Organic & Biomolecular Chemistry

PAPER

Cite this: *Org. Biomol. Chem.*, 2016, **14**, 6821

Cp*Rh(III)-catalyzed electrophilic amination of arylboronic acids with azo compounds for synthesis of arylhydrazides†

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Received 6th April 2016,
Accepted 14th June 2016

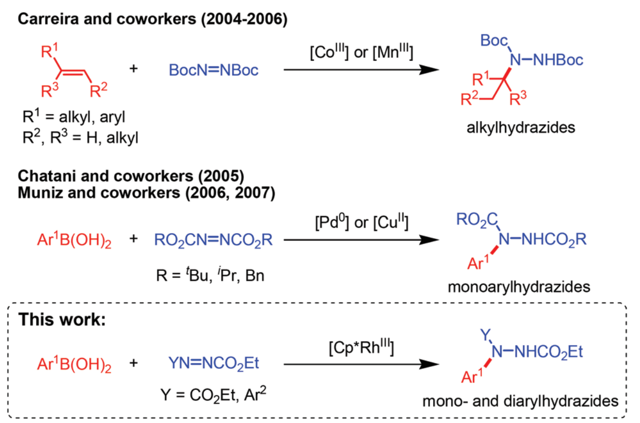
DOI: 10.1039/c6ob00719h

www.rsc.org/obc

A [Cp*Rh(III)]-catalyzed electrophilic amination of arylboronic acids with diethyl azodicarboxylate (DEAD) was developed, and arylhydrazides were produced in excellent yields and selectivity. The analogous amination with the arylazocarboxylates afforded the corresponding *N*,*N*-diarylhydrazides. The electrophilic amination of arylboronic acids with azocarboxylates proceeds readily under mild conditions with excellent functional group tolerance. Up to 99% yields were obtained. Preliminary mechanistic studies revealed that prior formation of an arylrhodium(III) intermediate for the azo coupling reaction can be ruled out.

Transition metal-catalyzed electrophilic (umpolung) aminations are attractive approaches for arylamine synthesis under mild conditions.[1] Characterized by weak N–X (X = leaving group) σ-bonds, haloamines and hydroxyamine derivatives have been extensively investigated for electrophilic amination with organolithium and -magnesium reagents.[2] Dialkyl azodicarboxylates are conceptually different classes of electrophilic amination reagents. Unlike the halo/hydroxyamine-type reagents, the azodicarboxylates react with carbanionic nucleophiles *via* N–N π-bond cleavage. While dialkyl azodicarboxylates are known to react with stoichiometric organometallic reagents for C–N bond coupling reactions,[3] examples involving transition metal catalysis are sparse in the literature (Scheme 1). About a decade ago, Carreira and coworkers reported a Co- and Mn-catalyzed alkene hydrohydrazination using di-*tert*-butyl azodicarboxylate and triphenylsilane as reagents.[3e–g] Recently, Chatani and coworkers reported a Cu-catalyzed hydroarylation of azodicarboxylates.[3h] Muniz and coworkers reported a Pd-catalyzed coupling of arylboronic acids with diethyl azodicarboxylate (DEAD). A palladadiaziridine complex was structurally characterized and was shown to mediate the C–N bond coupling reaction.[3i,j]

Owing to an interest in developing transition metal catalyzed C–H bond aminations under mild conditions,[4] we previously accomplished regioselective Pd-/Rh-catalyzed *ortho*-selective arene C–H amination with tosyloxycarbamates and *N*-chloroamines.[4k–o] The catalytic arene C–H amination should



Scheme 1 Recent examples of transition metal-catalyzed electrophilic amination with azo reagents.

proceed by coupling of reactive arylpalladium(II) and -rhodium(III) complexes with the amination reagents. By virtue of the weak N–N π-bond, we envisioned that dialkyl azodicarboxylates would be effective coupling partners with arylmetal complexes for C–N bond formation. Here we describe [Cp*Rh(III)]-catalyzed (Cp* = 1,2,3,4,5-pentamethyl-cyclopentadienyl) cross coupling of arylboronic acids with azo compounds for the synthesis of arylhydrazides.

When phenylboronic acid (**1a**; 0.3 mmol) was treated with DEAD (0.2 mmol) and [Cp*Rh(OAc)$_2$] (5 mol%) in THF at 80 °C under an N_2 atmosphere for 4 h, phenylhydrazide (**2a**) was obtained in 85% yield (Table 1, entry 1). In this work, we found that employing phenylboronic acid pinacol ester and potassium phenyltrifluoroborate alone did not bring about effective C–N coupling reactions (entries 2 and 3). The boron reagents were fully recovered with substantial decomposition

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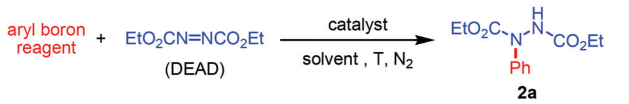
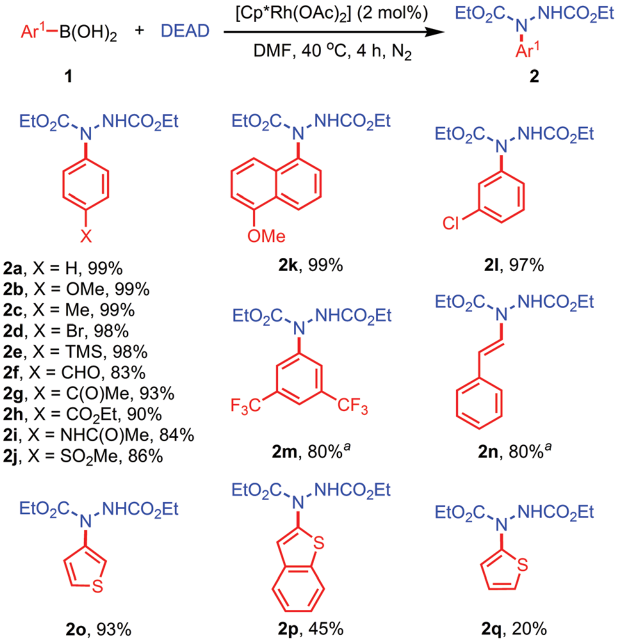
† Electronic supplementary information (ESI) available. CCDC 1455768–1455771. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6ob00719h

Table 1 Reaction optimization[a]



Entry	Aryl boron reagent	Catalyst	Solvent	T (°C)	Yield[b] (%)
1	$PhB(OH)_2$ (**1a**)	$[Cp^*Rh(OAc)_2]$	THF	80	85
2	PhB(pin)	$[Cp^*Rh(OAc)_2]$	THF	80	n.d.[c]
3	$KPhBF_3$	$[Cp^*Rh(OAc)_2]$	THF	80	n.d.[c]
4[d]	$KPhBF_3$	$[Cp^*Rh(OAc)_2]$	THF	80	70
5	**1a**	$[Cp^*RhCl_2]_2$	THF	80	10
6	**1a**	$[Rh(COD)Cl]_2$	THF	80	11
7	**1a**	$[Rh(COD)(OH)]_2$	THF	80	n.d.[c]
8	**1a**	$[Cp^*IrCl_2]_2$	THF	80	n.d.[c]
9	**1a**	$[Cp^*Rh(OAc)_2]$	^{t}BuOH	80	64
10	**1a**	$[Cp^*Rh(OAc)_2]$	MeCN	80	3
11	**1a**	$[Cp^*Rh(OAc)_2]$	Dioxane	80	50
12	**1a**	$[Cp^*Rh(OAc)_2]$	DCE	80	31
13[e]	**1a**	$[Cp^*Rh(OAc)_2]$	DMF	40	99
14[f]	**1a**	$[Cp^*Rh(OAc)_2]$	THF	80	42

[a] Conditions: aryl boron reagent (0.3 mmol), DEAD (0.2 mmol), catalyst (5 mol%), solvent (1 mL), 4 h in an N_2 atmosphere. [b] Isolated yield. [c] n.d. = not detected. [d] $B(OH)_3$ (0.3 mmol) was added. [e] $[Cp^*Rh(OAc)_2]$ (2 mol%) was used. [f] Di-*tert*-butyl azodicarboxylate (0.2 mmol) was used instead.



Scheme 2 Scope of the arylation of DEAD. Yields of isolated products are given. General reaction conditions: **1** (0.3 mmol), DEAD (0.2 mmol), $[Cp^*Rh(OAc)_2]$ (2 mol%), DMF (1 mL), 40 °C for 4 h in an N_2 atmosphere. [a] The reaction was performed at 80 °C.

of the DEAD. Interestingly, when potassium phenyltrifluoroborate was employed together with $B(OH)_3$ as additives and DMF as the solvent, **2a** was formed in 70% yield (entry 4).

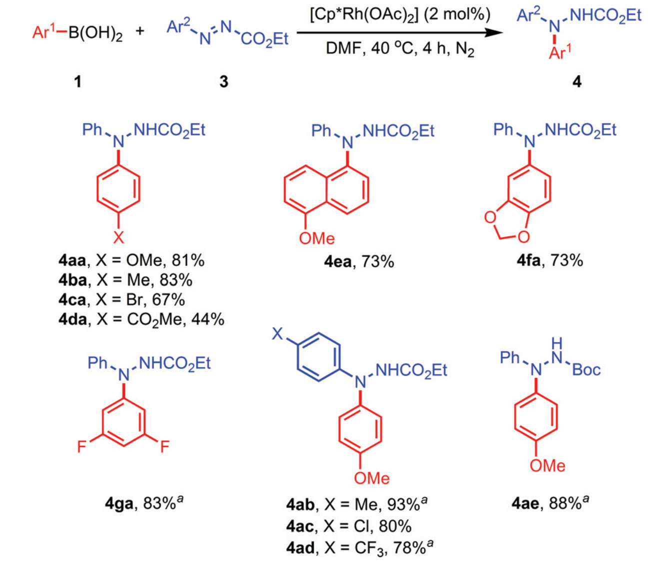
Other rhodium catalysts such as $[Cp^*RhCl_2]_2$ are less effective catalysts (entry 5). According to the literature, rhodium(I) diene complexes such as $[Rh(COD)X]_2$ (X = Cl, OH) are known to catalyze arylation of enones with arylboron reagents.[5] However, these Rh(I)–diene complexes were found to be ineffective catalysts for the reaction of **1a** with DEAD (entries 6 and 7). In this work, the related $[Cp^*IrCl_2]_2$ complex exhibited negligible catalytic activities under our reaction conditions (entry 8).

Other solvents such as ^{t}BuOH, MeCN, dioxane and DCE gave inferior results compared to THF (entries 9–12). After several trials, we found that DMF gave the best result with **2a** being formed in a nearly quantitative yield.[6] Upon further refinement of several experimental parameters, an optimized reaction protocol was established: $[Cp^*Rh(OAc)_2]$ (2 mol%), **1a** (0.3 mmol), DEAD (0.2 mmol) in DMF at 40 °C (entry 13). It is noteworthy that the azo coupling reaction is sensitive to the ester substituents on the azocarboxylates. For instance, the amination of **1a** with di-*tert*-butyl azodicarboxylate produced the corresponding arylhydrazides in only 42% yield (entry 14). The coupling with azobenzene was unsuccessful, and no C–N coupled products were obtained.[6]

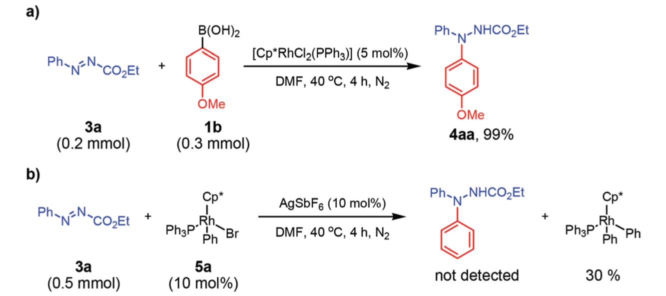
With DEAD as the model substrate, the scope of the arylboronic acids was examined (Scheme 2). The reactions of arylboronic acids containing electron-donating and -withdrawing groups (*e.g.* OMe, Me and Br) afforded the corresponding hydrazides (**2a–2d**) in excellent yields. Other functionalized arylboronic acids bearing TMS, CHO, C(O)Me, CO_2Et, NHC(O)Me and SO_2Me were converted to **2e–2j** in 83–98% yields. Fruitful results were achieved for the analogous amidation of 6-methoxy-1-naphthyl, 3-chloro and 3,5-bis(trifluoromethyl) phenylboronic acids with **2k–2m** being formed in excellent yields. Likewise, effective transformations of styrylboronic acid and heteroaromatic boronic acids were also achieved to give the corresponding products (**2n–2q**) in good to moderate yields.

Diarylamines are prevalent scaffolds found in many natural products, pharmaceuticals and functional materials.[7] The Pd- and Cu-catalyzed arylation of anilines with haloarenes are widely employed for diarylamine synthesis.[8] Yet, examples of diarylamine synthesis *via* electrophilic amination are sparse.[9] Lei and coworkers reported the synthesis of diarylamines by Cu-catalyzed arylation of *N*-chloroanilides with arylboronic acids.[9e] Recently, Chang and coworkers reported a reaction of aryl azides with aryliridium(III) complexes for diarylamine synthesis.[9f–h] In this work, we developed the catalytic arylation of arylazocarboxylates for the synthesis of *N*,*N*-diarylhydrazides.

The arylazocarboxylate was prepared by reacting arylhydrazine with ethyl chloroformate, followed by NBS oxidation. When phenylazocarboxylate (**3a**) was treated with 4-methoxyphenylboronic acid (**1b**) and $[Cp^*Rh(OAc)_2]$ (2 mol%) in DMF at 40 °C under an N_2 atmosphere, *N*,*N*-diarylhydrazides (**4aa**) was isolated as a single regioisomer in 81% yield (Scheme 3). The molecular structure of **4aa** has been established by single-crystal X-ray crystallography. Arylboronic acids containing elec-



Scheme 3 Scope of the arylation of arylazocarboxylate. Yields of isolated products are given. General reaction conditions: **1** (0.3 mmol), **3** (0.2 mmol), [Cp*Rh(OAc)$_2$] (2 mol%), DMF (1 mL), 40 °C for 4 h in an N_2 atmosphere. [a]The reaction was performed at 80 °C.



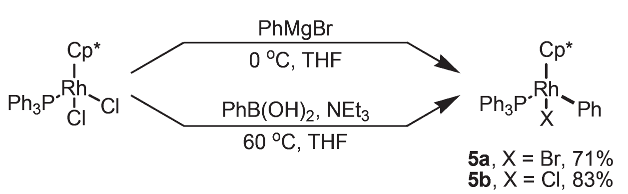
Scheme 5 Investigation of the stoichiometric reaction of arylrhodium(III) complexes with phenylazocarboxylate.

tron-donating and -withdrawing substituents were well tolerated (see results for **4ba–4da**). Similarly, amidation of 6-methoxy-1-naphthyl, 3,4-(methylenedioxy) and 3,5-ditrifluorophenylboronic acids furnished **4ea–4ga** in excellent yields.

With 4-methoxyphenylboronic acid as the arylating reagent, the reactions of some substituted arylazocarboxylates were examined. Effective C–N coupling was observed in all cases, and the diarylhydrazides (**4ab–4ae**) were formed in 78–93% yields.

Arylrhodium(III) complexes are known to mediate catalytic C–N bond coupling reactions.[4m,10] To examine the involvement of the arylrhodium(III) complexes, we prepared the well-defined [Cp*Rh(Ph)(Br)(PPh$_3$)] complex **5a** (71% yield) by reacting [Cp*RhCl$_2$(PPh$_3$)] with PhMgBr.[11] The analogous [Cp*Rh(Ph)(Cl) (PPh$_3$)] complex **5b** (83% yield) was also prepared by employing phenylboronic acid as the aryl source (Scheme 4).[12] The molecular structures of **5a** and **5b** have been confirmed by single-crystal X-ray crystallography.[6]

In this work, when [Cp*Rh(Ph)(Br)(PPh$_3$)] (**5a**) (10 mol%) was treated with AgSbF$_6$ (10 mol%) and phenylazocarboxylate (0.5 mmol) in DMF at 40 °C for 4 h, no *N*,*N*-diphenylhydrazide was formed. Notably, [Cp*Rh(Ph)$_2$(PPh$_3$)] was isolated in 30% yield, and 18% of the starting [Cp*Rh(Ph)(Br)(PPh$_3$)] was recovered (Scheme 5). Notwithstanding, [Cp*RhCl$_2$(PPh$_3$)] was found to be an effective catalyst for the arylation reaction. For example, reacting [Cp*RhCl$_2$(PPh$_3$)] (5 mol%) with 4-methoxyphenylboronic acid (**1b**) and phenylazocarboxylate (**3a**) in DMF at 40 °C afforded **4aa** in 99% yield. Based on the above findings, direct coupling of arylrhodium(III) with the azo reagent may not be a productive step for the arylation reaction.



Scheme 4 Synthesis of [Cp*Rh(Ph)(X)(PPh$_3$)].

Previously, Muniz and coworkers reported the Pd-catalyzed arylation of DEAD by arylboronic acids, and palladadiaziridine complexes have been characterized as the key intermediate. However, the attempt to characterize well-defined rhodalladiaziridine complexes was unsuccessful. The preparation and characterization of some reactive metalladiaziridine complexes are currently in progress, and the results will be reported separately.

Conclusions

In conclusion, we developed a [Cp*Rh(III)]-catalyzed electrophilic amination of arylboronic acids by employing azo reagents. Effective coupling of DEAD and the aryl azocarboxylates with arylboronic acids afforded mono- and diarylhydrazides in good yields under mild conditions.

Acknowledgements

We thank the Hong Kong Research Grants Council (PolyU5032/13P, C5023/14G) for financial support.

Notes and references

1 For transition metal-catalyzed electrophilic amination, see: (*a*) A. Ricci, *Amino Group Chemistry: From Synthesis to the Life Sciences*, Wiley-VCH, Weinheim, 2008; (*b*) A. Ricci, *Modern Amination Methods*, Wiley-VCH, Weinheim, 2000.
2 For a selected review on electrophilic amination of carbanions, see: (*a*) E. Erdik and M. Ay, *Chem. Rev.*, 1989, **89**, 1947. For selected articles on the stoichiometric addition of organometallic reagents: for the use of organolithium reagents, see: (*b*) P. Beak and B. J. Kokko, *J. Org. Chem.*,

1982, **47**, 2823. For the use of Grignard reagents, see: (*c*) M. J. Campbell and J. S. Johnson, *Org. Lett.*, 2007, **9**, 1521; (*d*) E. Erdik and S. Ates, *Synth. Commun.*, 2006, **36**, 2813; (*e*) M. Kitamura, T. Suga, S. Chiba and K. Narasaka, *Org. Lett.*, 2004, **6**, 4619. For the use of organozinc reagents, see: (*f*) A. M. Berman and J. S. Johnson, *J. Org. Chem.*, 2006, **71**, 219; (*g*) A. M. Berman and J. S. Johnson, *J. Org. Chem.*, 2005, **70**, 364; (*h*) E. Erdik and T. J. Daskapan, *Chem. Soc., Perkin Trans. 1*, 1999, 3139. For the use of cuprates, see: (*i*) P. Bernardi, P. Dembech, G. Fabbri, A. Ricci and G. Seconi, *J. Org. Chem.*, 1999, **64**, 641; (*j*) A. Alberti, F. Cane, P. Dembech, D. Lazzari, A. Ricci and G. Seconi, *J. Org. Chem.*, 1996, **61**, 1677; (*k*) A. Casarini, P. Dembech, D. Lazzari, E. Marini, G. Reginato, A. Ricci and G. Seconi, *J. Org. Chem.*, 1993, **58**, 5620. For the use of organostannane reagents, see: (*l*) Z. Zhang, Y. Yu and L. S. Liebeskind, *Org. Lett.*, 2008, **10**, 3005.

3 For stoichiometric addition of organometallic reagents reacting with azo compounds: for the use of Grignard reagents, see: (*a*) I. Sapountzis and P. Knochel, *Angew. Chem., Int. Ed.*, 2004, **43**, 897. For the use of organozinc reagents, see: (*b*) P. Sinha, C. C. Kofink and P. Knochel, *Org. Lett.*, 2006, **8**, 3741; (*c*) H. Mitchell and Y. Leblanc, *J. Org. Chem.*, 1994, **59**, 682. For the use of organotitanium reagents, see: (*d*) D. K. An, K. Hirakawa, S. Okamoto and F. Sato, *Tetrahedron Lett.*, 1999, **40**, 3737. For transition metal catalyzed C–N bond formation employing azo compounds: for Co- and Mn-catalyzed alkene hydrohydrazination, see: (*e*) J. Waser, B. Gaspar, H. Nambu and E. M. Carreira, *J. Am. Chem. Soc.*, 2006, **128**, 11693; (*f*) J. Waser, J. C. Gonzalez-Gomez, H. Nambu, P. Huber and E. M. Carreira, *Org. Lett.*, 2005, **7**, 4249; (*g*) J. Waser and E. M. Carreira, *J. Am. Chem. Soc.*, 2004, **126**, 5676. For Cu-mediated C–N bond coupling of arylboronic acid with azo compounds, see: (*h*) T. Uemura and N. Chatani, *J. Org. Chem.*, 2005, **70**, 8631. For Pd-catalyzed C–N bond coupling of arylboronic acid with azo compounds, see: (*i*) K. Muniz and A. Iglesias, *Angew. Chem., Int. Ed.*, 2007, **46**, 6350; (*j*) K. Muniz and M. Nieger, *Angew. Chem., Int. Ed.*, 2006, **45**, 2305.

4 Here our recent studies on catalytic C–H bond cross coupling reactions are depicted. For transition metal-catalyzed *ortho*-selective arene C–H bond carbenoid insertion, see: (*a*) H.-W. Lam, K.-Y. Man, W.-W. Chan, Z. Zhou and W.-Y. Yu, *Org. Biomol. Chem.*, 2014, **12**, 4112; (*b*) W.-W. Chan, S.-F. Lo, Z. Zhou and W.-Y. Yu, *J. Am. Chem. Soc.*, 2012, **134**, 13565; (*c*) W.-W. Chan, T.-L. Kwong and W.-Y. Yu, *Org. Biomol. Chem.*, 2012, **10**, 3749; (*d*) W.-W. Chan, S.-H. Yeung, Z. Zhou, A. S. C. Chan and W.-Y. Yu, *Org. Lett.*, 2010, **12**, 604. For transition metal-catalyzed C2-/*ortho*-selective arene C–H bond coupling with carboradical, see: (*e*) C.-W. Chan, P.-Y. Lee and W.-Y. Yu, *Tetrahedron Lett.*, 2015, **56**, 2559; (*f*) W.-W. Chan, Z. Zhou and W.-Y. Yu, *Chem. Commun.*, 2013, **49**, 8214; (*g*) C.-W. Chan, Z. Zhou and W.-Y. Yu, *Adv. Synth. Catal.*, 2011, **353**, 2999; (*h*) C.-W. Chan, Z. Zhou, A. S. C. Chan and W.-Y. Yu, *Org. Lett.*, 2010, **12**, 3926; (*i*) W.-Y. Yu, W. N. Sit, Z. Zhou and A. S. C. Chan, *Org. Lett.*, 2009, **11**, 3174; (*j*) W.-Y. Yu, W. N. Sit, K.-M. Lai, Z. Zhou and A. S. C. Chan, *J. Am. Chem. Soc.*, 2008, **130**, 3304. For Pd-catalyzed *ortho*-selective arene C–H bond amination with tosyloxycarbamates, see: (*k*) K.-H. Ng, F.-N. Ng and W.-Y. Yu, *Chem. Commun.*, 2012, **48**, 11680; (*l*) K.-H. Ng, A. S. C. Chan and W.-Y. Yu, *J. Am. Chem. Soc.*, 2010, **132**, 12862. For Rh-catalyzed *ortho*-selective arene C–H amination with *N*-chloramines, see: (*m*) F.-N. Ng, Z. Zhou and W.-Y. Yu, *Chem. – Eur. J.*, 2014, **20**, 4474; (*n*) K.-H. Ng, Z. Zhou and W.-Y. Yu, *Chem. Commun.*, 2013, **49**, 7031; (*o*) K.-H. Ng, Z. Zhou and W.-Y. Yu, *Org. Lett.*, 2012, **14**, 272.

5 For selective examples of rhodium(I) diene complexes catalyzed arylation of enones, see: (*a*) S. Gosiewska, J. A. Raskatov, R. Shintani, T. Hayashi and J. M. Brown, *Chem. – Eur. J.*, 2012, **18**, 80; (*b*) H. J. Edwards, J. D. Hargrave, S. D. Penrose and C. G. Frost, *Chem. Soc. Rev.*, 2010, **39**, 2093; (*c*) R. Shintani and T. Hayashi, *Aldrichimica Acta*, 2009, **42**, 31; (*d*) T. Hayashi, K. Ueyama, N. Tokunaga and K. Yoshida, *J. Am. Chem. Soc.*, 2003, **125**, 11508.

6 Refer to the ESI† for detailed experimental data.

7 (*a*) A. Kleeman, J. Engel, B. Kutscher and D. Reichert, *Pharmaceutical Substances: Syntheses, Patents, Applications of the most relevant APIs*, Thieme, Stuttgart, 5th edn, 2009; (*b*) S. M. Wilhelm, L. Adnane, P. Newell, A. Villanueva, J. M. Llovet and M. Lynch, *Mol. Cancer Ther.*, 2008, **7**, 3129; (*c*) R. Sordella, D. W. Bell, D. A. Haber and J. Settleman, *Science*, 2004, **305**, 1163; (*d*) M. W. N. Deininger and B. J. Druker, *Pharmacol. Rev.*, 2003, **55**, 401.

8 For Pd-catalyzed nucleophilic amination for diarylamine synthesis, see: (*a*) F. Paul, J. Patt and J. F. Hartwig, *Organometallics*, 1995, **14**, 3030; (*b*) A. S. Guram, R. A. Rennels and S. L. Buchwald, *Angew. Chem.*, 1995, **107**, 1456, (*Angew. Chem. Int. Ed. Engl.*, 1995, **34**, 1348); (*c*) J. Louie and J. F. Hartwig, *Tetrahedron Lett.*, 1995, **36**, 3609; (*d*) F. Paul, J. Patt and J. F. Hartwig, *J. Am. Chem. Soc.*, 1994, **116**, 5969. For Cu-catalyzed nucleophilic amination for diarylamine synthesis, see: (*e*) D. M. T. Chan, K. L. Monaco, R.-P. Wang and M. P. Winters, *Tetrahedron Lett.*, 1998, **39**, 2933; (*f*) D. A. Evans, J. L. Katz and T. R. West, *Tetrahedron Lett.*, 1998, **39**, 2937; (*g*) P. Y. S. Lam, C. G. Clark, S. Saubern, J. Adams, M. P. Winters, D. M. T. Chan and A. Combs, *Tetrahedron Lett.*, 1998, **39**, 2941.

9 For transition metal-catalyzed electrophilic amination for diarylamine synthesis: for stoichiometric addition of organoaluminum reagents reacting with *O*-protected hydroxamic acid, see: (*a*) S. Zhou, Z. Yang, X. Chen, Y. Li, L. Zhang, H. Fang, W. Wang, X. Zhu and S. Wang, *J. Org. Chem.*, 2015, **80**, 6323; (*b*) H. Yoon and Y. Lee, *J. Org. Chem.*, 2015, **80**, 10244. For Cu-catalyzed electrophilic amination for diarylamine synthesis, see: (*c*) R. Sakae, K. Hirano and M. Miura, *J. Am. Chem. Soc.*, 2015, **137**, 6460; (*d*) T. Kawano, K. Hirano, T. Satoh and M. Miura, *J. Am. Chem. Soc.*, 2010, **132**, 6900; (*e*) C. He, C. Chen, J. Cheng, C. Liu, W. Liu, Q. Li and A. Lei, *Angew. Chem., Int. Ed.*, 2008, **47**, 6414. For Rh-

catalyzed electrophilic amination for diarylamine synthesis, see: (*f*) S. H. Park, J. Kwak, K. Shin, J. Ryu, Y. Park and S. Chang, *J. Am. Chem. Soc.*, 2014, **136**, 2492; (*g*) K. Shin, Y. Baek and S. Chang, *Angew. Chem., Int. Ed.*, 2013, **52**, 1; (*h*) J. Ryu, K. Shin, S. H. Park, J. Y. Kim and S. Chang, *Angew. Chem., Int. Ed.*, 2012, **51**, 9904.

10 For arylrhodium(III)-mediated catalytic C–N bond coupling reactions, see: (*a*) G. Song, F. Wang and X. Li, *Chem. Soc. Rev.*, 2012, **41**, 3651; (*b*) K. Shin, Y. Baek and S. Chang, *Angew. Chem., Int. Ed.*, 2013, **52**, 1; (*c*) C. Grohmann, H. Wang and F. Glorius, *Org. Lett.*, 2012, **14**, 656; (*d*) J. Y. Kim, S. H. Park, J. Ryu, S. H. Cho, S. H. Kim and S. Chang, *J. Am. Chem. Soc.*, 2012, **134**, 9110; (*e*) C. Grohmann, H. Wang and F. Glorius, *Org. Lett.*, 2013, **15**, 3014. For arylrhodium(III)-mediated catalytic carbenoid C–C bond coupling reactions, see: (*f*) Y.-S. Lu and W.-Y. Yu, *Org. Lett.*, 2016, **18**, 1350; (*g*) F.-N. Ng, Y.-F. Lau, Z. Zhou and W.-Y. Yu, *Org. Lett.*, 2015, **17**, 1676.

11 J. W. Kang, K. Moseley and P. M. Maitlis, *J. Am. Chem. Soc.*, 1969, **91**, 5970.

12 E. J. Farrington, C. F. J. Barnard, E. Rowsell and J. M. Brown, *Adv. Synth. Catal.*, 2005, **347**, 185.