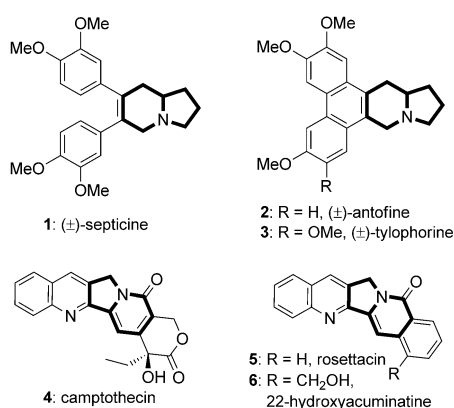


Rhodium(III)-Catalyzed Intramolecular Annulation through C–H Activation: Total Synthesis of (±)-Antofine, (±)-Septicine, (±)-Tylophorine, and Rosettacin**

Xianxiu Xu, Yu Liu, and Cheol-Min Park*

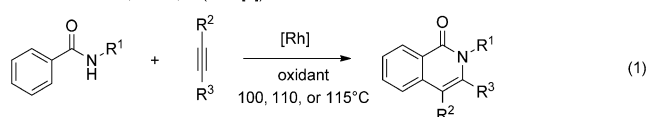
The indolizidine structural motif forms the core of many natural products with pharmacological relevance, such as indolizidine^[1] and phenanthroindolizidine^[2] alkaloids (septicine (1), antofine (2), and tylophorine (3)), camptothecin (4, CPT),^[3] and aramathecine alkaloids^[4] (rosettacin (5) and 22-hydroxyacuminatine (6)). While a number of synthetic methods for the construction of these scaffolds have been reported,^[1–4] the development of conceptually different synthetic approaches is still of great interest.



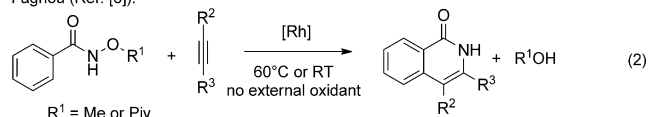
The rhodium(III)-catalyzed oxidative C–H activation has received significant interest in recent years because of its high efficiency, selectivity, and functional-group tolerance.^[5] Generally, these reactions require stoichiometric amounts of external oxidants [Eq. (1)],^[6] thus resulting in the generation of undesired waste. Recently, Fagnou et al. reported an oxidizing-directing-group strategy^[7] for the rhodium-catalyzed synthesis of isoquinolones by intermolecular C–H activation of *N*-methoxy/pivaloyloxy benzamides and alkynes [Eq. (2); Piv = pivaloyl],^[8] which not only obviates the need

for an external oxidant, but also increases the reactivity and selectivity under mild conditions. During our investigation of the reactivity of α -oximino carbenoids,^[9] we observed facile intramolecular N–O insertion of oxime ether moieties, which results in the formation of 2-alkoxy/aryloxy-2*H*-azirines.^[10] The cleavage of the N–O bond plays an important role in Fagnou's rhodium-catalyzed intermolecular C–H activation of *N*-methoxy/pivaloyloxy benzamides and in our N–O insertion of α -oximino carbenes. Based on this observation, we became interested in the intramolecular reaction of alkyne-tethered hydroxamic esters [Eq. (3)]. The successful development of this reaction would lead to a general and facile synthesis of hydroxyalkyl-substituted isoquinolone/2-pyridone derivatives, which could be readily transformed into indolizidine scaffolds. Herein, we wish to report these results, and the total synthesis of (±)-antofine, (±)-septicine, (±)-tylophorine, and rosettacin based on rhodium(III)-catalyzed C–H bond functionalization as the key step.

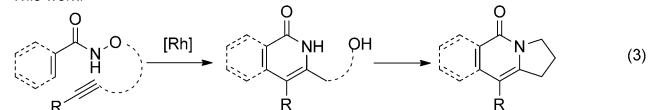
Satoh and Miura, Rovis, Li (Ref. [6]):



Fagnou (Ref. [8]):



This work:



Our synthetic attempts began with the reaction of **7a** by employing Fagnou's intermolecular reaction conditions^[7] (Table 1, entries 1 and 2). We found that treatment of **7a** with [(Cp**Rh*Cl₂)₂] (2.5 mol %) and CsOAc (30 mol %) in MeOH at 60 °C gave isoquinolones **8a** and **8a'** (29:1) in 98 % yield in 0.2 hours (Table 1, entry 1). Similar results were obtained with a reduced catalyst loading (0.5 mol %) and reaction temperature, however, a longer reaction time was required in this case (12 h; Table 1, entry 2). Improved

[*] Dr. X. Xu,^[†] Y. Liu,^[†] Prof. C.-M. Park
Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University
Singapore 637371 (Singapore)
E-mail: cmpark@ntu.edu.sg

[†] These authors contributed equally to this work.

[**] We gratefully acknowledge the Nanyang Technological University for the funding of this research. We thank Dr. Rakesh Ganguly for X-ray crystallographic analysis.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201204970>.

Table 1: Optimization of reaction conditions.

Entry	Catalyst (x mol%)	Additive	t [h]	Yield [%] ^[a] (8a : 8a')
1 ^[b]	[(Cp*RhCl ₂) ₂] (2.5)	CsOAc	0.2	98 (29:1)
2	[(Cp*RhCl ₂) ₂] (0.5)	CsOAc	12	98 (27:1)
3	[(Cp*RhCl₂)₂] (1.0)	CsOAc	4.0	98 (54:1)
4 ^[c]	[(Cp*RhCl ₂) ₂] (1.0)	CsOAc	10	98 (98:1)
5	[(RuCl ₂ { <i>p</i> -cymene}) ₂] (3.0)	NaOAc	8	96 (3:1)

[a] Yields determined by ¹H NMR spectroscopy. [b] Reaction at 60 °C.

[c] Reaction at 0.01 M. The entry in bold marks optimized reaction conditions. Cp* = pentamethylcyclopentadienyl.

regioselectivity (54:1) and reaction time (4 h) was achieved by using 1 mol% of catalyst at RT (Table 1, entry 3). The regioselectivity could be further improved under high-dilution conditions (0.01 M), although a longer reaction time (10 h) was again needed (Table 1, entry 4). A ruthenium catalyst ([RuCl₂{*p*-cymene})₂, 3.0 mol%]^[11] also gave the isoquinolones in excellent yields, however, with poor regioselectivity (3:1; Table 1, entry 5). The structure of **8a** was unambiguously assigned by ¹H/¹³C NMR spectroscopy and X-ray crystallography.^[12]

It is noteworthy that this intramolecular rhodium-catalyzed C–H/N–O bond functionalization reaction provides isoquinolones with reverse regioselectivity compared to the reported intermolecular version. In the latter case, when internal alkynes substituted with alkyl and aryl groups are employed, aryl groups are typically installed at the 3 position of isoquinolones.^[5–8,13] In contrast, our intramolecular reaction allows the installation of aryl groups at the 4 position of isoquinolones. This reverse regioselectivity offers a great synthetic potential for the construction of benzoindolizidine and indolizidine frameworks [Eq. (3)].

With the optimal conditions in hand, we surveyed various substrates to determine the scope of the reaction. The annulation reactions proceeded smoothly to afford isoquinolones and heteroaryl analogues in good to excellent yields (Table 2). A wide range of important functional groups on the aryl moieties of benzamides **7**, such as chloro, bromo, nitro, ester, and cyano groups, were well tolerated under the reaction conditions. Substrates with both electron-donating and electron-withdrawing groups at the *para* position of aryl groups participated in this reaction; electron-deficient substrates generally reacted faster than electron-rich ones (**8a–g**). Reactions with *ortho*-substituted benzamides also smoothly proceeded to give the corresponding products in excellent yields, albeit with diminished reaction rates (**8h** and **8i**). *meta*-Substituted benzamides smoothly reacted to give the corresponding isoquinolones in excellent yields with regioisomers (**8j** and **8k**) in a ratio of approximately 10:1. Extension of this reaction to heteroaryl carboxamides, such as thiophene and indole, proved successful when the reaction was performed in the presence of 2.5 mol% of catalyst at

Table 2: Scope for aryl and heteroaryl substrates.^[a]

8a : R = H; 4 h, 98% 8b : R = Me; 5 h, 97% 8c : R = OMe; 3.5 h, 97% 8d : R = Cl; 1 h, 96% 8e : R = CF ₃ ; 1 h, 96% 8f : R = CN; 1 h, 97% 8g : R = NO ₂ ; 1 h, 95%	8h : R = Me; 30 h, 98% 8i : R = Br; 30 h, 96% 8j : R = Me; 4 h, 97% ^[b] 8k : R = CO ₂ Me; 0.5 h, 97% ^[b] 8l : 2 h, 98% ^[c] 8m : 3.5 h, 80% ^[d] 8n : 3.5 h, 85% ^[d] 8o : R = TMS; 1 h, 98% ^[e] 8p : R = 4-MeOPh; 7 h, 98% 8q : R = 4-ClPh; 4 h, 97% 8r : R = Me; 6 h, 97% ^[c] 8s : R = Ph; 12 h, 94% ^[f] 8t : 12 h, 62% ^[c] 8u : 4 h, 95%	

[a] Yields of isolated products are given. [b] Isolated as a 10:1 mixture of regioisomers. [c] Reaction at 60 °C. [d] 2.5 mol% [(Cp*RhCl₂)₂] used; reaction at 60 °C. [e] 2.2 mmol scale reaction was also performed in the presence of 0.5 mol% catalyst at RT to complete in 3 h in 98% yield. [f] Regioselectivity of 11:1. TMS = trimethylsilyl.

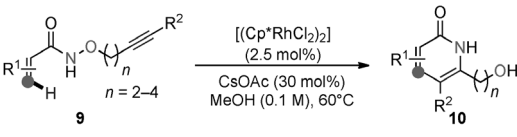
60 °C (**8m** and **8n**). Variation of the substituents on the phenyl group or replacement of the phenyl group with an alkyl group (such as methyl) showed that the electronic environment of the alkyne moiety had little impact on the reaction efficiency; **8p**, **8q**, and **8r** were obtained in 98%, 97%, and 97% yield, respectively. The reaction with TMS-protected alkyne turned out to be more efficient than that with phenyl-substituted alkyne and afforded **8o** in excellent yield, thus providing a useful handle for further transformation.

Next, we investigated the length of the tethers between the oxygen atom and the alkyne. All of the substrates with three-carbon-atom tethers gave the corresponding isoquinolones in excellent yields (**8a–q**). Furthermore, a rigid tether bearing an aryl group was well tolerated (**8u**). While the substrate with the two-carbon-atom tether also afforded **8s** in high yield with 11:1 regioselectivity, that with the four-carbon-atom tether was less effective and provided **8t** in moderate yield.

In 2010, Li and co-workers reported the rhodium(III)-catalyzed synthesis of 2-pyridones through oxidative alkene C(sp²)–H activation of *N*-arylacrylamides.^[14] While this represents a remarkable progress, the regioselectivity of the coupling with unsymmetrical alkynes is moderate. Later, Rovis et al. developed a new rhodium(III) catalyst with a bulkier ligand (1,3-di-*tert*-butylcyclopentadienyl) to improve regioselectivity, still favoring the normal regioselectivity in which aryl groups are substituted adjacent to nitrogen atoms.^[15] We reasoned that our new intramolecular rhodium-

(III)-catalyzed reaction of alkyne-tethered hydroxamic esters could provide 2-pyridones with an alternative substitution pattern. The results of the annulation reaction of various *N*-(pent-4-yn-1-yloxy)acrylamides are summarized in Table 3.

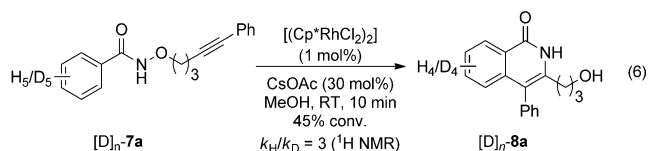
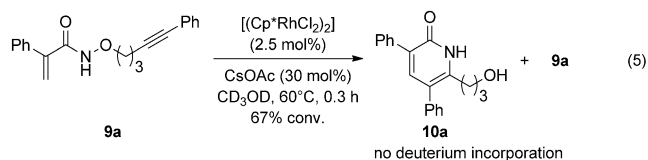
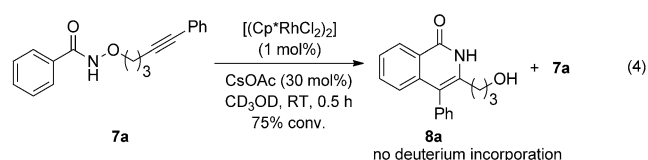
Table 3: Scope for alkenes.^[a]

	
10a: R = H; 4 h, 96% 10b: R = Me; 6 h, 91% 10c: R = Ph; 1 h, 94% 10d: R = 4-BrC₆H₄; 1 h, 95% 10e: R = 2-BrC₆H₄; 1 h, 89% 10f: R = 4-MeOC₆H₄; 1 h, 92% 10g: R = 4-MeC₆H₄; 1 h, 98% 10h: R = 3-MeC₆H₄; 1 h, 98% 10i: R = 2-MeC₆H₄; 1 h, 97%	10j: R = Me; 48 h, 55%^[b] 10k: R = Et; 48 h, 50%^[b] 10l: R = Ph; 24 h, 94% 10m: R = 4-MeC₆H₄; 24 h, 95% 10n: R = 4-ClC₆H₄; 17 h, 96% 10o: R = 2-thienyl; 10 h, 95%
10t: R = 4-MeOC₆H₄; 1 h, 96% 10u: R = TMS; 0.5 h, 90% 10v: R = Ph; 0.5 h, 95% 10w: R = Me; 0.5 h, 95%	10p: R¹ = R² = Ph; 5 h, 96% 10q: R¹ = Me, R² = Ph; 7 h, 97% 10r: R¹ = Me, R² = Et; 24 h, 92% 10s: R¹, R² = -(CH₂)₄-; 30 h, 94%

[a] Yield of isolated products. [b] 5 mol % [(Cp*RhCl₂)₂] used.

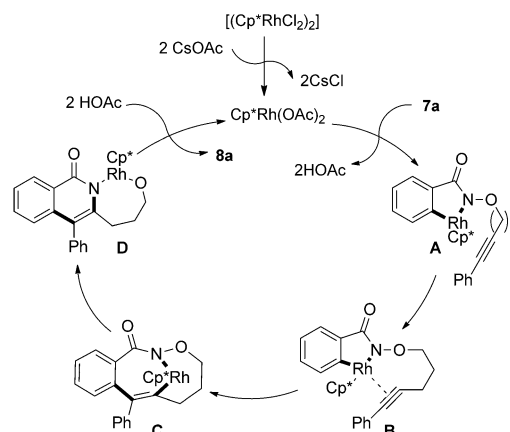
We were delighted to find that in the presence of [(Cp*RhCl₂)₂] (2.5 mol %) and CsOAc (30 mol %), the reaction smoothly proceeded at 60°C to afford 2-pyridones in a regioselective manner in good to excellent yields. Extensive substitution on the acrylamide at both α and β positions is tolerated well. α Substitution facilitates the reaction with shorter reaction time compared with β substitution and α,β disubstitution under identical conditions (**10b–i** vs. **10j–s**). Aryl substitution results in shorter reaction time compared to alkyl substitution (**10b** vs. **10c–i** and **10j**, **10k** vs. **10l–o**). Various substituents on the alkyne, including 4-MeOC₆H₄, TMS, and methyl groups, also afforded the corresponding 2-pyridones in excellent yields (**10t**, **10u**, and **10w**). In addition to the substrates with three-carbon-atom tether (**10a–u**), those with two-carbon-atom tether also gave the corresponding products in excellent yields (**10v** and **10w**); the substrate with the four-carbon-atom tether afforded **10x** in a slightly decreased yield (81 %).

To shed light on the reaction mechanism of this intramolecular redox-neutral process, deuterium-labeling experiments were performed. Reactions with **7a** and **9a** were performed under identical conditions in deuterated CH₃OH. No deuterium incorporation was detected in the recovered starting materials **7a** and **9a** and the products **8a** and **10a** [Eq. (4) and (5)]. These results indicate that the C–H bond-metalation step is irreversible under the reaction conditions, and the results are consistent with those from the intermolecular version of the reaction of benzhydroxamic ester with alkyne.^[8b] Moreover, a competition between protio and deutero **7a** showed a 3:1 product ratio at early conversions,



thus demonstrating that the product determining step is the C–H bond cleavage.^[16]

Based on the above results, a mechanistic pathway is proposed (Scheme 1). First, an irreversible C–H bond cleav-

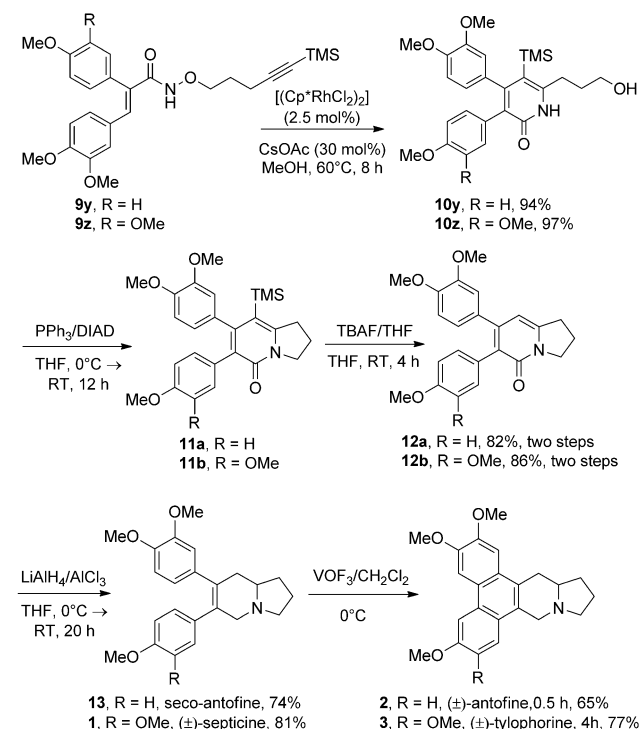


Scheme 1. Proposed mechanism.

age occurs to produce a five-membered rhodacycle intermediate **A** with concomitant loss of acetic acid. Next, coordination of alkyne affords intermediate **B**, which undergoes insertion into the Rh–C bond to form seven-membered rhodacycle **C**. Reductive elimination followed by oxidative addition into the N–O bond gives intermediate **D**. Upon protonation by acetic acid, product **8a** is released with regeneration of the catalyst. The formation of minute quantities of regioisomers from certain substrates could be ascribed to the presence of a minor pathway in which N–O bond cleavage occurs prior to alkyne insertion.

With this efficient route to 6-hydroxyalkyl-substituted 2-pyridones in hand, we next turned our attention to the synthetic utility of these compounds. Because of both their remarkable biological profiles and unusual pentacyclic archi-

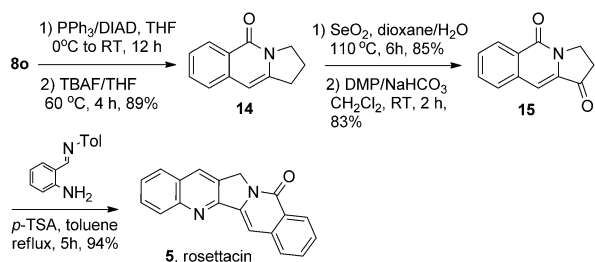
tures, phenanthroindolizidine alkaloids, such as antofine (**2**) and tylophorine (**3**), are attractive targets for total synthesis.^[2,17] Alkaloids **1**, **2**, and **3** could be readily prepared from amides **9y** and **9z** (Scheme 2). In the presence of



Scheme 2. Total synthesis of (±)-septicine (**1**), (±)-antofine (**2**), and (±)-tylophorine (**3**).

$[(\text{Cp}^*\text{RhCl}_2)_2]$ (2.5 mol%), the reaction of **9y** and **9z** produced 2-pyridones **10y** and **10z** in excellent yields. Under the standard Mitsunobu conditions, **10y** and **10z** were converted to indolizidines, from which the TMS group was easily removed to give **12a** and **12b** in 82% and 86% yields, respectively. Reduction of **12a** and **12b** under Moore's conditions^[18] provided seco-antofine (**13**) and alkaloid septicine (**1**) in high yields. Finally, synthesis of antofine (**2**) and tylophorine (**3**) was achieved by oxidative coupling of seco-antofine (**13**) and septicine (**1**) under the Liepa conditions.^[19]

The synthetic utility of our methodology is further illustrated by the synthesis of rosettacin (**5**; Scheme 3). Benzoindolizidine **14** could be obtained from isoquinolone **8o** in excellent yield through the Mitsunobu reaction and



Scheme 3. Synthesis of rosettacin (**5**).

subsequent deprotection of the TMS group. Sequential oxidation of **14** by SeO₂ and DMP afforded ketone **15** in good yield; **15** was further reacted with *N*-(2-aminobenzyl)-*p*-toluidine to produce rosettacin in 94% yield.

In summary, we have developed an efficient and practical rhodium(III)-catalyzed intramolecular annulation of alkyne-tethered hydroxamic esters for the synthesis of 3-hydroxyalkyl isoquinolones and 6-hydroxyalkyl-2-pyridones. This reaction features high reverse regioselectivity, broad substrate scope, and excellent functional-group tolerance, proceeds under mild reaction conditions with low catalyst loading and obviates the use of external oxidants. Furthermore, the highly efficient total synthesis of (±)-antofine, (±)-septicine, and (±)-tylophorine, and rosettacin, involving rhodium(III)-catalyzed C–H bond functionalization as a key step, was accomplished. We expect this intramolecular protocol to complement existing intermolecular methods and to gain broad applications in chemical synthesis.

Experimental Section

Without any particular precautions to extrude oxygen or moisture, the starting material (0.25 mmol), the indicated amount of $[(\text{Cp}^*\text{RhCl}_2)_2]$, and CsOAc (14.4 mg, 30 mol%) were weighed into a screw-cap vial equipped with a stirrer bar. MeOH (2.5 mL, 0.1 M) was added, and the mixture was stirred for the indicated time at RT, or the vial was placed in a preheated aluminum block and the mixture was stirred at 60°C and then cooled to RT (reactions monitored by TLC). The solvent was removed in vacuo, and the residue was purified by flash column chromatography on silica gel (eluent: EtOAc/MeOH = 100:1→50:1) to give the desired product.

Received: June 25, 2012

Published online: August 21, 2012

Keywords: 2-pyridones · annulation · C–H activation · isoquinolones · rhodium

- [1] For reviews, see: a) J. P. Michael, *Nat. Prod. Rep.* **2008**, 25, 139–165; b) J. P. Michael, *Nat. Prod. Rep.* **2007**, 24, 191–222.
- [2] For reviews, see: a) J. P. Michael, *Nat. Prod. Rep.* **2005**, 22, 603–626; b) J. P. Michael, *Nat. Prod. Rep.* **2001**, 18, 520–542; c) Z. G. Li, Z. Jin, R. Q. Huang, *Synthesis* **2001**, 2365–2378.
- [3] For reviews, see: a) W. Du, *Tetrahedron* **2003**, 59, 8649–8687; b) C. J. Thomas, N. J. Rahier, S. M. Hecht, *Bioorg. Med. Chem.* **2004**, 12, 1585–1604.
- [4] For synthesis and biological activity of rosettacin, see: a) F. Pin, S. Comesse, M. Sanselme, A. Daïch, *J. Org. Chem.* **2008**, 73, 1975–1978; b) B. M. Fox, X. Xiao, S. Antony, G. Kohlhausen, Y. Pommier, B. L. Staker, L. Stewart, M. Cushman, *J. Med. Chem.* **2003**, 46, 3275–3282; for synthesis and biological activity of 22-hydroxyacuminatine, see: c) X. Xiao, S. Antony, Y. Pommier, M. Cushman, *J. Med. Chem.* **2006**, 49, 1408–1412; d) H.-B. Zhou, G.-S. Liu, Z.-J. Yao, *J. Org. Chem.* **2007**, 72, 6270–6272; e) M. Babjak, A. Kanazawa, R. J. Anderson, A. E. Greene, *Org. Biomol. Chem.* **2006**, 4, 407–409.
- [5] For recent reviews, see: a) T. Satoh, M. Miura, *Chem. Eur. J.* **2010**, 16, 11212–11222; b) T. Satoh, M. Miura, *Synthesis* **2010**, 3395–3409; c) D. A. Colby, A. S. Tsai, R. G. Bergman, J. A. Ellman, *Acc. Chem. Res.* **2012**, 45, 814–825; d) G. Song, F. Wang, X. Li, *Chem. Soc. Rev.* **2012**, 41, 3651–3678; for important recent progress, see: e) N. Schröder, J. Wencel-Delord, F. Glorius, *J.*

- Am. Chem. Soc.* **2012**, *134*, 8298–8301; f) M. P. Huestis, L. Chan, D. R. Stuart, K. Fagnou, *Angew. Chem.* **2011**, *123*, 1374–1377; *Angew. Chem. Int. Ed.* **2011**, *50*, 1338–1341; g) S. Rakshit, C. Grohmann, T. Besset, F. Glorius, *J. Am. Chem. Soc.* **2011**, *133*, 2350–2353; h) D. R. Stuart, P. Alsabeh, M. Kuhn, K. Fagnou, *J. Am. Chem. Soc.* **2010**, *132*, 18326–18339; i) S. Rakshit, F. W. Patureau, F. Glorius, *J. Am. Chem. Soc.* **2010**, *132*, 9585–9587; j) K. Morimoto, K. Hirano, T. Satoh, M. Miura, *Org. Lett.* **2010**, *12*, 2068–2071; k) N. Guimond, K. Fagnou, *J. Am. Chem. Soc.* **2009**, *131*, 12050–12051; l) N. Umeda, H. Tsurugi, T. Satoh, M. Miura, *Angew. Chem.* **2008**, *120*, 4083–4086; *Angew. Chem. Int. Ed.* **2008**, *47*, 4019–4022.
- [6] a) S. Mochida, N. Umeda, K. Hirano, T. Satoh, M. Miura, *Chem. Lett.* **2010**, *39*, 744–746; b) T. K. Hyster, T. Rovis, *J. Am. Chem. Soc.* **2010**, *132*, 10565–10569; c) G. Song, D. Chen, C.-L. Pan, R. H. Crabtree, X. Li, *J. Org. Chem.* **2010**, *75*, 7487–7490.
- [7] For a highlight, see: F. W. Patureau, F. Glorius, *Angew. Chem.* **2011**, *123*, 2021–2023; *Angew. Chem. Int. Ed.* **2011**, *50*, 1977–1979.
- [8] a) N. Guimond, C. Gouliaras, K. Fagnou, *J. Am. Chem. Soc.* **2010**, *132*, 6908–6909; b) N. Guimond, S. I. Gorelsky, K. Fagnou, *J. Am. Chem. Soc.* **2011**, *133*, 6449–6457.
- [9] a) E. Lourdasamy, L. Yao, C.-M. Park, *Angew. Chem.* **2010**, *122*, 8135–8139; *Angew. Chem. Int. Ed.* **2010**, *49*, 7963–7967; b) Y. Jiang, W. C. Chan, C.-M. Park, *J. Am. Chem. Soc.* **2012**, *134*, 4104–4107; c) X. Qi, Y. Jiang, C.-M. Park, *Chem. Commun.* **2011**, *47*, 7848–7850.
- [10] X. Qi, X. Xu, C.-M. Park, *Chem. Commun.* **2012**, *48*, 3996–3998.
- [11] B. Li, H. Feng, S. Xu, B. Wang, *Chem. Eur. J.* **2011**, *17*, 12573–12577.
- [12] CCDC 886764 (**8a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [13] For comparison, the intermolecular reaction of *N*-methoxybenzamide and 5-phenylpent-4-yn-1-ol was performed under Fagnou's conditions. As expected, the reaction gave the 3-phenyl-substituted isoquinolone.
- [14] Y. Su, M. Zhao, K. Han, G. Song, X. Li, *Org. Lett.* **2010**, *12*, 5462–5465.
- [15] T. K. Hyster, T. Rovis, *Chem. Sci.* **2011**, *2*, 1606–1610.
- [16] E. M. Simmons, J. F. Hartwig, *Angew. Chem.* **2012**, *124*, 3120–3126; *Angew. Chem. Int. Ed.* **2012**, *51*, 3066–3072.
- [17] For recent syntheses of antofine, see: a) S. V. Pansare, R. Lingampally, R. Dyapa, *Eur. J. Org. Chem.* **2011**, 2235–2238; b) M. J. Niphakis, G. I. Georg, *J. Org. Chem.* **2010**, *75*, 6019–6022; c) X. Yang, Q. Shi, K. F. Bastow, K. H. Lee, *Org. Lett.* **2010**, *12*, 1416–1419; d) Z. Wang, Z. Li, K. Wang, Q. Wang, *Eur. J. Org. Chem.* **2010**, 292–299; e) S. Yamashita, N. Kurono, H. Senboku, M. Tokuda, K. Orito, *Eur. J. Org. Chem.* **2009**, 1173–1180; f) S. Kim, Y. M. Lee, J. Lee, T. Lee, Y. Fu, Y. Song, J. Cho, D. Kim, *J. Org. Chem.* **2007**, *72*, 4886–4891; g) A. Camacho-Davila, J. W. Herndon, *J. Org. Chem.* **2006**, *71*, 6682–6685; h) A. Fürstner, J. W. J. Kennedy, *Chem. Eur. J.* **2006**, *12*, 7398–7410; for recent syntheses of tylophorine, see: i) L. M. Rossiter, M. L. Slater, R. E. Giessert, S. A. Sakwa, R. J. Herr, *J. Org. Chem.* **2009**, *74*, 9554–9557; j) see ref. [17e]; k) A. McIver, D. D. Young, A. Deiters, *Chem. Commun.* **2008**, *39*, 4750–4752; l) W. Zeng, S. R. Chemler, *J. Org. Chem.* **2008**, *73*, 6045–6047; m) K. Wang, Q. Wang, R. Huang, *J. Org. Chem.* **2007**, *72*, 8416–8421.
- [18] B. R. Yersa, K. Yang, H. W. Moore, *Tetrahedron* **1994**, *50*, 6173–6180.
- [19] M. A. Ciufolini, F. Roschangar, *J. Am. Chem. Soc.* **1996**, *118*, 12082–12089.

