VIP Heterocycles Very Important Paper

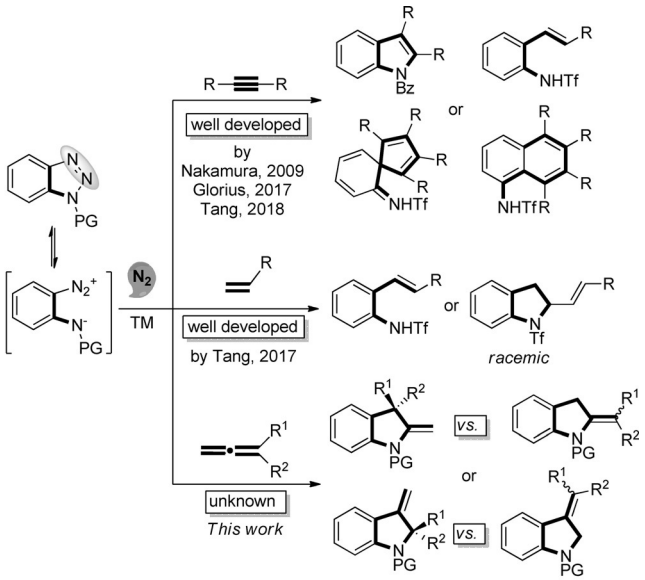
International Edition: DOI: 10.1002/anie.201904805
German Edition: DOI: 10.1002/ange.201904805

Pd/PC-Phos-Catalyzed Enantioselective Intermolecular Denitrogenative Cyclization of Benzotriazoles with Allenes and N-Allenamides

*Pei-Chao Zhang, Jie Han, and Junliang Zhang**

Abstract: *Reported herein is an asymmetric Pd/PC-Phos-catalyzed denitrogenative cyclization of benzotriazoles with allenes and N-allenamides, representing the first example of enantioselective denitrogenative cyclizations of benzotriazoles. A series of optically active 3-methyleneindolines were obtained in good yields with high ee values. The use of inexpensive and readily available starting materials, high regio- and enantioselectivity, a broad substrate scope, mild reaction conditions, no need for base, as well as versatile functionalization of the 3-methyleneindolines make this approach attractive.*

Benzotriazoles can undergo ring-chain isomerization to form the corresponding diazonium or diazo species by a Dimroth-type equilibrium. Over the past years, many methodologies have been developed by the use of this unique denitrogenation of benzotriazoles.[1–3] In this context, the development of new denitrogenative reactions of benzotriazoles with readily accessible unsaturated hydrocarbons have received much attention, and provide rapid access to various synthetically valuable compounds (Scheme 1). For example, the group of Nakamura[1c] demonstrated a Pd-catalyzed denitrogenative cyclization of benzotriazoles with internal alkynes. The group of Glorius[2b] then used iridium photocatalysis to achieve the denitrogenation of benzotriazoles and reaction with terminal alkynes. Recently, Tang and co-workers[3] developed an alternative seminal synergistic activating-stabilizing strategy to realize the denitrogenative reaction of benzotriazoles with alkynes[3a] and 1,3-dienes.[3b] Allenes and N-allenamides are readily available unsaturated hydrodcarbons bearing two units of cumulative unsaturation and have emerged as highly important building blocks in organic synthesis.[4] However, to the best of our knowledge, allenes have not been applied to the denitrogenative cyclization of benzotriazoles so far.[5] As a part of our program on the discovery of new asymmetric cyclization reactions of allenes and N-allenamides,[6] we became interested in the enantioselective intermolecular denitrogenative cyclization reaction of benzotriazoles with allenes and N-allenamides. If successful, 3-methyleneindolines and related skeletons, which are ubiquitous structural motifs found in an array of biologically active natural products and pharmaceuticals, would become easily accessible (Figure 1).[7] Despite the many methodologies developed in the last seven years,[8–15] the development of denitrogenative cyclization of benzotriazoles with allenes, especially in an enantioselective manner, still poses considerable considerations: 1) up to eight isomers (*er*, *rr*, *Z*/*E*) might be obtained in theory, so control of the product



Scheme 1. Denitrogenative reactions of benzotriazoles with unsaturated hydrocarbons. PG = protecting group, Tf = trifluoromethanesulfonyl.

[*] P.-C. Zhang, J. Han, Prof. Dr. J. Zhang
Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, East China Normal University, Shanghai, 200062 (P. R. China)
Prof. Dr. J. Zhang
Department of Chemistry, Fudan University
2005 Songhu Road, Shanghai, 200438 (P. R. China)
E-mail: junliangzhang@fudan.edu.cn
Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/anie.201904805.

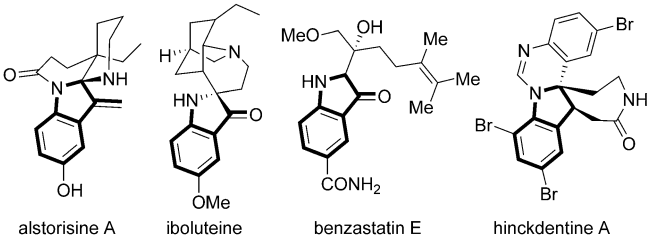
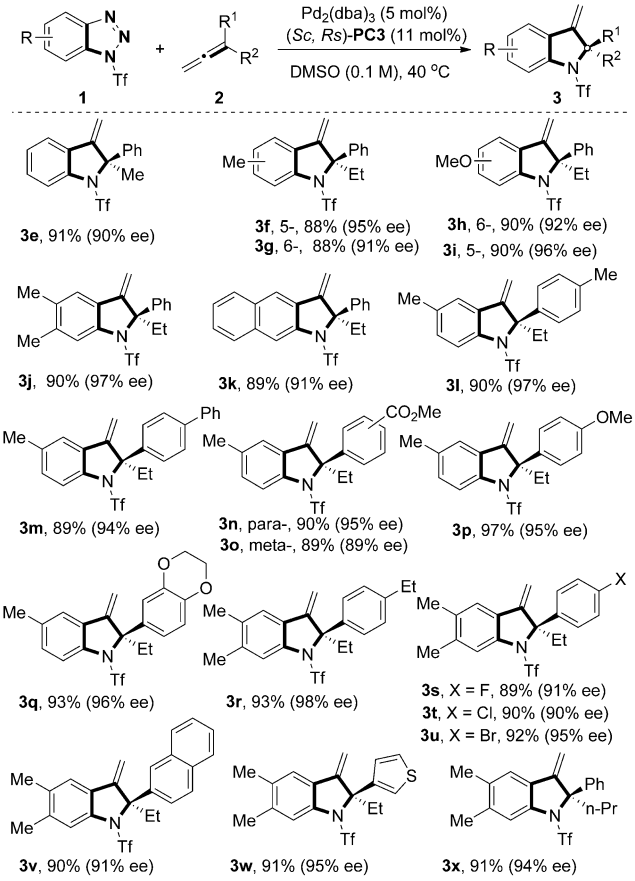


Figure 1. Biologically active natural products featuring functionalized indolines.

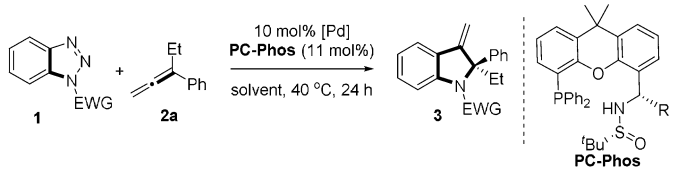
distribution is a challenge, 2) dimerization of the allenes, and especially the allenamides, would require control,[16] 3) potential compatibility issue between the phosphine ligands and diazonium salt intermediates would have to be addressed,[17] and 4) achieving high enantioselectivity would be key.

Our investigation began with the cyclization of the N1-Tf benzotriazole **1a** and allene **2a** (for structure see Table 1) with $Pd_2(dba)_3$ as a precatalyst. A series of commercially or readily available chiral ligands were systematically investigated, and our developed chiral sulfinamidephosphine-type ligands[18–20] delivered **3a** in up to 90% yield and up to 75% *ee* (see Figure S1 in the Supporting Information). Further screening showed that **PC-Phos**[6a,21] could give relatively higher *ee* values (Table 1). For example, (*Sc*, *Rs*)-**PC3** gave **3a** in 91% yield with 92% *ee* (entry 3). Moreover, (*Sc*, *Rs*)-N-Me-**PC3**, lacking the hydrogen-bonding site, delivered 31% *ee* (entry 4). However, (*Rs*)-**PC7** with chirality only at the sulfur atom gave racemic product, indicating that carbon chirality is quite important for obtaining high enantioselectivity (entry 6). Other palladium salts such as $Pd(dba)_2$, $Pd_2(dba)_3{\cdot}CHCl_3$, and $Pd(OAc)_2$ were then examined as precatalysts under identical reaction conditions (entries 7–9), among which $Pd_2(dab)_3$ exhibited the best enantioselectivity. Subsequently, other polar solvents such as DMF, MeOH, and CH_3CN were then examined but failed to give better results (entries 10–12). Lowering the temperature to 30°C slightly decreased the *ee* value to 89% (entry 13). Finally, the adjustment of the N1-electron-withdrawing group of benzotriazole (**1b–d**) from Tf to Ts, Bz, and Tfb did not deliver the corresponding products **3b–d**, indicating that the electron-withdrawing group also plays crucial role in this denitrogentive cyclization (entries 14–16).[3c]



Scheme 2. Cyclization reaction of benzotriazoles with allenes.

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



PC1: R = Ph; **PC2**: R = 4-$MeOC_6H_4$; **PC3**: R = 4-^{t}BuC_6H_4; **PC4**: R = 2-^{i}PrC_6H_4; **PC7**: R = H

Entry	EWG	[M]	L	Solvent	Yield [%][b]	*ee* [%][c]
1	Tf (**1a**)	$Pd_2(dba)_3$	**PC1**	DMSO	90	82
2	Tf (**1a**)	$Pd_2(dba)_3$	**PC2**	DMSO	89	86
3	Tf (**1a**)	$Pd_2(dba)_3$	**PC3**	DMSO	91	92
4	Tf (**1a**)	$Pd_2(dba)_3$	N-Me-**PC3**	DMSO	87	31
5	Tf (**1a**)	$Pd_2(dba)_3$	**PC4**	DMSO	88	37
6	Tf (**1a**)	$Pd_2(dba)_3$	**PC7**	DMSO	85	0
7	Tf (**1a**)	$Pd(dba)_2$	**PC3**	DMSO	89	91
8	Tf (**1a**)	$Pd_2(dba)_3{\cdot}CHCl_3$	**PC3**	DMSO	90	91
9	Tf (**1a**)	$Pd(OAc)_2$	**PC3**	DMSO	–	–
10	Tf (**1a**)	$Pd_2(dba)_3$	**PC3**	DMF	85	73
11	Tf (**1a**)	$Pd_2(dba)_3$	**PC3**	MeOH	86	78
12	Tf (**1a**)	$Pd_2(dba)_3$	**PC3**	CH_3CN	–	–
13[d]	Tf (**1a**)	$Pd_2(dba)_3$	**PC3**	DMSO	90	89
14	Ts (**1b**)	$Pd_2(dba)_3$	**PC3**	DMSO	–	–
15	Bz (**1c**)	$Pd_2(dba)_3$	**PC3**	DMSO	–	–
16	Tfb (**1d**)	$Pd_2(dba)_3$	**PC3**	DMSO	–	–

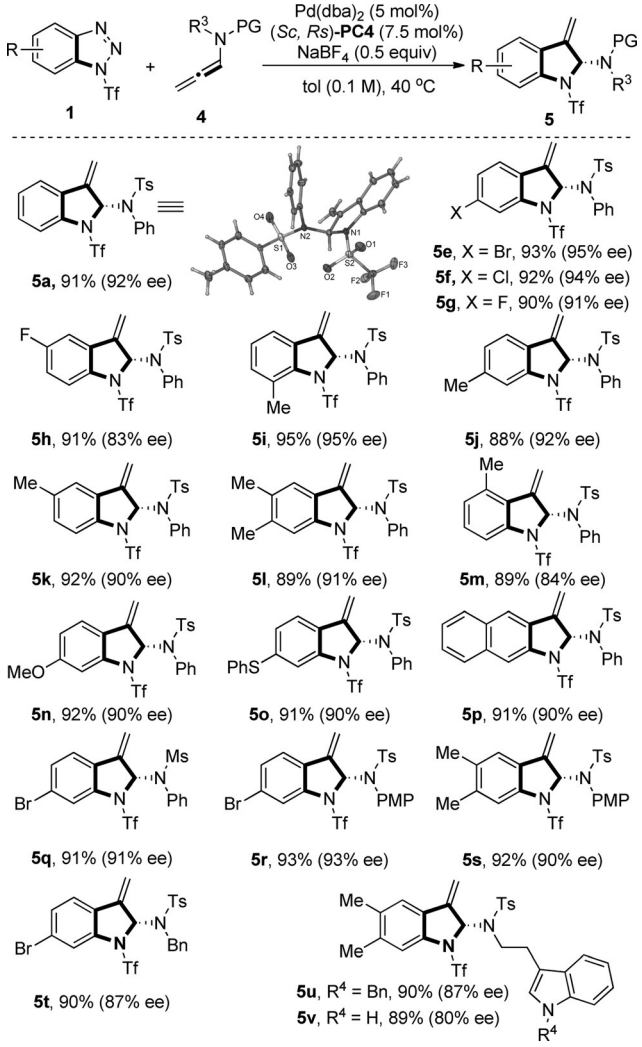
[a] Unless otherwise noted, all reactions were carried out with 0.1 mmol of **1**, 0.12 mmol of **2a**, and 10 mol% of catalyst ([Pd] to **PC-Phos** = 1:1.1) in 1.0 mL of solvent at 40°C for 24 h. [b] Yield of isolated product. [c] Determined by chiral HPLC. [d] At 30°C. Bz = benzoyl, dba = dibenzylideneacetone, DMF = *N*,*N*-dimethylformamide, DMSO = dimethylsufoxide, EWG = electron-withdrawing group, Tfb = 4-(trifluoromethyl)phenylsulfonyl, Ts = *p*-tolylsulfonyl.

With the optimized reaction conditions in hand, the scope of this asymmetric denitrogenative cyclization reaction was then investigated, and the results are shown in Scheme 2. In general, high yields (88–97%) with 89–98% *ee* values were exclusively obtained for the new aza-quaternary stereogenic center. For example, the benzotriazoles bearing one or two electron-donating groups (Me, OMe; *para*-positions to either N1 or N3) on the aryl ring of the benzotriazoles generally react well to furnish the desired products **3f–j** in 88–90% yields with 91–97% *ee* values. Notably, naphthotriazole also worked well, furnishing the corresponding product **3k** in 89% yield with 91% *ee*. Next, the scope with respect to the 1,1-disubstituted

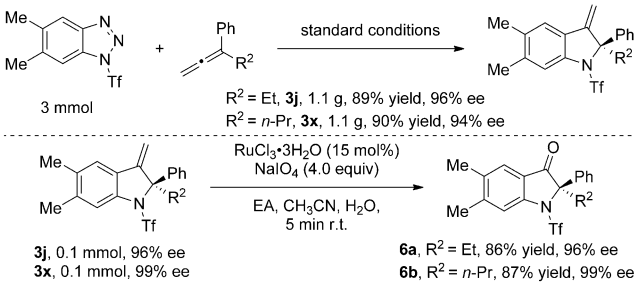
allene **2** was further investigated. A tolerance towards both electron-donating and electron-withdrawing groups on the aryl unit of the allene was observed, furnishing **3l–r** in excellent yields (89–97%) with 89–98% *ee* values. In particular, halogens (F, Cl, Br) on the phenyl ring are compatible to deliver the desired **3s–u** in high yields with 90–95% *ee* values. Gratifyingly, 2-naphthyl- and 3-thienyl-derived allenes delivered the cyclization products **3v,w** in 90–91% yields with 91–95% *ee* values. The structure and absolute configuration of **3x** were determined by single-crystal X-ray diffraction analysis.[22]

We next turned to examine whether N-allenamides[23] (**4**) were applicable to the present reaction. We found that only trace amounts of the corresponding cyclization product **5a** were detected under the above reaction conditions (see Scheme 3). After many attempts (see Figure S2 and Table S1), we finally identified the following reaction conditions : $Pd(dba)_2$ (5 mol%), **PC4** (7.5 mol%), **1a**, and 1.2 equivalents of **4a** in toluene at 40 °C for 48 hours delivered **5a** in 91% yield and 92% *ee*. The structure and absolute configuration of **5a** were determined by single-crystal X-ray diffraction analysis.[22] The scope of this reaction was then examined (Scheme 3). Notably, those benzotriazoles bearing diverse functional groups (R), such as halogens (F, Cl, Br) and electron-donating groups (Me, OMe, SPh) at various positions on the phenyl ring were compatible and delivered the desired **5a–o** in high yields with 84–95% *ee* values. Naphthotriazole also worked well, furnishing the corresponding product **5p** in 91% yield with 90% *ee*. Then, by changing the substitution on the sulfonyl group (PG), the reaction gave **5q** in 91% yield with 91% *ee*. Next, variation of R^3 on the N-allenamides from phenyl to PMP and Bn did not have an effect on the reaction, and the desired products **5r–t** were produced in high yields with good *ee* values. Interestingly, R^4 of the indoles appended to the N-allenamide,[6a] which is several bonds away, still affect the enantioselectivity in some sense (**5u,v**).

To demonstrate the practical utility of our protocol, gram-scale reactions were carried out under standard reaction conditions, furnishing 1.1 grams of **3j** in 89% yield with 97% *ee* and 1.1 grams of **3x** in 90% yield with 94% *ee*, respectively (Scheme 4). Treatment of **3j** and **3x** with $RuCl_3/NaIO_4$ gave good yields of the chiral ketones **6**, which are common skeleton in biologically relevant products.[24]



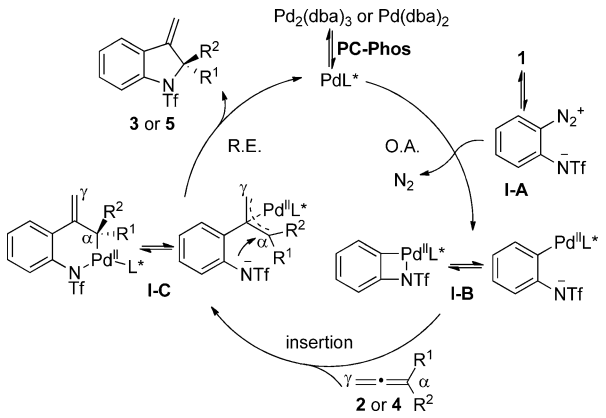
Scheme 3. Cyclization reaction of benzotriazoles with N-allenamides.



Scheme 4. Gram-scale synthesis and synthetic derivatization of the products.

To elucidate the proposed mechanism, several control reactions were conducted by addition of either external nucleophiles or by using 1,3-disubstituted allenes with or without a nucleophile, but no other types of products were detected (see the Supporting Information). Based on the above results and some relevant precedents,[3b,25] we propose a plausible mechanism to account for this palladium-catalyzed denitrogenative cyclization reaction (Scheme 5). Benzotriazoles (**1**) undergo a ring-chain isomerization to form the corresponding diazonium **I-A** by a Dimroth-type equilibrium.[3c,26] Oxidative addition of **I-A** to a palladium complex and extrusion of nitrogen gas would generate the intermediate **I-B**. The insertion of either the allene or allenamide into the C–Pd bond would deliver a π-allylpalladium complex **I-C**, which upon allylic substitution would produce the cyclization products **3** or **5**, respectively, and regenerate the palladium catalyst.

In summary, we have developed the first highly chemo-, regio-, and enantioselective palladium-catalyzed denitrogenative cyclization reaction of benzotriazoles with either allenes or N-allenamines using the chiral sulfinamidephosphine-type ligand **PC-Phos**. A series of optically active 3-



Scheme 5. Proposed mechanism.

methyleneindolines were obtained in high yields and with excellent *ee* values. This method can be expected to find wide synthetic application in view of its high efficiency, simple operation, mild reaction conditions, no use of base, and high chemo- and enantioselectivity. Inspired by this work, we anticipate that more catalytic asymmetric and synthetically valuable transformations of benzotriazoles will be developed in the near future.

Acknowledgements

We gratefully acknowledge the funding support of NSFC (21425205, 21672067) and the 973 Program (2015CB-856600).

Conflict of interest

The authors declare no conflict of interest.

Keywords: allenamides · allenes · cyclization · heterocycles · palladium

How to cite: *Angew. Chem. Int. Ed.* **2019**, *58*, 11444–11448
Angew. Chem. **2019**, *131*, 11566–11570

[1] For selected examples of the ring opening of benzotriazoles upon pyrolysis: a) Z. P. Yin, Z. C. Wang, X. F. Wu, *Org. Lett.* **2017**, *19*, 6232; b) A. S. Singh, N. Mishra, D. Kumar, V. K. Tiwari, *ACS Omega* **2017**, *2*, 5044; c) I. Nakamura, T. Nemoto, N. Shiraiwa, M. Terada, *Org. Lett.* **2009**, *11*, 1055; d) H. Al-Awadi, M. R. Ibrahim, N. A. Al-Awadi, Y. A. Ibrahim, *J. Heterocycl. Chem.* **2008**, *45*, 723; e) N. A. Al-Awadi, B. J. George, H. H. Dib, M. R. Ibrahim, Y. A. Ibrahim, O. M. E. El-Dusouqui, *Tetrahedron* **2005**, *61*, 8257; f) S. J. Barker, R. C. Storr, *J. Chem. Soc. Perkin Trans. 1* **1990**, 485.

[2] For selected examples of the ring opening of benzotriazoles by photolysis, see: a) M. Teders, A. Gómez-Suárez, L. Pitzer, M. N. Hopkinson, F. Glorius, *Angew. Chem. Int. Ed.* **2017**, *56*, 902; *Angew. Chem.* **2017**, *129*, 921; b) M. Teders, L. Pitzer, S. Buss, F. Glorius, *ACS Catal.* **2017**, *7*, 4053; c) N. A. Al-Jalal, M. R. Ibrahim, N. A. Al-Awadi, M. H. Elnagdi, Y. A. Ibrahim, *Molecules* **2014**, *19*, 20695; d) J. K. Dutton, D. P. M. Pleynet, A. P. Johnson, *Tetrahedron* **1999**, *55*, 11927; e) E. M. Burgess, R. Caithers, L. McCullagh, *J. Am. Chem. Soc.* **1968**, *90*, 1923.

[3] Ring opening of benzotriazoles by a synergistic activating-stabilizing effect: a) Y. Wang, Z. Wang, X. Chen, Y. Tang, *Org. Chem. Front.* **2018**, *5*, 2815; b) Y. H. Wang, Y. H. Li, Y. J. Fan, Z. G. Wang, Y. Tang, *Chem. Commun.* **2017**, *53*, 11873; c) Y. H. Wang, Y. F. Wu, Y. H. Li, Y. Tang, *Chem. Sci.* **2017**, *8*, 3852.

[4] For recent reviews, see: a) J. L. Mascareñas, I. Varela, F. López, *Acc. Chem. Res.* **2019**, *52*, 465; b) J. Ye, S. Ma, *Acc. Chem. Res.* **2014**, *47*, 989; c) S. Yu, S. Ma, *Angew. Chem. Int. Ed.* **2012**, *51*, 3074; *Angew. Chem.* **2012**, *124*, 3128; d) S. Ma, *Aldrichimica Acta* **2007**, *40*, 91; e) S. Ma, *Chem. Rev.* **2005**, *105*, 2829; f) S. Ma, *Acc. Chem. Res.* **2003**, *36*, 701; g) F. López, J. L. Mascareñas, *Chem. Soc. Rev.* **2014**, *43*, 2904.

[5] N1-selective nucleophilic addition of benzotriazoles to allenes: a) D. Berthold, B. Breit, *Org. Lett.* **2018**, *20*, 598; Denitrogenative annulation with allenes: b) M. Yamauchi, M. Morimoto, T. Miura, M. Murakami, *J. Am. Chem. Soc.* **2010**, *132*, 54; c) Denitrogenative annulation of 1,2,3,4-benzothiatriazine-1,1-(2*H*)-dioxides with allenes: T. Miura, M. Yamauchi, A. Kosaka, M. Murakami, *Angew. Chem. Int. Ed.* **2010**, *49*, 4955; *Angew. Chem.* **2010**, *122*, 5075.

[6] a) Y. Wang, P.-C. Zhang, X. Di, Qi. Dai, Z.-M. Zhang, J. Zhang, *Angew. Chem. Int. Ed.* **2017**, *56*, 15905; *Angew. Chem.* **2017**, *129*, 16121; b) T.-Y. Lin, C.-Z. Zhu, P.-C. Zhang, Y. Wang, H.-H. Wu, J.-J. Feng, J. Zhang, *Angew. Chem. Int. Ed.* **2016**, *55*, 10844; *Angew. Chem.* **2016**, *128*, 11002; c) Y. Wang, P.-C. Zhang, Y. Liu, F. Xia, J. Zhang, *Chem. Sci.* **2015**, *6*, 5564; d) Y. Wang, P.-C. Zhang, D. Qian, J. Zhang, *Angew. Chem. Int. Ed.* **2015**, *54*, 14849; *Angew. Chem.* **2015**, *127*, 15062.

[7] a) E. Fattorusso, O. Taglialatela-Scafati, *Modern Alkaloids: Structure, Isolation, Synthesis and Biology*, Wiley-VCH, Weinheim, **2008**; b) G. W. Gribble, *Indole Ring Synthesis: From Natural Products to Drug Discovery*, Wiley, Hoboken, **2016**.

[8] For selected examples using C–H activation strategies, see: a) M. Font, B. Cendón, A. Seoane, J. L. Mascareñas, M. Gulías, *Angew. Chem. Int. Ed.* **2018**, *57*, 8255; *Angew. Chem.* **2018**, *130*, 8387; b) X. Wen, Y. Wang, X. P. Zhang, *Chem. Sci.* **2018**, *9*, 5082; c) B.-S. Zhang, Y. Li, Y. An, Z. Zhang, C. Liu, X.-G. Wang, Y.-M. Liang, *ACS Catal.* **2018**, *8*, 11827; d) S.-S. Chen, M.-S. Wu, Z.-Y. Han, *Angew. Chem. Int. Ed.* **2017**, *56*, 6641; *Angew. Chem.* **2017**, *129*, 6741; e) L. Yang, R. Melot, M. Neuburger, O. Baudoin, *Chem. Sci.* **2017**, *8*, 1344; f) O. Villanueva, N. M. Weldy, S. B. Blakey, C. E. MacBeth, *Chem. Sci.* **2015**, *6*, 6672; g) Y. He, C. Zhang, M. Fan, Z. Wu, D. Ma, *Org. Lett.* **2015**, *17*, 496; h) D. Katayev, M. Nakanishi, T. Bürgi, E. P. Kündig, *Chem. Sci.* **2012**, *3*, 1422; i) S. Rousseaux, M. Davi, J. Sofack-Kreutzer, C. Pierre, C. E. Kefalidis, E. Clot, K. Fagnou, O. Baudoin, *J. Am. Chem. Soc.* **2010**, *132*, 10706.

[9] For selected examples using heteroannulation, see: a) R. O. Torres-Ochoa, T. Buyck, Q. Wang, J. Zhu, *Angew. Chem. Int. Ed.* **2018**, *57*, 5679; *Angew. Chem.* **2018**, *130*, 5781; b) J. I. Murray, N. J. Flodén, A. Bauer, N. D. Fessner, D. L. L. Dunklemann, O. Bob-Egbe, H. S. Rzepa, T. Bgrgi, J. Richardson, A. C. Spivey, *Angew. Chem. Int. Ed.* **2017**, *56*, 5760; *Angew. Chem.* **2017**, *129*, 5854; c) K. Saito, T. Akiyama, *Angew. Chem. Int. Ed.* **2016**, *55*, 3148; *Angew. Chem.* **2016**, *128*, 3200; d) B. W. Turnpenny, S. R. Chemler, *Chem. Sci.* **2014**, *5*, 1786; e) R. Miyaji, K. Asano, S. Matsubara, *Org. Lett.* **2013**, *15*, 3658; f) Q.-Q. Yang, Q. Wang, J. An, J.-R. Chen, L.-Q. Lu, W.-J. Xiao, *Chem. Eur. J.* **2013**, *19*, 8401; g) X.-L. Hou, B.-H. Zheng, *Org. Lett.* **2009**, *11*, 1789; h) C. D. Gilmore, K. M. Allan, B. M. Stoltz, *J. Am. Chem. Soc.* **2008**, *130*, 1558.

[10] For selected examples using hydrogenation, see: a) Y. Duan, L. Li, M.-W. Matsubara Chen, C.-B. Yu, H.-J. Fan, Y.-G. Zhou, *J. Am. Chem. Soc.* **2014**, *136*, 7688; b) L. Greb, S. Tamke, J. Paradies, *Chem. Commun.* **2014**, *50*, 2318; c) A. Kulkarni, W.

Zhou, B. Török, *Org. Lett.* **2011**, *13*, 5124; d) R. Kuwano, M. Kashiwabara, *Org. Lett.* **2006**, *8*, 2653.
[11] For selected examples using dearomative Heck reactions, see: a) X. Li, B. Zhou, R.-Z. Yang, F.-M. Yang, R.-X. Liang, R.-R. Liu, Y.-X. Jia, *J. Am. Chem. Soc.* **2018**, *140*, 13945; b) R.-R. Liu, Y.-G. Wang, Y.-L. Li, B.-B. Huang, R.-X. Liang, Y.-X. Jia, *Angew. Chem. Int. Ed.* **2017**, *56*, 7475; *Angew. Chem.* **2017**, *129*, 7583; c) K. Douki, H. Ono, T. Taniguchi, J. Shimokawa, M. Kitamura, T. Fukuyama, *J. Am. Chem. Soc.* **2016**, *138*, 14578;
[12] For examples by cyclization of 2-iodoaniline with unsaturated hydrocarbons, see: a) S.-S. Chen, J. Meng, Y.-H. Li, Z.-Y. Han, *J. Org. Chem.* **2016**, *81*, 9402; b) W. Shu, Q. Yu, S. Ma, *Adv. Synth. Catal.* **2009**, *351*, 2807; c) J. M. Zenner, R. C. Larock, *J. Org. Chem.* **1999**, *64*, 7312; d) J. M. Zenner, R. C. Larock, *J. Org. Chem.* **1995**, *60*, 482.
[13] For selected examples by cycloaddition, see: a) K.-M. Jiang, U. Luesakul, S.-Y. Zhao, K. An, N. Muangsin, N. Neamati, Y. Jin, J. Lin, *ACS Omega* **2017**, *2*, 3123; b) R. Alam, C. Diner, S. Jonker, L. Eriksson, K. J. Szabó, *Angew. Chem. Int. Ed.* **2016**, *55*, 14417; *Angew. Chem.* **2016**, *128*, 14629; c) S. Arai, M. Nakajima, A. Nishida, *Angew. Chem. Int. Ed.* **2014**, *53*, 5569; *Angew. Chem.* **2014**, *126*, 5675; d) Q. Yin, S.-L. You, *Chem. Sci.* **2011**, *2*, 1344; e) R. Viswanathan, E. N. Prabhakaran, M. A. Plotkin, J. N. Johnston, *J. Am. Chem. Soc.* **2003**, *125*, 163.
[14] For selected examples by rearrangement, see: a) B. Alcaide, P. Almendros, S. Cembellín, T. M. del Campo, A. Muñoz, *Chem. Commun.* **2016**, *52*, 6813; b) X. Chen, H. Fan, S. Zhang, C. Yu, W. Wang, *Chem. Eur. J.* **2016**, *22*, 716; c) B. Prasad, R. Adepu, A. K. Sharma, M. Pal, *Chem. Commun.* **2015**, *51*, 1259; d) G. Zhang, V. J. Catalano, L. Zhang, *J. Am. Chem. Soc.* **2007**, *129*, 11358; e) Y. Liu, W. W. McWhorter, Jr., *J. Am. Chem. Soc.* **2003**, *125*, 4240.
[15] Chiral 2-substituted indolines could be used in the enantioselective hydrogenation: a) K. Saito, H. Miyashita, T. Akiyama, *Org. Lett.* **2014**, *16*, 5312; b) C. Pasquier, S. Naili, A. Mortreux, F. Agbossou, L. Pélinski, J. Brocard, J. Eilers, I. Reiners, V. Peper, J. Martens, *Organometallics* **2000**, *19*, 5723.
[16] Four types of the dimerization of allenamides: a) W.-F. Zheng, P. P. Bora, G.-J. Sun, Q. Kang, *Org. Lett.* **2016**, *18*, 3694; b) X.-X. Li, L.-L. Zhu, W. Zhou, Z. Chen, *Org. Lett.* **2012**, *14*, 436; c) E. Bustelo, C. Guerot, A. Hercouet, B. Carboni, L. Toupet, P. H. Dixneuf, *J. Am. Chem. Soc.* **2005**, *127*, 11582; d) S. Saito, K. Hirayama, C. Kabuto, Y. Yamamoto, *J. Am. Chem. Soc.* **2000**, *122*, 10776.
[17] Phosphine compounds do react with diazonium salts: a) A. Roglans, A. Pla-Quintana, M. Moreno-Mañas, *Chem. Rev.* **2006**, *106*, 4622; b) S. Yasui, M. Fujii, C. Kawano, Y. Nishimura, A. Ohno, *Tetrahedron Lett.* **1991**, *32*, 5601; c) S. Yasui, M. Fujii, C. Kawano, Y. Nishimura, K. Shioji, A. Ohno, *J. Chem. Soc. Perkin Trans. 2* **1994**, 177.
[18] a) Y. Wang, Z.-M. Zhang, F. Liu, Y. He, J. Zhang, *Org. Lett.* **2018**, *20*, 6403; b) B. Xu, Z.-M. Zhang, S. Xu, B. Liu, Y. Xiao, J. Zhang, *ACS Catal.* **2017**, *7*, 210; c) Z.-M. Zhang, B. Xu, S. Xu, H.-H. Wu, J. Zhang, *Angew. Chem. Int. Ed.* **2016**, *55*, 6324; *Angew. Chem.* **2016**, *128*, 6432; d) M. Chen, Z.-M. Zhang, Z. Yu, H. Qiu, B. Ma, H.-H. Wu, J. Zhang, *ACS Catal.* **2015**, *5*, 7488; e) Z.-M. Zhang, P. Chen, W. Li, Y. Niu, X. Zhao, J. Zhang, *Angew. Chem. Int. Ed.* **2014**, *53*, 4350; *Angew. Chem.* **2014**, *126*, 4439.
[19] a) P.-C. Zhang, Y. Wang, Z.-M. Zhang, J. Zhang, *Org. Lett.* **2018**, *20*, 7049; b) H. Hu, Y. Wang, D. Qian, Z.-M. Zhang, L. Liu, J. Zhang, *Org. Chem. Front.* **2016**, *3*, 759.
[20] Z.-M. Zhang, B. Xu, Y. Qian, L. Wu, Y. Wu, L. Zhou, Y. Liu, J. Zhang, *Angew. Chem. Int. Ed.* **2018**, *57*, 10373; *Angew. Chem.* **2018**, *130*, 10530.
[21] L. Wang, M. Chen, P.-C. Zhang, W. Li, J. Zhang, *J. Am. Chem. Soc.* **2018**, *140*, 3467.
[22] CCDC 1910858, 1910859, and 1922456 [(*R*)-**3x**, (*R*)-**5a**, Me-**3z**] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.
[23] For general reviews on N-allenamides, see: a) E. Manoni, M. Bandini, *Eur. J. Org. Chem.* **2016**, 3135; b) T. Lu, Z. Lu, Z.-X. Ma, Y. Zhang, R. P. Hsung, *Chem. Rev.* **2013**, *113*, 4862; c) L.-L. Wei, H. Xiong, R. P. Hsuang, *Acc. Chem. Res.* **2003**, *36*, 773.
[24] For examples of total syntheses of biologically active products with a 3-oxoindoline core, see: a) M. Nakajima, S. Arai, A. Nishida, *Angew. Chem. Int. Ed.* **2016**, *55*, 3473; *Angew. Chem.* **2016**, *128*, 3534; b) Z. Xu, Q. Wang, J. Zhu, *J. Am. Chem. Soc.* **2015**, *137*, 6712; c) A. Karadeolian, M. A. Kerr, *Angew. Chem. Int. Ed.* **2010**, *49*, 1133; *Angew. Chem.* **2010**, *122*, 1151; d) J. Lee, J. S. Panek, *J. Org. Chem.* **2015**, *80*, 2959; e) S. Han, M. Movassaghi, *J. Am. Chem. Soc.* **2011**, *133*, 10768; f) P. S. Baran, E. J. Corey, *J. Am. Chem. Soc.* **2002**, *124*, 7904.
[25] F. Yan, H. Liang, J. Song, J. Cui, Q. Liu, S. Liu, P. Wang, Y. Dong, H. Liu, *Org. Lett.* **2017**, *19*, 86.
[26] a) D. S. Bohle, Z. Chua, I. Perepichka, *ChemPlusChem* **2013**, *78*, 1304; b) M. Uhde, T. Ziegler, *Synth. Commun.* **2010**, *40*, 3046; c) X. Àlvarez Micó, T. Ziegler, L. R. Subramanian, *Angew. Chem. Int. Ed.* **2004**, *43*, 1400; *Angew. Chem.* **2004**, *116*, 1424; d) A. R. Katritzky, F. B. Ji, W. Q. Fan, J. K. Gallos, J. V. Greenhill, R. W. King, P. J. Steel, *J. Org. Chem.* **1992**, *57*, 190.

Manuscript received: April 17, 2019
Accepted manuscript online: June 13, 2019
Version of record online: July 3, 2019

