Multiple C–H Activation Hot Paper

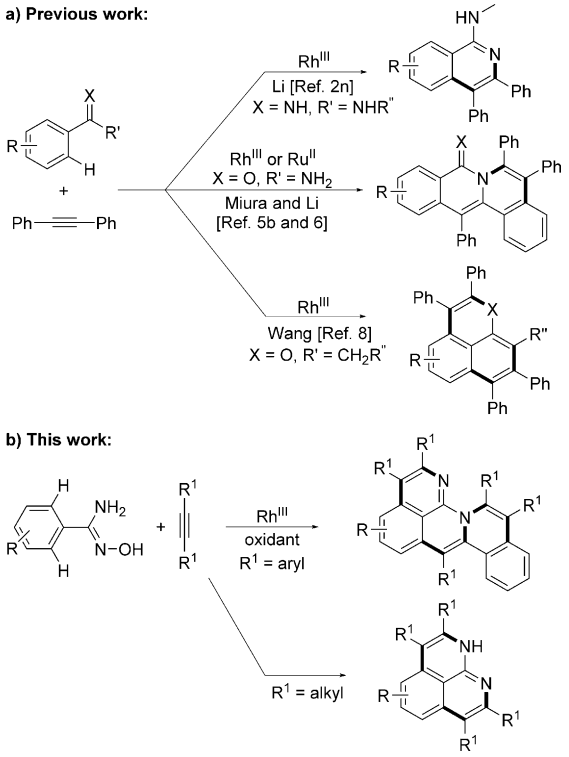
DOI: 10.1002/anie.201405183

One-Pot Synthesis of Highly Substituted Polyheteroaromatic Compounds by Rhodium(III)-Catalyzed Multiple C–H Activation and Annulation**

Jayachandran Jayakumar, Kanniyappan Parthasarathy, Yi-Hsiang Chen, Tai-Hua Lee, Shih-Ching Chuang, and Chien-Hong Cheng**

Abstract: *A new method for the synthesis of highly substituted naphthyridine-based polyheteroaromatic compounds in high yields proceeds through rhodium(III)-catalyzed multiple C–H bond cleavage and C–C and C–N bond formation in a one-pot process. Such highly substituted polyheteroaromatic compounds have attracted much attention because of their unique π-conjugation, which make them suitable materials for organic semiconductors and luminescent materials. Furthermore, a possible mechanism, which involves multiple chelation-assisted ortho C–H activation, alkyne insertion, and reductive elimination, is proposed for this transformation.*

Transition-metal-catalyzed C–H bond activation is an excellent method for the construction of various heteroaromatic molecules from readily available starting materials, which is generally difficult to achieve by using traditional synthetic methods.[1] Numerous examples of the rhodium(III)- or ruthenium(II)-catalyzed cleavage of C–H/N–H or C–H/O–H bonds followed by annulation reactions with alkynes to form diverse heterocyclic compounds have been reported.[2,3,4] Thus far, only a few examples of double C–H bond activation and subsequent C–C and C–X (X = N or O) bond formation reactions have been described (Scheme 1 a). For example, Miura, Satoh et al. reported the synthesis of polyarylated naphthyl-/anthrylazole,[5a] isoquinolinoisoquinolinone,[5b] and acene[5c] derivatives by Rh^{III}-catalyzed C–H activation. In 2010, Li and co-workers reported a [RhCp*]-catalyzed facile synthesis of polycyclic amides by double C–H activation of benzamides and coupling with alkynes (Cp* = pentamethyl cyclopentadienyl).[6] Very recently, efficient syntheses of complex aza-fused polycyclic quinolines[7] and naphthapyrans[8] by Rh^{III} catalysis have also been described. Our continuous interest in metal-catalyzed multiple C–H activation processes[9a–e] and in the synthesis of heterocycles[9f–j] prompted us to explore the synthesis of polyheteroaromatic compounds through multiple C–H activation and annulation. Herein, we wish to report an efficient Rh^{III}-catalyzed reaction of (*Z*)-*N*-hydroxybenzamidines (**1**) with alkynes to afford benzo[*de*](isoquinolino[2,1-*a*])[1,8]naphthyridines and 1*H*-benzo[*de*][1,8]naphthyridines (Scheme 1 b).



Scheme 1. Previous and current work.

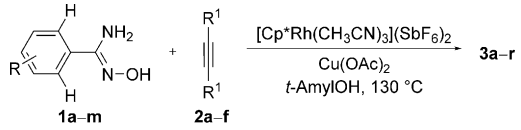
Treatment of **1a** (0.25 mmol) with diphenylacetylene (**2a**; 0.80 mmol) in the presence of $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$[10] (6.0 mol%) and $Cu(OAc)_2$ (4.5 equiv) in *tert*-amyl alcohol at 130 °C for 18 hours afforded benzo(isoquinolino)naphthyridine **3a** in 83% yield (Table 1, entry 1). The structure of **3a** was confirmed by ^1H and ^{13}C NMR spectroscopy and mass spectrometry. To the best of our knowledge, this is the first synthesis of benzo(isoquinolino)naphthyridines by catalytic multiple C–H bond activation and annulation in a one-pot process. Highly substituted polyheteroaromatic compounds are useful π-conjugated functional materials, which have been used as organic semiconductors or luminescent materials.[11] Furthermore, some heteroaromatic derivatives are versatile building blocks for natural products.[12]

[*] J. Jayakumar, Dr. K. Parthasarathy, Y.-H. Chen, Prof. Dr. C.-H. Cheng
Department of Chemistry, National Tsing Hua University
Hsinchu 30013 (Taiwan)
E-mail: chcheng@mx.nthu.edu.tw
Homepage: http://mx.nthu.edu.tw/%7Echcheng
T.-H. Lee, Prof. Dr. S.-C. Chuang
Department of Applied Chemistry, National Chiao Tung University
Hsinchu 30013 (Taiwan)
E-mail: jscchuang@faculty.nctu.edu.tw

[**] We thank the Ministry of Science and Technology of the Republic of China (NSC 102-2628-M-007-005) for support of this research.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201405183.

Table 1: Rhodium-catalyzed multiple C–H bond activation of *N*-hydroxybenzamidines and annulation with alkynes.[a]



1a: R = H
1b: R = 4-Me
1c: R = 4-*t*Bu
1d: R = 4-OMe
1e: R = 4-F
1f: R = 4-Cl
1g: R = 4-Br
1h: R = 4-I
1i: R = 4-CF_3
1j: R = 4-$N(Me)_2$
1k: R = 4-Ph
1l: R = 3,4,5-$(OMe)_3$
1m: R = 3-OMe

2a: R^1 = Ph
2b: R^1 = 4-MeC_6H_4
2c: R^1 = 4-$MeOC_6H_4$
2d: R^1 = 4-BrC_6H_4
2e: R^1 = 4-$CF_3C_6H_4$
2f: R^1 = 2-thienyl

	1	2	Product 3	Yield [%][b]
1	**1a**	**2a**	**3a**: R = H	83
2	**1b**	**2a**	**3b**: R = 4-Me	78
3	**1c**	**2a**	**3c**: R = 4-*t*Bu	70
4	**1d**	**2a**	**3d**: R = 4-OMe	66
5	**1e**	**2a**	**3e**: R = 4-F	86
6	**1f**	**2a**	**3f**: R = 4-Cl	75
7	**1g**	**2a**	**3g**: R = 4-Br	72
8	**1h**	**2a**	**3h**: R = 4-I	78
9	**1i**	**2a**	**3i**: R = 4-CF_3	63
10	**1j**	**2a**	**3j**: R = 4-NMe_2	68
11	**1k**	**2a**	**3k**: R = 4-Ph	81
12	**1l**	**2a**	**3l**: R = 3,4,5-$(OMe)_3$	81
13	**1m**	**2a**	**3m**: R = 3-OMe/ **3m′**: R = 5-OMe	70[c]
14	**1a**	**2b**	**3n**: R^1 = Me	76
15	**1a**	**2c**	**3o**: R^1 = OMe	80
16	**1a**	**2d**	**3p**: R^1 = Br	73
17	**1a**	**2e**	**3q**: R^1 = CF_3	68
18	**1a**	**2f**	**3r**	60

[a] Unless otherwise mentioned, all reactions were carried out using **1** (0.25 mmol), **2** (0.80 mmol), $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (6.0 mol%), $Cu(OAc)_2$ (1.12 mmol), and *tert*-amyl alcohol (3.5 mL) at 130°C for 18 h. [b] Yields of isolated products. [c] **3m**/**3m′** = 60:40.

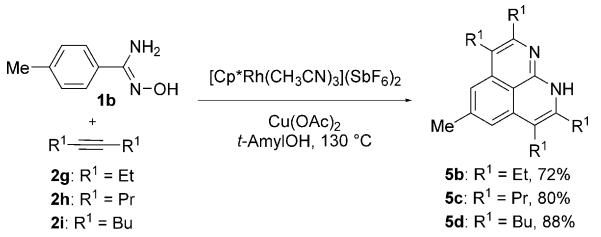
Other metal complexes, such as $[\{RhCp^*Cl_2\}_2]$ and $[\{RuCl_2(p\text{-cymene})\}_2]$ were also effective catalysts, giving **3a** in 68% and 43% yield, respectively. The presence of an oxidant was crucial for this transformation. In the absence of an oxidant, **3a** was not formed. $Cu(OAc)_2$ appeared to be the best oxidant, giving **3a** in 83% yield. The addition of other copper(II) salts, such as $Cu(OAc)_2{\cdot}H_2O$ or $Cu(OTf)_2$, also led to the formation of **3a**, but a longer reaction time of 24 hours was required, and **3a** was only formed in 62% and 15% yield, respectively. The choice of solvent was also crucial for the efficiency of this process. *tert*-Amyl alcohol was found to be the ideal solvent affording **3a** in 83% yield. Other solvents, such as DMF, *ortho*-xylene, dichloroethane (DCE), and CH_3CN, were less suitable for this reaction, giving **3a** in 70, 64, 58, and 45% yield, respectively (Table 1; see also the Supporting Information).

Under similar reaction conditions, various *para*-substituted (*Z*)-*N*-hydroxybenzamidines (**1b–k**) reacted with diphenylacetylene (**2a**) to give the corresponding products. The benzamidine derivatives **1b–d** underwent multiple C–H activation and annulation with **2a** to afford **3b–d** in 78, 70, and 66% yield, respectively (Table 1, entries 2–4). This transformation is also compatible with halogen substituents on the aromatic ring of **1**. Thus, the reaction of the fluoro-, chloro-, bromo-, or iodo-substituted benzamidines **1e–h** with **2a** gave **3e–h** in 86, 75, 72, and 78% yield, respectively (entries 5–8). Both electron-poor and electron-rich benzamidines (**1i**,**j**) were suitable substrates (entries 9 and 10). Furthermore, *N*-hydroxy-4-phenylbenzamidine (**1k**) reacted with alkyne **2a** to provide **3k** in 81% yield (entry 11). In a similar manner, *N*-hydroxy-3,4,5-trimethoxybenzamidine **1l** reacted with **2a** to give **3l** in 81% yield (entry 12). However, the reaction of *meta*-methoxy-substituted *N*-hydroxybenzamidine **1m** with **2a** provided two regioisomeric products **3m** and **3m′** in a 60:40 ratio in a combined yield of 70% (entry 13). The structures of **3c** and **3i** were confirmed by single-crystal X-ray diffraction.[13]

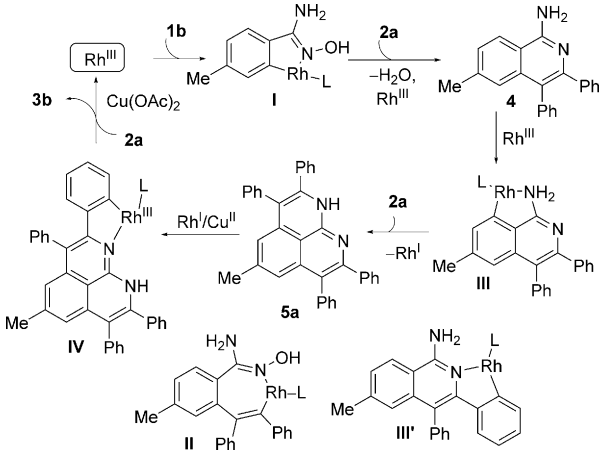
Aside from **2a**, other symmetric alkynes (**2b–e**) were also tested in the present reaction. Thus, the di-aryl-substituted acetylenes **2b–2e** reacted with **1a** to afford the corresponding products **3n–q** in good yields (entries 14–17). Interestingly, di(2-thienyl)acetylene **2f** also reacted smoothly with **1a** to give the annulated product **3r** in 60% yield (entry 18).

To further expand the substrate scope of this rhodium-catalyzed reaction, aliphatic alkynes **2g–i** were also subjected to the reaction with benzamidine **1b** (Scheme 2). However, when **1b** was treated with hex-3-yne (**2g**) under the standard reaction conditions (see Table 1), only a trace amount of the cyclization product benzonaphthyridine **5b** was observed. Fortunately, **5b** was isolated in 72% yield when the reaction time was increased to 48 hours. Under similar reaction conditions, oct-4-yne (**2h**) and dec-5-yne (**2i**) also reacted smoothly with **1b** to give substituted benzonaphthyridines **5c** and **5d** in 80 and 88% yield, respectively (Scheme 2).

To account for the present catalytic reaction, a possible mechanism involving Rh^{III}-catalyzed multiple C–H bond activation and annulation is proposed for **1b** and **2a** as the model substrates (Scheme 3).[1,2,4] The first step likely involves coordination of the oxime nitrogen atom of **1** to the Rh^{III} center, followed by *ortho* C–H activation to form five-membered rhodacycle **I**. Coordinative insertion of alkyne **2a** into the rhodium–carbon bond of **I** gives seven-membered rhodacycle **II**. Reductive elimination affords 1-aminoisoquinoline **4** and a Rh^{III} species. Further coordination of the amine nitrogen atom of **4** to the Rh^{III} species followed by C–H activation, insertion of **2a**, and reductive elimination affords **5a** and a Rh^{I} species. The latter is reoxidized by $Cu(OAc)_2$ to regenerate the active Rh^{III} species. Similar steps that include C–H bond activation, alkyne insertion, reductive elimination,



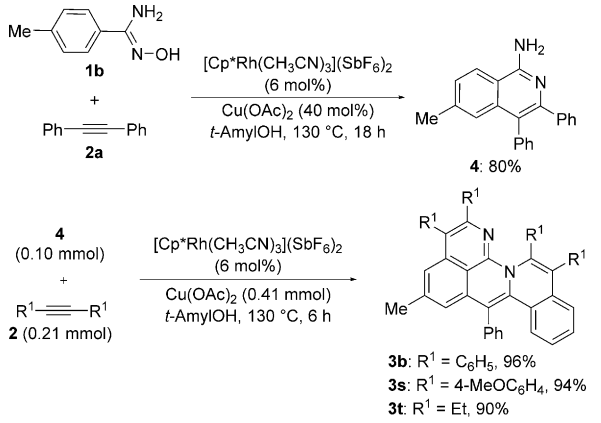
Scheme 2. Synthesis of substituted naphthyridines. Reaction conditions: **1** (0.25 mmol), **2** (0.80 mmol), $[RhCp^*(CH_3CN)_3](SbF_6)_2$ (6.0 mol%), $Cu(OAc)_2$ (1.10 mmol), *t*-AmylOH (3.5 mL), 130°C, 48 h.



Scheme 3. Proposed mechanism for the formation of **3b**. L = Cp*.

and oxidation of the Rh^I intermediate, afford the final product **3b** and a Rh^{III} species as the catalyst of the next cycle.

Substrate **1** has two possible sites (the amine and oxime nitrogen atoms) for coordination to the Rh^{III} species. To determine which atom is coordinating and to support the mechanism that is proposed in Scheme 3, we isolated **4** from the reaction of **1b** (0.25 mmol) and diphenylacetylene **2a** (0.30 mmol) under the standard conditions in 80% yield (18 h; Scheme 4, top). It is noteworthy that a relatively small amount of **2a** was used in this reaction. Based on this result, it appears that the oxime nitrogen atom coordinates to the rhodium center first to form intermediate **I** as shown in the proposed mechanism. Furthermore, the oxime group in **1** also



Scheme 4. Isolation of intermediate **4** and its reaction with alkynes.

acts as a redox-neutral directing group.[4,9h] As a result, the formation of **4** from **1b** and **2a** does in principle not require an oxidant.

Compound **4** (0.10 mmol) reacted with **2a** (0.21 mmol) under the standard reaction conditions to give product **3b** (96%; Scheme 4). Similarly, **4** also reacted with diaryl and dialkyl ethynes **2c** and **2g** to give **3s** and **3t** in 94 and 90% yield, respectively (Scheme 4, bottom). We were unable to isolate intermediate **5**, even when **4** was treated with aryl or alkyl alkynes **2** in a 1:1 ratio. The reactions afforded only the corresponding products **3** in 45–48% yield. The structures of **3s** and **3t** were determined by single-crystal X-ray diffraction.[13] It is noteworthy that the reaction of **4** with different alkynes provides an efficient method for the introduction of different substituents onto the final product **3**. There are two nitrogen atoms in **4** that can coordinate to the Rh^{III} species to undergo C–H bond activation and annulation with alkyne. The two corresponding intermediates are **III** and **III′** (Scheme 3), which can both give product **3**.

The solubility of **3** is reasonably good in dichloromethane and toluene. For example, the solubilities of the representative species **3i**, **3j**, **3l**, and **3r** are all greater than 10^{-3} M in these solvents at ambient temperature. To further understand the physical properties of these products, we measured the absorption and emission spectra of these species in dichloromethane (Figure 1; see also the Supporting Information, page S19). The fluorescence spectra of **3i**, **3j**, and **3r** show emission maxima at 500–530 nm with broad bandwidths (full width at half maximum $\geq$100 nm) and weak intensities. On the other hand, product **3l** (R = 3,4,5-$(OMe)_3$) shows very strong green photoluminescence with a narrower bandwidth of 75 nm. Furthermore, we also measured the absorption and emission spectra of **3t** and **5d** (page S20). Strong deep-blue emission was observed for **5d**, but only weak emission was found for **3t**.

In conclusion, we have successfully developed a simple and effective method for the synthesis of highly substituted naphthyridine-based polyheteroaromatic compounds in high yields from *N*-hydroxybenzamidines and alkynes. This transformation appears to proceed through multiple rhodium(III)-catalyzed C–H bond activation steps and annulation in a one-

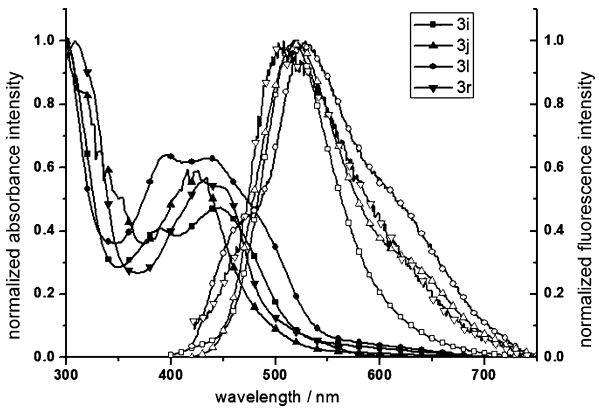


Figure 1. Absorption (1.0×10^{-5} M) and fluorescence (1.0×10^{-4} M, excitation at 400 nm) spectra of **3i** (R = 4-CF_3), **3j** (R = 4-NMe_2), **3l** (R = 3,4,5-$(OMe)_3$), and **3r** in dichloromethane.

pot fashion. Further applications of this method for the synthesis of organic materials and a detailed investigation of the reaction mechanism are currently in progress.

Experimental Section

General procedure for the rhodium-catalyzed synthesis of benzo[*de*](isoquinolino[2,1-*a*])[1,8]naphthyridine. A sealed tube containing *N*-hydroxybenzamidine **1** (0.25 mmol), alkyne **2** (0.80 mmol), $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (6.0 mol%), and $Cu(OAc)_2$ (1.12 mmol) was evacuated and purged with nitrogen gas three times. Then, *tert*-amyl alcohol (3.5 mL) was added to the system via syringe under nitrogen atmosphere, and the reaction mixture was stirred at 130°C for 18 hours. The mixture was cooled and diluted with CH_2Cl_2 (10 mL). The mixture was filtered through a Celite pad, which was washed with CH_2Cl_2 (50 mL). The filtrate was concentrated, and the residue was purified by column chromatography on silica gel using hexane/EtOAc (5–15%) as the eluent to afford **3** as a pure product.

Received: May 11, 2014
Revised: June 12, 2014
Published online: July 17, 2014

Keywords: alkynes · annulation · benzamidines · C–H activation · rhodium

[1] a) M. Catellani, *Top. Organomet. Chem.* **2005**, *8*, 21; b) M. Catellani, E. Motti, N. D. Ca, *Acc. Chem. Res.* **2008**, *41*, 1512; c) C.-H. Jun, C. W. Moon, D.-Y. Lee, *Chem. Eur. J.* **2002**, *8*, 2422; d) Y. J. Park, C.-H. Jun, *Bull. Korean Chem. Soc.* **2005**, *26*, 877; e) L. Ackermann, R. Vicente, *Top. Curr. Chem.* **2009**, *292*, 211; f) K. Fagnou, *Top. Curr. Chem.* **2009**, *292*, 35; g) X. Chen, K. M. Engle, D.-H. Wang, J.-Q. Yu, *Angew. Chem.* **2009**, *121*, 5196; *Angew. Chem. Int. Ed.* **2009**, *48*, 5094; h) D. A. Colby, R. G. Bergman, J. A. Ellman, *Chem. Rev.* **2010**, *110*, 624; i) T. W. Lyons, M. S. Sanford, *Chem. Rev.* **2010**, *110*, 1147.

[2] For selected examples of rhodium-catalyzed C–H activation and annulation with alkynes, see: a) K. Ueura, T. Satoh, M. Miura, *Org. Lett.* **2007**, *9*, 1407; b) K. Ueura, T. Satoh, M. Miura, *J. Org. Chem.* **2007**, *72*, 5362; c) D. R. Stuart, M. Bertrand-Laperle, K. M. N. Burgess, K. Fagnou, *J. Am. Chem. Soc.* **2008**, *130*, 16474; d) S. Mochida, K. Hirano, T. Satoh, M. Miura, *J. Org. Chem.* **2009**, *74*, 6295; e) T. Fukutani, N. Umeda, K. Hirano, T. Satoh, M. Miura, *Chem. Commun.* **2009**, 5141; f) P. Too, Y. F. Wang, S. Chiba, *Org. Lett.* **2010**, *12*, 5688; g) Y. Su, M. Zhao, K. Han, G. Song, X. Li, *Org. Lett.* **2010**, *12*, 5462; h) J. Chen, G. Song, C. Pan, X. Li, *Org. Lett.* **2010**, *12*, 5426; i) K. Morimoto, K. Hirano, T. Satoh, M. Miura, *Org. Lett.* **2010**, *12*, 2068; j) D. R. Stuart, P. Alsabeh, M. Kuhn, K. Fagnou, *J. Am. Chem. Soc.* **2010**, *132*, 18326; k) S. Rakshit, F. W. Patureau, F. Glorius, *J. Am. Chem. Soc.* **2010**, *132*, 9585; l) N. Guimond, C. Gouliaras, K. Fagnou, *J. Am. Chem. Soc.* **2010**, *132*, 6908; m) S. Mochida, M. Shimizu, K. Hirano, T. Satoh, M. Miura, *Chem. Asian J.* **2010**, *5*, 847; n) X. Wei, M. Zhao, Z. Du, X. Li, *Org. Lett.* **2011**, *13*, 4636; o) P. C. Too, S. H. Chua, S. H. Wong, S. Chiba, *J. Org. Chem.* **2011**, *76*, 6159; p) N. Umeda, K. Hirano, T. Satoh, N. Shibata, H. Sato, M. Miura, *J. Org. Chem.* **2011**, *76*, 13; q) X. Zhang, D. Chen, M. Zhao, J. Zhao, A. Jia, X. Li, *Adv. Synth. Catal.* **2011**, *353*, 719; r) L. Zheng, J. Ju, Y. Bin, R. Hua, *J. Org. Chem.* **2012**, *77*, 5794; s) W. Dong, L. Wang, K. Parthasarathy, F. F. Pan, C. Bolm, *Angew. Chem.* **2013**, *125*, 11787; *Angew. Chem. Int. Ed.* **2013**, *52*, 11573; t) M. V. Pham, N. Cramer, *Angew. Chem.* **2014**, *126*, 3552; *Angew. Chem. Int. Ed.* **2014**, *53*, 3484.

[3] a) L. Ackermann, A. V. Lygin, N. Hofmann, *Angew. Chem.* **2011**, *123*, 6503; *Angew. Chem. Int. Ed.* **2011**, *50*, 6379; b) B. Li, H. Feng, S. Xu, B. Wang, *Chem. Eur. J.* **2011**, *17*, 12573; c) L. Ackermann, A. V. Lygin, N. Hofmann, *Org. Lett.* **2011**, *13*, 3278; d) L. Ackermann, S. Fenner, *Org. Lett.* **2011**, *13*, 6548; e) R. K. Chinnagolla, M. Jeganmohan, *Chem. Commun.* **2012**, *48*, 2030; f) L. Ackermann, L. Wang, A. V. Lygin, *Chem. Sci.* **2012**, *3*, 177; g) K. R. Chinnagolla, M. Jeganmohan, *Eur. J. Org. Chem.* **2012**, 417; h) L. Ackermann, A. V. Lygin, *Org. Lett.* **2012**, *14*, 764; i) L. Ackermann, J. Pospech, K. Graczyk, K. Rauch, *Org. Lett.* **2012**, *14*, 930; j) R. K. Chinnagolla, S. Pimparkar, M. Jeganmohan, *Org. Lett.* **2012**, *14*, 3032; k) V. S. Thirunavukkarasu, M. Donati, L. Ackermann, *Org. Lett.* **2012**, *14*, 3416.

[4] a) T. Satoh, M. Miura, *Chem. Eur. J.* **2010**, *16*, 11212; b) J. Wencel-Delord, T. Dröge, F. Liu, F. Glorius, *Chem. Soc. Rev.* **2011**, *40*, 4740; c) G. Song, F. Wang, X. Li, *Chem. Soc. Rev.* **2012**, *41*, 3651; d) F. W. Patureau, J. Wencel-Delord, F. Glorius, *Aldrichimica Acta* **2012**, *45*, 31; e) L. Ackermann, *Acc. Chem. Res.* **2014**, *47*, 281; f) P. B. Arockiam, C. Bruneau, P. H. Dixneuf, *Chem. Rev.* **2012**, *112*, 5879; g) J. Li, M. John, L. Ackermann, *Chem. Eur. J.* **2014**, *20*, 5403.

[5] a) N. Umeda, H. Tsurugi, T. Satoh, M. Miura, *Angew. Chem.* **2008**, *120*, 4083; *Angew. Chem. Int. Ed.* **2008**, *47*, 4019; b) S. Mochida, N. Umeda, K. Hirano, T. Satoh, M. Miura, *Chem. Lett.* **2010**, *39*, 744; c) T. Fukutani, K. Hirano, T. Satoh, M. Miura, *J. Org. Chem.* **2011**, *76*, 2867.

[6] a) G. Song, D. Chen, C. Pan, R. H. Crabtree, X. Li, *J. Org. Chem.* **2010**, *75*, 7487; b) G. Song, X. Gong, X. Li, *J. Org. Chem.* **2011**, *76*, 7583.

[7] J. Huang, L. Dong, B. Han, C. Peng, Y. Chen, *Chem. Eur. J.* **2012**, *18*, 8896.

[8] X. Tan, B. Liu, X. Li, B. Li, S. Xu, H. Song, B. Wang, *J. Am. Chem. Soc.* **2012**, *134*, 16163.

[9] a) V. S. Thirunavukkarasu, K. Parthasarathy, C.-H. Cheng, *Angew. Chem.* **2008**, *120*, 9604; *Angew. Chem. Int. Ed.* **2008**, *47*, 9462; b) V. S. Thirunavukkarasu, K. Parthasarathy, C.-H. Cheng, *Chem. Eur. J.* **2010**, *16*, 1436; c) P. Gandeepan, K. Parthasarathy, C.-H. Cheng, *J. Am. Chem. Soc.* **2010**, *132*, 8569; d) J. Karthikeyan, C.-H. Cheng, *Angew. Chem.* **2011**, *123*, 10054; *Angew. Chem. Int. Ed.* **2011**, *50*, 9880; e) J. Karthikeyan, R. Haridharan, C.-H. Cheng, *Angew. Chem.* **2012**, *124*, 12509; *Angew. Chem. Int. Ed.* **2012**, *51*, 12343; f) K. Parthasarathy, M. Jeganmohan, C.-H. Cheng, *Org. Lett.* **2008**, *10*, 325; g) K. Parthasarathy, C.-H. Cheng, *J. Org. Chem.* **2009**, *74*, 9359; h) J. Jayakumar, K. Parthasarathy, C.-H. Cheng, *Angew. Chem.* **2012**, *124*, 201; *Angew. Chem. Int. Ed.* **2012**, *51*, 197.

[10] C. White, A. Yates, P. M. Maitlis, *Inorg. Synth.* **1992**, *29*, 228.

[11] a) J. E. Anthony, *Angew. Chem.* **2008**, *120*, 460; *Angew. Chem. Int. Ed.* **2008**, *47*, 452; b) M. D. Watson, A. Fechtenkötter, K. Müllen, *Chem. Rev.* **2001**, *101*, 1267; c) U. Mitschke, P. Bäuerle, *J. Mater. Chem.* **2000**, *10*, 1471; d) R. G. Harvey, *Polycyclic aromatic hydrocarbons*, Wiley-VCH, Weinheim, **1996**; e) M. Kimura, K. Tanaka, *Angew. Chem.* **2008**, *120*, 9914; *Angew. Chem. Int. Ed.* **2008**, *47*, 9768.

[12] a) B. Clement, M. Weide, U. Wolschendorf, I. Kock, *Angew. Chem.* **2005**, *117*, 641; *Angew. Chem. Int. Ed.* **2005**, *44*, 635; b) C. Bailly, *Chem. Rev.* **2012**, *112*, 3611; c) J. Deguchi, T. Shoji, A. E. Nugroho, Y. Hirasawa, T. Hosoya, O. Shirota, K. Awang, A. H. A. Hadi, H. Morita, *J. Nat. Prod.* **2010**, *73*, 1727.

[13] See the Supporting Information. CCDC 997429 (**1b**), CCDC 997432 (**3c**), CCDC 997433 (**3i**), CCDC 997430 (**3q**), CCDC 997431 (**3s**), and CCDC 998572 (**3t**) contain 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.

