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Rh(III)-Catalyzed Intramolecular Redox-Neutral or Oxidative Cyclization of Alkynes: Short, Efficient Synthesis of 3,4-Fused Indole Skeletons

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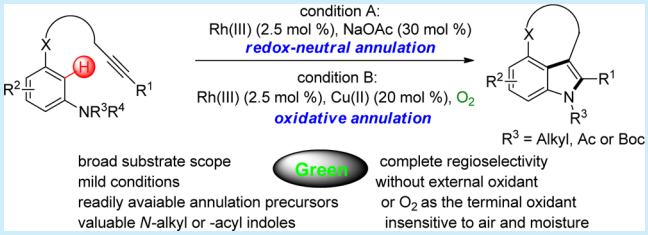
Supporting Information

ABSTRACT: A Rh(III)-catalyzed intramolecular redox-neutral or oxidative annulation of a tethered alkyne has been developed to efficiently construct 3,4-fused indoles via a C−H activation pathway. The advantages of this process are (1) ready availability of annulation precursors; (2) broad substrate scope; (3) complete regioselectivity; (4) simple and mild reaction conditions; and (5) no need for an external oxidant or to employ molecular oxygen as the stoichiometric terminal oxidant.



Indoles are of great interest to organic synthesis because of their presence in numerous natural products, pharmaceuticals, and agrochemicals.[1] Among them, 3,4-fused indole is particularly noteworthy because it presents a key structural motif of numerous bioactive natural products, such as the well-known lysergic acid,[2] hapalindole U,[3] chuangxinmycin,[4] dehydrobufotenine,[5] aurantioclavine,[6] *N*-methylwelwistatin,[7] communesin F,[8] and dragmacidin E.[9] As a consequence, there is a continued interest in the development of new methods to access this scaffold.[2−10] Despite these advances, most of these approaches are limited to cyclization of 3- or 4-functionalized indoles or generally require multistep synthesis to prepare their annulation precursors. Thus, methods for general and rapid preparation of 3,4-fused indoles would be highly desirable.

In 2012, Cho et al. reported the first intramolecular Fischer indolization reaction of aryl hydrazide with a tethered carbonyl group, followed by a tandem aromatic [3,3] sigmatropic rearrangement, to provide 3,4-fused indoles.[11] Recently, Boger and Jia reported an elegant synthesis of 3,4-fused indoles through an intramolecular Larock annulation reaction of 2-halide-3-substituted anilines (Scheme 1a).[12] Given that selective installation of a halide usually requires several steps, it would be highly desirable and attractive if we can take advantage of arene C−H bonds by a transition-metal-catalyzed C−H activation pathway. Indeed, transition-metal-catalyzed C−H bond activation has become an increasingly viable tool to functionalize aromatic C−H bonds during the past decade because it removes the need for time-consuming and tedious substrate prefunctionalization, thus enhancing the efficiency and scope as well. In this context, Rh(III)-catalyzed C_{sp^2} C−H activation with subsequent cross-coupling with alkynes and alkenes is a rapidly evolving research field.[13−15] Inspired by these reports and in continuation of our interest in Rh(III)-catalyzed C−H functionalization,[16] we herein report the

Scheme 1. Synthesis of 3,4-Fused Indoles

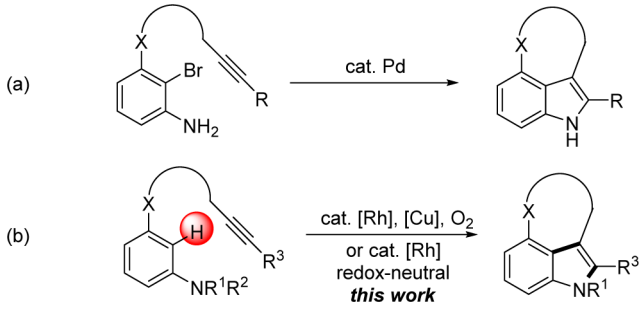
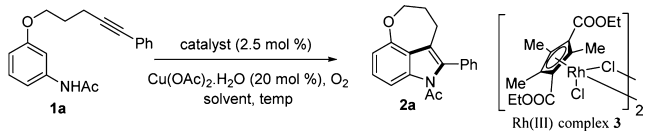


Table 1. Reaction Optimization[a]



entry	catalyst (2.5 mol %)	solvent	t (°C)	yield (%)[b]
1	$[RhCp^*(MeCN)_3](SbF_6)_2$	DMF	60	50
2	$[RhCp^*(MeCN)_3](SbF_6)_2$	*t*-AmOH	60	70
3	$[RhCp^*(MeCN)_3](SbF_6)_2$	CH_3CN	60	40
4	$[RhCp^*(MeCN)_3](SbF_6)_2$	dioxane	60	30
5	$[RhCp^*(MeCN)_3](SbF_6)_2$	DCE	60	21
6	catalyst **3**/$AgSbF_6$	acetone	20	70

[a]Reaction conditions: 0.2 mmol of **1a**, catalyst (2.5 mol %), $Cu(OAc)_2{\cdot}H_2O$ (20 mol %), solvent (2 mL) at the indicated temperature for 15 h. [b]Yield of isolated product.

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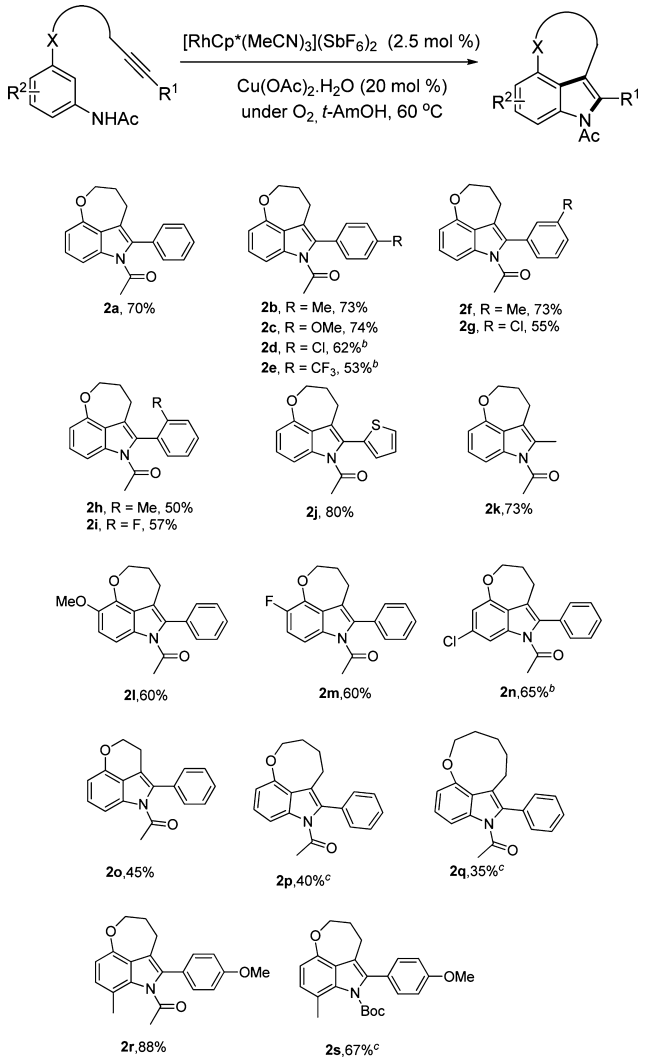
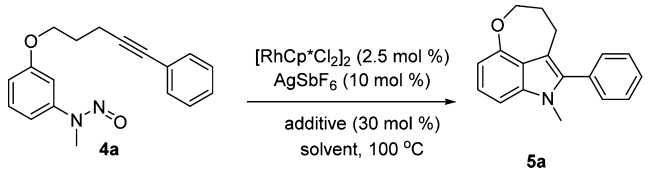
Scheme 2. Substrate Scope for the Rh-Catalyzed Oxidative Annulation Reaction[a]



[a]Reaction conditions: 0.2 mmol of **1**, $[RhCp^*(MeCN)_3](SbF_6)_2$ (2.5 mol %), $Cu(OAc)_2{\cdot}H_2O$ (20 mol %), *t*-AmOH (2 mL) at 60 °C under O_2 for 15 h. Yield of isolated product. [b] The reaction was conducted with $(Cp^*RhCl_2)_2$ (2.5 mol %), $AgSbF_6$ (10 mol %), $Cu(OAc)_2{\cdot}H_2O$ (2 equiv), *t*-AmOH (2 mL) at 110 °C for 0.5 h. [c] The reaction was conducted with **3** (2.5 mol %), $AgSbF_6$ (10 mol %), $Cu(OAc)_2{\cdot}H_2O$ (0.2 equiv), acetone (2 mL) at rt for 15 h.

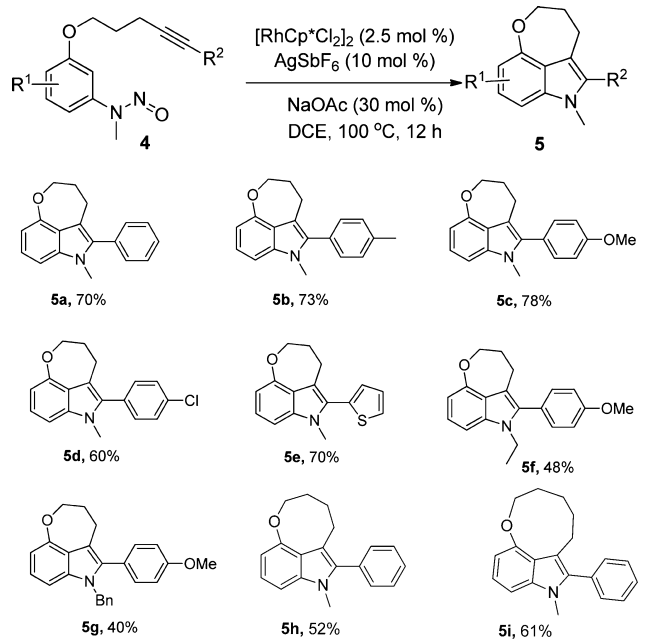
Table 2. Optimization of the Intramolecular Redox-Neutral Annulation Reaction[a]



entry	additive (30 mol %)	solvent	yield (%)[b]
1	AcOH	CH_3CN	0
2	PivOH	CH_3CN	0
3	NaOAc	CH_3CN	35
4	Na_2CO_3	CH_3CN	<10
5	CsOAc	CH_3CN	20
6	AgOAc	CH_3CN	<10
7	NaOAc	THF	17
8	NaOAc	DCE	70

[a]Reaction conditions: 0.2 mmol of **4a**, $[RhCp^*Cl_2]_2$ (2.5 mol %), $AgSbF_6$ (10 mol %), additive (30 mol %), and solvent (2 mL) at 100 °C for 12 h. [b]Yield of isolated product.

Scheme 3. Substrate Scope for the Rh-Catalyzed Redox-Neutral Annulation Reaction[a]



[a]Reaction conditions: 0.2 mmol of **4**, $[RhCp^*Cl_2]_2$ (2.5 mol %), $AgSbF_6$ (10 mol %), NaOAc (30 mol %), and DCE (2 mL) at 100 °C for 12 h. Yield of isolated product.

rhodium-catalyzed intramolecular annulation of alkynes via a C−H bond activation pathway to efficiently construct 3,4-fused indoles (Scheme 1b).[17]

We initiated our studies by exploring various reaction conditions for the desired annulation of substrate **1a** (Table 1). Initial experiments were performed with $[RhCp^*(MeCN)_3](SbF_6)_2$ (2.5 mol %) and $Cu(OAc)_2$ (20 mol %) in DMF under oxygen at 60 °C for 15 h. To our delight, the desired annulation product **2a** was obtained in 50% yield (entry 1). Among the solvents tested (entries 2−5), *tert*-amyl alcohol was proven to be optimal, affording the desired product **2a** in 70% yield (entry 2). In addition, the same reaction proceeded even at room temperature in 70% yield by using an electron-deficient rhodium(III) complex **3** as a catalyst and air/a catalytic amount of Cu $(OAc)_2$ as oxidants (entry 6).[15e,f]

With the optimal conditions established, we next investigated the substrate scope in this oxidative annulation reaction (Scheme 2). Various functional groups in the phenyl substituent of the alkyne, such as chloro, fluoro, and trifluoromethyl groups, were well tolerated. Substrates containing both electron-donating (**2b**, **2c**, **2f**, **2h**) and -withdrawing (**2d**, **2e**, **2g**, **2i**) groups at the *para* (**2b**−**2e**), *meta* (**2f** and **2g**) and *ortho* (**2h** and **2i**) positions of the phenyl ring were all viable for this intramolecular annulation reaction, affording the corresponding products in good yields. To our delight, heteroaromatic groups, such as thiophene, and alkyl groups could be accommodated in the reaction, giving products **2j** and

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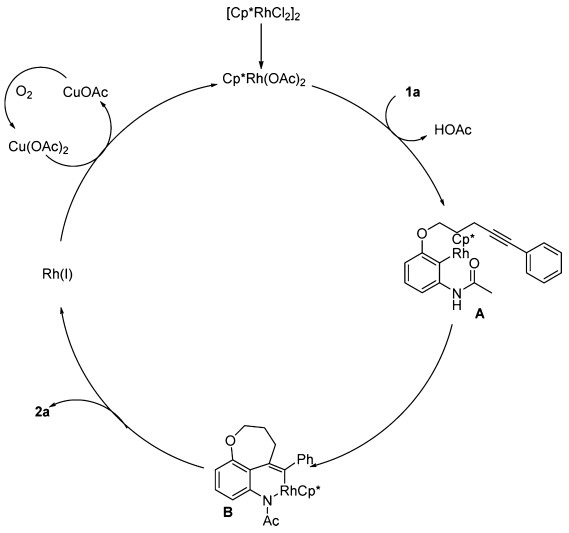
Scheme 4. Proposed Mechanism



2k in good yields. Substrates with electron-donating or -withdrawing R^2 groups also participated in this reaction (**2l**–**2n**, **2r**). Satisfyingly, the intramolecular reaction could be extended to generate 3,4-fused indoles with 6- to 9-membered rings (**2o**–**2q**), albeit in relatively low yields. More importantly, Boc-protected anilide was also well tolerated, providing the Boc-protected indole **2s** in good yield.

Next, the intramolecular redox-neutral annulation reaction was also investigated (Table 2).[18] When **4a** was treated with $[RhCp^*Cl_2]_2$ (2.5 mol %), $AgSbF_6$ (20 mol %), and an acid additive (30 mol %) in CH_3CN at 100 °C for 12 h, no desired annulation product **5a** was observed (entries 1–2). To our delight, when NaOAc (30 mol %) was added, product **5a** was obtained in 35% yield. Other bases, such as Na_2CO_3, CsOAc, and AgOAc, did not improve the yield of **5a** (entries 4–6). Next, we tested some solvents (entries 7–8), and DCE proved to be optimal as a solvent, improving the yield of **5a** to 70% (entry 8).

Next the optimized conditions were used to survey the scope of the reaction with various substrates (Scheme 3). Diverse functional groups were tolerated on the *para* positions of the ethynylphenyl substituent, including electron-donating (**5b**, **5c**) and electron-withdrawing (**5d**) groups, all providing their corresponding products in good yields. To our delight, heteroaromatic groups were well tolerated, giving products **5e** in good yields and demonstrating the versatility of this annulation. Various *N*-alkyl groups were next examined. *N*-Et and *N*-Bn substrates could be accommodated in the reaction, providing indoles **5f** and **5g** in moderate yields. To our delight, this intramolecular reaction could be extended to generate 3,4-fused indoles with 8- to 9-membered rings (**5h** and **5i**).

Based on the previous work,[14,15] we tentatively propose the following mechanism (Scheme 4). First, a Rh(III)-catalyzed *ortho*-directed C–H bond cleavage occurs to form intermediate **A**, followed by coordination and alkyne insertion to give rhodacycle **B**. Then reductive elimination occurs to provide the desired indole **2a** and the Rh(I) catalyst. Oxidation of the Rh(I) catalyst with Cu(II) regenerates the Rh(III) catalyst.

In summary, we have developed a novel, mild, and rapid method for the construction of 3,4-fused indoles based on a rhodium(III)-catalyzed C–H bond activation and subsequent intramolecular redox-neutral or oxidative annulation of tethered alkynes. The reactions feature a good substrate scope and complete regioselectivity and employ molecular oxygen as the stoichiometric terminal oxidant. More importantly, an intramolecular redox-neutral annulation reaction was also developed by utilizing the directing group as an internal oxidant. Given the importance of 3,4-fused indoles, we expect this intramolecular annulation reaction to gain broad synthetic utility.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization of products, and copies of ^1H and ^{13}C NMR spectra are provided. The material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Humphrey, G. R.; Kuethe, J. T. *Chem. Rev.* **2006**, *106*, 2875. (b) Cacchi, S.; Fabrizi, G. *Chem. Rev.* **2005**, *105*, 2873. (c) Gribble, G. W. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1045. (d) Saxton, J. E. *The Chemistry of Heterocyclic Compounds*, Vol. *25*, Part IV; Wiley: New York, 1983.

(2) For recent total synthesis of lysergic acid, see: (a) Liu, Q.; Jia, Y. *Org. Lett.* **2011**, *13*, 4810. (b) Iwata, A.; Inuki, S.; Oishi, S.; Fujii, N.; Ohno, H. *J. Org. Chem.* **2011**, *76*, 5506. (c) Kurokawa, T.; Isomura, M.; Tokuyama, H.; Fukuyama, T. *Synlett* **2009**, 775.

(3) For its selected total syntheses: (a) Baran, P. S.; Maimone, T. J.; Richter, J. M. *Nature* **2007**, *446*, 404. (b) Rafferty, R. J.; Williams, R. M. *J. Org. Chem.* **2012**, *77*, 519.

(4) For its selected total syntheses: (a) Kato, K.; Ono, M.; Akita, H. *Tetrahedron* **2001**, *57*, 10055. (b) Xu, X.-B.; Liu, J.; Zhang, J.-J.; Wang, Y.-W.; Peng, Y. *Org. Lett.* **2013**, *15*, 550.

(5) For its selected total syntheses: (a) Peat, A. J.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 1028. (b) Stoffman, E. J. L.; Clive, D. L. J. *Tetrahedron* **2010**, *66*, 4452.

(6) (a) Yamada, F.; Makita, Y.; Suzuki, T.; Somei, M. *Chem. Pharm. Bull.* **1985**, *33*, 2162. (b) Hegedus, L. S.; Toro, J. L.; Miles, W. H.; Harrington, P. J. *J. Org. Chem.* **1987**, *52*, 3319. (c) Somei, M.; Yamada, F. *Heterocycles* **2007**, *74*, 943. (d) Krishnan, S.; Bagdanoff, J. T.; Ebner, D. C.; Ramtohul, Y. K.; Tambar, U. K.; Stoltz, B. M. *J. Am. Chem. Soc.* **2008**, *130*, 13745. (e) Behenna, D. C.; Krishnan, S.; Stoltz, B. M. *Tetrahedron Lett.* **2011**, *52*, 2152. (f) Brak, K.; Ellman, J. A. *Org. Lett.* **2010**, *12*, 2004. (g) Xu, Z.; Hu, W.; Liu, Q.; Zhang, L.; Jia, Y. *J. Org. Chem.* **2010**, *75*, 7626.

(7) For total synthesis of *N*-methylwelwitindolinone, see: (a) Huters, A. D.; Quasdorf, K. W.; Styduhar, E. D.; Garg, N. K. *J. Am. Chem. Soc.* **2011**, *133*, 15797. (b) Bhat, V.; Allan, K. M.; Rawal, V. H. *J. Am. Chem. Soc.* **2011**, *133*, 5798.

(8) For total synthesis of communesin F, see: (a) Yang, J.; Wu, H.; Shen, L.; Qin, Y. *J. Am. Chem. Soc.* **2007**, *129*, 13794. (b) Zuo, Z.; Xie, W.; Ma, D. *J. Am. Chem. Soc.* **2010**, *132*, 13226. (c) Liu, P.; Seo, J. H.; Weinreb, S. M. *Angew. Chem., Int. Ed.* **2010**, *49*, 2000. (d) Belmar, J.; Funk, R. L. *J. Am. Chem. Soc.* **2012**, *134*, 16941.

(9) For total synthesis of dragmacidin E, see: Feldman, K. S.; Ngernmeesri, P. *Org. Lett.* **2011**, *13*, 5704.

(10) For other methods, see: (a) Xu, Q.; Dai, L.; You, S. *Chem. Sci.* **2013**, *4*, 97. (b) Hellal, M.; Singh, S.; Cuny, G. D. *J. Org. Chem.* **2012**, *77*, 4123. (c) Lim, H. J.; Gallucci, J. C.; RajanBabu, T. V. *Org. Lett.* **2010**, *12*, 2162. (d) Kalinin, A. V.; Chauder, B. A.; Rakhit, S.; Snieckus, V. *Org. Lett.* **2003**, *5*, 3519. (e) Katayama, S.; Ae, N.; Nagata, R. *J. Org. Chem.* **2001**, *66*, 3474. (f) Horwell, D. C.; Nichols, P. D.; Ratcliffe, G. S.; Roberts, E. *J. Org. Chem.* **1994**, *59*, 4418. (g) Lauchli, R.; Shea, K. J. *Org. Lett.* **2006**, *8*, 5287. (h) Bur, S. K.; Padwa, A. *Org. Lett.* **2002**, *4*, 4135. (i) Schçnherr, H.; Leighton, J. L. *Org. Lett.* **2012**, *14*, 2610. (j) Cheng, D.-J.; Wu, H.-B.; Tian, S.-K. *Org. Lett.* **2011**, *13*, 5636. (k) Greshock, T. J.; Funk, R. L. *J. Am. Chem. Soc.* **2006**, *128*, 4946.

(11) Park, I.-K.; Park, J.; Cho, C.-G. *Angew. Chem., Int. Ed.* **2012**, *51*, 2496.

(12) (a) Breazzano, S. P.; Poudel, Y. B.; Boger, D. L. *J. Am. Chem. Soc.* **2013**, *135*, 1600. (b) Shan, D.; Gao, Y.; Jia, Y. *Angew. Chem., Int. Ed.* **2013**, *52*, 4902.

(13) For reviews on Rh(III) catalyzed C−H activation, see: (a) Lewis, J. C.; Bergman, R. G.; Ellman, J. A. *Acc. Chem. Res.* **2008**, *41*, 1013. (b) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *Chem. Rev.* **2010**, *110*, 624. (c) Bouffard, J.; Itami, K. *Top. Curr. Chem.* **2010**, *292*, 231. (d) Satoh, T.; Miura, M. *Chem.—Eur. J.* **2010**, *16*, 11212. (e) Colby, D. A.; Tsai, A. S.; Bergman, R. G.; Ellman, J. A. *Acc. Chem. Res.* **2012**, *45*, 814. (f) Song, G.; Wang, F.; Li, X. *Chem. Soc. Rev.* **2012**, *41*, 3651. (g) Patureau, F. W.; Wencel-Delord, J.; Glorius, F. *Aldrichimica Acta* **2012**, *45*, 31. For reviews on other transition-metal-catalyzed C−H activation: (h) Ackermann, L.; Vicente, R.; Kapdi, A. R. *Angew. Chem., Int. Ed.* **2009**, *48*, 9792.

(14) For selected Rh(III)-catalyzed C−H functionalization by using alkynes and alkenes as substrates, see: (a) Liu, B.; Fan, Y.; Gao, Y.; Sun, C.; Xu, C.; Zhu, J. *J. Am. Chem. Soc.* **2013**, *135*, 468. (b) Feng, C.; Feng, D.; Loh, T.-P. *Org. Lett.* **2013**, *15*, 3670. (c) Wang, H.; Schroder, N.; Glorius, F. *Angew. Chem., Int. Ed.* **2013**, *52*, 5386. (d) Wang, H.; Grohmann, C.; Nimphius, C.; Glorius, F. *J. Am. Chem. Soc.* **2012**, *134*, 19592. (e) Zhen, W.; Wang, F.; Zhao, M.; Du, Z.; Li, X. *Angew. Chem., Int. Ed.* **2012**, *51*, 11819. (f) Li, B.-J.; Wang, H.-Y.; Zhu, Q.-L.; Shi, Z.-J. *Angew. Chem., Int. Ed.* **2012**, *51*, 3948. (g) Wang, D.; Wang, F.; Song, G.; Li, X. *Angew. Chem., Int. Ed.* **2012**, *51*, 12348. (h) Zhang, J.; Loh, T.-P. *Chem. Commun.* **2012**, *48*, 11232. (i) Ye, B.; Cramer, N. *Science* **2012**, *338*, 504. (j) Patureau, F. W.; Besset, T.; Kuhl, N.; Glorius, F. *J. Am. Chem. Soc.* **2011**, *133*, 2154. (k) Guimond, N.; Gorelsky, S. I.; Fagnou, K. *J. Am. Chem. Soc.* **2011**, *133*, 6449. (l) Li, H.; Li, Y.; Zhang, X.-S.; Chen, K.; Wang, X.; Shi, Z.-J. *J. Am. Chem. Soc.* **2011**, *133*, 15244. (m) Patureau, F. W.; Glorius, F. *Angew. Chem., Int. Ed.* **2011**, *50*, 1977. (n) Too, P. C.; Wang, Y.-F.; Chiba, S. *Org. Lett.* **2010**, *12*, 5688. (o) Rakshit, S.; Grohmann, C.; Besset, T.; Glorius, F. *J. Am. Chem. Soc.* **2011**, *133*, 2350. (p) Hyster, T. K.; Rovis, T. *J. Am. Chem. Soc.* **2010**, *132*, 10565. (q) Rakshit, S.; Patureau, F. W.; Glorius, F. *J. Am. Chem. Soc.* **2010**, *132*, 9585. (r) Guimond, N.; Fagnou, K. *J. Am. Chem. Soc.* **2009**, *131*, 12050. (s) Umeda, N.; Tsurugi, H.; Satoh, T.; Miura, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 4019. (t) Pham, M. V.; Ye, B.; Cramer, N. *Angew. Chem., Int. Ed.* **2012**, *51*, 10610. (u) Ueura, K.; Satoh, T.; Miura, M. *Org. Lett.* **2007**, *9*, 1407. (v) Ueura, K.; Satoh, T.; Miura, M. *J. Org. Chem.* **2007**, *72*, 5362. For intramolecular reaction: (w) Xu, X.; Liu, Y.; Park, C.-M. *Angew. Chem., Int. Ed.* **2012**, *51*, 9372. (x) Davis, T. A.; Hyster, T. K.; Rovis, T. *Angew. Chem., Int. Ed.* **2013**, *52*, 14181. (y) Ye, B.; Donets, P. A.; Cramer, N. *Angew. Chem., Int. Ed.* **2014**, *53*, 507. (z) Shi, Z.; Boultadakis-Arapinis, M.; Koester, D. C.; Glorius, F. *Chem. Commun.* **2014**, *50*, 2650.

(15) For Rh(III)-catalyzed oxidative indole synthesis: (a) Stuart, D. R.; Bertrand-Laperle, M.; Burgess, K. M. N.; Fagnou, K. *J. Am. Chem. Soc.* **2008**, *130*, 16474. (b) Stuart, D. R.; Alsabeh, P.; Kuhn, M.; Fagnou, K. *J. Am. Chem. Soc.* **2010**, *132*, 18326. (c) Chen, J.; Song, G.; Pan, C.-L.; Li, X. *Org. Lett.* **2010**, *12*, 5426. (d) Huestis, M. P.; Chan, L. N.; Stuart, D. R.; Fagnou, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 1338. (e) Hoshino, Y.; Shibata, Y.; Tanaka, K. *Adv. Synth. Catal.* **2014**, *356*, 1577. (f) Shibata, Y.; Tanaka, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 10917. For Ru(II) catalyzed indole synthesis, see: (g) Ackermann, L.; Lygin, A. V. *Org. Lett.* **2012**, *14*, 764.

(16) (a) Hou, W.; Zhou, B.; Yang, Y.; Feng, H.; Li, Y. *Org. Lett.* **2013**, *15*, 1814. (b) Zhou, B.; Hou, W.; Yang, Y.; Li, Y. *Chem.—Eur. J.* **2013**, *19*, 4701. (c) Zhou, B.; Yang, Y.; Shi, J.; Feng, H.; Li, Y. *Chem.—Eur. J.* **2013**, *19*, 10511. (d) Zhou, B.; Du, J.; Yang, Y.; Feng, H.; Li, Y. *Org. Lett.* **2013**, *15*, 6302. (e) Zhou, B.; Yang, Y.; Lin, S.; Li, Y. *Adv. Synth. Catal.* **2013**, *355*, 360. (f) Zhou, B.; Du, J.; Yang, Y.; Feng, H.; Li, Y. *Org. Lett.* **2014**, *16*, 592. (g) Yang, Y.; Hou, W.; Qin, L.; Du, J.; Feng, H.; Zhou, B.; Li, Y. *Chem.—Eur. J.* **2014**, *20*, 416. (h) Zhou, B.; Yang, Y.; Li, Y. *Chem. Commun.* **2012**, *48*, 5163. (i) Zhou, B.; Du, J.; Yang, Y.; Li, Y. *Org. Lett.* **2013**, *15*, 2934. (j) Yang, Y.; Zhou, B.; Li, Y. *Adv. Synth. Catal.* **2012**, *354*, 2916. (k) Du, J.; Yang, Y.; Feng, H.; Li, Y.; Zhou, B. *Chem.—Eur. J.* **2014**, *20*, 5727. (l) Du, J.; Zhou, B.; Yang, Y.; Li, Y. *Chem.—Asian J.* **2013**, *8*, 1386.

(17) During our manuscript preparation, a Rh-catalyzed intramolecular oxidative annulation reaction of a tethered alkyne was reported; see: (a) Zhang, X.; Li, Y.; Shi, H.; Zhang, L.; Zhang, S.; Xu, X.; Liu, Q. *Chem. Commun.* **2014**, *50*, 7306. (b) Tao, P.; Jia, Y. *Chem. Commun.* **2014**, *50*, 7367.

(18) For rhodium-catalyzed C−H activation using oxidizing directing groups, see: (a) Guimond, N.; Gouliaras, C.; Fagnou, K. *J. Am. Chem. Soc.* **2010**, *132*, 6908. (b) Too, P. C.; Wang, Y.-F.; Chiba, S. *Org. Lett.* **2010**, *12*, 5688. (c) Guimond, N.; Gorelsky, S. I.; Fagnou, K. *J. Am. Chem. Soc.* **2011**, *133*, 6449. (d) Rakshit, S.; Grohmann, C.; Besset, T.; Glorius, F. *J. Am. Chem. Soc.* **2011**, *133*, 2350. (e) Too, P. C.; Chua, S. H.; Wong, S. H.; Chiba, S. *J. Org. Chem.* **2011**, *76*, 6159. (f) Zhang, X.; Chen, D.; Zhao, M.; Zhao, J.; Jia, A.; Li, X. *Adv. Synth. Catal.* **2011**, *353*, 719. (g) Hyster, T. K.; Rovis, T. *Chem. Commun.* **2011**, *47*, 11846. (h) Wang, H.; Glorius, F. *Angew. Chem., Int. Ed.* **2012**, *51*, 7318. (i) Hyster, T. K.; KnÅrr, L.; Ward, T. R.; Rovis, T. *Science* **2012**, *338*, 500. (j) Ye, B.; Cramer, N. *Science* **2012**, *338*, 504. (k) Wang, H.; Grohmann, C.; Nimphius, C.; Glorius, F. *J. Am. Chem. Soc.* **2012**, *134*, 19592. (l) Neely, J. M.; Rovis, T. *J. Am. Chem. Soc.* **2013**, *135*, 66. (m) Hyster, T. K.; Ruhl, K. E.; Rovis, T. *J. Am. Chem. Soc.* **2013**, *135*, 5364. (n) Liu, G.; Shen, Y.; Zhou, Z.; Lu, X. *Angew. Chem., Int. Ed.* **2013**, *52*, 6033. (o) Qi, Z.; Wang, M.; Li, X. *Org. Lett.* **2013**, *15*, 5440. (p) Liu, B.; Song, C.; Sun, C.; Zhou, S.; Zhu, J. *J. Am. Chem. Soc.* **2013**, *135*, 16625. (q) Zhao, D.; Shi, Z.; Glorius, F. *Angew. Chem., Int. Ed.* **2013**, *52*, 12426. (r) Wang, C.; Huang, Y. *Org. Lett.* **2013**, *15*, 5294.