanistic investigations. DCM = dichloromethane.

minimized steric interactions. Rhodacycles **10**/**10′** proved catalytically active for the coupling of **4a** and **2a** under conditions B (61% yield, 95:5 e.r.), thus indicating the relevance of C–H activation.

A plausible pathway of the coupling of benzamide **1a** and olefin **2a** is proposed (Scheme 6). Cyclometalation of **1a** affords a rhodacycle, whereby the arene ring is oriented toward the back wall. Subsequently, olefin **2a** approaches



Scheme 6. Proposed reaction pathway.

with the NTs group pointed upward to minimize steric interactions with the ligated arene.[4k,12a] Stereodetermining *cis* insertion occurs *syn* to the NTs group to give intermediate **A**.[12a,14] The second (*meta*) C–H activation occurs through DG dechelation to produce rhodacycle **B**, which undergoes β-nitrogen elimination to deliver a Rh^{III} amidate **C**. C–N reductive elimination then furnishes product **3aa** together with a Rh^{I} intermediate, which is oxidized to regenerate the Rh^{III} catalyst.

In conclusion, by employing a flexible chelating group and a strong oxidant, we have developed a rhodium(III)-catalyzed oxidative [3+2] annulation of arenes and azabenzonorbornadienes for the enantioselective synthesis of *cis*-fused dihydrocarbazoles through rare enantioselective twofold C–H activation. Two distinct classes of arenes have been established as viable substrates on the basis of rational design and extensive screening. Mechanistic studies have been performed, and a chiral rhodacycle was isolated as an active intermediate. Studies on enantioselective C–H activation are ongoing in our laboratory.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: [3+2] annulation · asymmetric catalysis · C–H activation · rhodium · strained olefins

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[19] CCDC 1947357 (**3ga**), 1947359 (**5a**), and 1947477 (**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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