Advanced Synthesis & Catalysis

DOI: 10.1002/adsc.201500792

Rhodium(II)-Catalyzed Regioselective Carbenoid Insertion Reaction of Simple Indoles with *N*-Sulfonyltriazoles: A Rapid Access to Tryptamine Vinylogues

Jiapian Huang,[a] Yi Yang,[a] and Zhiyuan Chen[a,*]

[a] Key Laboratory of Functional Small Organic Molecules, Ministry of Education, and College of Chemistry & Chemical Engineering, Jiangxi Normal University, Nanchang, Jiangxi 330022, People's Republic of China
E-mail: zchen@jxnu.edu.cn

Received: August 23, 2015; Revised: October 28, 2015; Published online: December 9, 2015

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201500792.

Abstract: A synthetically useful 1,3-insertion reaction of a rhodium-carbenoid into the C(sp^2)–H bond of simple indole is disclosed, which produces structurally divergent 2-indolylenamides in good to excellent yields and decent chemo- and regioselectivities. The obtained tryptamine vinylogues can be transformed into biologically important tryptamine derivatives or 3,3′-biindoles with ease.

Keywords: carbenoid insertion reaction; indoles; *N*-sulfonyltriazoles; rhodium catalysis; tryptamine

Tryptamine is a monoamine alkaloid that is formed in plants, fungi, microbes, and amphibian tissues, and displays agonist action at multiple receptors, including non-selective serotonin receptors,[1a,b] 5HT2a-1a-2c receptors[1c] and ion channels.[1d] The tryptamine structure as a potent template has been found in many psychoactive compounds, such as serotonin, sumatriptan, amphetamine, psilocybin, bufotenine, and so forth (Figure 1).[2] Therefore, it is not surprising that the development of flexible procedures for the selective generation of tryptamine derivatives from easily accessible starting materials is of high interest.

The synthetic transformations of carbenoids derived from metal-catalyzed diazo decomposition have undergone a renaissance in the past few decades. Up to now, remarkable advancements have been made in the exploitation of the chemo- and regioselective intramolecular carbenoid insertion catalyzed by various transition metals such as Rh,[3] Pd,[4] Ni,[5] and Cu,[6] into simple arene C–H bonds.[7] For the intermolecular carbenoid insertion reaction, studies revealed that electron-rich arenes are very susceptible to the direct alkylation by carbenes. This was demonstrated by means of acceptor and acceptor/acceptor carbenes in the 1970s,[8] and then for donor/acceptor carbenes by Davies in the 1990s.[7a,9] Recently, intermolecular asymmetric insertion reactions of metal carbenoids into X–H (X = C,[10a] O,[10b–d] and B[10e]), and also C–C[10f] σ-bonds assisted by various chiral ligands have been successfully developed. Hu has exploited such reactions to initiate cascade sequences.[11] Also this chemistry has been used as key steps in the total synthesis of dictyodendrins A and F by Itami and Davies.[12]

Employment of *N*-sulfonyl-1,2,3-triazoles as a source of the metalla-carbenoid in Rh-catalyzed denitrogenative conditions has received considerable attention recently.[13] The *in-situ* generated electrophilic α-imino rhodium carbene species can serve as a versatile building block to construct various aza-heterocyclic molecules.[14] In 2012, the group of Fokin developed a Rh-catalyzed α-imino carbene insertion reaction of arylboronic acids as nucleophile with *N*-sulfonyl-1,2,3-triazoles, which represents a good example of the metal-catalyzed direct arylation of simple arenes using carbenoid insertion strategies.[15] Davies and co-workers disclosed an enantioselective synthesis

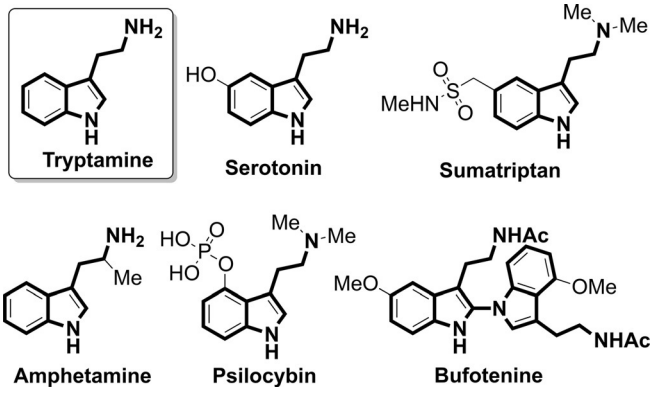


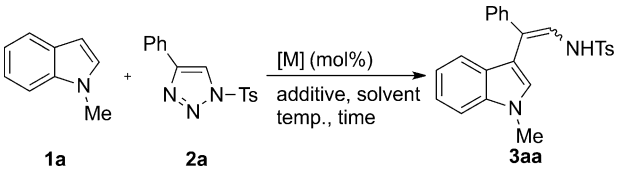
Figure 1. Tryptamine and its valuable derivatives.

of pyrroloindolines *via* Rh(II)-tetracarboxylate catalyzed formal [3+2] cycloaddition reaction of C-3 substituted indoles with triazole carbenoid precursors.[16] Anbarasan reported the carbenoid insertion and arylation reaction of α-imino rhodium carbenoids with *N*,*N*-dialkylamines.[17] Most recently, Lee and coworkers developed the Rh-catalyzed direct arylation of azulenes and alkoxyarylation reaction of aryl ethers with triazoles.[18] These diversity-oriented approaches displayed impressive flexibility with respect to variations of the aromatic substrates and triazoles, and the chemo- and regioselective functionalization of simple arenes deserve noticeable attention.

As part of our continuing interest toward the discovery of natural product-like alkaloids or carbocycles,[19] we have recently developed a Cu(I)-catalyzed tandem reaction of terminal alkynes, sulfonyl azides, and nitroolefins, which generates 2-amino-3-(2-nitroethyl)indoles as potential HCT-116 inhibitors with high efficiency.[19a] Keeping the biological importance of the 2-indolylethanamine protocols in mind, we herein present a novel Rh-catalyzed carbenoid insertion reaction of simple indoles with *N*-sulfonyl-1,2,3-triazoles.[20] The current reaction could serve as a rapid access to substituted 2-indolylethanamine vinylogues, which could be easily transformed into tryptamine derivatives under hydrogenative conditions.

We chose *N*-methylindole (**1a**) as a nucleophile and 4-phenyl-1-tosyl-1*H*-1,2,3-triazole (**2a**) as a carbenoid source in the presence of dirhodium tetracarboxylate, $Rh_2(OAc)_4$, to study the reaction (Table 1). Pleasingly, the desired product **3aa** was formed in good yield after the mixture of **1a** and **2a** had reacted in anhydrous toluene at 80 °C for 12 h (Table 1, entry 1). For the major product, the *Z*-configurated structure of **3aa** was confirmed based on an X-ray diffraction analysis.[21] The other metal catalysts were screened. No desired product was detected when catalysts such as CuOTf, $Cu(OTf)_2$,[22] $RhCl_2(PPh_3)_2$, Rh(COD)(acac), $Rh_2Cl_2(COD)_2$, or $Cp^*Rh_2Cl_4$ were employed (Table 1, entries 2–7). While a slightly higher yield of product **3aa** was observed when 5.0 mol% of $Rh_2(Oct)_4$ was used (92%), decreasing the catalyst loading to 2.5 mol% led to a drastic decline in efficiency (Table 1, entries 8 and 9). A blank reaction clearly demonstrated the importance of the rhodium catalyst in this reaction (Table 1, entry 10). For the solvent effect, the conversions of compound **1a** were only moderate when the reactions were carried out in PhCl and *p*-xylene, however, full conversion was observed in refluxing DCE, the reaction can reach completion in 12 h and 91% yield of **3aa** was isolated (Table 1, entries 11–14). Finally, we have also evaluated the reaction temperature and concentration, however, no superior result was observed.

Table 1. Optimization of the reaction conditions.[a]



1a 2a 3aa

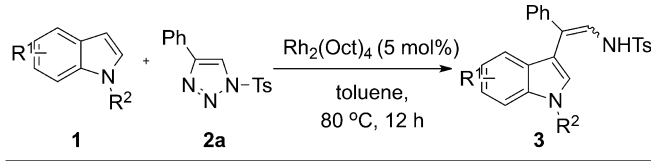
Entry	[M] (mol%)	Solvent	Temp. [°C]	Yield [%][b]
1	$Rh_2(OAc)_4$ (5)	toluene	80	88
2	CuOTf (10)	toluene	80	0
3	$Cu(OTf)_2$ (10)	toluene	80	0
4	$RhCl_2(PPh_3)_2$ (5)	toluene	80	0
5	Rh(COD)(acac) (5)	toluene	80	0
6	$Rh_2Cl_2(COD)_2$ (5)	toluene	80	0
7	$Cp^*Rh_2Cl_4$ (5)	toluene	80	0
8	$Rh_2(Oct)_4$ (5)	toluene	80	92
9	$Rh_2(Oct)_4$ (2.5)	toluene	80	52
10	–	toluene	80	0
11	$Rh_2(Oct)_4$ (5)	PhCl	80	64
12	$Rh_2(Oct)_4$ (5)	*p*-xylene	80	75
13	$Rh_2(Oct)_4$ (5)	DCE	80	91
14	$Rh_2(Oct)_4$ (5)	toluene	100	64

[a] Reactions were carried out with **1a** (0.3 mmol) and **2a** (0.45 mmol) in the presence of [Rh] catalyst in 3.0 mL of solvent under N_2 atmosphere.
[b] Isolated product. *E*/*Z* = 6:1. Cp* = 1,2,3,4,5-pentamethylcyclopenta-1,3-dienyl.

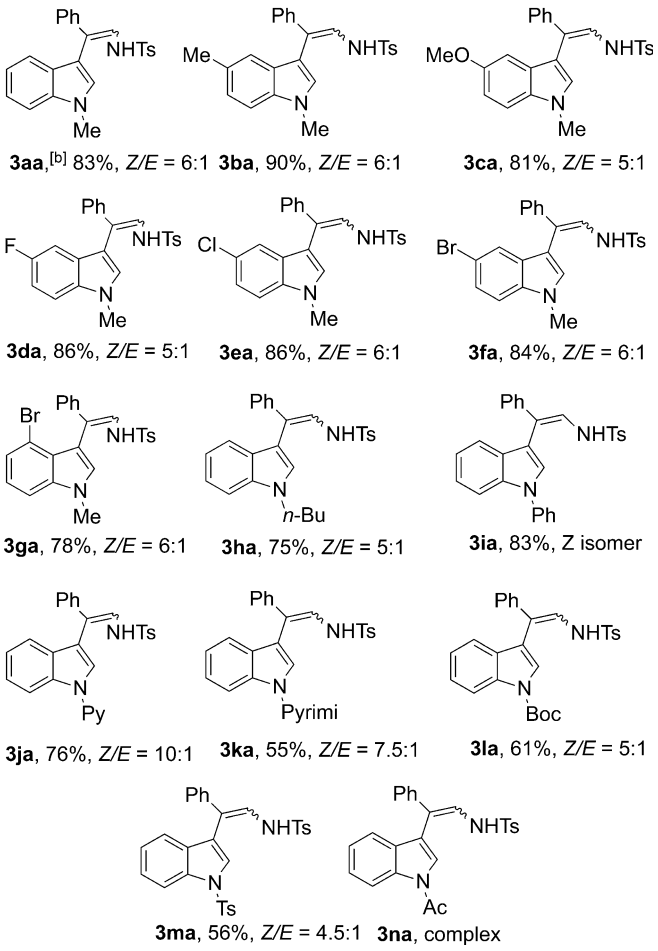
The scope of substituted indoles was subsequently examined under the optimized conditions (Table 2). The utility of this reaction can be demonstrated by a preparative gram-scale reaction, as the product **3aa** can be isolated in 83% yield with a *Z*/*E* isomer ratio of 6:1 on the 10.0 mmol scale. Different substituents which were attached on the benzenoid ring of indole with electron-donating (**1b** and **1c**), or electron-withdrawing (**1d**–**1g**) properties were all tolerated, affording the corresponding products **3aa**–**3ga** in good to excellent yields. It is worth noting that the halogen groups, such as fluoride (**3da**), chloride (**3ea**), and bromide (**3fa** and **3ga**) were compatible in the reaction, which could serve as potential synthetic handles for further elaborations. The reaction of *N*-butylindole **1h** with **2a** afforded product **3ha** as an inseparable mixture of isomers in 75% yield. To further probe the substituent diversity of the indole substrates, *N*-aryl-substituted indoles were synthesized. The *N*-phenyl-substituted product (*Z*)-**3ia** was formed in good yield, the (*E*)-**3ia** isomer was unavailable due to its formation in merely trace amounts in the reaction. It is well-known that N-heterocyclic moieties are useful directing groups in the C-2 functionalization of indoles in C–H activation reactions.[23] The N-pyridine and N-pyrimidine substitutents were tolerated in the current reaction, thus delivering the targeted products **3ja** to **3ka** in serviceable yields, respectively. For the

Advanced Synthesis & Catalysis

Table 2. Scope of the rhodium-catalyzed carbenoid insertion reaction of indole **1** with *N*-tosyl-1,2,3-triazole **2a**.[a]



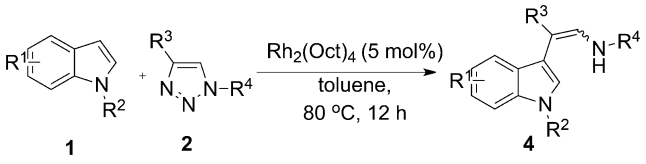
1 2a 3



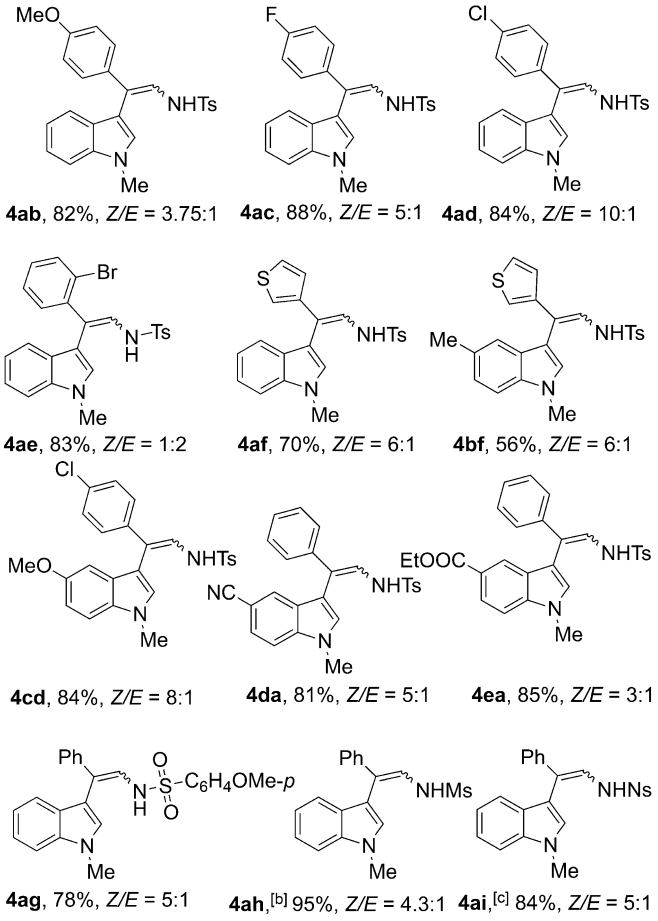
[a] *Reaction conditions:* indole **1** (0.30 mmol), triazole **2a** (0.45 mmol), $Rh_2(Oct)_4$ (0.015 mmol), toluene (3.0 mL), N_2, 80 °C, 10–12 h. Isolated yield based on **1**. *E*/*Z* ratio was determined by ^{1}H NMR.

[b] Gram scale reaction, using 1.31 g (10 mmol) of **1a** and 4.50 g (15 mmol) of **2a** as starting materials.

Table 3. Scope of the rhodium-catalyzed carbene insertion reactions of substituted indoles **1** with various triazoles **2**.[a]



1 2 4



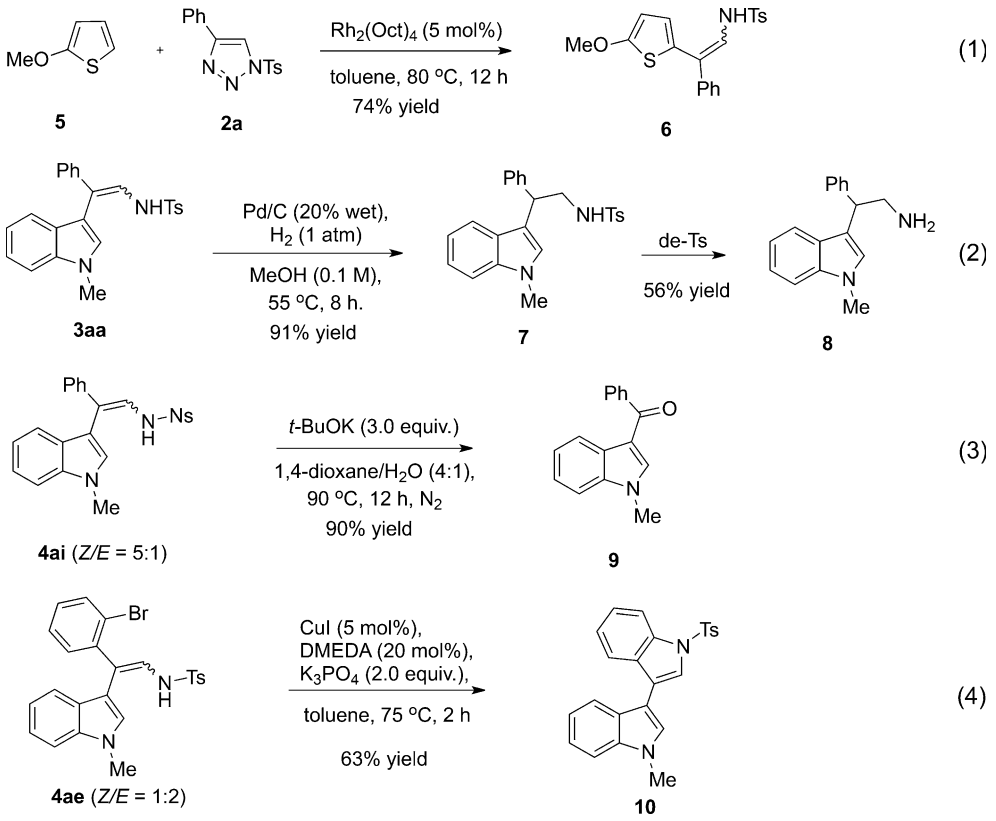
[a] *Reaction conditions:* indole **1** (0.30 mmol, 1.0 equiv.), triazole **2** (0.45 mmol, 1.5 equiv.), $Rh_2(Oct)_4$ (0.015 mmol), toluene (3.0 mL), N_2, 80 °C, 10–12 h. Isolated yield based on **1**. *E*/*Z* ratio was determined by ^{1}H NMR.

[b] Ms = methanesulfonyl.

[c] Ns = 4-nitrobenzenesulfonyl.

various protecting groups which were located at the R^2 position, we were delighted to observe that the Boc and Ts groups were well tolerated, the corresponding products **3la** and **3ma** were isolated in 61% and 56% yields, respectively. A complex outcome was observed for the reaction of triazole **2a** with acetyl-substituted indole **1n**.

The substituent effects of R^3 and R^4 in 1,2,3-triazoles **2** are summarized in Table 3. Good yields were observed whenever the aromatic groups of R^3 were attached with electron-donating (**2b**) or withdrawing (**2c**–**d**) moieties, the corresponding products **4ab**–**4ae** and **4cd** were isolated in up to 88% yields, albeit as inseparable mixtures of isomers in variable ratios. Note that for the production of compound **4ae**, the *E* isomer was isolated as the major product, presumably due to the steric congestion effect which was caused by the *ortho*-substution of bromide in the phenyl group. Heteroaromatic such as 3-thienyl substituted products **4af** and **4bf** were isolated in good yields. For substitutions on the indole ring, reactive electron-withdrawing groups, such as CN and COOEt were tolerated under the optimized conditions to give the



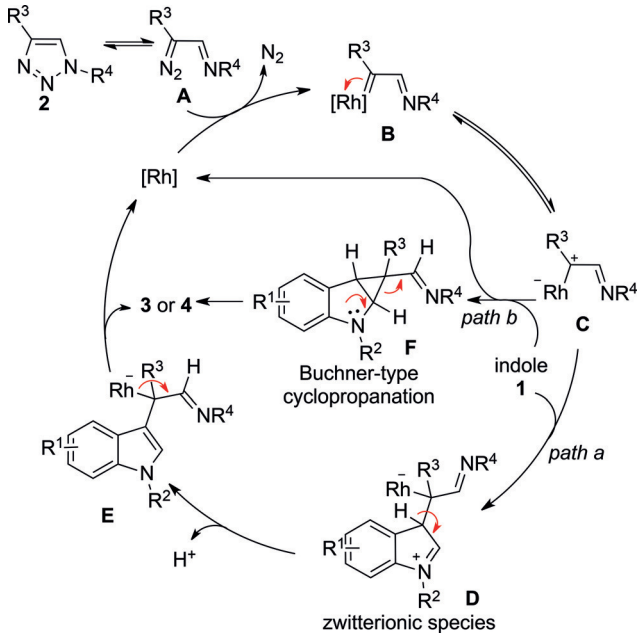
Scheme 1. Reaction extensions.

corresponding products **4da** and **4ea** in good yields. However, the reaction displayed some limitations with alkyl substitution in the R^3 position of 1,2,3-triazole **2**, whereas no reaction occurred in the Rh-catalyzed reactions of **1a** with alkylated 1,2,3-triazoles. The alkyl-substituted 1,2,3-triazoles were consumed at elevated temperatures, however, indole **1a** was untouched and no desired product could be detected. Finally, changing the sulfonyl group of R^4 in 1,2,3-triazole substrates **2** from Ts to 4-methoxybenzenesulfonyl (**2g**), methanesulfonyl (Ms, **2h**), or 4-nitrobenzenesulfonyl (Ns, **2i**) gave the corresponding enamides **4ag**, **4ah** and **4ai** in 78%, 95%, and 84% yields, respectively.

It is also noticeable that a substituted indole is not a limitation to the current carbenoid insertion chemistry; other electron-rich arenes can also be used as a nucleophile to participate in the Rh-catalyzed reaction. As shown in Eq. (1) (Scheme 1), in the presence of 5.0 mol% $Rh_2(Oct)_4$, the reaction of 2-methoxythiophene **5** with 1,2,3-triazole **2a** proceeded smoothly to afford compound **6** as an inseparable *Z*/*E* mixture of isomers (1:1) in 74% yield. This result was conceptually different from the previously reported reactions of *N*-sulfonyl-1,2,3-triazoles with furans[24] or hydrofurans,[25] from which highly substituted pyrroles or medium-sized dioxazocines were obtained, respectively.

The synthetic potential of the obtained 2-indolylenamide products can be illustrated by a series of extension reactions. For instance, treatment of compound **3aa** under Pd/C conditions with 1 atm of H_2 at 55 °C for 8 h gave a Ts-protected product **7** in 91% yield, deprotection of the tosyl group from compound **7** using Na-Naph as a reducing agent[26] afforded tryptamine derivative **8** in a synthetically useful yield [Eq. (2), Scheme 1]. In addition, treatment of the Ns-protected tryptamine vinylogue **4ai** with *t*-BuOK gave (1-methyl-1*H*-indol-3-yl)(phenyl)methanone **9** in 90% yield [Eq. (3), Scheme 1].[27] Furthermore, the 3,3′-biindole **10** can be synthesized in 63% yield from a Cu-catalyzed C–N bond formation reaction using the *Z*/*E* isomer mixture of **4ae** as starting material [Eq. (4), Scheme 1].[28] 3,3′-Biindoles are found in many natural products and biologically active compounds, their derivatives have been used in the treatment of protein folding disorder, such as Alzheimer's disease, dementia, and spongiform encephalopathy.[29]

The mechanistic rationale is outlined in Scheme 2. The catalytic cycle is believed to initiate with the rhodium-catalyzed nitrogen extrusion from diazoimine species **A** to form a highly reactive rhodium(II) azavinyl carbene **B**, and its zwitterionic isomer **C**.[30] The carbenoid carbon of intermediate **C** is highly electrophilic, thus capable of inducing the following intermolecular nucleophilic attack of indole **1** to give the



Scheme 2. Proposed mechanism.

zwitterionic intermediate **D** (path a). Finally, intramolecular aromatization and protodemetallation reactions of **E** occurred to give the observed products **3** or **4**, and meanwhile regenerate the reactive rhodium catalyst. An alternative possible mechanism, involving Buchner-type cyclopropanation followed by ring opening of the strained intermediate **F** cannot be ruled out (path b).[31,32] This reaction pathway was considered as being reasonable when taking the excellent chemo- and regioselectivites of the resulting products into account. The intermediates **E** and **F** with less substitution hindrance between R^3 and NR^4 groups would be formed with priority, which finally resulted in the formation of the (*E*)-isomer as the main product in the observed compounds **3** or **4**.

In conclusion, we have developed a novel Rh-catalyzed carbenoid insertion reaction of simple indoles with *N*-sulfonyl-1,2,3-triazoles, to provide structurally divergent 2-indoylenamides in good to excellent yields. A highly regioselective insertion process of the α-imino rhodim carbene species into indole C(sp^2)–H bond was involved in the reaction. Unlike the previous cycloaddition reaction of C-3 substituted indoles with Rh-carbenoid precursors to give pyrroloindolines,[16] the current reaction was informative with respect to the substituent-dependent reactivity profile of simple indoles toward rhodium-carbenoid species. Moreover, the obtained indole-based enamides can be easily transformed into tryptamine and 3,3′-biindole derivatives, therefore, this reaction might serve as a valuable strategy for the expedient synthesis of biologically active compounds. Further studies on the biological evaluations of the products are currently underway.

Experimental Section

General Procedure for the Synthesis of Compound 3 or 4

To a stirred solution of indole **1** (0.3 mmol) and *N*-sulfonyl-1,2,3-triazole **2** (0.45 mmol) in anhydrous toluene (3.0 mL) was added the rhodium catalyst (0.015 mmol) under N_2 at room temperature. The reaction tube was sealed and the mixture heated to 80 °C for 12 h, or overnight. After completion of the reaction as indicated by TLC, the reaction mixture was allowed to cool to room temperature. The mixture was concentrated under reduced pressure, and the residue was purified *via* silica-gel column chromatography (petroleum ether:EtOAc = 50:1) to afford the desired compound **3** or **4**.

Acknowledgements

We thank the 'National NSFC (21202065, 21462022) and the Natural Science Foundation of Jiangxi Province (20142BAB203005) for financial support.

References

[1] a) F. Nagai, R. Nonaka, K. Satoh, H. Kaminura, *Eur. J. Pharmacol.* **2007**, *559*, 132; b) B. Blough, A. Landavazo, J. Partilla, A. Decker, K. Page, M. Baumann, R. Rothman, *Bioorg. Med. Chem. Lett.* **2014**, *24*, 4754; c) W. Fantegrossi, A. Murnane, C. Reissig, *Biochem. Pharmacol.* **2008**, *75*, 17; d) T.-S. Ray, *PLoS One* **2010**, *5*, e9019.

[2] a) U. Anthoni, C. Christophersen, P. H. Nielsen, in: *Alkaloids: Chemical and Biological Perspectives*, (Ed.: S. W. Pelletier), Pergamon, New York **1999**, Vol. 13, p 163; b) T. Pvenet, J. Pusset, in: *The Alkaloids: Chemistry and Pharmacology*, (Ed.: G. A. Cordell), Academic Press, New York **1996**, Vol. 48, p 1.

[3] M. P. Doyle, M. A. McKervey, T. Ye, *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*, Wiley, New York **1998**.

[4] a) Q. Xiao, Y. Zhang, J. Wang, *Acc. Chem. Res.* **2013**, *46*, 236; b) J. Barluenga, C. Valdés, *Angew. Chem.* **2011**, *123*, 7626; *Angew. Chem. Int. Ed.* **2011**, *50*, 7486; c) T. Ye, M. McKervey, *Chem. Rev.* **1994**, *94*, 1091.

[5] T. Yao, K. Hirano, T. Satoh, M. Miura, *Angew. Chem.* **2012**, *124*, 799; *Angew. Chem. Int. Ed.* **2012**, *51*, 775.

[6] a) E. Park, S. Kim, S. Chang, *J. Am. Chem. Soc.* **2008**, *130*, 17268; b) F. Ye, X. Ma, Q. Xiao, H. Li, Y. Zhang, J. Wang, *J. Am. Chem. Soc.* **2012**, *134*, 5742.

[7] For reviews, see: a) H. M. L. Davies, D. Morton, *Chem. Soc. Rev.* **2011**, *40*, 1857; b) C. Slattery, A. Ford, A. R. Maguire, *Tetrahedron* **2010**, *66*, 6681; c) M. Doyle, R. Duffy, M. Ratnikov, L. Zhou, *Chem. Rev.* **2010**, *110*, 704.

[8] For early comprehensive reviews, see: a) M. P. Doyle, *Chem. Rev.* **1986**, *86*, 919; b) H. M. L. Davies, R. E. J. Beckwith, *Chem. Rev.* **2003**, *103*, 2861.
[9] For selected examples, see: a) H. M. L. Davies, O. Loe, *Synthesis* **2004**, 2595; b) J. Alford, H. M. L. Davies, *Org. Lett.* **2012**, *14*, 6020; c) S. Hansen, J. Spangler, J. Hansen, H. M. L. Devies, *Org. Lett.* **2012**, *14*, 4626; d) S. Ovalles, J. Hansen, H. M. L. Devies, *Org. Lett.* **2011**, *13*, 4284.
[10] a) T. Nishimura, Y. Maeda, T. Hayashi, *Angew. Chem.* **2010**, *122*, 7482; *Angew. Chem. Int. Ed.* **2010**, *49*, 7324; b) T. Maier, G. C. Fu, *J. Am. Chem. Soc.* **2006**, *128*, 4594; c) C. Chen, S. Zhu, B. Liu, L. Wang, Q. L. Zhou, *J. Am. Chem. Soc.* **2007**, *129*, 12616; d) Y. Liang, H. Zhou, Z. Yu, *J. Am. Chem. Soc.* **2009**, *131*, 17783; e) D. Chen, X. Zhang, W. Qi, B. Xu, M. Xu, *J. Am. Chem. Soc.* **2015**, *137*, 5268; f) A. Yada, S. Fujita, M. Murakami, *J. Am. Chem. Soc.* **2014**, *136*, 7217.
[11] X. Ma, J. Jiang, S. Lv, W. Yao, Y. Yang, S. Liu, F. Xia, W.-H. Hu, *Angew. Chem.* **2014**, *126*, 13352; *Angew. Chem. Int. Ed.* **2014**, *53*, 13136.
[12] A. Yamaguchi, K. Chepiga, J. Yamaguchi, K. Itami, H. M. L. Davies, *J. Am. Chem. Soc.* **2015**, *137*, 644.
[13] a) H. M. L. Davies, J. Alford, *Chem. Soc. Rev.* **2014**, *43*, 5151; b) A. Gulevich, V. Gevorgyan, *Angew. Chem.* **2013**, *125*, 1411; *Angew. Chem. Int. Ed.* **2013**, *52*, 1371.
[14] a) X. Ma, F. Wu, X. Yi, H. Wang, W. Chen, *Chem. Commun.* **2015**, *51*, 6862; b) E. Lee, T. E. Ryu, S. Shin, W. Choi, P. Lee, *Org. Lett.* **2015**, *17*, 2470; c) S. Chuprakov, B. T. Worrell, N. Selander, R. Sit, V. V. Fokin, *J. Am. Chem. Soc.* **2014**, *136*, 195; d) K. Chen, Z. Zhu, Y. Zhang, X. Tang, M. Shi, *Angew. Chem.* **2014**, *126*, 6763; *Angew. Chem. Int. Ed.* **2014**, *53*, 6645; e) B. Parr, S. Green, H. M. L. Davies, *J. Am. Chem. Soc.* **2013**, *135*, 4716; f) E. Schultz, R. Sarpong, *J. Am. Chem. Soc.* **2013**, *135*, 4696.
[15] N. Selander, B. T. Worrell, S. Chuprakov, S. Velaparthi, V. V. Fokin, *J. Am. Chem. Soc.* **2012**, *134*, 14670.
[16] J. E. Spangler, H. M. L. Davies, *J. Am. Chem. Soc.* **2013**, *135*, 6802.
[17] D. Yadagiri, P. Anbarasan, *Org. Lett.* **2014**, *16*, 2510.
[18] a) S. Park, W.-S. Yong, S. Kim, P. H. Lee, *Org. Lett.* **2014**, *16*, 4468; b) S. Shin, Y. Park, C. Kim, J. Son, P. H. Lee, *J. Org. Chem.* **2015**, *80*, 5859.
[19] Indole: a) Z. Chen, D. Zheng, J. Wu, *Org. Lett.* **2011**, *13*, 848; isoquinoline: b) P. Huang, Z. Chen, Q. Yang, Y. Peng, *Org. Lett.* **2012**, *14*, 2790; c) P. Huang, Q. Yang, Z. Chen, Q. Ding, J. Xu, Y. Peng, *J. Org. Chem.* **2012**, *77*, 8092; benzofluorenol: d) Z. Chen, M. Zeng, J. Yuan, Q. Yang, Y. Peng, *Org. Lett.* **2012**, *14*, 3588; methyleneindene: e) Q. Xiao, H. Zhu, G. Li, Z. Chen, *Adv. Synth. Catal.* **2014**, *356*, 3809; f) H. Zhu, J. Huang, C. Fan, Z. Chen, *Chem. Asian J.* **2015**, *10*, 1463.
[20] L. Li, C. Shu, B. Zhou, Y. Yu, X. Xiao, L. Ye, *Chem. Sci.* **2014**, *5*, 4057.
[21] CCDC 1400835 (**3aa**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.
[22] A copper catalyst was demonstrated to be the most appropriate catalyst in the cyclopropanation reaction of diazo compounds, see: a) J. Yang, H. Wu, L. Shen, Y. Qin, *J. Am. Chem. Soc.* **2007**, *129*, 13794; b) L. Shen, M. Zhang, Y. Wu, Y. Qin, *Angew. Chem.* **2008**, *120*, 3674; *Angew. Chem. Int. Ed.* **2008**, *47*, 3618.
[23] a) Z. Ding, N. Yoshikai, *Angew. Chem.* **2012**, *124*, 4776; *Angew. Chem. Int. Ed.* **2012**, *51*, 4698; b) M. Nishino, K. Hirano, T. Satoh, M. Miura, *Angew. Chem.* **2012**, *124*, 7099; *Angew. Chem. Int. Ed.* **2012**, *51*, 6993; c) W. Song, L. Ackermann, *Angew. Chem.* **2012**, *124*, 8376; *Angew. Chem. Int. Ed.* **2012**, *51*, 8251.
[24] B. Parr, S. Green, H. M. L. Davies, *J. Am. Chem. Soc.* **2013**, *135*, 4716.
[25] F. Medina, C. Besnard, J. Lacour, *Org. Lett.* **2014**, *16*, 3232.
[26] C. Schöttle, P. Bockstaller, R. Popescu, D. Gerthsen, C. Feldmann, *Angew. Chem.* **2015**, *127*, 10004; *Angew. Chem. Int. Ed.* **2015**, *54*, 9866.
[27] G. Sankar, K. Maneesh, K. Harshad, *J. Org. Chem.* **2011**, *76*, 4753.
[28] A. Klapars, X. Huang, S. L. Buchwald, *J. Am. Chem. Soc.* **2002**, *124*, 7421.
[29] M. D. Carter, M. Hadden, D. Weaver, S. M. Jacobo, *Patent E.W.O.* 125324 A1, **2006**.
[30] H. M. L. Davies, S. J. Hedley, *Chem. Soc. Rev.* **2007**, *36*, 1109.
[31] E. Buchner, T. Curtius, *Ber. Dtsch. Chem. Ges.* **1885**, *18*, 2377.
[32] A. DeAngelis, V. W. Shurtleff, O. Dmitrenko, J. M. Fox, *J. Am. Chem. Soc.* **2011**, *133*, 1650.

