Tetrahedron Letters 55 (2014) 1859–1862

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Synthesis of indoles through Rh(III)-catalyzed C–H cross-coupling with allyl carbonates

Tian-Jun Gong, Wan-Min Cheng, Wei Su, Bin Xiao, Yao Fu *

Department of Chemistry, University of Science and Technology of China, Hefei 230026, China

ARTICLE INFO

Article history:
Received 23 September 2013
Revised 5 November 2013
Accepted 14 November 2013
Available online 22 November 2013

Keywords:
Rh(III)-catalyzed
C–H activation
Indoles

ABSTRACT

A practical Rh-catalyzed reaction was developed to achieve 2-alkyl-substituted indole synthesis. The reaction can tolerate a variety of synthetically important functional groups. The indole products can also be transformed into other important skeletons. Two bioactive compounds, that is indomethacin and pravadoline were prepared using the new method.

The indole ring system represents a key structural component that occurs ubiquitously in biologically active natural and unnatural compounds.[1] As a result, the development of new synthetic strategies for the synthesis of functionalized indoles[2] has been intensively studied in synthetic organic chemistry. Recently, an increasing number of examples have appeared in the literature featuring transition metal (Pd,[3] Rh,[4] Cu,[5] Ru[6] Fe,[7] Au,[8] Ni[9]) catalyzed oxidative C–H bond functionalization event as a fundamental step in the synthesis of various indoles. Despite these advances, further development of methods for synthesis of indoles is needed to expand the scope and utility of this category of synthetically valuable transformations. Herein, we developed a Rh(III)-catalyzed C–H activation with allyl carbonates for the synthesis of 2-aliphatic-substituted indoles.[10–12] This process allows quick assembly of indole rings from inexpensive and readily available amides and allyl carbonates and tolerates a broad range of functional groups (aryl-Br, heterocycle, amino acid).

Initially, we chose acetanilide (**1a**) and allyl acetate (**2a**) as model substrates to screen the reaction conditions (Table 1). When the substrates were treated with $[RhCp^*Cl_2]_2$, $AgSbF_6$, and $Cu(OAc)_2$ in dioxane at 110 °C for 24 h, we were delighted to obtain the desired product **3a** in 67% yield (Table 1, entry 1). To improve the yield we tested other solvents (i.e., DMF, DMSO, PhCl, DCE, and THP), where little product was obtained in DMF and DMSO (entries 2 and 3) whereas moderate yields were obtained in THP, PhCl, and DCE (60%, 53%, and 34%, entries 4–6). By changing the oxidants we then found that AgOAc, Ag_2CO_3, Ag_2O, and $Cu(OTFA)_2$ diminished the reactivity (entries 7–10). When $Cu(OAc)_2$ (1 equiv)/Ag_2CO_3 (1 equiv) was used the yield increased to 80% (entry 11). The yield was further improved to 88% by using allyl carbonate (**2b**) instead of allyl acetate (**2a**) (entries 12). The present reaction does not proceed by using allyl bromide (**2c**) (entry 13). Moreover, we carried out control experiments (entry 14 and 15), finding that the present reaction does not proceed with $[IrCp^*Cl_2]_2$ and $[Ru(p\text{-cymene})Cl_2]_2$. Furthermore, without adding $[RhCp^*Cl_2]_2$ catalyst we obtained no product (entry 16).

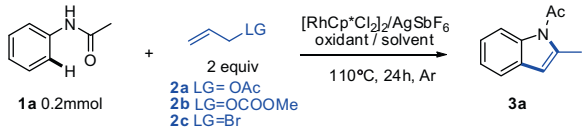
With the optimized reaction conditions in hand ($[RhCp^*Cl_2]_2$, $AgSbF_6$, and $Cu(OAc)_2/Ag_2CO_3$ in dioxane at 110 °C for 24 h), a variety of amides were examined to test the scope of the reaction (Table 2). Both electron-donating and withdrawing groups could be tolerated in this reaction. Electron-donating groups (**3b–d**) including 4-OMe, OAc, and OPiv gave isolated yields of 77%, 52%, and 50%, respectively. Electron withdrawing groups, such as 4-CF_3, 4-CN, and 4-SO_2Me can also be tolerated in the reaction (**3e–g**). Moreover, the aryl-halogen (Cl, Br, F) and OTs groups were well compatible with the Rh-catalyzed processes (**3h–k**), which made additional functionalization possible at these positions. When 3-substituted derivative was used, we saw the production of a less sterically crowded isomer in 50% yield (**3l**) and 74% yield (**3m**). In addition, acetanilides containing alkyl carboxylate, alkyl chloride, alkyl phosphate ester, and alkyl toluenesulfonate side chains (**3n–q**) were well tolerated in the reaction. Also interestingly, disubstituted acetanilides were also successfully tolerated in the reaction, with high regioselectivity (**3r**, **3s**).

Heterocycle compounds are highly interesting building blocks in the drug design. Accordingly we were interested in using heterocycle substituted acetanilides. We were delighted to find that kinds

* Corresponding author.
E-mail address: fuyao@ustc.edu.cn (Y. Fu).

http://dx.doi.org/10.1016/j.tetlet.2013.11.065
0040-4039/

Table 1
Optimization of the reaction conditions[a]



Entry	2	Oxidant	Solvent	Yield[b] (%)
1	**2a**	$Cu(OAc)_2$ (2 equiv)	Dioxane	67
2	**2a**	$Cu(OAc)_2$ (2 equiv)	DMF	8
3	**2a**	$Cu(OAc)_2$ (2 equiv)	DMSO	0
4	**2a**	$Cu(OAc)_2$ (2 equiv)	THP	60
5	**2a**	$Cu(OAc)_2$ (2 equiv)	PhCl	53
6	**2a**	$Cu(OAc)_2$ (2 equiv)	DCE	34
7	**2a**	AgOAc (2 equiv)	Dioxane	12
8	**2a**	Ag_2O (2 equiv)	Dioxane	30
9	**2a**	$Cu(TFA)_2$ (2 equiv)	Dioxane	40
10	**2a**	Ag_2CO_3 (2 equiv)	Dioxane	48
11	**2a**	$Cu(OAc)_2$ (1 equiv) Ag_2CO_3 (1 equiv)	Dioxane	80
12	**2b**	**$Cu(OAc)_2$ (1 equiv) Ag_2CO_3 (1 equiv)**	**Dioxane**	**88**
13	**2c**	$Cu(OAc)_2$ (1 equiv) Ag_2CO_3 (1 equiv)$_3$	Dioxane	0
14[c]	**2b**	$Cu(OAc)_2$ (1 equiv) Ag_2CO_3 (1 equiv)	Dioxane	0
15[d]	**2b**	$Cu(OAc)_2$ (1 equiv) Ag_2CO_3 (1 equiv)	Dioxane	<5
16[e]	**2b**	$Cu(OAc)_2$ (1equiv) Ag_2CO_3 (1 equiv)	Dioxane	0

[a] All the reactions were carried out with 5 mol % $[RhCp^*Cl_2]_2$, 20 mol % $AgSbF_6$ 0.2 mmol of **1a**, and 0.4 mmol of **2**, in 1 mL solvent, 110 °C.
[b] Isolated yield.
[c] $[IrCp^*Cl_2]_2$ instead of $[RhCp^*Cl_2]_2$.
[d] $[Ru(p\text{-cymene})Cl_2]_2$ instead of $[RhCp^*Cl_2]_2$.
[e] Without using $[RhCp^*Cl_2]_2$.

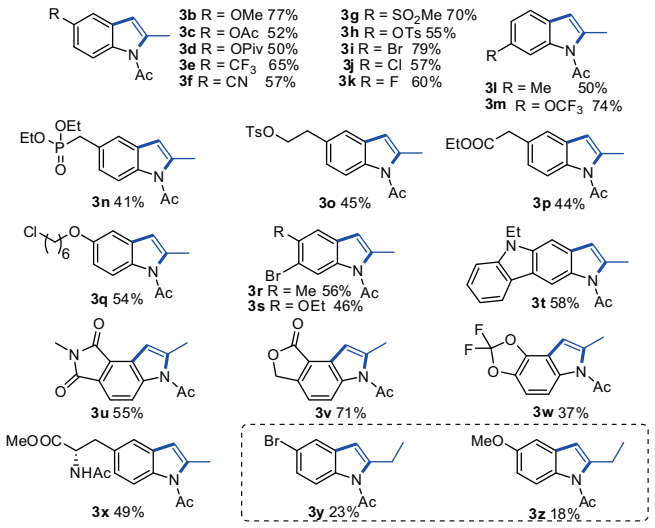
of heterocycle substituted acetanilides can successfully proceed in the reaction. Carbazole substituted acetanilides can afford the desired products **3t** in 58% yield. We obtained the indole product **3u** in 55% yield when phthalimide substituted acetanilides was used, high regioselectivity was observed. We also found that C–H activation indole synthesis process can be applied to valerolactone and acetal substituted acetanilides (**3v**, **3w**). Finally, we were surprised to find that an amino acid group can smoothly survive the indole synthesis process (**3x**). This finding is synthetically useful because amino acids are highly important skeletons in the biologically active compounds.

Other substituted allyl carbonates were used in the reaction. Unfortunately, only very low yields of product were obtained (**3y**, **3z**).

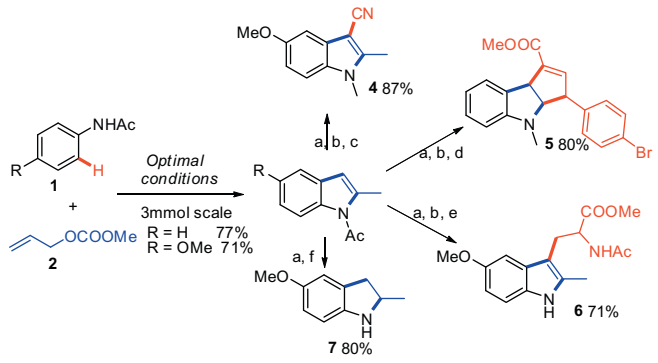
To demonstrate the synthetic utility of our reaction, we first tested and found that the reaction could be scaled up to a gram-scale (Scheme 1). Moreover, the products were converted to a number of important molecules. Direct cyanation of indole with *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide (NCTS)[13] by using Wang's conditions[13b] was developed. Moreover, Lewis acid promoted highly regioselective electrophilic substitution of indoles with N-acetylated α,β-dehydroalanine methyl ester synthesis of 3-indolyl-α-amino acids can successfully proceed.[14] An Rh(II) catalyzed [3+2] reaction was also reported, by using Davies's conditions.[15] Finally, $NaBH_3CN$ reduction of the 2-methylindole can give indoline **7**.[16] Such conversions are important for the synthesis of biologically active compounds.

To further show the utility of the 2-aliphatic-substituted indole process, this method allowed quick access to a number of drug molecules (Scheme 2). Product **3b** was converted to indomethacin **10**, an nonsteroidal anti-inflammatory drug, in four steps:[17] First, removal of acetyl protecting group; Second, introduction of a substituent at the 3-position on the indole ring was accomplished by

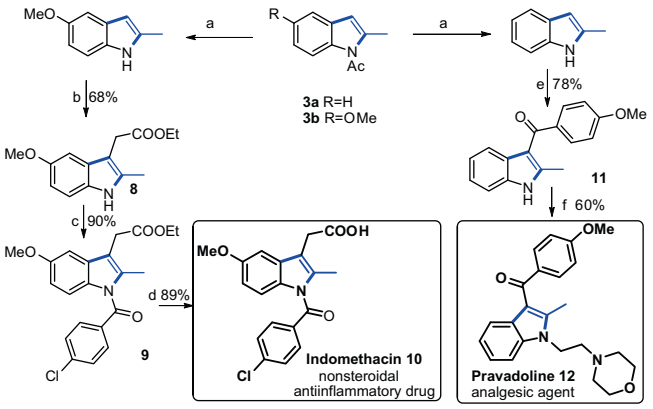
Table 2
Scope of acetanilides and allyl carbonates[a]



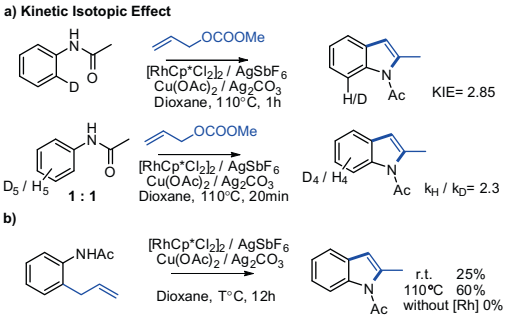
[a] Reactions were carried out at 110 °C for 24 h on a 0.2 mmol scale. Isolated yields.



Scheme 1. Further transformation of 2-methyl indoles. Reaction conditions: (a) KOH, EtOH, THF, reflux; (b) THF, NaH, then MeI; (c) NCTS, $BF_3{\cdot}OEt_2$, DCE, 80 °C, 12 h; (d) (*E*)-methyl 4-(4-bromophenyl)-2-diazobut-3-enoate, $Rh_2(S\text{-}DOSP)_4$, toluene, −45 °C; (e) N-acetylated α-dehydroalanine methyl ester, $ZrCl_4$ (2 equiv), CH_2Cl_2, 0 °C to rt, 12 h; (f) $NaBH_3CN$ (3 equiv), HOAc.



Scheme 2. Application to the synthesis of indomethacin and pravadoline. Reaction conditions: (a) KOH, EtOH, THF, reflux; (b) $BrCH_2CO_2Et$, *n*-BuLi, $ZnCl_2$, THF, 0 °C to rt; (c) $4\text{-}ClC_6H_4COCl$, *t*-BuOK, THF, rt; (d) LiOH (10 equiv), H_2O, THF, 25 °C, 6 h; (e) MeMgBr, CH_2Cl_2, Et_2O, then $4\text{-}OMeC_6H_4COCl$; (f) $ClCH_2CH_2$-4-morpholinyl, KOH, DMSO.



Scheme 3. Mechanism experiments.

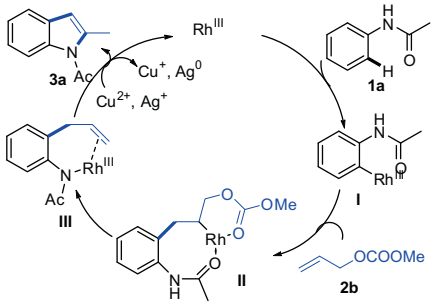


Figure 1. Proposed mechanism.

conventional 3-alkylation; Third, 4-chlorobenzoylation to give product **9** and Fourth, subsequent hydrolysis led to **10**. Along the same line, product **3a** was converted to Pravadoline **12**, an analgesic agent, in three steps:[18] removal of the acetyl protecting group, the C-3 aroyl group was introduced to give **11** followed by N-alkylation to afford the target **12**.

To comprehend the mechanism of the reaction we carried out the kinetic isotope effect experiment.[19a] First, an intramolecular kinetic isotope effect ($k_{H/D}$ = 2.85) was observed (Scheme 3). Moreover, an intramolecular kinetic isotope effect (k_H/k_D = 2.3) was also observed. This observation indicates that C–H bond activation is the rate-determining step in the catalytic cycle.[19] We prepared the 2-allylacetanilide (possible reaction intermediates).[20] 2-Allylacetanilide can be converted to the indole product, even under room temperature, which is consistent with Saá's work.[11] Furthermore, no product was obtained without using Rh^{III} catalyst, Rh^{III} is necessary for the oxidant oxidative cyclization step.

On the basis of experiments we proposed that the mechanism is as follows (Fig. 1): First, the Rh(III) catalyst reacted with the substrate (**1a**) through a rate-determining C–H activation step (mostly likely via a concerted metalation–deprotonation process) to generate a six-membered rhodacycle(III) intermediate (**I**). Second, Rh(III) in **I** reacts with allyl carbonates to produce Rh(III) species **II**, followed by decarboxylative β-oxygen elimination.[21] Finally, oxidative cyclization took place to generate the target product (**3a**). The Rh(III) complex then went back to the catalytic cycle.

In summary, we have developed an unprecedented Rh-catalyzed C–H activation with allyl carbonate synthesis of 2-aliphatic-substituted indoles. The reaction tolerated a variety of synthetically important functional groups (e.g., aryl-Br, heterocycle, amino acid). The indoles can be readily converted to many synthetically useful skeletons, and the present reaction may provide a practical tool for rapid synthesis of functional molecules (indomethacin and pravadoline). Further exploration of the synthetic utilities of this chemistry and in-depth mechanistic study are currently in progress.

Experimental

^{1}H NMR spectra were recorded at 400 MHz on an ARX 400 Bruker spectrometer. Chemical shifts are reported in parts per million referenced to the residual proton resonances of the solvents. Coupling constants are expressed in Hertz.

General procedure for rhodium-catalyzed indoles synthesis

A 10 mL Schlenk tube equipped with a magnetic stirrer was charged with $[RhCp^*Cl_2]_2$(5 mol %), $AgSbF_6$(20 mol %), $Cu(OAc)_2$(1 equiv), Ag_2CO_3(1 equiv), and sub-stituted acetanilides **1** (0.2 mmol). The tube was evacuated and backfilled with argon three times. Then allyl carbonate (0.4 mmol) in dioxane (1 mL) was added. After addition of all substrates, the reaction mixture was stirred and heated at 110 °C for 24 h. Then reaction was cooled to room temperature. Solvent and volatile reagents were removed by rotary evaporation and the residue was purified by flash column chromatography on silica gel to give the target product.

1-(2-Methyl-1*H*-indol-1-yl)ethanone (3a)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 7.8, 1H), 7.51–7.38 (m, 1H), 7.31–7.14 (m, 2H), 6.35 (s, 1H), 2.70 (s, 3H), 2.62 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.42, 137.44, 136.66, 129.90, 123.68, 123.25, 119.96, 115.39, 109.86, 27.46, 17.74.

1-(5-Methoxy-2-methyl-1*H*-indol-1-yl)ethanone (3b)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 9.1, 1H), 6.92 (d, J = 2.6, 1H), 6.84 (dd, J = 9.1, 2.6, 1H), 6.32–6.24 (m, 1H), 3.84 (s, 3H), 2.68 (s, 3H), 2.61 (d, J = 1.0, 3H).

1-Acetyl-2-methyl-1*H*-indol-5-yl acetate (3c)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 9.0, 1H), 7.16 (d, J = 2.4, 1H), 6.95 (dd, J = 9.0, 2.4, 1H), 6.34 (s, 1H), 2.69 (s, 3H), 2.61 (d, J = 0.9, 3H), 2.31 (s, 3H).

1-Acetyl-2-methyl-1*H*-indol-5-yl pivalate (3d)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 9.0, 1H), 7.13 (d, J = 2.4, 1H), 6.91 (dd, J = 9.0, 2.4, 1H), 6.32 (s, 1H), 2.69 (s, 3H), 2.61 (d, J = 1.0, 3H), 1.37 (s, 9H).

1-(5-Trifluoromethyl-2-methyl-1*H*-indol-1-yl)ethanone (3e)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.8, 1H), 7.63 (s, 1H), 7.40 (dd, J = 8.8, 1.4, 1H), 6.35 (s, 1H), 2.65 (s, 3H), 2.57 (d, J = 0.9, 3H).

Diethyl (1-acetyl-2-methyl-1*H*-indol-5-yl)methylphosphonate (3n)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.6, 1H), 7.32 (s, 1H), 7.10 (d, J = 8.6, 1H), 6.26 (s, 1H), 4.02–3.82 (m, 4H), 3.15 (d, J = 21.3, 2H), 2.64 (s, 3H), 2.55 (s, 3H), 1.16 (t, J = 7.1, 6H).

2-(1-Acetyl-2-methyl-1*H*-indol-5-yl)ethyl 4-methylbenzenesulfonate (3o)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.6, 1H), 7.66 (d, J = 8.3, 2H), 7.22 (d, J = 8.0, 2H), 7.17 (d, J = 1.2, 1H), 6.97 (dd, J = 8.6, 1.7, 1H), 6.28 (s, 1H), 4.23 (t, J = 7.1, 2H), 3.01 (t, J = 7.0, 2H), 2.70 (s, 3H), 2.63 (d, J = 0.7, 3H), 2.40 (s, 3H).

1-(5-(6-Chlorohexyloxy)-2-methyl-1*H*-indol-1-yl)ethanone (3q)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 9.1, 1H), 6.91 (d, J = 2.5, 1H), 6.83 (dd, J = 9.1, 2.6, 1H), 6.28 (s, 1H), 3.99 (t, J = 6.4, 2H), 3.54 (t, J = 6.7, 2H), 2.67 (s, 3H), 2.60 (d, J = 1.0, 3H), 1.81 (m, 4H), 1.56–1.47 (m, 4H).

(*S*)-Methyl 2-acetamido-3-(1-acetyl-2-methyl-1*H*-indol-5-yl)propanoate (3x)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.5, 1H), 7.10 (s, 1H), 6.89 (d, J = 8.5, 1H), 6.24 (s, 1H), 5.94 (d, J = 7.5, 1H), 4.82 (dd, J = 13.5, 5.8, 1H), 3.65 (s, 3H), 3.10 (m, 2H), 2.62 (s, 3H), 2.54 (s, 3H), 1.90 (s, 3H).

Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.11.065.

References and notes

1. (a) Kochanowska-Karamyan, A. J.; Hamann, M. T. *Chem. Rev.* **2010**, *110*, 4489; (b) Bandini, M.; Eichholzer, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 9608; (c) Arisawa, M.; Kasaya, Y.; Obata, T.; Sasaki, T.; Nakamura, T.; Araki, T.; Yamamoto, K.; Sasaki, A.; Yamano, A.; Ito, M.; Abe, H.; Ito, Y.; Shuto, S. *J. Med. Chem.* **2012**, *55*, 8152.
2. (a) Cacchi, S.; Fabrizi, G. *Chem. Rev.* **2005**, *105*, 2873; (b) Humphrey, G. R.; Kuethe, J. T. *Chem. Rev.* **2006**, *106*, 2875; (c) Cui, X.; Li, J.; Fu, Y.; Liu, L.; Guo, Q.-X. *Tetrahedron Lett.* **2008**, *49*, 3458; (d) Inman, M.; Moody, C. *J. Chem. Sci.* **2013**, *4*, 29.
3. For Pd-catalyzed direct C–H indoles synthesis, see: (a) Tan, Y.; Hartwig, J. F. *J. Am. Chem. Soc.* **2010**, *132*, 3676; (b) Neumann, J. J.; Rakshit, S.; Dröge, T.; Würtz, S.; Glorius, F. *Chem. Eur. J.* **2011**, *17*, 7298; (c) Wei, Y.; Deb, I.; Yoshikai, N. *J. Am. Chem. Soc.* **2012**, *134*, 9098.
4. For Rh-catalyzed direct C–H indoles synthesis, see: (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) Huestis, M. P.; Chan, L.; Stuart, D. R.; Fagnou, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 1338; (d) Wang, C.; Sun, H.; Fang, Y.; Huang, Y. *Angew. Chem., Int. Ed.* **2013**, *52*, 5795.
5. For Cu-catalyzed direct C–H indoles synthesis, for see: (a) Bernini, R.; Fabrizi, G.; Sferrazza, A.; Cacchi, S. *Angew. Chem., Int. Ed.* **2009**, *48*, 8078–8081; (b) Li, Y.-M.; Sun, M.; Wang, H.-L.; Tian, Q.-P.; Yang, S.-D. *Angew. Chem., Int. Ed.* **2013**, *52*, 3972.
6. For Ru-catalyzed direct C–H indoles synthesis, see: Ackermann, L.; Lygin, A. V. *Org. Lett.* **2013**, *15*, 3670.
7. For Fe-catalyzed direct C–H indoles synthesis, see: Guan, Z.-H.; Yan, Z.-Y.; Ren, Z.-H.; Liu, X.-Y.; Liang, Y.-M. *Chem. Commun.* **2010**, 2823.
8. For Au-catalyzed direct C–H indoles synthesis, see: Wang, Y.; Ye, L.; Zhang, L. *Chem. Commun.* **2011**, 7815.
9. For Ni-catalyzed direct C–H indoles synthesis, see: Song, W.; Ackermann, L. *Chem. Commun.* **2013**, 6638.
10. For Rh(III)-catalyzed direct C–H allylation of arenes with allylic carbonates, see: (a) Wang, H.; Schröder, N.; Glorius, F. *Angew. Chem., Int. Ed.* **2013**, *52*, 5386; (b) Feng, C.; Feng, D.; Loh, T.-P. *Org. Lett.* **2012**, *14*, 764.
11. During the preparation of our manuscript, we noted a similar study has been published: Cajaraville, A.; López, S.; Varela, J. A.; Saá, C. *Org. Lett.* **2013**, *15*, 4576.
12. (a) Satoh, T.; Miura, M. *Chem. Eur. J.* **2010**, *16*, 11212; (b) Colby, D. A.; Tsai, A. S.; Bergman, R. G.; Ellman, J. A. *Acc. Chem. Res.* **2012**, *45*, 814; (c) Song, G.; Wang, F.; Li, X. *Chem. Soc. Rev.* **2012**, *41*, 3651.
13. (a) Anbarasan, P.; Neumann, H.; Beller, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 519; (b) Gong, T.-J.; Xiao, B.; Cheng, W.-M.; Su, W.; Xu, J.; Liu, Z.-J.; Liu, L.; Fu, Y. *J. Am. Chem. Soc.* **2013**, *135*, 10630.
14. Angelini, E.; Balsamini, C.; Bartoccini, F.; Lucarini, S.; Piersanti, G. *J. Org. Chem.* **2008**, *73*, 5654.
15. Lian, Y.; Davies, H. M. L. *J. Am. Chem. Soc.* **2010**, *132*, 440.
16. Arp, F. O.; Fu, G. C. *J. Am. Chem. Soc.* **2006**, *128*, 14264.
17. Haag, B. A.; Zhang, Z.-G.; Li, J.-S.; Knochel, P. *Angew. Chem., Int. Ed.* **2010**, *49*, 9513.
18. Bell, M. R.; D'Ambra, T. E.; Kumar, V.; Eissenstat, M. A.; Herrmann, J. L.; Wetzel, J. R.; Rosi, D.; Philion, R. E.; Daum, S. J.; Hlasta, D. J.; Kullnig, R. K.; Ackerman, H. J.; Haubrich, D. R.; Luttinger, D. A.; Baizman, E. R.; Miller, M. S.; Ward, S. J. *J. Med. Chem.* **1991**, *34*, 1099.
19. (a) Simmons, E. M.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **2012**, *51*, 3066; (b) Li, L.; Brennessel, W. W.; Jones, W. D. *J. Am. Chem. Soc.* **2008**, *130*, 12414; (c) Xiao, B.; Gong, T.-J.; Xu, J.; Liu, Z.-J.; Liu, L. *J. Am. Chem. Soc.* **2011**, *133*, 1466; (d) Gong, T.-J.; Xiao, B.; Liu, Z.-J.; Wan, J.; Xu, J.; Luo, D.-F.; Fu, Y.; Liu, L. *Org. Lett.* **2011**, *13*, 3235; (e) Brasse, M.; Cámpora, J.; Ellman, J. A.; Bergman, R. G. *J. Am. Chem. Soc.* **2013**, *135*, 6427.
20. Yip, K.-T.; Yang, D. *Chem. Asian J.* **2011**, *6*, 2166.
21. (a) Weaver, J. D.; Recio, A., III; Grenning, A. J.; Tunge, J. A. *Chem. Rev.* **2011**, *111*, 1846; (b) Shang, R.; Liu, L. *Sci. China Chem.* **2011**, *54*, 1670.