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Rh/Cu-catalyzed multiple C–H, C–C, and C–N bond cleavage: facile synthesis of pyrido[2,1-*a*]-indoles from 1-(pyridin-2-yl)-1*H*-indoles and γ -substituted propargyl alcohols†

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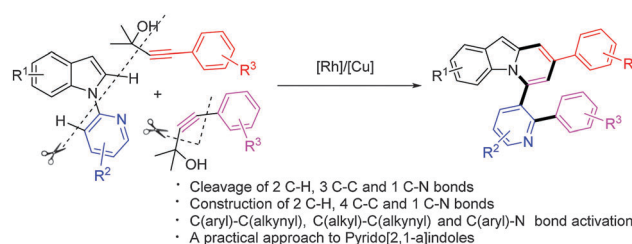
An unusual Rh/Cu-catalyzed synthesis of pyrido[2,1-*a*]indoles starting from 1-(pyridin-2-yl)-1*H*-indoles and γ -substituted propargyl alcohols was presented. The multi-step cascade transformations formally involve the cleavage of two C–H, three C–C, and one C–N bonds with concomitant construction of two C–H, four C–C, and one C–N bonds with excellent chemoselectivity in one-pot reaction.

The selective cleavage and construction of chemical bonds has always been a central topic in modern synthetic organic chemistry.¹ In recent decades, transition metal-catalyzed direct cleavage of inert chemical bonds such as C–H, C–C and C–N bonds, and thus associated transformations have garnered increasing attention by the synthetic community. In particular, significant developments have been acquired in the area of C–H activation.² However, reports of C–C activation are less prominent in the literature probably owing to the thermodynamic stability of these bonds and the kinetic factors arising from the greater steric hindrance as well as the competing C–H activation.^{3,4} Therefore, examples for C–C bond activation are still mostly limited to strained C–C bonds, decarboxylation reactions, or performed with the help of strong chelation assistants.^{3,4} Similarly, due to the high C–N bond dissociation energy, catalytic transformations involving selective cleavage of C–N bonds have been scarce so far.^{5,6} Not surprisingly, the simultaneous cleavage of both C–C and C–N bonds under one set of conditions would be even more challenging, which is limited to a few reports.⁷

On the other hand, transition-metal mediated direct C–H alkynylation for the introduction of the alkynyl functionality has received much attention recently.⁸ Although terminal alkynes,⁹ alkynylhalides¹⁰ as well as benziodoxolone-based hypervalent iodine reagents¹¹ have been used as alkynyl coupling partners to achieve direct C–H alkynylation of intrinsically different arenes, the substrate scope remains limited. It is still necessary to develop highly efficient and general

alkynylation methods for broadly defined arenes *via* a C–H activation pathway. In this context, it is worth noting that *tert*-propargyl alcohols have been involved in Sonogashira-type reactions as masked terminal alkynes.¹² Moreover, Miura discovered that [Rh(OH)(COD)]₂ could catalyze regio- and stereo-selective homo-coupling of γ -arylated *tert*-propargyl alcohols *via* β -carbon elimination with liberation of ketone, in which an alkynyl rhodium generated *in situ* was proposed as the key intermediate.¹³ Furthermore, given the great success and advantages of rhodium catalysis in the construction of C–X bonds (X = C, N, O, *etc.*) based on C–H activation in recent years,^{14,15} we were prompted to design the Rh-catalyzed direct C–H alkynylation of arenes utilizing γ -substituted *tert*-propargyl alcohols as the alkynyl coupling partner. Following this idea, we have thus examined the reactions of 1-(pyridin-2-yl)-1*H*-indoles with *tert*-propargyl alcohols under the Rh/Cu catalyst system, which serendipitously led to the formation of pyrido[2,1-*a*]indoles instead of the expected alkynylation products (Scheme 1). Herein, we communicate this unusual cascade reaction, whereby at least six bonds, including two C–H, three C–C and one C–N bonds, were cleaved and seven bonds (two C–H, four C–C and one C–N bonds) were constructed in one pot. The reaction reported here is unprecedented especially when the efficiency is considered.¹⁶

We initiated our study by choosing 1-(pyridin-2-yl)-1*H*-indole **1a** and 2-methyl-4-phenyl-3-butyn-2-ol **2a** as model substrates. Surprisingly, when [Cp*RhCl₂]₂ and Cu(OAc)₂·H₂O were employed as the catalytic system, the unexpected product **3aa**, which contains a pyrido[2,1-*a*]indole skeleton, was isolated in 24% yield (Table 1, entry 1). The definite structures of **3** came from the X-ray



Scheme 1 Rh/Cu-catalyzed facile synthesis of pyrido[2,1-*a*]indoles *via* multiple C–H, C–C, and C–N bond cleavage.

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Table 1 Optimization of reaction conditions^a

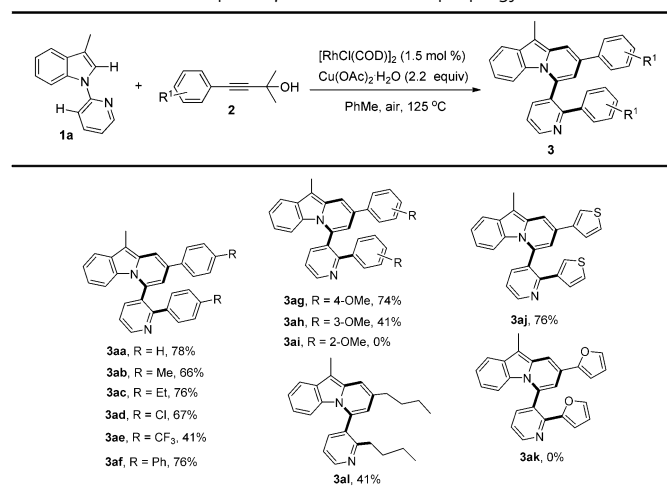
Entry	[M]	Oxidant	Solvent	Temp. (°C)	Yield (%) 3aa ^b
1	[Cp*RhCl ₂] ₂	Cu(OAc) ₂ ·H ₂ O	PhMe	125	24/(4a 64°)
2	[Cp*Rh(CH ₃ CN) ₃]	Cu(OAc) ₂ ·H ₂ O	PhMe	125	32
3	[SbF ₆] ₂	Cu(OAc) ₂ ·H ₂ O	PhMe	125	40
4	[RhOH(COD)] ₂	Cu(OAc) ₂ ·H ₂ O	PhMe	125	57/(4a 54)
5	[RhCl(COD)] ₂	Cu(OAc) ₂ ·H ₂ O	PhMe	125	78/(4a 41)
6	[RhCl(COD)] ₂	Cu(OAc) ₂ ·H ₂ O	Xylene	125	67
7	[RhCl(COD)] ₂	Cu(OAc) ₂ ·H ₂ O	DCE	125	56
8	[RhCl(COD)] ₂	Cu(OAc) ₂ ·H ₂ O	Dioxane	125	20
9	[RhCl(COD)] ₂	NO	PhMe	125	0
10	NO	Cu(OAc) ₂ ·H ₂ O	PhMe	125	0/(4a 98)
11	[RhCl(COD)] ₂	Cu(OAc) ₂ ·H ₂ O	PhMe	125	Trace ^d
12	[RhCl(COD)] ₂	AgOAc	PhMe	125	0
13	[RhCl(COD)] ₂	Ag ₂ CO ₃	PhMe	125	0
14	[RhCl(COD)] ₂	Cu(OAc) ₂ ·H ₂ O	PhMe	110	0/(4a 84)
15	[RhCl(COD)] ₂	Cu(OAc) ₂ ·H ₂ O	PhMe	140	Trace
16	[RhCl(COD)] ₂	Cu(OAc) ₂ ·H ₂ O	PhMe	125	21/(4a 71) ^e

^a Reaction conditions: **1a** (0.20 mmol), **2a** (0.80 mmol, 4 equiv.), [M] (1.5 mol%), oxidant (2.2 equiv.) and solvent (2 mL) under air for about 6 h.

^b Yield of isolated products based on **1a**. ^c Yield of isolated products based on **2a**. ^d 2.0 equiv. of K₂CO₃ was added. ^e Phenylacetylene instead of **2a**.

crystallographic studies of a series of pyrido[2,1-*a*]indole products **3af**, **3ag** (vide infra, see ESI[†]), **3la** (Table 3), and **3jga** (Scheme 3). To the best of our knowledge, efficient strategies for the construction of pyrido[2,1-*a*]indoles, a recurring structural motif found in many pharmaceuticals and functional materials, have rarely been reported.^{17,18} After screening of a variety of rhodium precatalysts, [RhCl(COD)]₂ was found to be the best choice and **3aa** was obtained in 78% isolated yield (entries 2–5). Investigation of solvent effects indicated that toluene was the most suitable solvent (entries 5–8). Control experiments revealed that no desired product **3aa** was detected in the absence of either [RhCl(COD)]₂ or Cu(OAc)₂·H₂O (entries 9 and 10). Notably, the reaction was suddenly shut down in the presence of an extra basic additive, K₂CO₃ (entry 11). The use of other common oxidants such as AgOAc or Ag₂CO₃ did not provide **3aa** at all (entries 12 and 13). 125 °C was found to be the optimal temperature (entries 14 and 15). We have also examined the possibility of employing a simple terminal alkyne instead of **2a** for this transformation, which gave **3aa** in only 21% yield accompanied by a large amount of Glaser coupling product **4a** in 71% yield (entry 16). This result clearly showed that Glaser coupling was inhibited effectively in this reaction by using *tert*-propargyl alcohol as the alkynylating reagent instead of phenylacetylene.

With these optimized reaction conditions in hand, the scope of this reaction was extensively studied. First, a series of γ -substituted *tert*-propargyl alcohols were investigated (Table 2). To our satisfaction, γ -arylated *tert*-propargyl alcohols with electron-donating or electron-withdrawing substituents, such as Me, Et, Cl, CF₃, and Ph, at the *para* position on the phenyl ring were well tolerated to provide the corresponding products in moderate to good yields (**3aa–3af**, 41–78% yield).

Table 2 Reaction scope of γ -substituted *tert*-propargyl alcohols^a

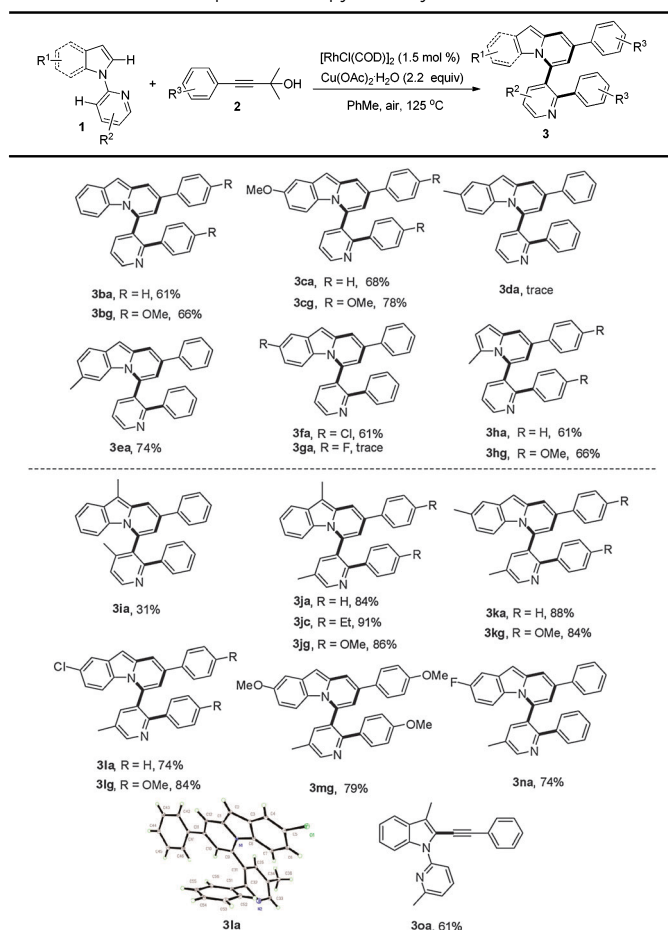
^a General reaction conditions: **1a** (0.2 mmol), **2** (0.8 mmol), [RhCl(COD)]₂ (1.5 mol%), Cu(OAc)₂·H₂O (2.2 equiv.), PhMe (2 mL), 125 °C, air, 6 h. Yield of isolated products based on **1a**.

Substrates bearing methoxy groups at the *meta* and *para* positions on the phenyl ring proceeded well (**3ag**, **3ah**), while that with a methoxy group at the *ortho* position on the phenyl ring failed to yield the desired product **3ai**, possibly due to the steric hindrance. It is worth noting that the methodology could be further extended to thiophene containing substrate **2j** to afford **3aj** in 76% yield, while γ -furan *tert*-propargyl alcohol **2k** did not work at all. Moreover, aliphatic 2-methyloct-3-yn-2-ol **2l** was also investigated to produce **3al** in 41% yield, which represents the first example of C(alkyl)–C(alkynyl) single bond cleavage.¹⁹

Subsequently, the scope of 1-(pyridin-2-yl)-1H-indoles was further investigated (Table 3). Gratifyingly, reactions of **1b** with γ -arylated *tert*-propargyl alcohols worked well to yield **3ba** and **3bg** in good yields. Other indoles with a substituent group such as OMe or Cl at the C-5 position on the indole ring were also compatible with this transformation, thus affording the corresponding products **3ca**, **3cg**, and **3fa**, while substrates with Me or F at the C-5 position on the indole ring did not work (**3da**, **3ga**). In contrast, when the Me group was at the C-6 position, the reaction proceeded smoothly to give **3ea** in 74% yield. More importantly, when 2-(2-methyl-1H-pyrrol-1-yl)pyridine, **1h**, was used as the substrate, indolizine derivatives **3ha** and **3hg** could be obtained in 61% and 66% yields respectively, which represent the rare examples of indolizine synthesis starting from pyrrole.^{18b,c}

We next examined the influence of the substituent at the pyridyl directing groups for the reaction (Table 3). Firstly, when the C-3 position of the pyridyl group, which is subject to the consequent C–C bond formation, was blocked with a Me group, the reaction was completely suppressed to yield only **4a**. In addition, installation of the Me substituent on the pyridyl C-4 position furnished product **3ia** in only 31% yield. Further studies revealed that the 5-methylpyridin-2-yl directing group gave the best result, providing the target products in particularly high yields (**3ja–3na**, 74–91%), and even substrates with Me or F at the C-5 position on the indole ring were converted into the corresponding target products **3la**, **3lg**, and **3na** effectively. It should be noted that changing the directing group from

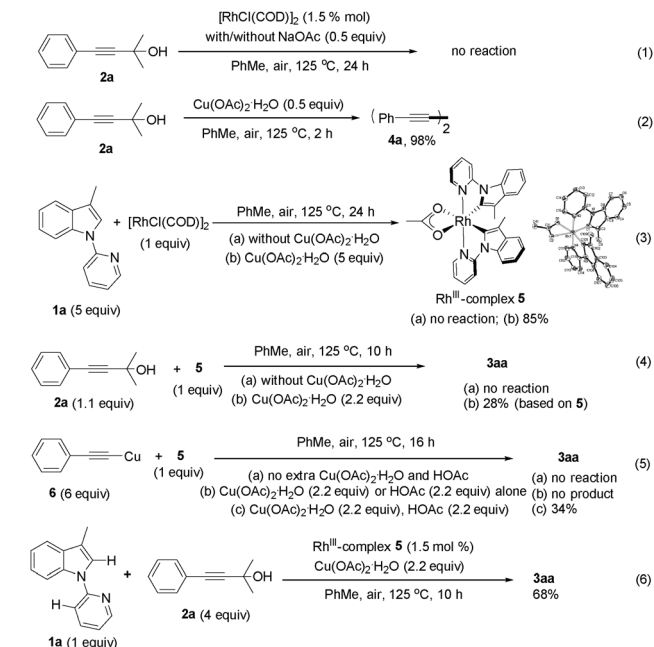


Table 3 Reaction scope of the 1-(pyridin-2-yl)-1H-indoles^a

^a General reaction conditions: **1** (0.2 mmol), **2** (0.8 mmol), [RhCl(COD)]₂ (1.5 mol %), Cu(OAc)₂·H₂O (2.2 equiv.), PhMe (2 mL), 125 °C, air, 6 h. Yield of isolated products based on **1**.

pyridin-2-yl to 6-methylpyridin-2-yl significantly affected the reactivity and only the alkynylation product **3oa** was isolated. The steric hindrance of the Me group at the C-6 position may account for this difference. Isolation of the alkynylation product **3oa** indicated that the alkynylation step was possibly involved in the catalytic cycle for the formation of pyrido[2,1-*a*]indoles **3**.

To get some mechanistic insights into this transformation, several experiments were carried out (Scheme 2). First, addition of TEMPO to the reaction mixture had a negligible effect on the reaction, which suggested that a free-radical pathway might be ruled out. Next, stoichiometric reaction of **2a** with [RhCl(COD)]₂ was performed and no reaction could be observed indeed, even if an excess of NaOAc was added (eqn (1)). Notably, it was found that the Glaser coupling product **4a** was generated quantitatively when Cu(OAc)₂·H₂O was mixed with **2a** at 125 °C (eqn (2)). These results indicated that it is Cu(OAc)₂·H₂O rather than [RhCl(COD)]₂ that is responsible for the C–C bond cleavage of **2a** via β-carbon elimination.¹³ Reaction of [RhCl(COD)]₂ with **1a** was also investigated and no appreciable reaction could be observed when the reaction was performed in the absence of Cu(OAc)₂·H₂O. However, the biscyclometalated Rh(III) complex **5** was obtained in 85% yield when the reaction was performed in the presence of



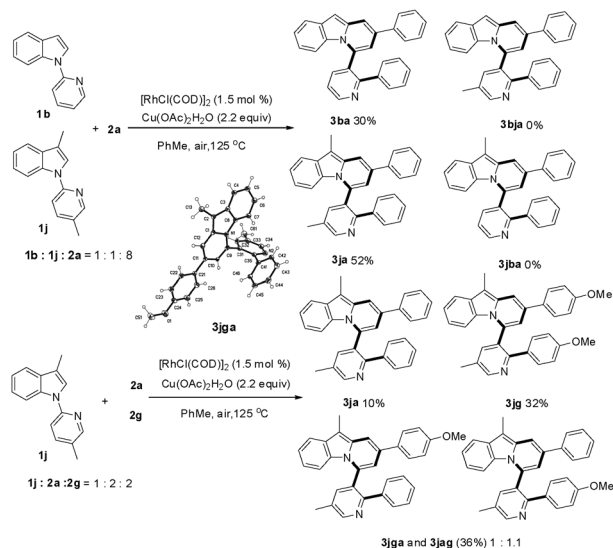
Scheme 2 Mechanistic studies.

Cu(OAc)₂·H₂O (eqn (3)), which clearly indicated that the Csp²–H bond cleavage of substrate **1a** was enforced by the Rh^{III} species. The structure of **5** was confirmed by single-crystal X-ray diffraction. Furthermore, the reactivity of complex **5** was tested. Again, no reaction took place when complex **5** was mixed with **2a** at 125 °C (eqn (4)). In sharp contrast, the reaction of **5** and **2a** in the ratio of 1 : 1.1 in the presence of Cu(OAc)₂·H₂O did proceed to yield the target product **3aa** (eqn (4)). However, further efforts to isolate intermediates from the reaction mixtures by adjusting the ratio of **5** and **2a** failed. Reaction of **5** with copper phenylacetylide **6** was also investigated to give product **3aa**, albeit in 34% yield. Of note, the addition of extra Cu(OAc)₂·H₂O as an oxidant and HOAc was essential to promote the reaction. No desired product could be observed in the absence of Cu(OAc)₂·H₂O or HOAc (eqn (5)). These observations implied that the acetylide copper species generated from the reaction of **2a** with Cu(OAc)₂·H₂O could undergo transmetalation of the alkynyl group to rhodium to afford acetylide rhodium, which then participated in the subsequent transformations. The catalytic activity of complex **5** under standard conditions was also tested to provide **3aa** in 68% yield, which indicated that complex **5** could be a possible intermediate in the catalytic cycle (eqn (6)).

The possibility of cross reactions between two different indoles or propargyl alcohols was also investigated (Scheme 3). The reaction of indole substrates **1b** and **1j** with **2a** afforded only the corresponding **3ba** and **3ja**, while the crossover products **3bja** and **3jba** were not detected at all, clearly indicating that the C–N bond cleavage and the concomitant transformations proceeded in an intramolecular manner. In contrast, reaction of **1j** with a mixture of **2a** and **2g** led to the isolation of products **3ja** and **3jg** as well as the expected crossover products **3jga** and **3jag** with the latter two as a mixture.

Given the results of the above control experiments, it is reasonable to believe that the reaction is presumably initiated by the cyclometallation of 1-(pyridin-2-yl)-1H-indoles with Rh^{III} species.





Scheme 3 Cross reactions.

Transmetalation of the alkynyl group from the acetylide copper species generated *in situ* to Rh followed by a reductive elimination yields the alkynylation product (see ESI†), which then proceeds to undergo a series of transformations to afford the target product finally. The mechanistic details for the further transformation of the alkynylation product to give the pyrido[2,1-*a*]indole skeleton are unclear yet.

In conclusion, we have discovered a novel Rh/Cu catalyzed cascade reaction involving multiple C–H, C–C, and C–N bond cleavage and formation, giving rise to a practical approach for the construction of pyrido[2,1-*a*]indoles. Remarkably, the highly selective cleavage of several types of extremely inert chemical bonds such as C(aryl)–C(alkynyl), C(alkyl)–C(alkynyl), and C(aryl)–N bonds was realized in this transformation. Further studies aimed at revealing the detailed mechanism of this complicated reaction and applications of this protocol are currently being investigated in our laboratory.

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Notes and references

- M. B. Smith and J. March, *March's Advanced Organic Chemistry: Reactions Mechanisms and Structure*, Wiley, Hoboken, NJ, 2007.
- Selected reviews: (a) R. Giri, B.-F. Shi, K. M. Engle, N. Maugel and J.-Q. Yu, *Chem. Soc. Rev.*, 2009, **38**, 3242; (b) C. I. Herrerias, X. Yao, Z. Li and C.-J. Li, *Chem. Rev.*, 2007, **107**, 2456; (c) T. W. Lyons and M. S. Sanford, *Chem. Rev.*, 2010, **110**, 1147; (d) C. S. Yeung and V. M. Dong, *Chem. Rev.*, 2011, **111**, 1215; (e) J. L. Bras and J. Muzart, *Chem. Rev.*, 2011, **111**, 1170; (f) C.-L. Sun, B.-J. Li and Z.-J. Shi, *Chem. Rev.*, 2011, **111**, 1293; (g) J. Wencel-Delord, T. Drge, F. Liu and F. Glorius, *Chem. Soc. Rev.*, 2011, **40**, 4740; (h) P. B. Arockiam, C. Bruneau and P. H. Dixneuf, *Chem. Rev.*, 2012, **112**, 5879; (i) L. Ackermann, *Acc. Chem. Res.*, 2014, **47**, 281.
- For selected reviews, see: (a) R. H. Crabtree, *Nature*, 2000, **408**, 415; (b) C.-H. Jun, *Chem. Soc. Rev.*, 2004, **33**, 610; (c) M. Rubin, M. Rubina and V. Gevorgyan, *Chem. Rev.*, 2007, **107**, 3117; (d) Y. Horino, *Angew. Chem., Int. Ed.*, 2007, **46**, 2144; (e) M. Tobisu and N. Chatani, *Chem. Soc. Rev.*, 2008, **37**, 300; (f) C. Winter and N. Krause, *Angew. Chem., Int. Ed.*, 2009, **48**, 2460; (g) F. Chen, T. Wang and N. Jiao, *Chem. Rev.*, 2014, **114**, 8613.
- For selected recent examples, see: (a) C.-H. Jun, H. Lee and S.-G. Lim, *J. Am. Chem. Soc.*, 2001, **123**, 751; (b) A. Sattler and G. Parkin, *Nature*, 2010, **463**, 523; (c) C. Qin, P. Feng, Y. Ou, T. Shen, T. Wang and N. Jiao, *Angew. Chem., Int. Ed.*, 2013, **52**, 7850; (d) M. Saydou and A. M. Echavarren, *Angew. Chem., Int. Ed.*, 2013, **52**, 13468; (e) H. M. Ko and G. Dong, *Nat. Chem.*, 2014, **6**, 739; (f) L. Souillart, E. Parker and N. Cramer, *Angew. Chem., Int. Ed.*, 2014, **53**, 3001; (g) X. Huang, X. Li, M. Zou, S. Song, C. Tang, Y. Yuan and N. Jiao, *J. Am. Chem. Soc.*, 2014, **136**, 14858.
- For reviews of C–N bond cleavage, see: (a) K. Khumtaveeporn and H. Alper, *Acc. Chem. Res.*, 1995, **28**, 414; (b) A. Roglans, A. Pla-Quintana and M. Moreno-Mañas, *Chem. Rev.*, 2006, **106**, 4622; (c) N. J. Turner, *Chem. Rev.*, 2011, **111**, 4073.
- For selected examples, see: (a) T. Koreeda, T. Kochi and F. Kakiuchi, *J. Am. Chem. Soc.*, 2009, **131**, 7238; (b) W. Geng, W.-X. Zhang, W. Hao and Z. Xi, *J. Am. Chem. Soc.*, 2012, **134**, 20230; (c) B.-J. Li, H.-Y. Wang, Q.-L. Zhu and Z.-J. Shi, *Angew. Chem., Int. Ed.*, 2012, **51**, 3948; (d) M. Tobisu, K. Nakamura and N. Chatani, *J. Am. Chem. Soc.*, 2014, **136**, 5587.
- For some recent reports on both C–C and C–N bond cleavage, see: (a) C. Li, W.-T. Zhang and X.-S. Wang, *J. Org. Chem.*, 2014, **79**, 5847; (b) P. Feng, X. Sun, Y. Su, X. Li, L.-H. Zhang, X. Shi and N. Jiao, *Org. Lett.*, 2014, **16**, 3388.
- (a) K. Sonogashira, *J. Organomet. Chem.*, 2002, **653**, 46; (b) E. Negishi and L. Anastasia, *Chem. Rev.*, 2003, **103**, 1979; (c) W. Shi, C. Liu and A. Lei, *Chem. Soc. Rev.*, 2011, **40**, 2761; (d) J. P. Brand and J. Waser, *Chem. Soc. Rev.*, 2012, **41**, 4165.
- Selected examples, see: (a) Y. Wei, H. Zhao, J. Kan, W. Su and M. Hong, *J. Am. Chem. Soc.*, 2010, **132**, 2522; (b) N. Matsuyama, M. Kitahara, K. Hirano, T. Satoh and M. Miura, *Org. Lett.*, 2010, **12**, 2358; (c) S. H. Kim, J. Yoon and S. Chang, *Org. Lett.*, 2011, **13**, 1474; (d) M. Shang, H.-L. Wang, S.-Z. Sun, H.-X. Dai and J.-Q. Yu, *J. Am. Chem. Soc.*, 2014, **136**, 11590.
- Selected examples, see: (a) K. Kobayashi, M. Arisawa and M. Yamaguchi, *J. Am. Chem. Soc.*, 2002, **124**, 8528; (b) I. V. Seregin, V. Ryabova and V. Gevorgyan, *J. Am. Chem. Soc.*, 2007, **129**, 7742; (c) Y. Ano, M. Tobisu and N. Chatani, *J. Am. Chem. Soc.*, 2011, **133**, 12984; (d) J. He, M. Wasa, K. S. L. Chan and J.-Q. Yu, *J. Am. Chem. Soc.*, 2013, **135**, 3387.
- (a) J. P. Brand, L. Charpentier and J. Waster, *Angew. Chem., Int. Ed.*, 2009, **48**, 9346; (b) C. Feng and T.-P. Loh, *Angew. Chem., Int. Ed.*, 2014, **53**, 2722; (c) F. Xie, Z. Qi, S. Yu and X. Li, *J. Am. Chem. Soc.*, 2014, **136**, 4780; (d) K. D. Collins, F. Lied and F. Glorius, *Chem. Commun.*, 2014, **50**, 4459.
- (a) T. Nishimura, H. Ariki, Y. Maeda and S. Uemura, *Org. Lett.*, 2003, **5**, 2997; (b) T. Nishimura, H. Ariki, Y. Maeda and S. Uemura, *Org. Lett.*, 2003, **5**, 2997.
- A. Funayama, T. Satoh and M. Miura, *J. Am. Chem. Soc.*, 2005, **127**, 15354.
- See for selected reviews: (a) T. Satoh and M. Miura, *Chem. – Eur. J.*, 2010, **16**, 11212; (b) D. A. Colby, R. G. Bergman and J. A. Ellman, *Chem. Rev.*, 2010, **110**, 624; (c) G. Song, F. Wang and X. Li, *Chem. Soc. Rev.*, 2012, **41**, 3651.
- Rh-catalyzed C–H alkynylation, see ref. 11b–d.
- (a) B. M. Trost, *Science*, 1991, **254**, 1471; (b) C.-J. Li and B. M. Trost, *Proc. Natl. Acad. Sci. U. S. A.*, 2008, **105**, 13197.
- (a) F. De Simone, J. Gertsch and J. Waser, *Angew. Chem., Int. Ed.*, 2010, **49**, 5767; (b) M. Mizutani, F. Inagaki, T. Nakanishi, C. Yangagihara, I. Tamai and C. Mukai, *Org. Lett.*, 2011, **13**, 1796.
- (a) A. Ohsawa, T. Kawaguchi and H. Igeta, *J. Org. Chem.*, 1982, **47**, 3497; (b) H. Zhu, J. Stöckigt, Y. Yu and H. Zou, *Org. Lett.*, 2011, **13**, 2792; (c) D. C. Rogness, N. A. Markina, J. P. Waldo and R. C. Larock, *J. Org. Chem.*, 2012, **77**, 2743; (d) S. Samala, P. Pallavi, R. Kumar, R. K. Arigela, G. Singh, R. S. Ampapathi, A. Priya, S. Datta, A. Patra and B. Kundu, *Chem. – Eur. J.*, 2014, **20**, 14344.
- Rare examples for C(aryl)–C(alkynyl) bond cleavage, see: (a) M. Gaydou and A. M. Echavarren, *Angew. Chem., Int. Ed.*, 2013, **52**, 13468; (b) X.-R. Song, Y.-P. Han, Y.-F. Qiu, Z.-H. Qiu, X.-Y. Liu, P.-F. Xu and Y.-M. Liang, *Chem. – Eur. J.*, 2014, **20**, 12046; (c) ref. 4c; (d) C. Müller, C. N. Iverson, R. J. Lachicotte and W. D. Jones, *J. Am. Chem. Soc.*, 2001, **123**, 9718.

