

Rhodium(III)-Catalyzed Synthesis of Cinnolinium Salts from Azobenzenes and Diazo Compounds

Xiaohong Chen,^a Guangfan Zheng,^b Guoyong Song,^{a,*} and Xingwei Li^{b,*}

^a Beijing Key Laboratory of Lignocellulosic Chemistry, Beijing Forestry University, Beijing 100083, People's Republic of China

E-mail: songg@bjfu.edu.cn

^b Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, People's Republic of China

E-mail: xwli@dicp.ac.cn

Received: March 14, 2018; Revised: May 21, 2018; Published online: June 20, 2018



Supporting information for this article is available on the WWW under <https://doi.org/10.1002/adsc.201800326>

Abstract: A Rh(III)-catalyzed C–H activation of azobenzenes in the coupling with diazo compounds has been realized, providing a straightforward strategy to access functionalized cinnolinium triflates in high yields. This protocol features silver free mild reaction conditions and compatibility with diverse functional groups. The coupling proceeds *via* initial Rh(III)-catalyzed C–H alkylation, followed by zinc triflate-mediated cyclization, where zinc triflate acts as a Lewis acid as well as a triflate source.

Keywords: rhodium; azobenzenes; C–H activation; diazo compounds; cinnolinium salts

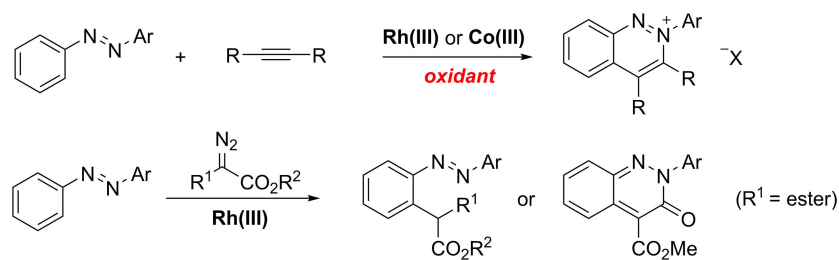
Cinnolinium salts are among the most important *N*-heterocyclic quaternary ammonium salts that have been widely found in the core structures of many bioactive compounds, pharmaceuticals, alkaloids, receptors, and inhibitors.^[1] Therefore, as a step-economic strategy, metal-catalyzed C–H activation has received increasing attention in the synthesis of functionalized cinnolinium and other quaternary ammonium salts. So far, only limited C–H activation strategies have been developed for the synthesis of quaternary ammonium salts.^[2–10] Mechanistically, reductive elimination of a neutral nitrogen ligand and an anionic carbon ligand consists of the predominant pathway in these coupling systems. Moreover, the coupling reagents are nearly always limited to internal alkynes.

In 2012, Cheng reported the first oxidative coupling of imines and alkynes for the synthesis of isoquinolinium salts.^[3] Cheng and You also independently realized oxidative coupling of azobenzenes with alkynes for the synthesis of cinnolinium salts.^[4] In

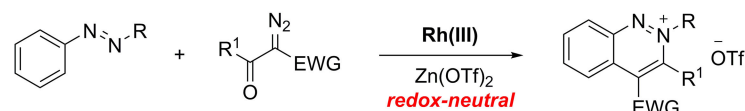
2013, Huang disclosed the synthesis of related salts *via* Rh(III)-catalyzed aerobic annulation between 2-arylpyridines and alkynes.^[5] Later, Choudhury and Wang explored Rh(III)-catalyzed C–H activation of imidazolium/benzimidazolium salts and annulative coupling with alkynes for the synthesis of fused salts, where an NHC acted as an efficient directing group.^[6] Our group reported the divergent annulative coupling of imidazo[1,2-*a*]pyridines with alkynes, where related fused salts could be formed under a controlled condition.^[7] Wang also explored the synthesis of conjugated polycyclic quinoliniums by Rh(III)-catalyzed multiple C–H activation and annulation of arylpyridiniums with alkynes.^[8] Under Rh(III)-catalysis, the You group successfully extended the directing group of arenes to neutral oxygen, where various oxonium salts have been accessed either as an intermediate or final products.^[9] Besides relying on rhodium(III) catalysis, Cheng and Wang also independently realized Co(III) version of some of the important annulation systems.^[10]

Cp*Rh(III) complexes have been recently recognized as competent catalysts for versatile C–H functionalization owing to their high catalytic activity, selectivity, and functional group compatibility.^[11] Under Rh(III) and Ir(III) catalysis, diazo compounds have been widely used as coupling partners in C–H activation systems because of their high reactivity and electrophilicity.^[12] Recently, Kim's, Lee's, Yao's and Lin's groups independently reported Rh(III)-catalyzed direct coupling of azobenzenes with diazo compounds to afford alkylation products or neutral cinnolines.^[13] Despite the high reactivity of diazo compounds, synthesis of salts *via* C–H activation has not been explored. Inspired by these outcomes,^[14] we reasoned that synthesis of cinnolinium salts might be realized using diazo compounds as coupling reagents through C–H activation. Herein, we report Rh(III)-

(a) Previous work:



(b) This work:

**Scheme 1.** Transition Metal-Catalyzed C–H Activation of Azobenzenes.**Table 1.** Optimization of Reaction Conditions.^[a]

entry	catalyst (mol%)	OTf salt (mol%)	solvent	temp. (°C)	yield ^[b] (%)
1	[Cp*RhCl ₂] ₂ (2.5)/AgOTf (10)	Zn(OTf) ₂ (60)	TFE	120	89
2	[Cp*Co(CO)I ₂] (10)/AgOTf (20)	Zn(OTf) ₂ (60)	TFE	120	31
3	[Cp*RhCl ₂] ₂ (2.5)	AgOTf (110)	TFE	120	64
4	[Cp*RhCl ₂] ₂ (2.5)	Zn(OTf) ₂ (60)	TFE	120	92
5	[Cp*RhCl ₂] ₂ (2.5)	Zn(OTf) ₂ (110)	TFE	120	93
6	[Cp*RhCl ₂] ₂ (2.5)	Zn(OTf) ₂ (60)	TFE	80	95
7	[Cp*RhCl ₂] ₂ (2.5)	Zn(OTf) ₂ (60)	TFE	60	96
8	[Cp*RhCl ₂] ₂ (2.5)	Zn(OTf) ₂ (60)	TFE	40	94
9	[Cp*RhCl ₂] ₂ (2.5)	Zn(OTf) ₂ (60)	TFE	25	97
10	[Cp*RhCl ₂] ₂ (2.5)	Zn(OTf) ₂ (60)	MeOH	25	76
11	[Cp*RhCl ₂] ₂ (2.5)	Zn(OTf) ₂ (60)	EtOH	25	70
12	[Cp*RhCl ₂] ₂ (2.5)	Zn(OTf) ₂ (60)	DCE	25	36
13	[Cp*RhCl ₂] ₂ (2.5)	Zn(OTf) ₂ (60)	HFIP	25	90
14	[Cp*RhCl ₂] ₂ (2.5)	Zn(OTf) ₂ (60)	PhCF ₃	25	30

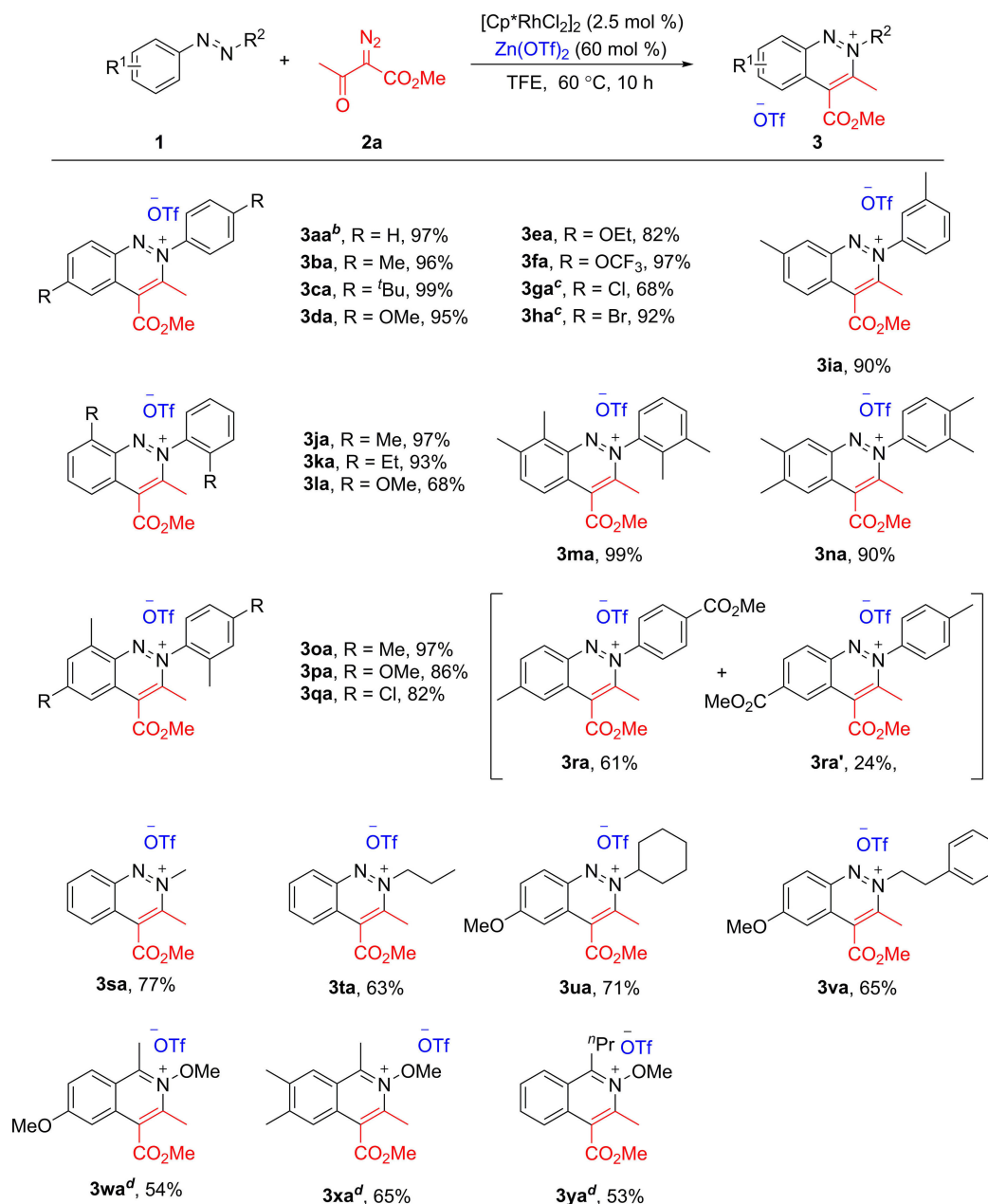
^[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), [Cp*RhCl₂]₂ (2.5 mol%), additive, solvent (2 mL), 25–120 °C, 10 h.

^[b] Isolated yield.

catalyzed mild and redox-neutral synthesis of cinnolinium salts with diazo compounds *via* C–H activation of azobenzenes^[11m,15] and related oxime ethers. In contrast to previous oxidative systems that rely on N(neutral)–C reductive elimination, this system follows a Lewis acid-assisted annulation pathway with the elimination of a hydroxy group under redox-neutral conditions.

First, the reaction of (*E*)-1,2-diphenyldiazene (**1a**) with methyl 2-diazo-3-oxobutanoate (**2a**) was examined under various reaction conditions (Table 1). By using the combination of [Cp*RhCl₂]₂ and AgOTf as a

catalyst and Zn(OTf)₂ as a triflate source,^[16] the C–H annulation product **3aa** was obtained in 89% yield in trifluoroethanol (TFE) at 120 °C (entry 1). Replacing the [Cp*RhCl₂]₂ with [Cp*Co(CO)I₂] led to a decreased yield of **3aa** (entry 2). When Zn(OTf)₂ was used as a sole triflate source in the absence of AgOTf, **3aa** was generated in high yield (92%), being superior to that from AgOTf as a sole triflate source (64%) (entries 3–4). To our surprise, decreasing the reaction temperature is applicable to the current C–H annulated reaction, and 97% yield of **3aa** was obtained at room temperature (entries 6–9). A range of solvents



^aReaction conditions: **1** (0.2 mmol), **2** (0.3 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (2.5 mol %), $\text{Zn}(\text{OTf})_2$ (60 mol %), TFE (2 mL), 60 °C, 10 h, isolated yield. ^bAt room temperature. ^cAt 80 °C. ^dReaction conditions: **1** (0.2 mmol), **2** (0.3 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (2.5 mol %), $\text{Zn}(\text{OTf})_2$ (1.1 equiv), HOAc (1.0 equiv) TFE (2 mL), 60 °C, 10 h.

Scheme 2. Substrate Scope of Azobenzenes.^[a]

was also tested. Obviously, the activity towards the formation of **3aa** increased with the solvent polarity. For example, TFE and hexafluoroisopropanol (HFIP) having high $E_T(30)$ values (59.8 and 65.3 kcal mol⁻¹, respectively) showed higher activity than those from ethanol ($E_T(30)$ = 51.9 kcal mol⁻¹, 70%), dichloroethane (DCE, $E_T(30)$ = 37.0 kcal mol⁻¹, 36%) and PhCF₃ ($E_T(30)$ = 38.5 kcal mol⁻¹, 30%) (entries 10–14).^[17] The molecular structure of **3aa** was unequiv-

ocally established by X-ray crystallography (CCDC 1814875).^[18]

With the establishment of the optimal reaction conditions, we next explored the scope of azobenzene substrate. Given the poor solubility of some azobenzenes in TFE, the reaction was conducted at 60 °C in most cases. As shown in Scheme 2, a range of substituted azobenzenes was examined to react with 2-diazo-3-oxobutanoate (**2a**). Introduction of electron-

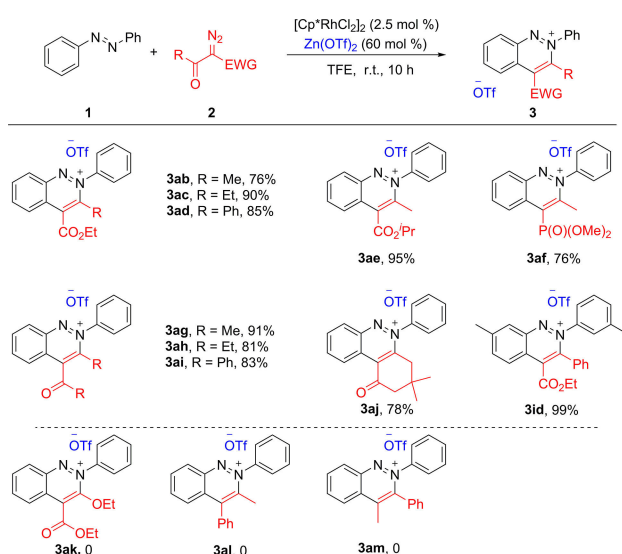
donating and -withdrawing groups at the C4-position of the azobenzene was tolerated, providing the corresponding cinnolinium salts (**3aa–3ha**) in good to excellent yields (68–99%). In the case of azobenzene having a methyl group at the C3 position, the annulation reaction took place only at the less sterically demanding C–H bond, to give **3ia** and **3na** exclusively in excellent yield (both 90%). C2-functionalized azobenzenes were also tolerated, affording the desired products **3ja–3la** in consistently good to excellent yields (68–97%). In order to understand the electronic effect, non-symmetrical azo compound **1r** was examined, yielding regioisomeric products **3ra/3ra'** (61%/24%), which indicates that the C–H annulation is favored for a more electron-rich aromatic ring. Various (phenylazo)alkanes were also

suitable substrates to give **3sa–3ua** in good yields. When alkyl group was replaced with phenethyl group, the cinnolinium salt **3va** was successfully synthesized in 65% yield. The arene substrate was further extended to oxime ethers, and isoquinolinium salts **3wa–3ya** were isolated in good yield although they were prone to decomposition in solution.

Subsequently, the coupling of azobenzenes **1a** and **1i** with various diazo compounds was examined under the optimal conditions at room temperature (Scheme 3). Various symmetrical and nonsymmetrical diazo compounds coupled smoothly with azobenzenes, thus affording the cinnolinium salts in 76–99% yields. In the case of an α -diazo phosphate **2f**, the coupling also reacted smoothly to give the target product **3af**. The cyclic diazo compound **2j** was a proper annulated reagent, which resulted in polycyclic product **3aj** in 78% yield. When diethyl 2-diazomalonate **2k** was used as a coupling reagent, no target product **3ak** was observed, indicating that the ketone group is essential in this catalytic reaction. Unfortunately, no cinnolinium salt (**3ai** or **3am**) was generated when the electron-donating group was introduced into the diazo compounds, indicating the crucial role of EWG.

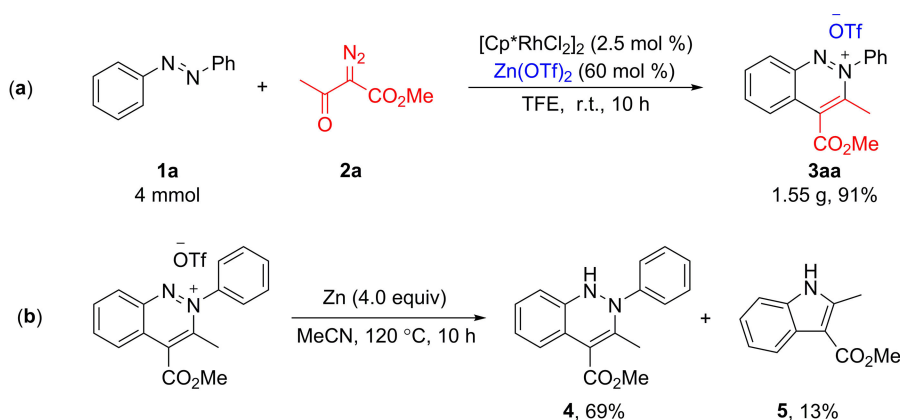
The synthetic utility of the reaction system was then demonstrated in a scale-up reaction. Thus, a 4 mmol-reaction of **1a** and **2a** afforded cinnolinium salt **3aa** in 91% yield (Scheme 4a). Reduction **3aa** with Zn in wet acetonitrile under N_2 atmosphere afforded a mixture of **4** and **5** in 69% and 13% yield, respectively (Scheme 4b). The possible pathway for the formation of product **5** involved a reductive cleavage of **4**, followed by condensation, which was described in supporting information (Scheme S1).

Several experiments have been conducted to probe the mechanism of C–H annulation of azobenzenes and diazo Compounds (Scheme 5). A competitive reaction between **1b** and **1g** with diazo ester **2a** yielded a single product **3ba** (>20:1), suggesting that the reaction is highly favored for a more electron-rich

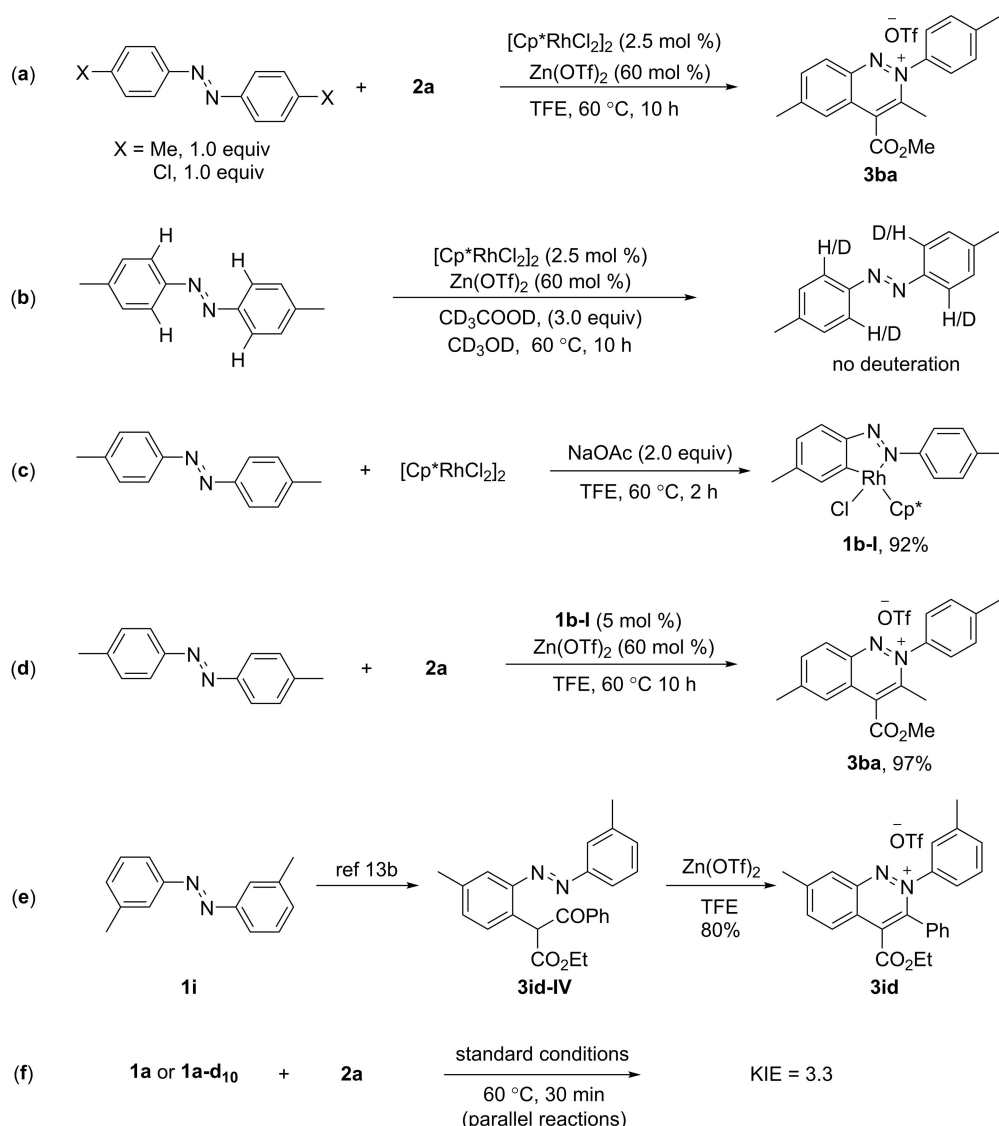


^aReaction Conditions: **1** (0.2 mmol), **2** (0.3 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %), $Zn(OTf)_2$ (60 mol %), and TFE (2 mL) were stirred at room temperature for 10 h.
^bIsolated yield.

Scheme 3. Substrate Scope of Diazo Compounds.^[a,b]



Scheme 4. Gram-Scale Synthesis and Synthetic Applications.

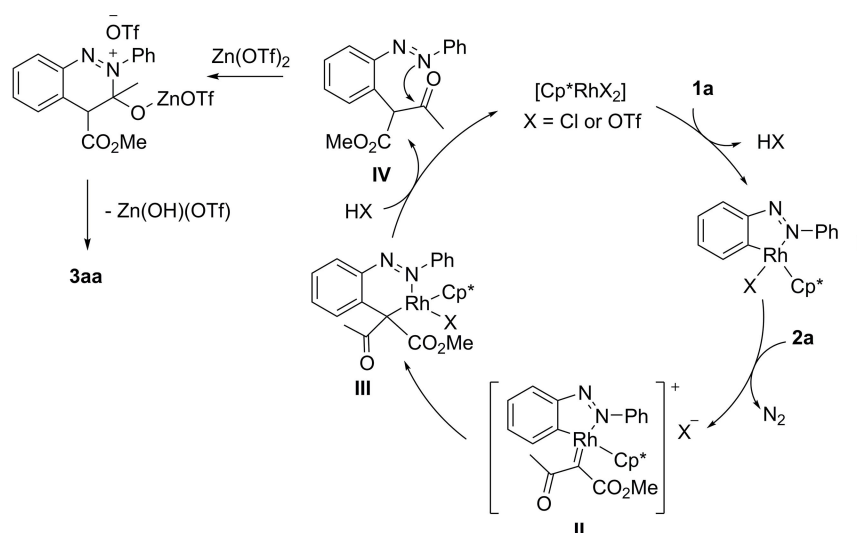


Scheme 5. Mechanistic Investigations.

azobenzene (Scheme 5a). This observation also agrees with the outcome of the intramolecular competitive reaction (**3ra/3ra'**). When **1b** was allowed to undergo H/D exchange under the standard conditions with methanol-*d*₄ and/or CD₃COOD in the absence of a diazo compound, no deuterium incorporation was observed at *ortho* position (Scheme 5b). Furthermore, the catalytic reaction of **1b** and **2a** in the presence of CD₃COOD led to recovered **1b**, with no observable deuteration. These results suggested that cyclorhodation is largely irreversible under these conditions. A putative rhodacyclic intermediate was synthesized from the reaction of **1b** and [RhCp*Cl₂]₂ with NaOAc in TFE, which afforded a five-membered rhodacycle **1b-I** in 92% yield (see SI). This complex was applied as a catalyst in the reaction of **1b** and **2a**, which afforded cinnolinium salt **3ba** in 97% yield. These

results suggested a C–H activation pathway. Moreover, another possible organic intermediate **3id-IV** was synthesized according to the literature (Scheme 5e),^[13b] and it was cleanly converted to the target product **3id** when treated with Zn(OTf)₂ in TFE at 60 °C. This clearly suggests that the cyclization step is mediated by Zn(OTf)₂ and the rhodium catalyst is not necessary. Kinetic isotope effect (KIE) value was measured as 3.3 by two parallel reactions of **1a** and **1a-d**₁₀ with **2a** (Scheme 5f), indicating that C–H bond cleavage is probably involved in the turnover-limiting step.

Based on our preliminary mechanistic studies and previous reports,^[19] the mechanism of this coupling is proposed in Scheme 6. Starting from an active catalyst Cp*RhX₂ (X=Cl or OTf), cyclometalation of azobenzene affords a rhodacyclic intermediate **I** together



Scheme 6. Proposed Catalytic Cycle.

with an acid HX. Coordination of an incoming diazo ester (**2a**) is followed by denitrogenation to afford a metal-carbene species **II**. Subsequent migratory insertion of the carbene moiety into Rh-aryl bond gives a 6-membered rhodacyclic **III**. Protonolysis of the intermediate **III** generates a 2-alkylated intermediate **IV** together with regeneration of the active Rh(III) catalyst. Finally, ketone carbonyl group is activated by the zinc salt and is nucleophilically attacked by the nitrogen to furnish the final annulated product **3aa**, where the Zn(OH)(OTf) can promote this cyclization to eventually give Zn(OH)₂.

In summary, we have developed a Rh(III)-catalyzed efficient C–H activation of azobenzenes with diazo compounds, affording the target salts in high yields. A variety of azobenzenes and diazo compounds are amenable to the coupling systems. This protocol features a relatively low catalyst loading, mild and sliver-free reaction conditions, and compatibility with diverse functional groups, thus providing straightforward access to functionalized cinnolinium salts.

Experimental Section

General procedure for the synthesis of compound 3: To a pressure tube (35 mL) charged with azobenzene **1** (0.2 mmol), diazo compound **2** (0.3 mmol), [Cp*RhCl₂]₂ (2.5 mol%), and Zn(OTf)₂ (60 mol%) was added TFE (2 mL), and the result mixture was stirred at the reaction temperature (r.t. –80 °C) for 10 h (monitored by TLC). After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography to afford the target product.

Acknowledgements

Financial support from the NSFC (Nos. 21472186 and 21525208) and the fund for new technology of methanol conversion of Dalian Institute of Chemical Physics (Chinese Academy of Sciences) are gratefully acknowledged.

References

- [1] a) W. Kalk, K. H. Schundehutte, US Patent, US4139530, **1979**. b) Y. Yu, S. K. Singh, A. Liu, T.-K. Li, L. F. Liub, E. J. LaVoiea, *Bioorg. Med. Chem.* **2003**, *11*, 1475–1491. c) W. Lewgowd, A. Stanczak, *Arch. Pharm. Chem. Life Sci.* **2007**, *340*, 65–80. d) B. Hu, R. Unwalla, M. Collini, E. Quinet, I. Feingold, A. G. Nilsson, A. Wilhelmsson, P. Nambi, J. Wrobel, *Bioorg. Med. Chem.* **2009**, *17*, 3519–3527. e) B. S. Young, J. L. Marshall, E. MacDonald, C. L. Vonnegut, M. M. Haley, *Chem. Commun.* **2012**, *48*, 5166–5168. f) Y. Shen, Z. Shang, Y. Yang, S. Zhu, X. Qian, P. Shi, J. Zheng, Y. Yang, *J. Org. Chem.* **2015**, *80*, 5906–5911.
- [2] a) H. J. Barber, E. Lunt, K. Washbourn, W. R. Wragg, *J. Chem. Soc. C* **1967**, 1657–1664. b) M. H. Palmer, E. R. Russell, *J. Chem. Soc. C* **1968**, 2621–2625. c) D. E. Ames, H. R. Ansari, A. D. G. France, A. C. Lovesey, B. Novitt, R. Simpson, *J. Chem. Soc. C* **1971**, 3088–3097. d) G. Wu, A. L. Rheingold, R. F. Heck, *Organometallics* **1986**, *5*, 1922–1924. e) G. Wu, A. L. Rheingold, R. F. Heck, *Organometallics* **1987**, *6*, 2386–2391. f) D. L. Davies, C. E. Ellul, S. A. Macgregor, C. L. McMullin, K. Singh, *J. Am. Chem. Soc.* **2015**, *137*, 9659–9669.
- [3] a) J. Jayakumar, K. Parthasarathy, C.-H. Cheng, *Angew. Chem. Int. Ed.* **2012**, *51*, 197–200. b) P. Gandeepan, C.-H. Cheng, *Chem. Asian J.* **2016**, *11*, 448–460.
- [4] a) K. Muralirajan, C.-H. Cheng, *Chem. Eur. J.* **2013**, *19*, 6198–6202. b) D. Zhao, Q. Wu, X. Huang, F. Song, T. Lv, J. You, *Chem. Eur. J.* **2013**, *19*, 6239–6244.

- [5] G. Zhang, L. Yang, Y. Wang, Y. Xie, H. Huang, *J. Am. Chem. Soc.* **2013**, *135*, 8850–8853.
- [6] a) D. Ghorai, J. Choudhury, *Chem. Commun.* **2014**, *50*, 15159–15162. b) D. Ghorai, J. Choudhury, *ACS Catal.* **2015**, *5*, 2692–2696. c) Q. Ge, B. Li, H. Song, B. Wang, *Org. Biomol. Chem.* **2015**, *13*, 7695–7710. d) R. Thenarukandiyil, J. Choudhury, *Organometallics* **2015**, *34*, 1890–1897.
- [7] Z. Qi, S. Yu, X. Li, *J. Org. Chem.* **2015**, *80*, 3471–3479.
- [8] Q. Ge, Y. Hu, B. Wang, *Org. Lett.* **2016**, *18*, 2483–2486.
- [9] a) Y. Zhao, S. Li, X. Zheng, J. Tang, Z. She, G. Gao, J. You, *Angew. Chem. Int. Ed.* **2017**, *56*, 4286–4289. b) J. Yin, M. Tan, D. Wu, R. Jiang, C. Li, J. You, *Angew. Chem. Int. Ed.* **2017**, *56*, 13094–13098.
- [10] a) S. Prakash, K. Muralirajan, C.-H. Cheng, *Angew. Chem. Int. Ed.* **2016**, *55*, 1844–1848. b) Y.-X. Lao, S.-S. Zhang, X.-G. Liu, C.-Y. Jiang, J.-Q. Wu, Q. Li, Z.-S. Huang, H. Wang, *Adv. Synth. Catal.* **2016**, *358*, 2186–2191.
- [11] For the examples of Cp*Rh(III)-catalyzed C–H activation, see: a) T. Satoh, M. Miura, *Chem. Eur. J.* **2010**, *16*, 11212–11222. b) D. A. Colby, R. G. Bergman, J. A. Ellman, *Chem. Rev.* **2010**, *110*, 624–655. c) G. Song, F. Wang, X. Li, *Chem. Soc. Rev.* **2012**, *41*, 3651–3678. d) D. A. Colby, A. S. Tsai, R. G. Bergman, J. A. Ellman, *Acc. Chem. Res.* **2012**, *45*, 814–825. e) Z. Shi, D. C. Koester, M. Bouladakis-Arapinis, F. Glorius, *J. Am. Chem. Soc.* **2013**, *135*, 12204–12207. f) N. Kuhl, N. Schröder, F. Glorius, *Adv. Synth. Catal.* **2014**, *356*, 1443–1460. g) G. Song, X. Li, *Acc. Chem. Res.* **2015**, *48*, 1007–1020. h) Y. Cheng, C. Bolm, *Angew. Chem. Int. Ed.* **2015**, *54*, 12349–12352. i) R. B. Dateer, S. Chang, *Org. Lett.* **2016**, *18*, 68–71. j) D. Das, A. Biswas, U. Karmakar, S. Chand, R. J. Samanta, *Org. Chem.* **2016**, *81*, 842–848. k) Z. Qi, S. Yu, X. Li, *Org. Lett.* **2016**, *18*, 700–703. l) S. Zhou, J. Wang, L. Wang, C. Song, K. Chen, J. Zhu, *Angew. Chem. Int. Ed.* **2016**, *55*, 9384–9388. m) Z. Long, Z. Wang, D. Zhou, D. Wan, J. You, *Org. Lett.* **2017**, *19*, 2777–2780. n) K. S. Halskov, H. S. Roth, J. A. Ellman, *Angew. Chem. Int. Ed.* **2017**, *56*, 9183–9187. o) X. Chen, S. Yang, H. Li, B. Wang, G. Song, *ACS Catal.* **2017**, *7*, 2392–2396.
- [12] Selected examples of C–H functionalization with diazo compounds, see: a) W.-W. Chan, S.-F. Lo, Z. Zhou, W.-Y. Yu, *J. Am. Chem. Soc.* **2012**, *134*, 13565–13568. b) T. K. Hyster, K. E. Ruhl, T. Rovis, *J. Am. Chem. Soc.* **2013**, *135*, 5364–5367. c) S. Cui, Y. Zhang, D. Wang, Q. Wu, *Chem. Sci.* **2013**, *4*, 3912–3196. d) W. Ai, X. Yang, Y. Wu, X. Wang, Y. Li, Y. Yang, B. Zhou, *Chem. Eur. J.* **2014**, *20*, 17653–17657. e) F. Hu, Y. Xia, F. Ye, Z. Liu, C. Ma, Y. Zhang, J. Wang, *Angew. Chem. Int. Ed.* **2014**, *53*, 1364–1367. f) S. Yu, S. Liu, Y. Lan, B. Wan, X. Li, J. Am. Chem. Soc. **2015**, *137*, 1623–1631. g) B. Zhou, Z. Chen, Y. Yang, W. Ai, H. Tang, Y. Wu, W. Zhu, Y. Li, *Angew. Chem. Int. Ed.* **2015**, *54*, 12121–12126. h) Y. Yang, X. Wang, Y. Li, B. Zhou, *Angew. Chem. Int. Ed.* **2015**, *54*, 15400–15404. i) J. Zhou, J. Shi, X. Liu, J. Jia, H. Song, H. E. Xu, W. Yi, *Chem. Commun.* **2015**, *51*, 5868–5871. j) X. Chen, G. Zheng, Y. Li, G. Song, X. Li, *Org. Lett.* **2017**, *19*, 6184–6187.
- [13] a) J.-Y. Son, S. Kim, W. H. Jeon, P. H. Lee, *Org. Lett.* **2015**, *17*, 2518–2521. b) S. Sharma, S. H. Han, S. Han, W. Ji, J. Oh, S.-Y. Lee, J. S. Oh, Y. H. Jung, I. S. Kim, *Org. Lett.* **2015**, *17*, 2852–2855. c) P. Sun, Y. Wu, Y. Huang, X. Wu, J. Xu, H. Yao, A. Lin, *Org. Chem. Front.* **2016**, *3*, 91–95.
- [14] For the references of synthesis of other quaternary ammonium salts, see: a) G. Wu, A. L. Rheingold, S. J. Geib, R. F. Heck, *Organometallics* **1987**, *6*, 1941–1946. b) G. Wu, S. J. Geib, A. L. Rheingold, R. F. Heck, *J. Org. Chem.* **1988**, *53*, 3238–3241. c) R. P. Korivi, C.-H. Cheng, *Org. Lett.* **2005**, *7*, 5179–5182. d) L. Li, W. W. Brennessel, W. D. Jones, *J. Am. Chem. Soc.* **2008**, *130*, 12414–12419. e) R. P. Korivi, Y.-C. Wu, C.-H. Cheng, *Chem. Eur. J.* **2009**, *15*, 10727–10731. f) R. P. Korivi, C.-H. Cheng, *Chem. Eur. J.* **2010**, *16*, 282–287. g) C.-Z. Luo, P. Gandeepan, C.-H. Cheng, *Chem. Commun.* **2013**, *49*, 8528–8530. h) C.-Z. Luo, P. Gandeepan, J. Jayakumar, K. Parthasarathy, Y.-W. Chan, C.-H. Cheng, *Chem. Eur. J.* **2013**, *19*, 14181–14186.
- [15] Selected reports on C–H activation of azobenzenes: a) Y. Lian, R. G. Bergman, L. D. Lavis, J. A. Ellman, *J. Am. Chem. Soc.* **2013**, *135*, 7122–7125. b) H. Li, P. Li, H. Tan, L. Wang, *Chem. Eur. J.* **2013**, *19*, 14432–14436. c) Y. Lian, J. R. Hummel, R. G. Bergman, J. A. Ellman, *J. Am. Chem. Soc.* **2013**, *135*, 12548–12551. d) H. Deng, H. Li, L. Wang, *Org. Lett.* **2015**, *17*, 2450–2453. e) J. R. Hummel, J. A. Ellman, *J. Am. Chem. Soc.* **2015**, *137*, 490–498. f) H. Deng, H. Li, L. Wang, *Org. Lett.* **2016**, *18*, 3110–3113.
- [16] F. Xie, Z. Qi, S. Yu, X. Li, *J. Am. Chem. Soc.* **2014**, *136*, 4780–4787.
- [17] C. Reichardt, *Chem. Rev.* **1994**, *94*, 2319–2358.
- [18] The CCDC number is 1814875. See Supporting Information for crystallographic information.
- [19] For a report on Rh(III)–Zn(II) relay catalysis, see: Q. Wang, F. Wang, X. Yang, X. Zhou, X. Li, *Org. Lett.* **2016**, *18*, 6144–6147.