Organic LETTERS

Letter

pubs.acs.org/OrgLett

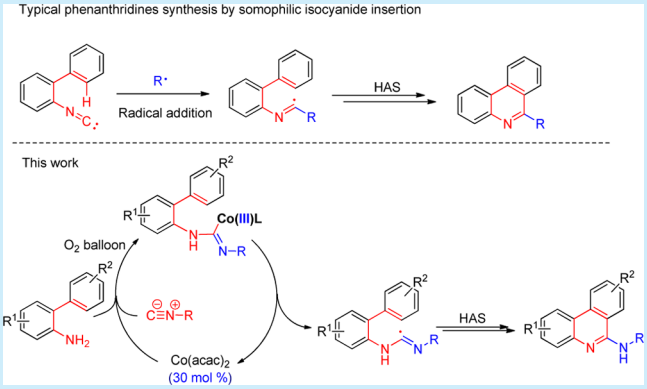
$Co(acac)_2/O_2$-Mediated Oxidative Isocyanide Insertion with 2-Aryl Anilines: Efficient Synthesis of 6-Amino Phenanthridine Derivatives

Tong-Hao Zhu, Shun-Yi Wang,* Yang-Qing Tao, Tian-Qi Wei, and Shun-Jun Ji*

Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China

Supporting Information

ABSTRACT: A novel and efficient protocol for the creation of 6-amino phenanthridine derivatives by $Co(acac)_2$-catalyzed isocyanide insertion with 2-aryl anilines under an O_2 atmosphere via homolytic aromatic substitution (HAS) type C−H functionalization has been developed. This reaction not only proceeds smoothly utilizing O_2 as the oxidant but also provides a new approach to construct phenanthridine derivatives utilizing readily available 2-aryl anilines with isocyanides instead of 2-isocyanobiaryls with different radical precursors.



Phenanthridines have attracted much attention, because they show versatile biological activities such as antibacterial, antitumoral, cytotoxic, and DNA intercalator (Figure 1).[1,2] Therefore, it is important to develop new methods for the synthesis of these compounds.[3,4] Transition-metal-catalyzed isocyanide insertion reactions[5] and somophilic isocyanide insertion reactions[3,6] have been well developed for the construction of heterocycles via cascade reactions.[7] Recently, a series of 6-substituted phenanthridines were easily prepared by radical addition to 2-isocyanobiaryls followed by a homolytic aromatic substitution (HAS) process.[3,8] However, there has been no report on the construction of 6-amino phenanthridines utilizing a similar strategy. There are also no reactions of 2-aryl anilines with isocyanides to construct 6-amino phenanthridines. More recently, we have developed a cobalt-catalyzed isocyanide insertion reaction of aromatic amine derivatives to synthesize 2-aminobenzimidazoles, 2-aminobenzothiazoles, and 2-aminobenzoxazoles.[9]

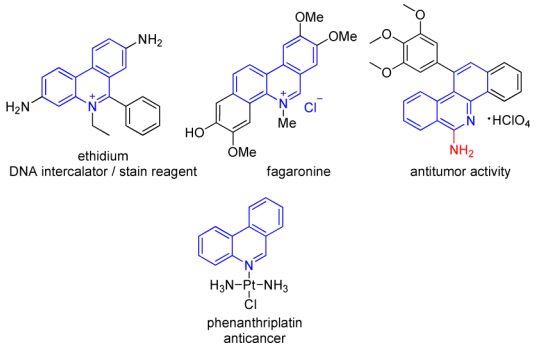
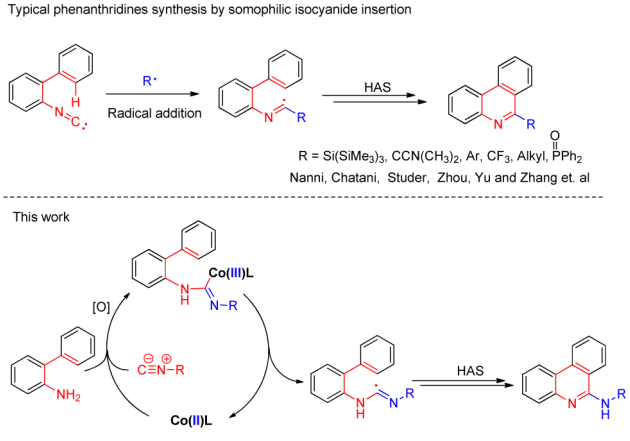


Figure 1. Biologically active phenanthridines.

As a continuation of our work on isocyanide insertion reactions,[9,10] herein, we plan to investigate the reaction of isocyanides with 2-aryl anilines catalyzed by a cobalt salt under oxidative conditions, which would concisely synthesize 6-amino phenanthridine derivatives via the formation of an imidoyl radical intermediate followed by HAS type C−H functionalization (Scheme 1). This reaction utilizes readily available 2-aryl anilines with isocyanides instead of 2-isocyanobiaryls with

Scheme 1. Phenanthridines Synthesis by Isocyanide Insertion



Received: January 27, 2014

   dx.doi.org/10.1021/ol500286x | *Org. Lett.* XXXX, XXX, XXX−XXX

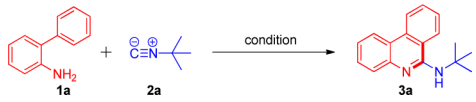
different radical precursors catalyzed by an inexpensive and low toxicity cobalt salt under oxidation conditions.

Our initial studies focused on developing a more efficient catalytic system by investigating the reaction of aniline **1a** and *tert*-butyl isocyanide **2a** as a model system. When the reaction of **1a** and **2a** was carried out in toluene at 100 °C without a catalyst under sealed tube conditions, no desired product was observed (Table 1, entry 1). To our surprise, the desired *N*-(*tert*-butyl)phenanthridin-6-amine **3a** could be obtained in 53% GC-yield by the reaction of **1a** and **2a** catalyzed by 20 mol % $Co(acac)_2$ in toluene at 100 °C under sealed tube conditions (Table 1, entry 2). However, other cobalt salts such as $Co(OAc)_2$, $CoCl_2{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}9H_2O$, and $CoSO_4{\cdot}7H_2O$ could not promote this reaction (Table 1, entries 3−6). The results of screening for solvent, catalyst loading, and reaction temperature conditions indicated that 1,4-dioxane, 30 mol % $Co(acac)_2$, and 100 °C were optimal for this reaction (Table 1, entries 7−16). When the reaction was carried out under an argon atmosphere, it was found that almost no desired product was formed (Table 1, entry 17). This result indicated that O_2 was critical for this reaction. To our delight, the reaction of **1a** and **2a** catalyzed by 30 mol % $Co(acac)_2$ in 1,4-dioxane at 100 °C could react smoothly under 1 atm of O_2 atmosphere (O_2 balloon) to afford the desired product **3a** in 66% GC-yield (60% isolated yield) (Table 1, entry 18).

With the optimized conditions in hand, the reaction scope of the 2-aryl anilines was investigated. The results are summarized in Schemes 2 and 3. The substituted 2-aryl anilines (**1a−k**) reacted well with *tert*-butyl isocyanide **2a** (Scheme 2), giving the desired products **3a−k** in moderate yields. It is noteworthy that not only the 2-aryl group bearing electron-donating groups could offer the desired products in moderate yields but also the 2-aryl group bearing electron-withdrawing groups could afford the desired products in moderate yields (30%-63%). When 3′-methylbiphenyl-2-amine **1h** was applied to the reaction, a mixture of the two isomers *N*-*tert*-butyl-9-methylphenanthridin-6-amine **3h** and *N*-*tert*-butyl-7-methylphenanthridin-6-amine **3h′** in the ratio 3:2 was obtained. 2-(Pyridin-4-yl)aniline could also react well and lead to the desired product **3i** in 49% yield. It should be noted that **3j** could also be observed in 42% yield with excellent regioselectivity, determined by NMR.

Then, we investigated the subtituent effects on the aniline aromatic ring. The results are listed in Scheme 3. The 2-aryl substituted anilines (**1l−s**) reacted well with *tert*-butyl isocyanide **2a**, furnishing the desired products **4a−h** in moderate yields. It is worth noting that the reaction of aniline bearing electron-donating groups (Me, OMe) could lead to the desired products in 31%−55% yields. When an aniline bearing an electron-withdrawing group such as NO_2 was applied to the reaction, the desired product **4d** could also be obtained in 35% yield. The reactions of halo-substituted anilines **1l** and **1m** afforded the products **4a** and **4b** in 54% and 57% yields, respectively. Furthermore, relatively bulky substrate **1p** could also undergo the transformation, generating the desired product **4e** in 31% yield. Unfortunately, when 3-methyl-biphenyl-2-amine **1q** reacted with **2a**, only a trace of product was formed. To our delight, *N*-(*tert*-butyl)benzo[*c*][1,5]naphthyridin-6-amine **4h** could also be observed in 47% yield by the

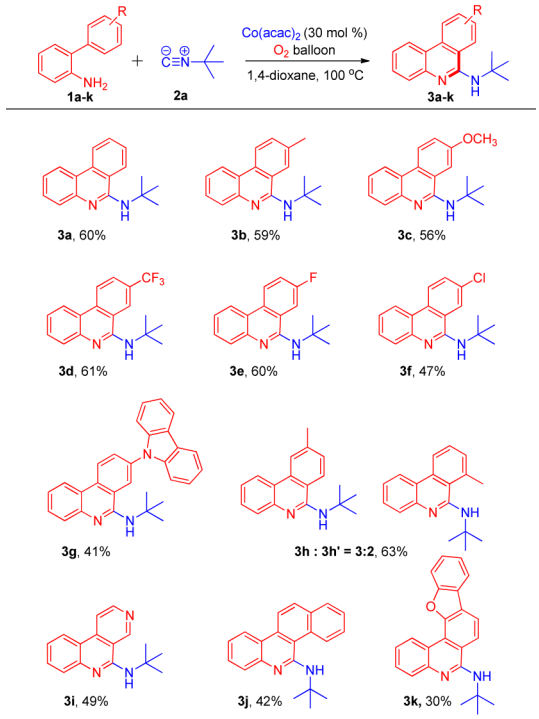
Table 1. Optimization of Isocyanide Insertion with 2-Aryl Anilines[a]



entry	catalyst (mol %)	temp (°C)	solvent	yield (%)[b]
1	–	100	toluene	0
2	$Co(acac)_2$ (20)	100	toluene	53
3	$Co(OAc)_2$ (20)	100	toluene	trace
4	$CoCl_2{\cdot}6H_2O$ (20)	100	toluene	trace
5	$Co(NO_3)_2{\cdot}9H_2O$ (20)	100	toluene	trace
6	$CoSO_4{\cdot}7H_2O$ (20)	100	toluene	trace
7	$Co(acac)_2$ (20)	100	benzene	39
8	$Co(acac)_2$ (20)	100	DMSO[e]	trace
9	$Co(acac)_2$ (20)	100	anisole	56
10	$Co(acac)_2$ (20)	100	1,4-dioxane	58
11	$Co(acac)_2$ (20)	100	DCE[f]	41
12	$Co(acac)_2$ (20)	100	DME[g]	53
13	$Co(acac)_2$ (10)	100	1,4-dioxane	24
14	$Co(acac)_2$ (30)	100	1,4-dioxane	63
15	$Co(acac)_2$ (30)	110	1,4-dioxane	44
16	$Co(acac)_2$ (30)	130	1,4-dioxane	43
17[c]	$Co(acac)_2$ (30)	100	1,4-dioxane	trace
18[d]	$Co(acac)_2$ (30)	100	1,4-dioxane	66

[a]Reaction conditions: biphenyl-2-amine **1a** (0.5 mol), *tert*-butyl isocyanide **2a** (0.6 mol, 1.2 equiv), cobalt catalyst, and solvent (3 mL) mixed in a 25 mL sealed tube with a magnetic stirrer for 12 h. [b]Yields were determined by GC analysis with biphenyl as the internal standard. [c]The atmosphere was argon. [d]The O_2 balloon was used, and a Schlenk tube was used instead of a sealed tube. [e]DMSO = dimethyl sulfoxide. [f]DCE = 1,2-dichloroethane. [g]DME = ethyleneglycol dimethyl ether.

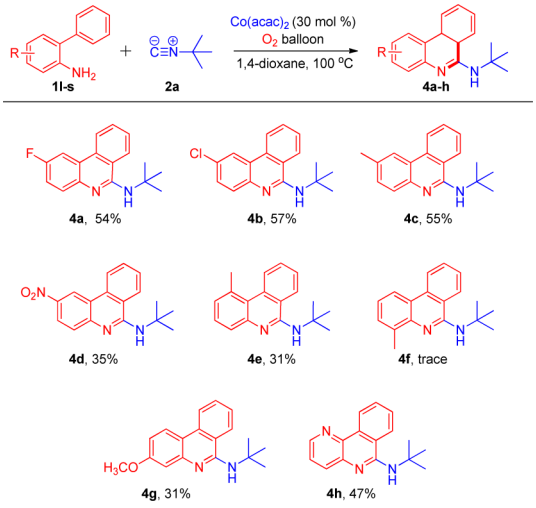
Scheme 2. Cobalt-Catalyzed Insertion Reactions of *tert*-Butyl Isocyanides 2a with Substituted 2-Phenyl Aniline 1a−k[a,b]



[a]Reaction conditions: substituted 2-phenyl aniline **1a−k** (0.5 mol), *tert*-butyl isocyanide **2a** (0.6 mol, 1.2 equiv), $Co(acac)_2$ (30 mol %), and 1,4-dioxane (3 mL) mixed in a Schlenk tube at 100 °C under O_2 balloon conditions. [b] Isolated yields.

dx.doi.org/10.1021/ol500286x | *Org. Lett.* XXXX, XXX, XXX−XXX

Scheme 3. Cobalt-Catalyzed Insertion Reactions of *tert*-Butyl Isocyanides 2a with Substituted 2-Phenyl Aniline 1l–s[a,b]

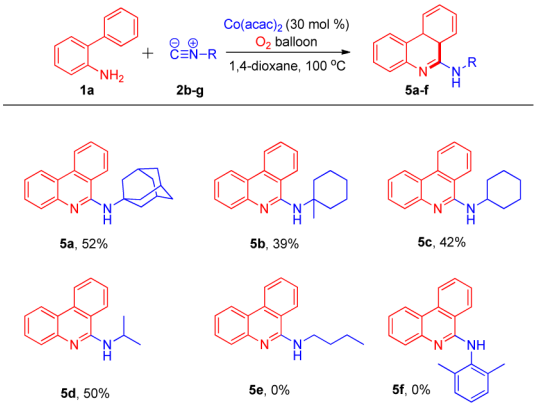


[a]Reaction conditions: substituted 2-phenyl aniline **1l–1s** (0.5 mol), *tert*-butyl isocyanide **2a** (0.6 mol, 1.2 equiv), $Co(acac)_2$ (30 mol %), and 1,4-dioxane (3 mL) mixed in a Schlenk tube at 100 °C under O_2 balloon conditions. [b] Isolated yields.

reaction of 2-phenylpyridin-3-amine **1k** with **2a** under the optimal conditions.

We further studied the reaction of several isocyanides with **1a** under identical conditions. When other secondary or tertiary aliphatic isocyanides **2b–e** were employed, the reactions also proceeded smoothly to give the desired products in moderate yields (39%–52%) (Scheme 4). However, the reactions of primary aliphatic isocyanide *n*-butyl isocyanide **2f** and aromatic isocyanide **2g** failed to give the desired products.

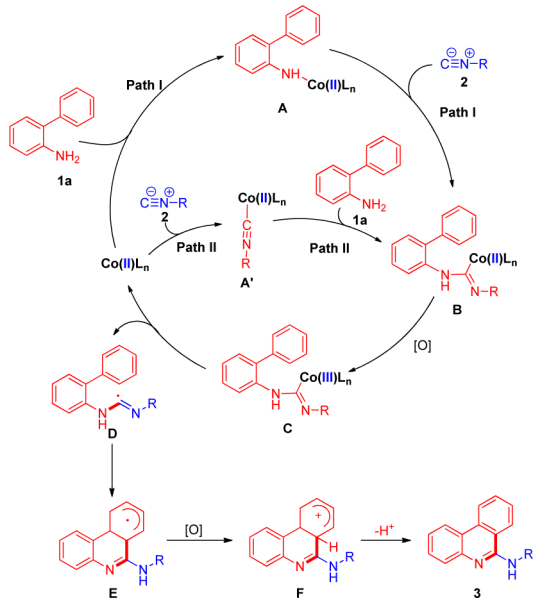
Scheme 4. Cobalt-Catalyzed Insertion Reactions of Substituted Isocyanides 2b–g with Biphenyl-2-amine 1a[a,b]



[a]Reaction conditions: substituted biphenyl-2-amine **1a** (0.5 mol), isocyanide **2b–g** (0.6 mol, 1.2 equiv), $Co(acac)_2$ (30 mol %), and 1,4-dioxane (3 mL) mixed in a Schlenk tube at 100 °C under O_2 balloon conditions. [b] Isolated yields.

Based on the literature reports[11−16] and the above results, we proposed a plausible mechanism via two possible pathways as shown in Scheme 5. Path I consists of a Co(II) salt reacting with **1a** to give cobalt(II) complex **A**.[11] **A** undergoes addition with **2**[12] to provide cobalt(II) carbene complex **B**[13] (Scheme 5, path I). The other possible pathway involves the Co(II) salt

Scheme 5. Proposed Mechanism



reacting with isocyanide **2** to furnish complex **A′**.[14,15] Then, **1a** adds to **A′** to give cobalt(II) carbene complex **B** (Scheme 5, path II). After the oxidation of **B**,[16] cobalt(III) complex **C** is formed, which may be cleaved homolytically to afford the active imidoyl radical **D** and the Co(II) catalyst. After the intramolecular cyclization of **D**, further oxidation, and subsequently deprotonation, the desired phenanthridine is formed.

In conclusion, we have developed a new, simple, and efficient $Co(acac)_2$-catalyzed cascade isocyanides insertion with 2-aryl anilines under an O_2 atmosphere to construct 6-amino phenanthridine derivatives in moderate to good yields via homolytic aromatic substitution (HAS) type C–H functionalization. In view of the important biological properties of phenanthridines, 6-amino substituted phenanthridines have potential biological properties. The mechanism of this reaction is different from the mechanisms of the Pd-catalyzed isocyanide insertion reaction and radical isocyanide insertion reaction, and further mechanism studies are underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and full spectroscopic data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: shunyi@suda.edu.cn.
*E-mail: shunjun@suda.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge the Natural Science Foundation of China (Nos. 21172162, 21372174), the Ph.D. Programs Foundation of Ministry of Education of China (2013201130004), the Young National Natural Science Foundation of China (No. 21202111), the Young Natural

dx.doi.org/10.1021/ol500286x | *Org. Lett.* XXXX, XXX, XXX–XXX

Science Foundation of Jiangsu Province (BK2012174), Key Laboratory of Organic Synthesis of Jiangsu Province (KJS1211), PAPD, and Soochow University for financial support.

REFERENCES

(1) (a) Theobald, R. S.; Schofield, K. *Chem. Rev.* **1950**, *46*, 170. (b) Stevenson, P.; Sones, K. R.; Gicheru, M. M.; Mwangi, E. K. *Acta Trop.* **1995**, *59*, 257. (c) Abdel-Halim, O. B.; Morikawa, T.; Ando, s.; Matsuda, H.; Yoshikawa, M. *J. Nat. Prod.* **2004**, *67*, 1119. (d) Bailly, C.; Arafa, R. K.; Tanious, F. A.; Laine, W.; Tardy, C.; Lansiaux, A.; Colson, P.; Boykin, D. W.; Wilson, W. D. *Biochemistry* **2005**, *44*, 1941. (e) Sripada, L.; Teske, J. A.; Deiters, A. *Org. Biomol. Chem.* **2008**, *6*, 263.

(2) (a) Krzysztof, J.; Sarangan, R.; Jack, R. C.; Irving, W. W. *J. Med. Chem.* **2004**, *47*, 4008. (b) Phillips, S. D.; Castle, R. N. *J. Heterocycl. Chem.* **1981**, *18*, 223. (c) Ilka, k.; Dieter, H.; Matthias, W.; Ulrich, W.; Bernd, C. *J. Med. Chem.* **2005**, *48*, 2772. (d) Park, G. Y.; Wilson, J. J.; Song, Y.; Lippard, S. J. *Proc. Natl. Acad. Sci. U.S.A.* **2012**, *109*, 11987.

(3) (a) Nanni, D.; Pareschi, P.; Rizzoli, C.; Sgarabotto, P.; Tundo, A. *Tetrahedron* **1995**, *51*, 9045. (b) Tobisu, M.; Koh, K.; Furukawa, T.; Chatani, N. *Angew. Chem., Int. Ed.* **2012**, *51*, 11363. (c) Zhang, B.; Mück-Lichtenfeld, C.; Daniliuc, C. G.; Studer, A. *Angew. Chem., Int. Ed.* **2013**, *52*, 10792. (d) Wang, Q.; Dong, X.; Xiao, T.; Zhou, L. *Org. Lett.* **2013**, *15*, 4846. (e) Leifert, D.; Daniliuc, C. G.; Studer, A. *Org. Lett.* **2013**, *15*, 6286. (f) Jiang, H.; Cheng, Y.; Wang, R.; Zheng, M.; Zhang, Y.; Yu, S. *Angew. Chem., Int. Ed.* **2013**, *52*, 13289.

(4) (a) Cheng, Y.; Jiang, H.; Zhang, Y.; Yu, S. *Org. Lett.* **2013**, *15*, 5520. (b) Janin, Y. L.; Croisy, A.; Riou, J.-F.; Bisagni, E. *J. Med. Chem.* **1993**, *36*, 3686. (c) Kock, I.; Heber, D.; Weide, M.; Wolchendorf, U.; Clement, B. *J. Med. Chem.* **2005**, *48*, 2772. (d) Liu, B.; Li, Y.; Jiang, H.; Yin, M.; Huang, H. *Adv. Synth. Catal.* **2012**, *354*, 2288.

(5) For recent selected examples, see: (a) Saluste, C.; Whitby, R.; Furber, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 4156. (b) Komeyama, K.; Sasayama, D.; Kawabata, T.; Takehira, K.; Takaki, K. *Chem. Commun.* **2005**, 634. (c) Tobisu, M.; Kitajima, A.; Yoshioka, S.; Hyodo, I.; Oshita, M.; Chatani, N. *J. Am. Chem. Soc.* **2007**, *129*, 11431. (d) Kuniyasu, H.; Sugoh, K.; Su, M.; Kurosawa, H. *J. Am. Chem. Soc.* **1997**, *119*, 4669. (e) Wang, Y.; Wang, H.; Peng, J.; Zhu, Q. *Org. Lett.* **2011**, *13*, 4604. (f) Zhu, C.; Xie, W.; Falck, J. *Chem.—Eur. J.* **2011**, *17*, 12591. (g) Baelen, G. V.; Kuijer, S.; Sergeyev, S.; Janssen, E.; Maes, U. W.; Ruijter, E.; Orru, R. V. A. *Chem.—Eur. J.* **2011**, *17*, 15039. (h) Vlaar, T.; Ruijter, E.; Znabet, A.; Janssen, E.; Maes, B. U. W.; Orru, R. V. A. *Org. Lett.* **2011**, *13*, 6496. (i) Qiu, G.; He, Y.-H.; Wu, J. *Chem. Commun.* **2012**, *48*, 3836. (j) Vlaar, T.; Cioc, R. C.; Mampuys, P.; Maes, B. U. W.; Orru, R. V. A.; Ruijter, E. *Angew. Chem., Int. Ed.* **2012**, *51*, 13058. (k) Vlaar, T.; Ruijter, E.; Maes, B. U. W.; Orru, R. V. A. *Angew. Chem., Int. Ed.* **2013**, *52*, 7084. (l) Qiu, G.; Liu, G.; Pu, S.; Wu, J. *Chem. Commun.* **2012**, *48*, 2903. (m) Qiu, G.; Chen, C.; Yao, L.; Wu, J. *Adv. Synth. Catal.* **2013**, *355*, 1579. (n) Ryn, I.; Sonoda, N.; Curran, D. P. *Chem. Rev.* **1996**, *96*, 177. (o) Qiu, G.; Ding, Q.; Wu, J. *Chem. Soc. Rev.* **2013**, *42*, 5257. (p) Lang, S. *Chem. Soc. Rev.* **2013**, *42*, 4867.

(6) For recent selected examples of a somophilic isocyanide insertion reaction, see: (a) Currn, D. P.; Liu, H. *J. Am. Chem. Soc.* **1991**, *113*, 2127. (b) Currn, D. P.; Liu, H. *J. Am. Chem. Soc.* **1992**, *114*, 5863. (c) Josien, H.; Ko, S.-B.; Currn, D. P. *Chem.—Eur. J.* **1998**, *4*, 67. (d) Fukuyama, T.; Chen, X.; Peng, G. *J. Am. Chem. Soc.* **1994**, *116*, 3127. (e) Kobayashi, S.; Peng, G.; Fukuyama, T. *Tetrahedron Lett.* **1999**, *40*, 1519. (f) Sumi, S.; Matsumoto, H.; Tokuyama, H.; Fukuyama, T. *Org. Lett.* **2003**, *5*, 1891. (g) Mitamura, T.; Iwata, K.; Ogawa, A. *Org. Lett.* **2009**, *11*, 3422. (h) Mitamura, T.; Ogawa, A. *J. Org. Chem.* **2011**, *76*, 1163. (i) Mitamura, T.; Iwata, K.; Ogawa, A. *J. Org. Chem.* **2011**, *76*, 3880.

(7) For recent selected examples, see: (a) Domling, A. *Chem. Rev.* **2006**, *106*, 17. (b) Zhu, J. H., Bienayme, H., Eds. *Multicomponent Reactions*; Wiley-VCH: Weinheim, 2005. (c) Wang, X.; Wang, S.-Y.; Ji, S.-J. *Org. Lett.* **2013**, *15*, 1954. (d) Zhao, L.-L.; Xu, X.-P.; Wang, S.-Y.; Ji, S.-J. *Chem. Commun.* **2013**, *49*, 2569. (e) Wang, X.; Wang, S.-Y.; Ji, S.-J. *Org. Lett.* **2013**, *15*, 4246. (f) Wang, R.; Xu, X.-P.; Meng, H.; Wang, S.-Y.; Ji, S.-J. *Tetrahedron* **2013**, *69*, 1600. (g) Wang, R.; Wang, S.-Y.; Ji, S.-J. *Tetrahedron* **2013**, *69*, 10836.

(8) (a) Studer, A.; Curran, D. P. *Angew. Chem., Int. Ed.* **2011**, *50*, 5018. (b) Bhakuni, B. S.; Kumar, A.; Balkrishna, S. J.; Sheikh, J. A.; Konor, S.; Kumar, S. *Org. Lett.* **2012**, *14*, 2838. (c) Chen, W.-C.; Hsu, Y.-C.; Shih, W.-C.; Ong, T.-G. *Chem. Commun.* **2012**, *48*, 6702. (d) Beaulieu, L.-P. B.; Roman, R. S.; Vallee, F.; Charette, A. B. *Chem. Commun.* **2012**, *48*, 8249.

(9) Zhu, T.-H.; Wang, S.-Y.; Wang, G.-N.; Ji, S.-J. *Chem.—Eur. J.* **2013**, *19*, 5850.

(10) (a) Gu, Z.-Y.; Zhu, T.-H.; Cao, J.-J.; Wang, S.-Y.; Ji, S.-J. *ACS Catal.* **2014**, *4*, 49. (b) Zhu, T.-H.; Zhu, X.; Xu, X.-P.; Ji, S.-J. *Tetrahedron Lett.* **2011**, *52*, 2771.

(11) (a) Schaefer, W. P. *Inorg. Chem.* **1968**, *7*, 725. (b) Saha, P.; Ali, M. A.; Ghosh, P.; Punniyamurthy, T. *Org. Biomol. Chem.* **2010**, *8*, 5692.

(12) (a) Periasamy, M. P.; Walborsky, H. M. *J. Org. Chem.* **1974**, *39*, 611. (b) Ito, Y.; Imai, H.; Matsuura, T.; Saegusa, T. *Tetrahedron Lett.* **1984**, *25*, 3091.

(13) (a) Liu, B.; Xia, Q.-Q.; Chen, W.-Z. *Angew. Chem.* **2009**, *121*, 5621. (b) Silvia, D.-G.; Nicolas, M.; Steven, P. N. *Chem. Rev.* **2009**, *109*, 3612. (c) Macarena, P.; Jose, A. M.; Eduardo, P. *Chem. Rev.* **2009**, *109*, 3677. (d) Simms, R. W.; Drewitt, M. J.; Baird, M. C. *Organometallics* **2002**, *21*, 2958. (e) Cowley, R. E.; Bontchev, R. P.; Duesler, E. N.; Smith, J. M. *Inorg. Chem.* **2006**, *45*, 9771. (f) Danopoulos, A. A.; Wright, J. A.; Motherwell, W. B.; Ellwood, S. *Organometallics* **2004**, *23*, 4807.

(14) (a) Hashmi, K. S. A.; Riedel, D.; Rudolph, M.; Rominger, F.; Oeser, T. *Chem.—Eur. J.* **2012**, *18*, 3827. (b) Hashmi, K. S. A.; Lothschütz, C.; Böhling, C.; Rominger, F. *Organometallics* **2011**, *30*, 2411. (c) Hashmi, K. S. A.; Lothschütz, C.; Böhling, C.; Hengst, T.; Hubbert, C.; Rominger, F. *Adv. Synth. Catal.* **2010**, *352*, 3001.

(15) (a) Cowley, R. E.; Golder, M. T.; Eckert, N. A.; Al-Afyouni, M. H.; Holland, P. L. *Organometallics* **2013**, *32*, 5289. (b) Odabachian, Y.; Tong, S.; Wang, Q.; Wang, M.-X.; Zhu, J. *Angew. Chem., Int. Ed.* **2013**, *52*, 10878. (c) Jones, W. D.; Kosar, W. P. *J. Am. Chem. Soc.* **1986**, *108*, 5640. (d) Ruiz, J.; Perandones, B. F.; Garcia, G.; Mosquera, M. E. G. *Organometallics* **2007**, *26*, 5687. (e) Ruiz, J.; Perandones, B. F. *Organometallics* **2009**, *28*, 830. (f) Ruiz, J.; Garcia, G.; Mosquera, M. E. G.; Perandones, B. F.; Gonzalo, M. P.; Vivanco, M. *J. Am. Chem. Soc.* **2005**, *127*, 8584.

(16) (a) Bjerrum, J.; McReynolds, J. P. *Inorg. Synth.* **1946**, *2*, 216. (b) Lindholm, R. D.; Bause, D. E. *Inorg. Synth.* **1978**, *18*, 67. (c) Fremy, M. E. *Annales de Chimie et de Physique* **1852**, *35*, 257.

dx.doi.org/10.1021/ol500286x | *Org. Lett.* XXXX, XXX, XXX−XXX