Published in final edited form as:
Angew Chem Int Ed Engl. 2014 December 15; 53(51): 14191–14195. doi:10.1002/anie.201408335.

Rhodium-Catalyzed N–H Insertion of Pyridyl Carbenes Derived from Pyridotriazoles: A General and Efficient Approach to 2-Picolylamines and Imidazo[1,2-*a*]pyridines

Yi Shi, **Anton V. Gulevich**, and **Vladimir Gevorgyan***
Department of Chemistry, University of Illinois at Chicago 845 W Taylor St., Room 4500, Chicago, IL 60607 (USA)

Abstract

A general and efficient N–H insertion reaction of rhodium pyridyl carbenes derived from pyridotriazoles was developed. Various N–H containing compounds, including amides, anilines, enamine and aliphatic amines, smoothly underwent the N–H insertion reaction to afford 2-picolylamine derivatives. The developed transformation was further utilized in a facile one-pot synthesis of imidazo[1,2-*a*]pyridines.

Keywords

N–H insertion; pyridotriazole; rhodium carbene; picolylamine; imidazopyridine; transannulation reaction

Transition-metal-catalyzed denitrogenative transannulation of pyridotriazoles[1] is a powerful method for synthesis of nitrogencontaining heterocycles.[2–4] As a convenient progenitor of metal carbene species, pyridotriazole **1** exists in the equilibrium with diazo-form **A**, which can be trapped with Rh(II) to form the reactive pyridyl carbene intermediate **B** (Scheme 1, eq. 1). In 2007, our group reported the transannulation reaction of pyridotriazoles based on the reaction of intermediate **B** with nitriles. It was shown that Cl, Br or OMe substituents at C-7 position (AG, activating group), as well as electron-withdrawing (EWG) groups at C-3 position, were requisite for efficient formation of the imidazo[1,2-*a*]pyridines (eq. 1).[1a] Naturally, we were interested in expanding the scope of imidazo[1,2-*a*]pyridines which can be accessed via transannulation reaction of pyridotriazoles. Herein, we report a general rhodiumcatalyzed N–H insertion reaction of pyridylcarbenes **B** derived from pyridotriazoles **1** to afford valuable picolylamine derivatives **3** (eq. 2);[5] and their application in a one-pot synthesis of imidazo[1,2-*a*]pyridines **4** (eq. 3).[6] This new method toward imidazo[1,2-*a*]pyridines features much broader scope, where the presence of AG and EWG in starting pyridotriazole **1** no longer required.

In continuation of our studies on application of diazocompounds for the synthesis of nitrogen-containing heterocycles,[7] we investigated the reaction of pyridotriazoles with

Fax: (+1) 312-355-0836, vlad@uic.edu, Homepage: http://www.chem.uic.edu/vggroup.

primary amides as a potential route to imidazo[1,2-*a*]pyridines (*vide infra*). 7-Cl-substituted triazole **1a**, which was proved to be an effective carbene precursor,[1] was tested in the Rh-catalyzed N–H insertion reaction first.[8] Indeed, the reaction of **1a** with $BocNH_2$ in the presence of $Rh_2(esp)_2$ catalyst at room temperature produced the corresponding piclolyl amine **3aa** in 74% yield (Table 1, entry 1).[9] Attempts to employ 7-unsubstituted pyridotriazole **1b** under these reaction conditions failed. However, we were pleased to find that at 120 °C it underwent insertion reaction to furnish picolylamine **3ab** in 90% yield (Entry 2).[10]

Next, we examined the scope of this N−H insertion reaction (Table 1). Thus, alkyl carbamates, such as *t*-$BuOCONH_2$, $EtOCONH_2$, and $BnOCONH_2$ produced picolyl amines **3ab–3ad** in high yields (entries 2–4). The reaction also worked efficiently with alkyl and aryl amides (entries 5–7), as well as with alkenyl amide (entry 8). Notably, cyano-group and alkenyl moiety, which normally react with metal carbenes, stayed intact under these reaction conditions (entries 6,8). Moreover, we found that phenyl urea and sulfonamide could also participate in this transformation to produce insertion products **3ai** and **3aj** (entries 9,10). Secondary amides, such as oxazolidin-2-one (entry 11) and 3(2-*H*)-pyridazinone (entry 12), were also competent reaction partners. Notably, the reaction also efficiently proceeded with pyridotriazoles containing different substituents at the C-3 poisition. Thus, 3-aryl pyridotriazoles (entries 13–16) and even 3-methyl pyridotriazole (entry 17) reacted smoothly to produce the desired N–H insertion products. In addition, 4-methyl pyridotriazole (entry 18), *N*-fused quinolinotriazole (entry 19) and benzoxazolotriazole (entry 20) also underwent an efficient N–H insertion reaction to afford the corresponding amides.

After developing the N–H insertion reaction with various amides, we turned our attention to more challenging aromatic and aliphatic amines, which, due to their high basicity, may potentially deactivate Rh(II) catalyst. To our delight, reasonable to good yields in the reaction of **1b** with anilines were achieved upon raising catalyst loading to 3 mol % (Table 2, entries 1–9). Thus, anilines bearing functional groups, such as halogen (entries 3 and 8), CF_3 (entries 4 and 7), and CO_2Me (entry 5), efficiently underwent the reaction with pyridotriazole **1b** to produce the insertion products. Moreover, sterically hindered 2,6-dichloro, and 2,6-diisopropylaniline reacted smoothly to give the corresponding insertion products in reasonable yield (entries 8,9). In addition, enamine also underwent the N–H insertion reaction to form the corresponding product **3bj** (entry 10). Among aliphatic amines, α-CF_3-substituted alkyl amines could undergo N–H insertion reaction, which was demonstrated by the reactions of **1b** with 2,2,2-trifluoro-1-phenylethane-1-amine (entry 11). Notably, the successful N–H insertion reaction with CF_3-amino acid (entry 12) opens access to fluorinated opine derivatives (i.e. **3bl**).[11]

Along the line of our studies on the development of new transformations toward heterocyclic molecules, we envisioned that the obtained picolylamides **3** could be cyclized into imidazopyridines **4** via a nucleophilic attack of the pyridine nitrogen at a suitably activated amide group (Table 3).[12] Accordingly, we developed a formal one-pot transannulation reaction of pyridotriazoles with primary amides that proceeds via the Rh-catalyzed N–H insertion reaction followed by a cyclization into imidazo[1,2-*a*]pyridines

(Table 3). Noteworthy, this transannulation reaction of pyridotriazoles **1** with amides has much broader scope compared to the previously developed transannulation reaction of **1** with nitriles (Scheme 1, eq. 1). Thus, the activating group AG is not necessary for the successful reaction, as well as substituent at C-3 position is notlimited to an electron-withdrawing group. Generally, the developed transannulation reaction is allowed for an efficient synthesis of imidazo[1,2-*a*]pyridines containing aryl, alkenyl and alkyl substituents (entries 1–6).

In order to understand the superior efficiency of the newly developed reaction of pyridotriazoles with amines over the previously reported reaction with nitriles, we performed reactions of pyridotriazoles **1a,b** with $BocNH_2$ and PhCN in the presence of different rhodium catalysts (Scheme 2). Thus, it was found that $Rh_2(esp)_2$, indeed, is a superior catalyst over the previously used $Rh_2(OAc)_2$ for reactions of pyridotriazole, both with amides (eq. 1) and nitriles (eq. 2). It was also verified that amides showed higher reactivity towards Rh-pyridocarbene (*i.e*. **B**, Scheme 1) over nitriles, since even $Rh_2(esp)_2$ catalyst was not efficient for transannulation of unactivated pyridotriazoles **1b**,**c**,**e** with nitriles (Scheme 2, eq. 3). It is believed that the N-H insertion reaction of pyridotriazoles, analogously to that of phenyldiazoacetates, proceeds via an ylide mechanism.[13,14] However, it requires higher temperatures to produce sufficient amounts of a reactive diazo-form (*i.e*. **B**, Scheme 1).[15] Overall, we believe that a superior efficiency of the newly developed reaction of pyridotriazoles with amines and amides over the previously reported reaction with nitriles is due to a combination of an increased potency of the Rh-catalyst and a higher reactivity of amines and amides over that of nitriles.

In conclusion, we have developed a general and efficient Rhcatalyzed reaction of pyridotriazoles with amides and amines producing valuable picolylamine derivatives. The subsequent cyclization provides an expeditious access to various disubstituted imidazopyridines in a one-pot manner. The developed protocol is allowed for the synthesis of polysubstituted imidazopyridines, which were not accessible via previously reported transannulation reaction of pyridotriazoles with nitriles. Further studies on the unique reactivity of pyridotriazoles are currently underway in our lab.

Experimental Section

An oven-dried 3.0 mL V-vial equipped with a stirring bar was charged with $Rh_2(esp)_2$ (1–3 mol %), pyridotriazole (0.2 mmol), amide or amine (1.5 equiv.) and DCE (2 mL) under N_2 atmosphere. The reaction vessel was capped with Mininert syringe valve and the reaction mixture was stirred at 120 °C for 3 hours. Upon completion, the reaction mixture was cooled to room temperature, concentrated under reduced pressure, and the crude product was purified by column chromatography to afford the corresponding N–H insertion products.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

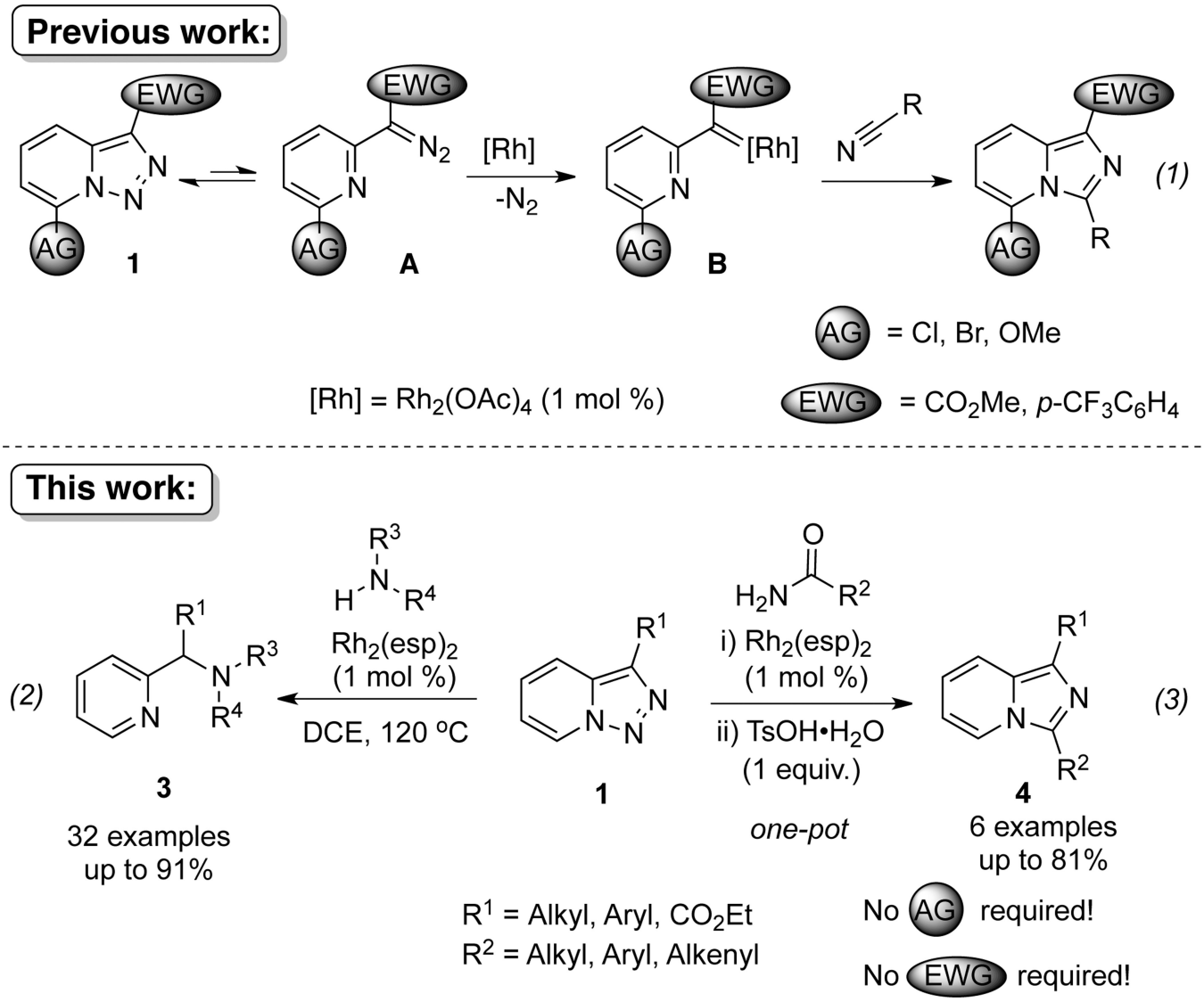
The support of the National Institutes of Health (GM 64444) and National Science Foundation (CHE-1362541) is gratefully acknowledged.

References

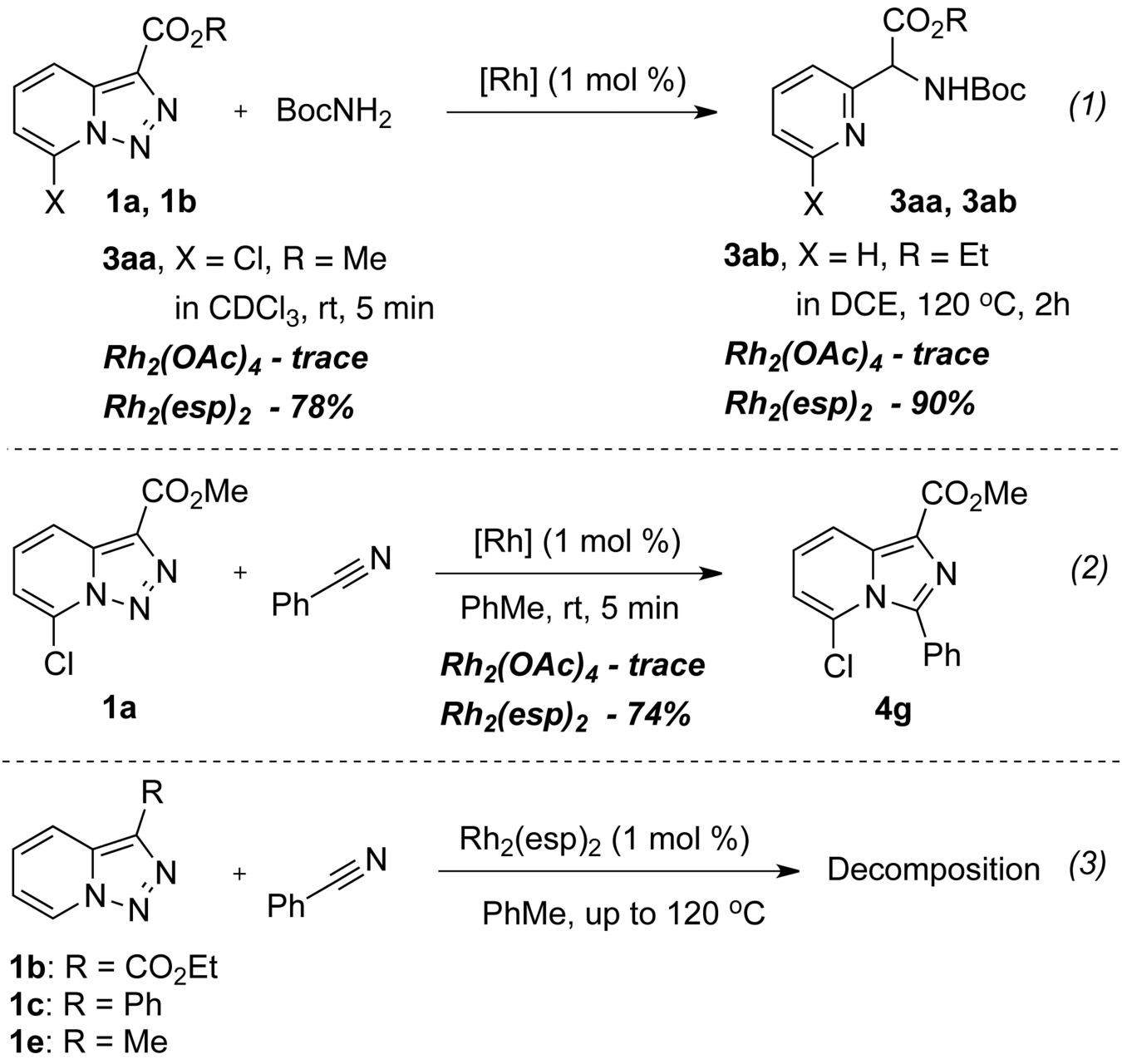
1. Chuprakov S, Hwang F, Gevorgyan V. Angew. Chem. 2007; 119:4841–4843. *Angew. Chem. Int. Ed.***2007**, *46*, 4757–4759; Chuprakov S, Gevorgyan V. Org. Lett. 2007; 9:4463–4466. [PubMed: 17892296] For review, see: Chattopadhyay B, Gevorgyan V. Angew. Chem. 2012; 124:886–896. *Angew. Chem. Int. Ed.***2012**, *51*, 862–872.
2. For reviews on reactions of metallocarbenes derived from *N*-sulfonyl 1,2,3-triazoles, see: Davies HML, Alford JS. Chem. Soc. Rev. 2014; 43:5151–5162. [PubMed: 24802192] Gulevich AV, Gevorgyan V. Angew. Chem. 2013; 125:1411–1413. *Angew. Chem. Int. Ed.***2013**, *52*, 1371–1373;
3. For transannulation reactions of *N*-sulfonyl triazoles, see: Horneff T, Chuprakov S, Chernyak N, Gevorgyan V, Fokin VV. J. Am. Chem. Soc. 2008; 130:14972–14974. [PubMed: 18855475] Miura T, Yamauchi M, Murakami M. Chem. Commun. 2009:1470–1471. Chattopadhyay B, Gevorgyan V. Org. Lett. 2011; 13:3746–3749. [PubMed: 21692488] Parr BT, Green SA, Davies HML. J. Am. Chem. Soc. 2013; 135:4716–4718. [PubMed: 23477809] Spangler JE, Davies HML. J. Am. Chem. Soc. 2013; 135:6802–6805. [PubMed: 23607705] Alford JS, Spangler JE, Davies HML. J. Am. Chem. Soc. 2013; 135:11712–11715. [PubMed: 23915171] Parr BT, Davies HML. Angew. Chem. 2013; 125:10228–10231. *Angew. Chem. Int. Ed.***2013**, *52*, 10044–10047; Zibinsky M, Fokin VV. Angew. Chem. 2013; 125:1547–1550. *Angew. Chem. Int. Ed.***2013**, *52*, 1507–1510; Chuprakov S, Kwok SW, Fokin VV. J. Am. Chem. Soc. 2013; 135:4652–4655. [PubMed: 23477345] Miura T, Tanaka T, Hiraga K, Stewart SG, Murakami M. J. Am. Chem. Soc. 2013; 135:13652–13655. [PubMed: 23988194] Miura T, Hiraga K, Biyajima T, Nakamuro T, Murakami M. Org. Lett. 2013; 15:3298–3301. [PubMed: 23777199] Schultz EE, Sarpong R. J. Am. Chem. Soc. 2013; 135:4696–4699. [PubMed: 23477843] Shi Y, Gevorgyan V. Org. Lett. 2013; 15:5394–5396. [PubMed: 24093728] Miura T, Funakoshi Y, Murakami M. J. Am. Chem. Soc. 2014; 136:2272–2275. [PubMed: 24437578] Kim C, Park S, Eom D, Seo B, Lee PH. Org. Lett. 2014; 16:1900–1903. [PubMed: 24660875] Yang J, Zhu C, Tang X, Shi M. Angew. Chem. 2014; 126:5242–5246. *Angew. Chem. Int. Ed.***2014**, *53*, 5142–5146; Shang H, Wang Y, Tian Y, Feng J, Tang Y. Angew. Chem. 2014; 126:5768–5772. *Angew. Chem. Int. Ed.***2014**, *53*, 5662–5666; Chen K, Zhu Z-Z, Zhang Y-S, Tang X-Y, Shi M. Angew. Chem. 2014; 126:6763–6767. *Angew. Chem. Int. Ed.***2014**, *53*, 6645–6649; Rajagopal B, Chou C-H, Chung C-C, Lin P-C. Org. Lett. 2014; 16:3752–3755. [PubMed: 24968224] Ran R-Q, He J, Xiu SD, Wang K-B, Li C-Y. Org. Lett. 2014; 16:3704–3707. [PubMed: 25004242] Medina F, Besnard C, Lacour J. Org. Lett. 2014; 16:3232–3235. [PubMed: 24885761]
4. For other reactions of *N*-sulfonyl triazoles, see: Grimster N, Zhang L, Fokin VV. J. Am. Chem. Soc. 2010; 132:2510–2511. [PubMed: 20131915] Chuprakov S, Kwok SW, Zhang L, Lercher L, Fokin VV. J. Am. Chem. Soc. 2009; 131:18034–18035. [PubMed: 19928917] Selander N, Worrell BT, Chuprakov S, Velaparthi S, Fokin VV. J. Am. Chem. Soc. 2012; 134:14670–14673. [PubMed: 22913576] Chuprakov S, Worrell BT, Selander N, Sit RK, Fokin VV. J. Am. Chem. Soc. 2014; 136:195–202. [PubMed: 24295389] Chuprakov S, Malik JA, Zibinsky M, Fokin VV. J. Am. Chem. Soc. 2011; 133:10352–10355. [PubMed: 21619004] Alford JS, Davies HML. Org. Lett. 2012; 14:6020–6023. [PubMed: 23153274] Muira T, Biyajima T, Fujii T, Murakami M. J. Am. Chem. Soc. 2012; 134:194–196. [PubMed: 22129424] Miura T, Tanaka T, Biyajima T, Yada A, Murakami M. Angew. Chem. 2013; 125:3975–3978. *Angew. Chem. Int. Ed.***2013**, *52*, 3883–3886. Miura T, Funakoshi Y, Morimoto M, Biyajima T, Murakami M. J. Am. Chem. Soc. 2012; 134:17440–17443. [PubMed: 23043352] Selander N, Worrell BT, Fokin VV. Angew. Chem. 2012; 124:13231–13234. *Angew. Chem. Int. Ed.***2012**, *51*, 13054–13057; Boyer A. Org. Lett. 2014; 16:1660–1663. [PubMed: 24575756] Jung DJ, Jeon HJ, Kim JH, Kim Y, Lee S. Org. Lett. 2014; 16:2208–2211. [PubMed: 24708029] Yadagiri D, Anbarasan P. Org. Lett. 2014; 16:2510–1513. [PubMed: 24724575] Miura T, Funakoshi Y, Tanaka T, Murakami M. Org. Lett. 2014; 16:2760–2763. [PubMed: 24773098] Miura T, Nakamuro T, Hiraga K, Murakami M. Chem. Commun. 2014; 50:10474–10477.
5. For selected reports on 2-pycolylamine-containing bioactive molecules, see: Tsuboi K, Bachovchin DA, Speers AE, Spicer TP, Fernandez-Vega V, Hodder P, Rosen H, Cravatt BF. J. Am. Soc. Chem.

2011; 133:16605–16616. Wood MR, Schirripa KM, Kim JJ, Kuduk SD, Chang RK, DiMarco CN, DiPardo RM, Wan B-L, Murphy KL, Ransom RW, Chang RSL, Holahan MA, Cook JJ, Lemaire W, Mosser SD, Bednar RA, Tang C, Prueksaritanont T, Wallace AA, Mei Q, Yu J, Bohn DL, Clayton FC, Adarayn ED, Sitko GR, Leonard YM, Freidinger RM, Pettibone DJ, Bock MG. Bioorg. Med. Chem. Lett. 2008:716–720. [PubMed: 18061443]

6. For reports on the biological activity of imidazopyridines, see: Kim D, Wang L, Hale JJ, Lynch CL, Budhu RJ, MacCoss M, Mills SG, Malkowitz L, Gould SL, DeMartino JA, Springer MS, Hazuda D, Miller M, Kessler J, Hrin RC, Carver G, Carella A, Henry K, Lineberger J, Schleif WA, Emini EA. Bioorg. Med. Chem. Lett. 2005; 15:2129–2134. [PubMed: 15808483] Nakahara S, Kubo A, Mikami Y, Ito J. Heterocycles. 2006; 68:515–520. Kamal A, Ramakrishna G, Ramaiah MJ, Viswanath A, Bao AVS, Bagul C, Mukhopadyay DVL, Pushpavalli SNC, Pal-Bhadra M. Bioorg. Med. Chem. 2013; 4:697–703.
7. a) Gulevich AV, Helan V, Wink DJ, Gevorgyan V. Org. Lett. 2013; 15:956–959. [PubMed: 23373731] b) Kuznetsov A, Gulevich AV, Wink DJ, Gevorgyan V. Angew. Chem. 2014; 126:9167–9171.Angew. Chem. Int. Ed. 2014; 53:9021–9025.
8. For a 1,3- N−H insertion reaction of iminocarbenes with non-basic N−H groups, see: Chuprakov S, Worrell BT, Selander N, Sit RK, Fokin VV. J. Am. Chem. Soc. 2014; 136:195–202. [PubMed: 24295389]
9. Other rhodium catalysts, such as $Rh_2(OAc)_4$ and $Rh_2(Oct)_4$, are also capable of catalyzing the reaction of pyridotriazole **1a** with $BocNH_2$.
10. The reaction of pyridotriazole **1b** with $BocNH_2$ in the presence of other rhodium catalysts, such as $Rh_2(OAc)_4$ and $Rh_2(Oct)_4$, did not give any product.
11. For selected reports on bioactive iminodicarboxylic acids and opines, see: Moore LW, Chilton WS, Canfield ML. Appl. Environ. Microbiol. 1997; 63:201–207. [PubMed: 16535484] Chilton WS, Petit A, Chilton M-D, Dessaux Y. Phytochemistry. 2001; 58:137–142. [PubMed: 11524123]
12. Kovtun YP, Prostota YA. Chem. Heterocycl. Compd. 2000; 36:557–559.
13. For selected reviews on the Rh-catalyzed N-H insertion reactions of diazocompounds, see: Gillingham D, Fei N. Chem. Soc. Rev. 2013; 42:4918–4931. [PubMed: 23407887] Zhang Z, Wang J. Tetrahedron. 2008; 64:6577–6605. Doyle MP, McKervey MA, Ye T. Modern Catalytic Methods for Organic Synthesis with Diazo Compounds: From Cyclopropanes to Ylides. 1998New YorkWiley
14. Analogously to pyridotriazole **1a**, phenyldiazoacetate quantitatively reacts with $BocNH_2$ in the presence of $Rh_2(esp)_2$ catalyst at room temperature.
15. Test experiments indicated no N-H insertion reaction of **1b** with $BocNH_2$ and $PhNH_2$ occurred under thermal conditions in the absence of Rh catalyst



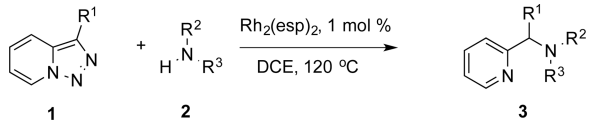
Scheme 1.
Transannulation reactions of pyridotriazoles.



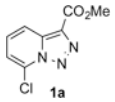
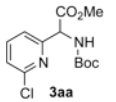
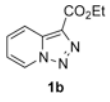
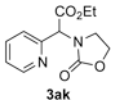
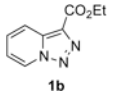
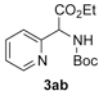
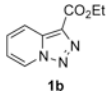
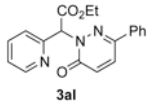
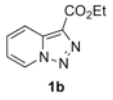
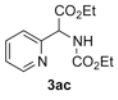
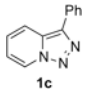
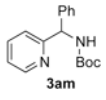
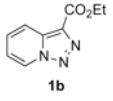
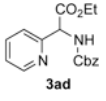
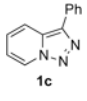
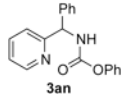
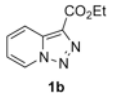
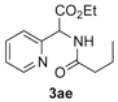
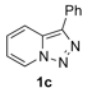
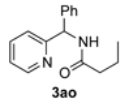
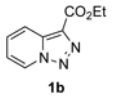
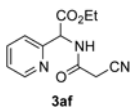
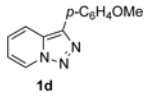
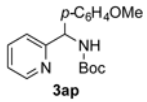
Scheme 2.
Reactions of pyridotriazoles with amides and nitriles.

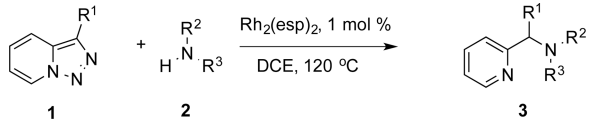
Table 1

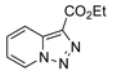
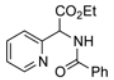
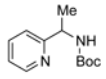
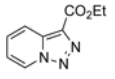
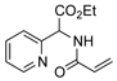
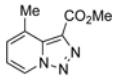
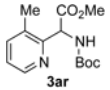
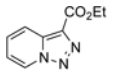
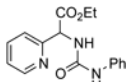
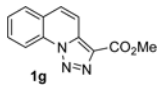
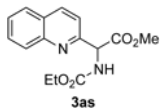
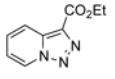
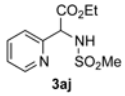
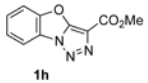
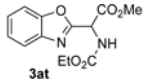
Substrate Scope for the Rh(II)-Catalyzed Reaction of Pyridotriazoles with Amides.[a,b]



1 2 3

Entry	Triazole 1	Product 3	Yield/%	Entry	Triazole 1	Product 3	Yield/%
1	 1a	 3aa	74[c]	11	 1b	 3ak	66
2	 1b	 3ab	90	12	 1b	 3al	75
3	 1b	 3ac	91	13	 1c	 3am	89
4	 1b	 3ad	65	14	 1c	 3an	75
5	 1b	 3ae	85	15	 1c	 3ao	81
6	 1b	 3af	87	16	 1d	 3ap	77



Entry	Triazole 1	Product 3	Yield/%	Entry	Triazole 1	Product 3	Yield/%
7	 1b	 3ag	76	17	 1e	 3aq	88
8	 1b	 3ah	85	18	 1f	 3ar	66
9	 1b	 3ai	75	19	 1g	 3as	63
10	 1b	 3aj	68[d]	20	 1h	 3at	91

[a] Conditions: triazole **1** (0.20 mmol), N–H compounds **2** (1.5 equiv.), and $Rh_2(esp)_2$ (1.0 mol %) were heated in 2 ml of dry DCE at 120 °C until completion.

[b] Isolated yields.

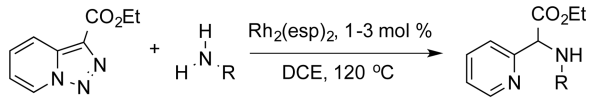
[c] Performed at room temperature.

[d] 3.0 mol % $Rh_2(esp)_2$.

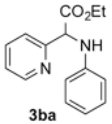
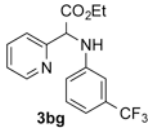
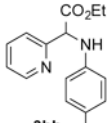
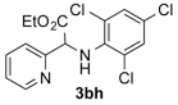
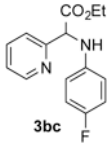
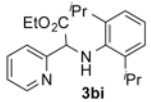
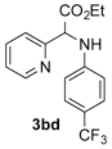
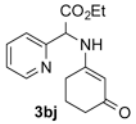
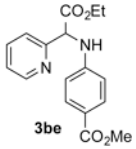
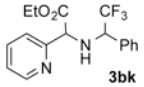
Angew Chem Int Ed Engl. Author manuscript; available in PMC 2015 December 15.

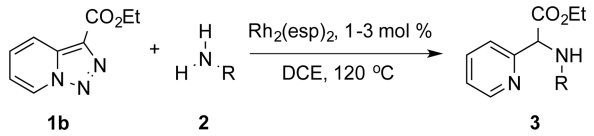
Table 2

Substrate Scope for the Rh(II)-Catalyzed Reaction of Pyridotriazoles with Anilines and Aliphatic Amines.[a,b]

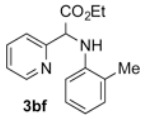
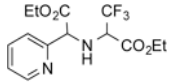


1b 2 3

Entry	Product	Yield, %	Entry	Product	Yield, %
1	 3ba	88	7	 3bg	71
2	 3bb	63	8	 3bh	90
3	 3bc	80	9	 3bi	47
4	 3bd	86	10	 3bj	91[c]
5	 3be	72	11	 3bk	87



1b **2** **3**

Entry	Product	Yield, %	Entry	Product	Yield, %
6	 **3bf**	76	12	 **3bl**	82

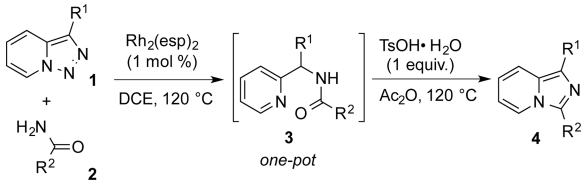
[a] Conditions: triazole **1** (0.20 mmol), N–H compounds **2** (1.5 equiv.), and $Rh_2(esp)_2$ (3.0 mol %) were heated in 2 ml of dry DCE at 120 °C until completion.

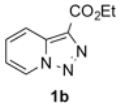
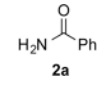
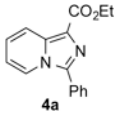
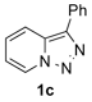
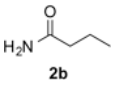
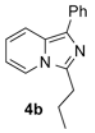
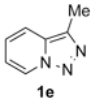
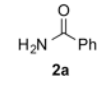
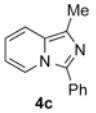
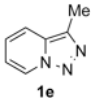
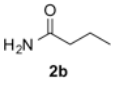
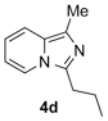
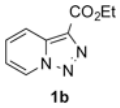
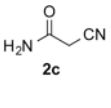
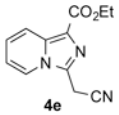
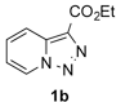
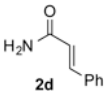
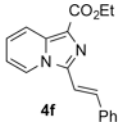
[b] Isolated yields.

[c] 1.0 mol % of $Rh_2(esp)_2$.

Table 3

One-Pot Synthesis of Imidazo[1,2-*a*]pyridines via N–H insertion/Cyclization Process. [*a*,*b*]



Entry	Triazole 1	Amide 2	Product 4	Yield/%
1	 **1b**	 **2a**	 **4a**	70
2	 **1c**	 **2b**	 **4b**	77
3	 **1e**	 **2a**	 **4c**	73
4	 **1e**	 **2b**	 **4d**	81
5	 **1b**	 **2c**	 **4e**	58
6	 **1b**	 **2d**	 **4f**	78

*[a]*Conditions: triazole **1** (0.20 mmol), amides **2** (1.5 equiv.), and $Rh_2(esp)_2$ (1.0 mol %) were heated in 2 ml of dry DCE at 120 °C until completion. Then TsOH•H_2O (1.0 equiv.) and Ac_2O (0.2 ml) were added and the reaction mixture was heated at 120 °C.

*[b]*Isolated yields.