Ring-Expansion Reactions

DOI: 10.1002/anie.201001237

Palladium-Catalyzed Ring-Expansion Reaction of Indoles with Alkynes: From Indoles to Tetrahydroquinoline Derivatives Under Mild Reaction Conditions**

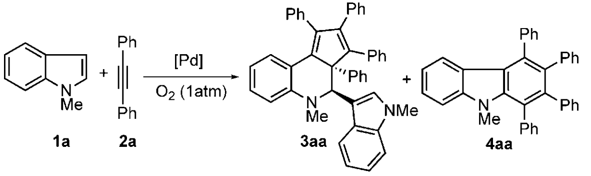
*Zhuangzhi Shi, Bo Zhang, Yuxin Cui, and Ning Jiao**

In memory of Xian Huang

Polyarylated aromatic and heteroaromatic compounds with condensed aromatic cores have attracted considerable attention in the electrochemical, photochemical, and functional materials fields because of their stability, their enhanced ability to transport charge, and their fluorescent properties in the solid state that are brought about by the aryl groups.[1] Alkynes are important building blocks and synthons for the construction of these multiply arylated compounds.[2] Recently, the cyclization reactions of alkynes through C–H activation[3] has presented an attractive and powerful strategy for the generation of aromatic and heteroaromatic compounds, such as naphthalenes, indoles, isoquinolines, carbazoles, benzothiazoles, and pyridines.[4] Herein, we describe an unprecedented palladium-catalyzed ring-expansion reaction of indoles with alkynes through dual C–H bond activations, using O_2 as the oxidant, which leads to tetrahydroquinoline derivatives with highly substituted cyclopentadienyl cores. To the best of our knowledge, only a few examples of ring-expansion reactions of indoles have been performed so far.[5] This chemistry not only offers a new approach to polysubstituted 4,5-dihydrocyclopenta[*c*]quinolines, but also valuable mechanistic insights into this novel ring-expansion reaction.

Recently, we developed the direct dehydrogenative anulation (DDA) reaction of simple anilines or biaryl compounds with internal alkynes to generate indoles and carbazole derivatives, respectively,[6] using O_2 as the oxidant.[7,8] Our continued efforts in metal-catalyzed C–H bond activation and cycloaromatization reactions prompted us to explore the reaction of indoles and alkynes. When *N*-methylindole (**1a**) was treated with diphenylethyne (**2a**) in the presence of $Pd(OAc)_2$ in acidic conditions at 100 °C under O_2 (1 atm), only 9-methyl-1,2,3,4-tetraphenyl-9*H*-carbazole (**4aa**) was obtained (Table 1, entries 1–2).[9] Interestingly, when the reaction was carried out at 20 °C, polysubstituted 4,5-dihydroquinoline **3aa** was selectively produced in 31 % yield (Table 1, entry 3). Subsequently, various parameters were screened in the presence of AcOH (Table 1, entries 4–9). When a mixture of acetonitrile and acetic acid (v/v = 1:1) was used as solvent, the reaction gave the highest efficiency with high diastereoselectivity (78 % yield; Table 1, entry 6). Use of a lower loading of $Pd(OAc)_2$ gave **3aa** in an acceptable yield (Table 1, entry 7). Control reactions confirmed that the reaction did not proceed in the absence of a palladium catalyst (Table 1, entry 8). Notably, a 59 % yield was achieved even when air was used as an oxidant instead of O_2 (Table 1, entry 9).

Table 1: Palladium-catalyzed ring-expansion reactions of **1a** with **2a**.[a]



Entry	Pd(OAc)$_2$ [eqiuv]	Solvent	*T* [°C]	*t* [h]	Yield [%][b] 3aa	Yield [%][b] 4aa
1	0.1	DMA/PivOH (4:1)	100	12	0	41
2	0.1	AcOH	100	12	0	18
3	0.1	AcOH	RT	36	31	trace
4	0.5	AcOH	RT	36	59	trace
5	0.1	DCE/AcOH (1:1)	RT	36	62	0
6	**0.1**	**CH_3CN/AcOH (1:1)**	**RT**	**36**	**78**	**0**
7	0.05	CH_3CN/AcOH (1:1)	RT	36	69	0
8	none	CH_3CN/AcOH (1:1)	RT	48	0	0
9[c]	0.1	CH_3CN/AcOH (1:1)	RT	48	59	0

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.5 mmol), $Pd(OAc)_2$, in solvent (1.0 mL), under an O_2 atmosphere (1 atm). [b] Yield of isolated product. The diastereoselectivity of this transformation is very high. [c] The reaction was carried out in air. DMA = N,N-dimethylacetamide, DCE = 1,2-dichloroethane.

Under these optimized reaction conditions, groups such as benzyl and hydroxyethyl, on the N were tolerated to give the desired products (**3ba** and **3ca**, 65 % and 63 %, respectively; Table 2). 1,5-dimethyl-1*H*-indole gave the corresponding polysubstituted tetrahydro-quinoline in 63 % yield (**3da**, Table 2). Notably, free (NH) indole (**1e**) was successfully transformed into the desired products in good yield (**3ea**, 74%, Table 2). In particular, the halogen-containing motifs (**3fa** and **3ga**; Table 2) work well in this transformation. Moreover, nitrile and nitro groups can also be incorporated into the benzene ring of the indole units for this reaction. As expected, indole derivative 2,3-dihydro-1*H*-pyrrolo[3,2,1-*ij*]quinoline **1j** can also be converted into the interesting **3ja** in 70 % yield (Table 2).

The scope of the internal alkynes was then investigated with *N*-methylindole (**1a**). These results indicated that both aryl- and alkyl-substituted internal alkynes were tolerant of this ring-expansion process. 1-Phenyl-1-hexyne (**2b**) reacted with **1a** to afford 2,3a-dibutyl-5-methyl-4-(1-methyl-1*H*-indol-3-yl)-1,3-diphenyl-4,5-dihydro-3a*H*-cyclopenta[*c*]quinoline (**3ab**), along with a small amount of an unidentified isomer[10] in 57 % yield and 64:36 regioselectivity (Table 3, entry 2). Similarly, the reaction of **1e** with **2b** afforded **3eb** and an isomer[10] (70:30) in a moderate combined yield (Table 3, entry 3). Even dialkyl-substituted dec-5-yne **2c**, were also converted into the desired product **3ac** with a

---

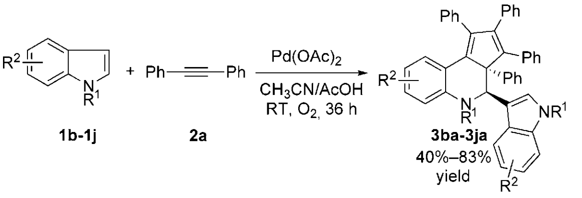
[*] Z. Shi, B. Zhang, Dr. Y. Cui, Dr. N. Jiao
State Key Laboratory of Natural and Biomimetic Drugs
School of Pharmaceutical Sciences, Peking University
Xue Yuan Rd. 38, Beijing 100191 (China)
Fax: (+86) 10-8280-5297
E-mail: jiaoning@bjmu.edu.cn

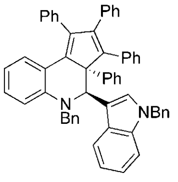
Dr. N. Jiao
State Key Laboratory of Organometallic Chemistry
Chinese Academy of Sciences
Shanghai 200032 (China)

[**] Financial support from Peking University, the National Science Foundation of China (Nos. 20702002 and 20872003), and the National Basic Research Program of China (973 Program; Grant No. 2009CB825300) is greatly appreciated. We thank Riyuan Lin in this group for reproducing the results of **3ba** and **3ga** in Table 2.

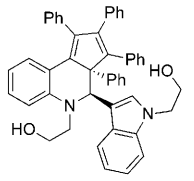
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201001237.

Table 2: Ring-expansion reactions of indoles **1** with alkynes **2a**.[a,b]

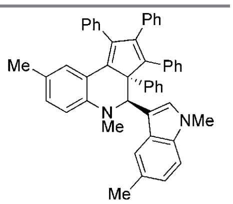




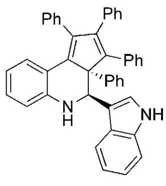
3ba: 65%



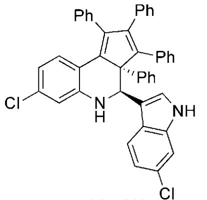
3ca: 63%



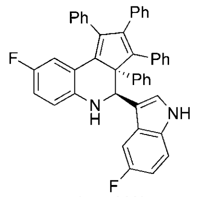
3da:63%



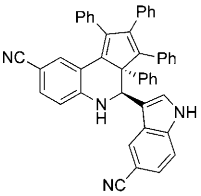
3ea: 74%



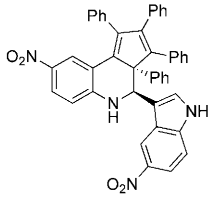
3fa: 59%



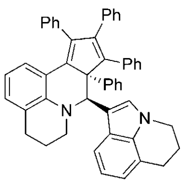
3ga: 83%



3ha: 60%



3ia: 40%



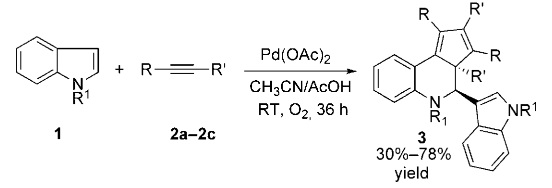
3ja: 70%

[a] Standard reaction conditions: **1** (0.20 mmol), **2** (0.50 mmol), Pd(OAc)$_2$ (0.02 mmol), CH$_3$CN/AcOH (1:1; 1.0 mL), RT, O$_2$ (1 atm), 36 h; [b] Yield of isolated product. The diastereoselectivity of this transformation is very high.

slight lower yield (Table 3, entry 4). Furthermore, the structure of **3aa** and **3eb** were confirmed by single-crystal X-ray analysis (see the Supporting Information, Figure S1 and S2).

The possibility of cross-reactions between two different indoles was also investigated. The reaction of **1a**, **1k**, and **2a** in a 1:1:5 molar ratio afforded three products (**3aa**:**5**:**3ka** = 4:5:1) in 78% overall yield with the indole product **5** as the major product (Scheme 1). However, the reaction of **1a** and **2a** in the presence of other electron-rich (hetero)arenes, such as 1,2-dimethyl-1*H*-indole, furan, 1-methyl-1*H*-pyrrole, benzo[*b*]thiophene, and *para*-xylene in our catalytic system, produced **3aa** as the sole product.

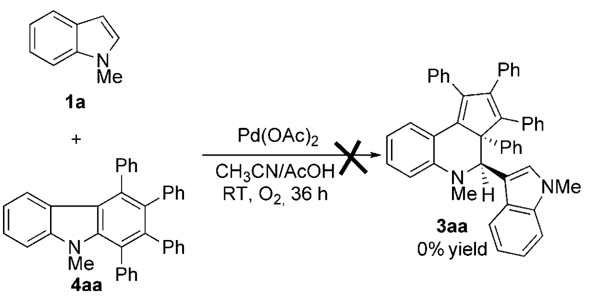
Table 3: Ring-expansion reactions of indoles **1** with alkynes **2a**–**2c**.[a]

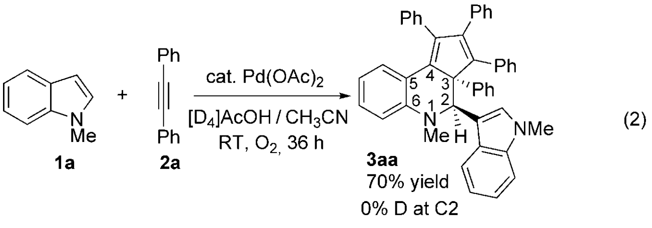


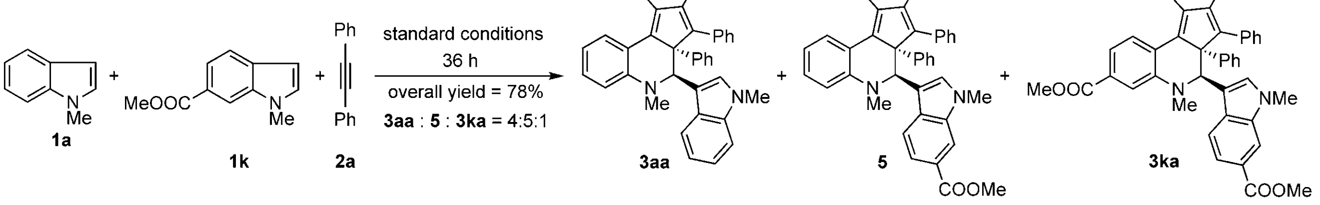
Entry	R^1	R, R′	Product	Yield [%][b]
1	Me (**1a**)	Ph, Ph (**2a**)	**3aa**	78
2	Me (**1a**)	Ph, *n*Bu (**2b**)	**3ab**	57 (64:36)[c]
3	H (**1e**)	Ph, *n*Bu (**2b**)	**3eb**	33 (70:30)[c]
4	Me (**1a**)	*n*Bu, *n*Bu (**2c**)	**3ac**	35

[a] Standard reaction conditions: **1** (0.20 mmol), **2** (0.50 mmol), Pd(OAc)$_2$ (0.02 mmol), CH$_3$CN/AcOH (1:1; 1.0 mL), RT, O$_2$ (1 atm), 36 h; [b] Yield of isolated product. [c] The ratio of the regioisomers was determined by ^{1}H NMR spectroscopy.

It was determined that product **3aa** was not generated from a rearrangement of **1a** and **4aa**. When **1a** and **4aa** were heated in our catalytic system, both starting materials were recovered [Eq. (1)]. Moreover, when a control experiment was carried out with [D$_4$]AcOH/CH$_3$CN, **3aa** was obtained in 70% yield, but no deuterium-labeled product was observed at the C2 position [Eq. (2)]. When 1,3-dideuteroindole [D]-**1e** was employed in the reaction under the standard conditions,

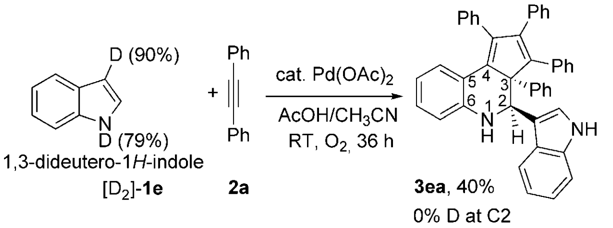




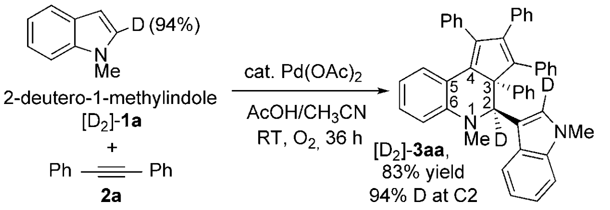


Scheme 1. The reaction of **1a** and **1k** with **2a**.

3ea was exclusively obtained in 40% yield, but again, no deuterated product was observed [Eq. (3)]. Further study showed that the reaction of 2-deutero-1-methylindole (94% D) and **2a** in our catalytic system gave [D$_2$]-**3aa** in 83% yield with 94% isotopic purity at the C2 position [Eq. (4)]. These results indicate that all of the hydrogen atoms at the C2 position in **3aa** come from the C2 position of **1a**.[11]

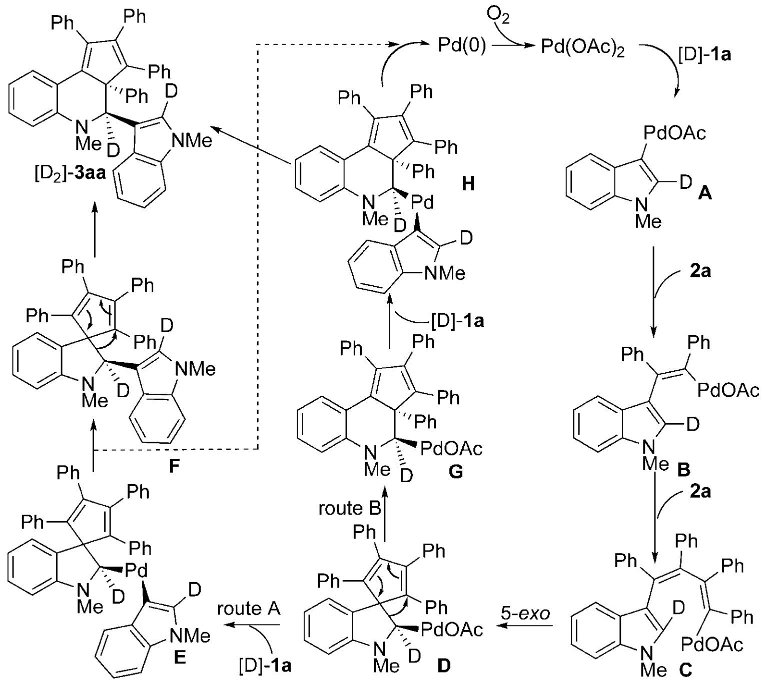


(3)



(4)

Given the result of the above control experiments, two plausible pathways were proposed for this kind of transformation (Scheme 2). In the initial step, regioselective direct electrophilic aromatic palladation at the 3-position of the indole forms an indol-3-ylpalladium species **A**.[12] The subsequent insertion of two alkyne molecules forms a dienylpalladium intermediate **C**.[13] Then, the intramolecular 5-*exo*-dig insertion[14] of an indole leads to spiro palladium intermediate **D**, with subsequent trapping by another indole ring to generate intermediate **E** (route A). Next, intermediate **E** undergoes reductive elimination to give intermediate **F** and the Pd^0 that is formed is reoxidized by O$_2$ to Pd^{II} to complete the catalytic cycle. Finally, the spiro intermediate **F** may highly selectively rearrange into the more stable ring-fused product **3aa**, having a *cis* relationship between the phenyl group and D owing to the steric hindrance. Alternatively, intermediate **D** may highly selectively rearrange into the more stable ring-fused intermediate **G** (route B). Then a successive second intermolecular electrophilic aromatic palladation of another indole molecule would generate intermediate **H**, which undergoes reductive elimination to give the product **3aa**.



Scheme 2. Proposed mechanism for the palladium-catalyzed ring-expansion reaction of indoles.

Some of the synthesized polysubstituted 4,5-dihydrocyclopenta[*c*]quinolines showed solid state fluorescence in the range of 500–560 nm (see the Supporting Information). Remarkably, **3aa** shows a strong emission compared with a typical emitter, such as tris(8-hydroxyquinolino)aluminum (Alq$_3$), which is a well-known green fluorescence emitter in the solid state (Figure 1, A versus B). In contrast, the free (NH) substrate **3ea** was found to exhibit weaker luminescence compared with that of Alq$_3$ (Figure 1, A versus C). In particular, compound **3aa** exhibits an intense green luminescence peak at around 520 nm, and the intensity is at least three times stronger than that of Alq$_3$. Furthermore, the bandwidth of **3aa** is much narrower than that of Alq$_3$, and is observed as a high-purity green emission. This strongly suggests that the remarkably intense luminescence of **3aa** may be applied to a green emitter for electroluminescence (EL) devices.

In summary, we have demonstrated the first palladium-catalyzed highly selective ring-expansion reaction of readily available indoles with alkynes, leading to polysubstituted tetrahydroquinoline products. Compound **3aa** displays an intense luminescence in the solid state. This kind of transformation involves dual C–H bond activations, one C–C bond cleavage, five new C–C bond formations, and uniquely, ring-expansion of the indole through a rearrangement pathway, under mild reaction conditions. Moreover, O$_2$ (1 atm) is used as the oxidant in this catalytic cycle. This work may broaden the research into the areas of palladium catalysis and the ring-expansion of indoles. Studies to clarify the reaction mechanism and additional synthetic applications of this reaction are ongoing in our laboratory.

Experimental Section

5-Methyl-4-(1-methyl-1*H*-indol-3-yl)-1,2,3,3a-tetraphenyl-4,5-dihydro-3a*H*-cyclopenta[*c*]quinoline (**3aa**): **1a** (25.0 μL, 0.20 mmol), **2a** (89.0 mg, 0.50 mmol), and Pd(OAc)$_2$ (4.50 mg, 0.02 mmol) were added to a 20 mL Schlenk tube and the tube was purged three times with O$_2$

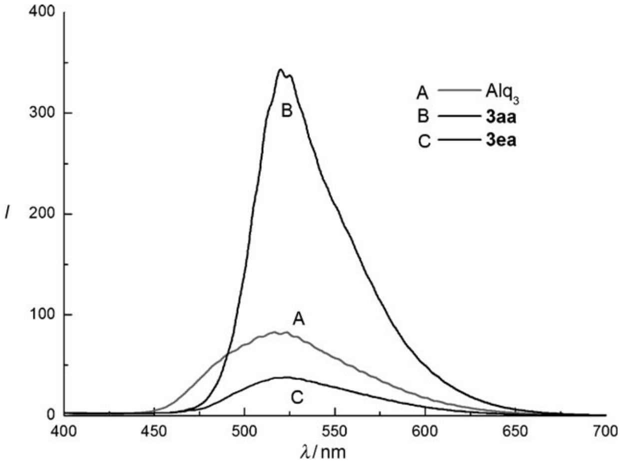


Figure 1. Fluorescence spectra of Alq$_3$ (A), **3aa** (B), and **3ea** (C) in the solid state upon excitation at 380 nm.

(1 atm), followed by addition of 1:1 CH_3CN/AcOH (v/v; 1.0 mL). The mixture was stirred at room temperature under O_2 (1 atm) for 36 hours and monitored by TLC. The solution was then quenched with H_2O (10 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic phases were washed with saturated sodium bicarbonate solution, dried over $MgSO_4$, filtered, and evaporated under vaccum. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1) to afford 48.0 mg (78%) of **3aa**: light-yellow/green solid; IR: (KBr) $\nu_{max} = 1596, 1484, 1296, 1199, 739, 694\ cm^{-1}$; ^1H NMR: (400 MHz, $CDCl_3$) $\delta = 7.56$ (d, $J = 7.6$ Hz, 2H), 7.29–7.13 (m, 9H), 7.10–6.85 (m, 8H), 6.80–6.67 (m, 4H), 6.60–6.48 (m, 3H), 6.31 (t, $J = 7.4$ Hz, 1H), 6.14 (d, $J = 7.6$ Hz, 2H), 5.49 (s, 1H), 3.61 (s, 3H), 2.91 ppm (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) $\delta = 146.8$, 145.9, 144.6, 144.4, 139.4, 136.2, 135.9, 135.83, 135.78, 129.6, 129.5, 129.1, 128.7, 128.6, 128.1, 127.9, 127.6, 127.1, 126.82, 126.78, 126.4, 126.3, 125.8, 120.7, 119.1, 118.5, 117.0, 115.0, 111.8, 110.7, 108.6, 62.4, 60.5, 37.6, 32.6 ppm; MS (70 eV): m/z (%): 616.6 (100) $[M]^+$; HRMS m/z (ESI) calcd for $C_{46}H_{36}N_2$ $[M]^+$ 616.2873, found 616.2869.

Received: March 1, 2010

Keywords: alkynes · C–H activation · indoles · oxidation · palladium

---

[1] a) J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Plenum, New York, **1999**; b) U. Mitschke, P. J. Bäuerle, *J. Mater. Chem. Phys.* **2000**, *10*, 1471; c) M. D. Watson, A. Fechtenkotter, K. Mullen, *Chem. Rev.* **2001**, *101*,1267; d) J. E. Anthony, *Angew. Chem.* **2008**, *120*, 460; *Angew. Chem. Int. Ed.* **2008**, *47*, 452; e) M. Mazur, P. Krysinski, G. J. Blanchard, *Langmuir* **2005**, *21*, 8802; f) W. Pisula, Z. Tomovic, M. Stepputat, U. Kolb, T. Pakula, K. Muellen, *Chem. Mater.* **2005**, *17*, 2641; g) S. Debnath, Q. Cheng, T. G. Hedderman, H. J. Byrne, *J. Phys. Chem. C* **2008**, *112*, 10418; h) T. Okazaki, K. K. Laali, *Adv. Org. Synth.* **2006**, *2*, 353; i) J. N. Moorthy, P. Natarajan, P. Venkatakrishnan, D.-F. Huang, T. J. Chow, *Org. Lett.* **2007**, *9*, 5215.

[2] a) *Acetylene Chemistry: Chemistry, Biology, and Material Science* (Eds.: P. J. Stang, R. R. Tykwinski, F. Diederich), Wiley-VCH, Weinheim, **2005**; b) R. G. Harvey, *Polycyclic Aromatic Hydrocarbons*, Wiley-VCH, Weinheim, **1997**.

[3] For recent reviews on C–H activation, see a) S. Beccalli, G. Broggini, M. Martinelli, S. Sottocornola, *Chem. Rev.* **2007**, *107*, 5318; b) L. Ackermann, R. Vicente, A. R. Kapdi, *Angew. Chem.* **2009**, *121*, 9976; *Angew. Chem. Int. Ed.* **2009**, *48*, 9792; c) X. Chen, K. M. Engle, D.-H. Wang, J.-Q. Yu, *Angew. Chem.* **2009**, *121*, 5196; *Angew. Chem. Int. Ed.* **2009**, *48*, 5094; d) B.-J. Li, S.-D. Yang, Z.-J. Shi, *Synlett* **2008**, *7*, 949; e) M. Lautens, P. Thansandote, *Chem. Eur. J.* **2009**, *15*, 5874; f) T. Kitamura, *Eur. J. Org. Chem.* **2009**, 1111; g) R. Giri, B.-F. Shi, K. M. Engle, N. Maugel, J.-Q. Yu, *Chem. Soc. Rev.* **2009**, *38*, 3242; h) O. Daugulis, H.-Q. Do, D. Shabashov, *Acc. Chem. Res.* **2009**, *42*, 1074; i) R. Jazzar, H. Julien, A. Renaudat, J. Sofack-Kreutzer, O. Baudoin, *Chem. Eur. J.* **2010**, *16*, 2654; j) T. W. Lyons, M. S. Sanford, *Chem. Rev.* **2010**, *110*, 1147; k) D. A. Colby, R. G. Bergman, J. A. Ellman, *Chem. Rev.* **2010**, *110*, 624.

[4] For some recent examples on the construction of aromatic and heteroaromatic compounds using C–H activation, see: a) N. Umeda, H. Tsurugi, T. Satoh, M, Miura, *Angew. Chem.* **2008**, *120*, 4083; *Angew. Chem. Int. Ed.* **2008**, *47*, 4019; b) Y.-T. Wu, K.-H. Huang, C.-C. Shin, T.-C. Wu, *Chem. Eur. J.* **2008**, *14*, 6697; c) T. Gerfaud, L. Neuville, J. Zhu, *Angew. Chem.* **2009**, *121*, 580; *Angew. Chem. Int. Ed.* **2009**, *48*, 572; d) N. Guimond, K. Fagnou, *J. Am. Chem. Soc.* **2009**, *131*, 12050; e) D. R. Stuart, M. Bertrand-Laperle, K. M. N. Burgess, K. Fagnou, *J. Am. Chem. Soc.* **2008**, *130*, 16474; f) K. Inamoto, C. Hasegawa, K. Hiroya, T. Doi, *Org. Lett.* **2008**, *10*, 5147; g) S. Würtz, S. Rakshit, J. J. Neumann, T. Dröge, F. Glorius, *Angew. Chem.* **2008**, *120*, 7340; *Angew. Chem. Int. Ed.* **2008**, *47*, 7230; h) N. Chernyak, V. Gevoorgyan, *J. Am. Chem. Soc.* **2008**, *130*, 5626; i) V. S. Thirunavukkarasu, K. Parthasarathy, C.-H. Cheng, *Angew. Chem.* **2008**, *120*, 9604; *Angew. Chem. Int. Ed.* **2008**, *47*, 9462; j) X. Wan, D. Xing, Z. Fang, B. Li, F. Zhao, K. Zhang, L. Yang, Z. Shi, *J. Am. Chem. Soc.* **2006**, *128*, 12046.

[5] a) M. Mentel, R. Breinbauer, *Curr. Org. Chem.* **2005**, *9*, 109; b) G. L. Closs, G. M. Schwartz, *J. Org. Chem.* **1961**, *26*, 2609.

[6] a) Z. Shi, C. Zhang, S. Li, D. Pan, S. Ding, Y. Cui, N. Jiao, *Angew. Chem.* **2009**, *121*, 4642; *Angew. Chem. Int. Ed.* **2009**, *48*, 4572; b) Z. Shi, Ding, Y. Cui, N. Jiao, *Angew. Chem.* **2009**, *121*, 8035; *Angew. Chem. Int. Ed.* **2009**, *48*, 7895.

[7] Dioxygen is an ideal oxidant and offers attractive industrial prospects in terms of green and sustainable chemistry. For selected reviews, see: a) M. Costas, M. P. Mehn, M. P. Jensen, L. Que, Jr., *Chem. Rev.* **2004**, *104*, 939; b) S. S. Stahl, *Angew. Chem.* **2004**, *116*, 3480; *Angew. Chem. Int. Ed.* **2004**, *43*, 3400; c) T. Punniyamurthy, S. Velusamy, J. Iqbal, *Chem. Rev.* **2005**, *105*, 2329; d) B. V. Popp, S. S. Stahl, *Top. Organomet. Chem.* **2007**, *22*, 149.

[8] For our other recent work using O_2 as oxidant, see: C. Zhang, N. Jiao, *J. Am. Chem. Soc.* **2010**, *132*, 28.

[9] a) M. Yamashita, K. Hirano, T. Satoh, M. Miura, *Org. Lett.* **2009**, *11*, 2337; b) M. Yamashita, H. Horiguchi, K. Hirano, T. Satoh, M. Miura, *J. Org. Chem.* **2009**, *74*, 7841.

[10] The minor isomers could not be isolated cleanly by recrystalization or chromatography. Therefore, the constitution of the minor products could not be determined yet. However, based on the ^1H NMR spectra and the high diastereoselectivity of other products, we believe that the minor products are more likely to be regioisomers than diastereomers.

[11] For recent examples of using deuterated indole in mechanistic studies, see: a) B. S. Lane, M. A. Brown, D. Sames, *J. Am. Chem. Soc.* **2005**, *127*, 8050; b) M.-Z. Wang, M.-K. Wong, C. -M, Che, *Chem. Eur. J.* **2008**, *14*, 8353; c) X. Cuo, S. Pan, J. Liu, Z. Li, *J. Org. Chem.* **2009**, *74*, 8848.

[12] a) D. R. Stuart, K. Fagnou, *Science* **2007**, *316*, 1172; b) R. J. Phipps, N. P. Grimster, M. J. Gaunt, *J. Am. Chem. Soc.* **2008**, *130*, 8172; c) E. M. Beck, R. Hatley, M. J. Gaunt, *J. Am. Chem. Soc.* **2006**, *128*, 2528; d) N. P. Grimster, C. Gauntlett, C. R. A. God-

frey, M. J. Gaunt, *Angew. Chem.* **2005**, *117*, 3185; *Angew. Chem. Int. Ed.* **2005**, *44*, 3125; e) E. M. Ferreira, B. M. Stoltz, *J. Am. Chem. Soc.* **2003**, *125*, 9578; f) T. A. Dwight, N. R. Rue, D. Charyk, R. Josselyn, B. Deboef, *Org. Lett.* **2007**, *9*, 3137; g) A. Kong, X. Han, X. Lu, *Org. Lett.* **2006**, *8*, 1339; h) Y. Fujiwara, I. Moritani, S. Danno, R. Asano, S. Teranishi, *J. Am. Chem. Soc.* **1969**, *91*, 7166; i) I. Moritanl, Y. Fujiwara, *Tetrahedron Lett.* **1967**, *8*, 1119.

[13] a) T. Satoh, S. Ogino, M. Miura, M. Nomura, *Angew. Chem.* **2004**, *116*, 5173; *Angew. Chem. Int. Ed.* **2004**, *43*, 5063; b) H. Horiguchi, T. Hayato, T. Satoh, M. Miura, *Adv. Synth. Catal.* **2008**, *350*, 509; c) H. Horiguchi, K. Hirano, T. Satoh, M. Miura, *Adv. Synth. Catal.* **2009**, *351*, 1432.

[14] Y.-T. Wu, M.-Y. Kuo, Y.-T. Chang, C.-C. Shin, T.-C. Wu, C.-C. Tai, T.-H. Cheng, W.-S. Liu, *Angew. Chem.* **2008**, *120*, 10039; *Angew. Chem. Int. Ed.* **2008**, *47*, 9891.