

Heterocycles

International Edition: DOI: 10.1002/anie.201605530
German Edition: DOI: 10.1002/ange.201605530

Regiodivergent Intermolecular [3+2] Cycloadditions of Vinyl Aziridines and Allenes: Stereospecific Synthesis of Chiral Pyrrolidines

Tao-Yan Lin, Chao-Ze Zhu, Peichao Zhang, Yidong Wang, Hai-Hong Wu, Jian-Jun Feng,* and Junliang Zhang*

Abstract: The first rhodium-catalyzed intermolecular [3+2] cycloaddition reaction of vinyl aziridines and allenes for the synthesis of enantioenriched functionalized pyrrolidines was realized. [3+2] cycloaddition with the proximal C=C bond of *N*-allenamides gave 3-methylene-pyrrolidines in high regio- and diastereoselectivity, whereas, 2-methylene-pyrrolidines were obtained as the major products by the cycloadditions of vinyl aziridines with the distal C=C bond of allenes. Use of readily available starting materials, a broad substrate scope, high selectivity, mild reaction conditions, as well as versatile functionalization of the cycloadducts make this approach very practical and attractive.

Chiral pyrrolidines are ubiquitous structural motifs found in an array of biologically active natural products and pharmaceuticals (Figure 1).^[1a-c] Meanwhile, they also serve as important building blocks in organic synthesis and are featured in the structures of versatile ligands and organocatalysts.^[1d,e] Therefore, many impressive strategies in the area of pyrrolidine synthesis have emerged,^[2] such as alkene hydroamina-

tion,^[3] iodocyclization,^[4] rearrangement,^[5] NH insertion reactions of metallocarbenes,^[6] cycloisomerization,^[7] and cycloaddition.^[8] Among them, the transition-metal-catalyzed [3+2] cycloadditions of aziridines represent powerful tools enabling quick and efficient access to pyrrolidines in an atom-economical fashion. However, almost all previous studies on this topic have been focused on 1,3-dipolar cycloadditions of either aryl or alkyl aziridines by selective C–C^[8b,c] and C–N bond^[8h-k] cleavage with alkynes^[8d-f] or alkenes^[8g] for the formation of pyrrolidine derivatives, substituted with saturated C–C bonds, in racemic form. In contrast, the [3+2] cycloaddition of an aziridine with an allene is rarely reported, and seriously limits the utilization of this method in the synthesis of the valuable 2-methylene- and 3-methylene-pyrrolidines containing a C=C bond.^[9] For example, the groups of Vo-Quang and Pinho e Melo have done seminal work on the [3+2] cycloadditions of azomethine ylides, generated from aryl aziridines, with the proximal C=C bond of allenes.^[10] Cycloaddition with the distal C=C bond of allenes remains unknown so far.

Despite the fact that vinyl aziridines are increasingly being exploited as versatile building blocks in organic synthesis, the [3+2] cycloaddition of vinyl aziridine with a two-atom partner has not been well developed.^[8i] Since 2000, the groups of Alper,^[11a,b] Trost,^[11c,d] Aggarwal,^[11e] Louie,^[11f] and Lee^[11g] demonstrated a series of [3+2] cycloadditions of vinylaziridines with heterocumulenes (e.g., isocyanates, carbodiimides, CO₂ and isothiocyanates, etc.), thus efficiently delivering diverse five-membered heterocycles with two heteroatoms. However, the [3+2] cycloaddition of vinylaziridines for the formation of pyrrolidines in the presence of doubly activated Michael acceptors was reported at 2002 by Yamamoto and co-workers.^[12] Subsequently, Aggarwal and co-workers extended this methodology to monoactivated alkenes and demonstrated its utility in a stereospecific synthesis of (–)-α-kainic acid.^[13] Recently, the more challenging enantioselective [3+2] cycloaddition of vinylaziridines with electron-deficient alkenes was reported by Hou, Ding, et al. and Lu and co-workers (Scheme 1).^[14] However, previous reports on the [3+2] cycloadditions of vinylaziridines were limited to alkenes with either one or two activators until Blum and co-workers reported the intramolecular [3+2] cycloadditions of vinyl aziridines bearing an unactivated olefin moiety, a reaction facilitated by a gold/palladium dual activation.^[15] Very recently, a thiyl-radical-catalyzed intermolecular [3+2] cyclizations of vinyl aziridine and electron-rich alkenes was developed by the group of Maruoka.^[16] As a part of our program in the discovery of new cycloaddition reactions of strained rings,^[17] we recently developed

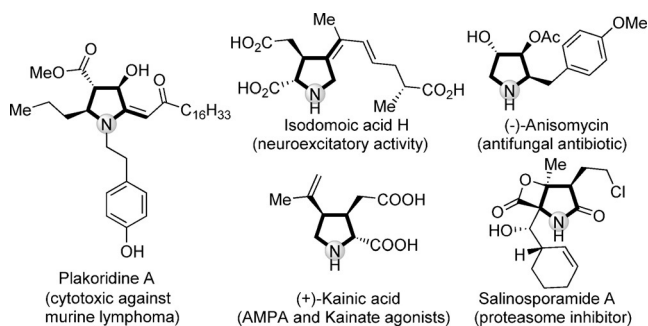
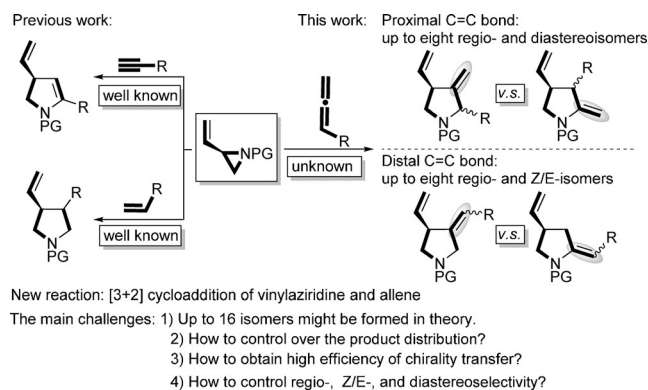


Figure 1. Biologically active natural products featuring chiral pyrrolidines.

[*] T.-Y. Lin, C.-Z. Zhu, P. Zhang, Y. Wang, Prof. Dr. H.-H. Wu, Dr. J.-J. Feng, 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)
E-mail: jjfeng@chem.ecnu.edu.cn
jlzhang@chem.ecnu.edu.cn

Prof. Dr. J. Zhang
State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, CAS
345 Lingling Road, Shanghai 200032 (China)
Homepage: <http://faculty.ecnu.edu.cn/s/1811/t/20975/main.jspy>

Supporting information for this article can be found under:
<http://dx.doi.org/10.1002/anie.201605530>.



Scheme 1. [3+2] cycloadditions of vinylaziridines with unsaturated hydrocarbons. PG = protecting group.

a rhodium(I)-catalyzed intermolecular [3+2] cycloaddition of optically pure vinyl aziridines and unactivated as well as activated alkynes for the synthesis of enantioenriched 2,3-dihydropyroles by a chirality transfer strategy.^[17a] Thus far, however, the more challenging [3+2] cycloadditions of vinyl aziridines with allenes for the construction of valuable chiral methylene pyrrolidines has not been realized. This transformation would be a highly valuable because an additional olefin moiety would be installed in the product and thus increases the structural flexibility given the number of subsequent transformations which could be accessed through the alkene bond.

Allenes are versatile dipolarophiles because of the presence of two cumulative unsaturations.^[18] In fact, both C=C bonds are suitable positions for dipolar attack which can proceed with two opposite orientations. Hence, compared to alkynes and alkenes, both regio-, Z/E, and diastereoselectivity can be involved in [3+2] cycloadditions of vinyl aziridines with allenes and up to sixteen isomers might be obtained in theory. So the main challenge is how to control the product distribution and the efficiency of chirality transfer. Herein, we report our efforts to address this issue and realize the divergent synthesis of enantioenriched methylenepyrrolidines (Scheme 1).

Our investigation began with (*R*)-**1a** and the allene **2a** (for structures see Table 1), considering that the π -donating ability of the nitrogen atom renders N-alleneamines more electron rich than simple allenes.^[19] Initially, (*R*)-**1a** and 1.5 equivalents of **2a** were subjected to a solution of [Rh(NBD)₂]₂BF₄ (5 mol %) in DCE at room temperature. To our surprise, the reaction gave the 3-methylene-pyrrolidines rather than 2-methylene-pyrrolidines in 64 % yield (NMR) as a single diastereomer together with recovery (*R*)-**1a** in 34 % yield (NMR) without loss of chiral information. The structure of **3aa** was confirmed by X-ray crystallographic analysis.^[20] Previous studies on [m+2] cycloadditions of N-allenamides have been focused on the distal C=C bond reactivity. In contrast, transition-metal-catalyzed [m+2] cycloadditions with the proximal C=C bond of N-allenamides is not well known.^[19,21] After many attempts, we found that the ratio of (*R*)-**1a** to **2a**, reaction temperature, and charging sequence have great effect on the reaction conversion (see Table S1 in

the Supporting Information), and thus, the final reaction conditions A are described as follows: to a solution of [Rh(NBD)₂]₂BF₄ (5 mol %) in DCE (0.5 mL) was added a mixture of **1** (1.5 equiv) and 0.2 mmol of **2** (1.0 equiv) in DCE (2.0 mL) dropwise over a period of 5 minutes at 0 °C.

Having the optimized reaction conditions in hand, we investigated the generality of the N-alleneamine (**2**). In general, the chirality of (*R*)-**1a** can be completely transferred to the chiral 3-methylene-pyrrolidines with 95–99 % *ee*. By changing the substitution on the sulfonyl group R⁵, the reaction proceeded in moderate to high yields (Table 1,

Table 1: [3+2] cycloadditions of vinylaziridine and alleneamines.^[a]

Nr.	1 R ¹ /R ² /R ³	<i>ee</i> [%]	2 R ⁴ /R ⁵	Yield [%] ^[b]	<i>ee</i> [%]
1	Ts/H/Me (1a)	98	Ph/Ts (2a)	3aa , 90	99
2	1a	98	Ph/Bs (2b)	3ab , 92	97
3	1a	98	Ph/Ns (2c)	3ac , 65	98
4	1a	98	Ph/Ms (2d)	3ad , 62	95
5	1a	98	4-MeOC ₆ H ₄ /Ts (2e)	3ae , 88	99
6	1a	98	4-BrC ₆ H ₄ /Ts (2f)	3af , 91	98
7	1a	98	Bn/Ts (2g)	3ag , 89	99
8	1a	98	4-FC ₆ H ₄ CH ₂ /Ts (2h)	3ah , 93	98
9	1a	98	Me/Ts (2i)	3ai , 90	97
10	Ts/H/H (1b)	99	2a	3ba , 91	99
11	Ms/H/H (1c)	86	2a	3ca , 62	86
12	Ts/H/ <i>i</i> Pr (1d)	90	2a	3da , 89	90
13	Ts/H/ <i>n</i> Bu (1e)	91	2a	3ea , 85	98
14	Ts/H/Ph (1f)	97	2a	3fa , 95	97
15	Ts/H/OTBS (1g)	95	2a	3ga , 60	94
16 ^[c]	Ts/Me/Me (1h)	88	2a	3ha , 71	88

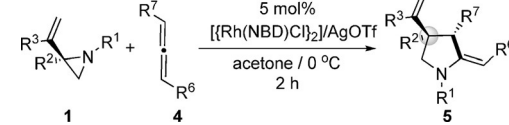
[a] Reaction conditions A: To a solution of [Rh(NBD)₂]₂BF₄ (5 mol %) in DCE (0.5 mL) was added a mixture of **1** (1.5 equiv) and 0.2 mmol of **2** (1.0 equiv) in DCE (2.0 mL) dropwise over a period of 5 mins at 0 °C, then it was stirred at 0 °C for another 15 min. [b] Yield of isolated product. [c] (*S*)-**1h** was used. Bs = 4-bromobenzenesulfonyl, DCE = 1,2-dichloroethane, NBD = norbornadiene, Ms = methanesulfonyl, Ns = 2-nitrobenzenesulfonyl, TBS = *tert*-butyldimethylsilyl, Ts = 4-toluenesulfonyl.

entries 1–4). Moreover, the sulfonyl alleneamine can be modified at the nitrogen atom (R⁴), thus resulting in a robust process for either aryl, benzyl, or alkyl N-substitution (entries 5–9). Next, the potential of the cycloaddition with respect to different substituted vinylaziridines was further evaluated. As depicted in Table 1, the reactions of the N-tosyl **1b** and N-mesyl **1c** proceeded smoothly, thus providing options for N protection and deprotection of the corresponding pyrrolidines (entries 10 and 11). The substituent R³ can be either H, isopropyl, *n*-butyl, phenyl, or OTBS groups, without a notable negative effect to the cycloadditions (entries 12–15). Notably, the vinylaziridine **1h** could also successfully deliver the desired cycloadduct, thus incorporating a chiral quaternary carbon center into the 3-methylene-pyrrolidine **3ha**.

Encouraged by the success of [3+2] cycloadditions of vinylaziridines and N-alleneamines at the proximal C=C bond, we then investigated the more general but challenging allenes **4** (for structure see Table 2) as they have a high formal concentration effect and bidentate coordination,^[18] and are almost unreactive under reaction conditions A. Various rhodium catalysts, silver salts, solvents, and temperatures were then screened (see Table S2). Finally, we identified reaction conditions B: 5 mol % [Rh(NBD)Cl]₂/AgOTf, 0.08 M **1a**, and 1.5 equivalents of **4a** in acetone at 0 °C as the optimal reaction conditions to afford **5aa** in 85 % yield and 96 % *ee*. Of note, the reaction occurs mainly at the distal C=C bond of the allene.

We then examined the scope of the reaction by conducting the cycloadditions of a range of aryl and alkyl allenes (**4**) with (*R*)-**1a** (Table 2, entries 1–18). A tolerance towards both electron-withdrawing and electron-donating substituents on the aryl moiety of the allenes (at the *ortho*, *meta*, and *para* positions) provided the corresponding chiral 2-methylene-pyrrolidines in moderate to excellent yields (54–94 %) with 93–98 % *ee* (entries 1–11). A suitable crystal of the substitu-

Table 2: [3+2] cycloadditions of vinylaziridine and allenes.^[a]

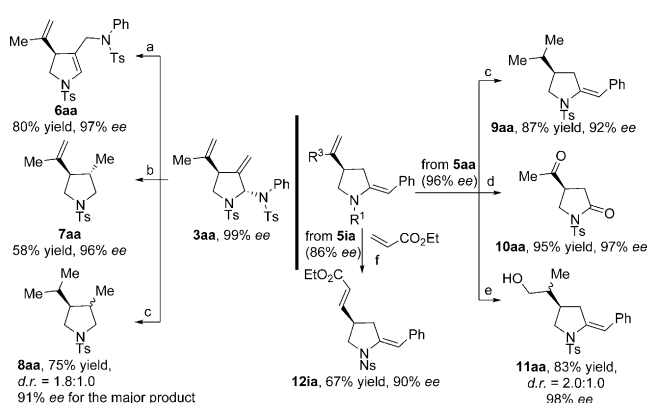


Nr.	1 R ¹ /R ² /R ³	<i>ee</i> [%]	4 R ⁶ /R ⁷	Yield [%] ^[b]	<i>ee</i> [%]
1	1a	98	Ph/H (4a)	5aa , 85	96
2	1a	98	4-MeOC ₆ H ₄ /H (4b)	5ab , 54	98
3	1a	98	4-MeC ₆ H ₄ /H (4c)	5ac , 83	97
4	1a	98	4- <i>t</i> BuC ₆ H ₄ /H (4d)	5ad , 84	96
5	1a	98	2,4,6-Me ₃ C ₆ H ₂ /H (4e)	5ae , 91	96
6	1a	98	4-FC ₆ H ₄ /H (4f)	5af , 81	96
7	1a	98	4-ClC ₆ H ₄ /H (4g)	5ag , 86	97
8	1a	98	3-ClC ₆ H ₄ /H (4h)	5ah , 93	98
9	1a	98	4-BrC ₆ H ₄ /H (4i)	5ai , 91	95
10	1a	98	4-MeCO ₂ C ₆ H ₄ /H (4j)	5aj , 94	93
11	1a	98	4-CNC ₆ H ₄ /H (4k)	5ak , 77	94
12 ^[c]	1a	98	1-naphthyl/H (4l)	5al , 92	96
13 ^[c]	1a	98	2-naphthyl/H (4m)	5am , 91	96
14	1a	98	CH ₂ C ₆ H ₅ /H (4n)	5an , 85	94
15	1a	98	CH ₂ CH ₂ C ₆ H ₅ /H (4o)	5ao , 82	94
16	1a	98	cyclopentyl/H (4p)	5ap , 80	96
17	1a	98	CH ₂ NTsBoc/H (4q)	5aq , 93	— ^[d]
18	1a	98	CH ₂ CH(CO ₂ Me) ₂ /H (4r)	5ar , 70	96
19	1a	98	CO ₂ Me/H (4s)	5as , 86	96
20	1a	98	SO ₂ Ph/H (4t)	5at , 91	95
21	1a	98	<i>n</i> Pr/ <i>n</i> Pr (4u)	5au , 34	96
22	Ts/H/H (1b)	99	4a	5ba , 42	86
23	Ns/H/H (1i)	88	4a	5ia , 74	86
24	Ms/H/H (1c)	86	4a	5ca , 53	83
25	Ts/H/ <i>i</i> Pr (1d)	90	4a	5da , 63	87
26	Ts/H/ <i>n</i> Bu (1e)	91	4a	5ea , 78	(94)

[a] Reaction conditions B: [Rh(NBD)Cl]₂ (5 mol %)/ AgOTf (10 mol %), 0.2 mmol **1** and **4** (1.5 equiv), acetone, 0 °C, 2 h. [b] Yield of isolated product. [c] The ratio of **5** to its regioisomer **5'** is listed as follows: **5al**/**5al'** = 23:1, **5am**/**5am'** = 18:1. [d] The *ee* value of **5aq** cannot be determined by HPLC analysis using a chiral stationary phase. Boc = *tert*-butoxycarbonyl, Tf = trifluoromethanesulfonyl.

tion product **5ak** was obtained to unambiguously establish the absolute stereochemistry and regioselectivity. In most cases, only one regioisomer is detected, except for the naphthyl-containing **4l,m**, thus affording the corresponding **5** and its regioisomer **5'** in high ratio. Notably, both nonfunctionalized aliphatic allenes (**4n–p**) and functionalized aliphatic allenes (**4q,r**) were compatible and afforded the desired products. Additionally, the reaction is not limited to unactivated allenes. The monoactivated allenes **4s** and **4t** were also compatible. Notably, the 1,3-disubstituted allene **4u** successfully gave the desired cycloadduct **5au**. Moreover, the substituted vinylaziridines **1c–e** and **1i** delivered the corresponding cycloadducts in acceptable yield and with highly efficient chirality transfer, except for **1b**.

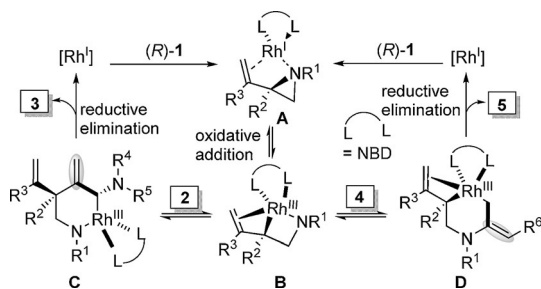
The rich functionalities in the [3+2] cycloadducts provide many opportunities for further synthetic transformations (Scheme 2). The compound **6aa** could be obtained by



Scheme 2. Reaction conditions: a) PhNHTs, [Pd₂(dba)₃·CHCl₃], PhCOONa, dppf, THF, 50 °C; b) Et₃SiH, BF₃·Et₂O, DCM, −78 °C to 0 °C; c) Pd/C, H₂, MeOH; d) 1. O₃, DCM; 2. PPh₃; e) 1. BH₃·THF, RT; 2. H₂O₂, NaOH; f) Grubbs-II, DCM, 40 °C. DCM = dichloromethane, dba = dibenzylideneacetone, dppf = 1,1-bis(diphenylphosphino)ferrocene.

palladium-catalyzed rearrangement of **3aa** in 80 % yield and 97 % *ee*. Moreover, treatment of **3aa** with Et₃SiH/BF₃·Et₂O selectively gives **7aa** as a single diastereomer. By contrast, both double bonds and the aminal group can be reduced to afford **8aa** in 75 % yield with a 1.8:1.0 d.r. value, by treatment of **3aa** with Pd/C under 1 atm hydrogen. Transformations with respect to the [3+2] cycloadducts of **5aa** and **5ia** have also been conducted. The disubstituted double bond could be selectively hydrogenated to produce the corresponding **9aa** in 87 % yield with the same *ee* value. The oxidative cleavage of the double bond of **5aa** was realized by treatment with O₃/PPh₃ in dichloromethane to give the multifunctionalized chiral pyrrolidine **10aa** in 95 % yield with complete chirality transfer. In addition, the hydroboration of the double bond of **5aa** and subsequent oxidation delivered the primary alcohol **11aa** with two contiguous chiral stereocenters in 83 % yield, 98 % *ee*, and 2:1 d.r. Finally, a cross-metathesis reaction converts **5ia** into the unsaturated ester **12ia** in a highly stereoselective fashion.

As shown in Table 2 and Table S2, in most cases the erosion of the *ee* value (1–13%) and trace amounts of the [5+2] cycloadducts were observed. In contrast, there was no [5+2] cycloadduct observed in the cycloaddition of vinylaziridines and N-allenamides. Moreover, the chirality of vinylaziridines can be completely transferred to the [3+2] cycloadducts **3** as described in Table 1. Based on the results above, we propose a plausible mechanism to account for this rhodium-catalyzed [3+2] cycloaddition (Scheme 3). Both the



Scheme 3. Proposed mechanism.

olefin and the nitrogen atom in (*R*)-**1** can coordinate to the rhodium catalyst, and leads to the enyl ($\sigma + \pi$) rhodium species **B** with retention of configuration formed by oxidative addition.^[17a,22] Subsequently, **B** can be regioselectively captured by the distal C=C bond of **4** through insertion into the Rh–N bond to deliver another enyl ($\sigma + \pi$) rhodium species (**D**). Finally, the irreversible reductive elimination of **D** produces **5** and regenerates the rhodium catalyst. Alternatively, in the presence of **2**, regioselective interception of **B** by the proximal C=C bond of an N-allenamide through insertion into the Rh–C bond affords the intermediate **C**, which might evolve into the final 3-methylene-pyrrolidine **3** by reductive elimination.^[23]

In summary, we have developed a regiodivergent approach to 2- or 3-methylene-pyrrolidines by the rhodium-catalyzed intermolecular stereospecific [3+2] cycloadditions of vinyl aziridines and either general allenes or N-allenamides. This method delivers valuable chiral pyrrolidines with broad substrate scope, and high diastereoselectivity and enantioselectivity (up to 99% *ee*) by a chirality-transfer strategy. Moreover, the products can be further functionalized to give a set of functionalized chiral pyrrolidines with high efficiency and selectivity. Further mechanism studies and synthetic applications of this transformation are underway.

Acknowledgements

We are grateful to the funding support of STCSM (15YF1403600), NSFC(21373088, 21425205).

Keywords: cycloaddition · allenes · chirality · heterocycles · rhodium

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 10844–10848
Angew. Chem. **2016**, *128*, 11002–11006

- a) J. P. Michael, *Nat. Prod. Rep.* **1999**, *16*, 675; b) C. Bhat, S. G. Tilve, *RSC Adv.* **2014**, *4*, 5405; c) F. J. Sardina, H. Rapoport, *Chem. Rev.* **1996**, *96*, 1825; d) S. Mukherjee, J. W. Yang, S. Hoffmann, B. List, *Chem. Rev.* **2007**, *107*, 5471; e) F. Fache, E. Schultz, M. L. Tomasino, M. Lemaire, *Chem. Rev.* **2000**, *100*, 2159.
- a) I. Nakamura, Y. Yamamoto, *Chem. Rev.* **2004**, *104*, 2127; b) J. Yu, F. Shi, L.-Z. Gong, *Acc. Chem. Res.* **2011**, *44*, 1156; c) M.-Y. Han, J.-Y. Jia, W. Wang, *Tetrahedron Lett.* **2014**, *55*, 784.
- a) X. Han, R. A. Widenhoefer, *Angew. Chem. Int. Ed.* **2006**, *45*, 1747; *Angew. Chem.* **2006**, *118*, 1779; b) K. D. Hesp, M. Stradiotto, *Org. Lett.* **2009**, *11*, 1449; c) Z. Liu, J. F. Hartwig, *J. Am. Chem. Soc.* **2008**, *130*, 1570.
- a) A. Feula, S. S. Dhillon, R. Byravan, M. Sangha, R. Ebanks, M. A. Hama Salih, N. Spencer, L. Male, I. Magyary, W.-P. Deng, F. Muller, J. S. Fossey, *Org. Biomol. Chem.* **2013**, *11*, 5083; b) M. C. Marcotullio, V. Campagna, S. Sternativo, F. Costantino, M. Curini, *Synthesis* **2006**, 2760.
- a) D. J. Mack, J. T. Njardarson, *ACS Catal.* **2013**, *3*, 272; b) E. A. Ilardi, J. T. Njardarson, *J. Org. Chem.* **2013**, *78*, 9533; c) M. Brichacek, D. E. Lee, J. T. Njardarson, *Org. Lett.* **2008**, *10*, 5023; d) M. Brichacek, M. N. Villalobos, A. Plichta, J. T. Njardarson, *Org. Lett.* **2011**, *13*, 1110; e) D. J. Mack, J. T. Njardarson, *Chem. Sci.* **2012**, *3*, 3321.
- a) C. Jing, D. Xing, Y. Qian, T. Shi, Y. Zhao, W. Hu, *Angew. Chem. Int. Ed.* **2013**, *52*, 9289; *Angew. Chem.* **2013**, *125*, 9459; b) C. Jing, D. Xing, L. Gao, J. Li, W. Hu, *Chem. Eur. J.* **2015**, *21*, 19202; c) S. M. Nicolle, W. Lewis, C. J. Hayes, C. J. Moody, *Angew. Chem. Int. Ed.* **2016**, *55*, 3749; *Angew. Chem.* **2016**, *128*, 3813.
- a) A. K. Å. Persson, J. E. Bäckvall, *Angew. Chem. Int. Ed.* **2010**, *49*, 4624; *Angew. Chem.* **2010**, *122*, 4728; b) W. Rao, S. N. Berry, P. W. H. Chan, *Chem. Eur. J.* **2014**, *20*, 13174.
- For selected reviews on the [3+2] cycloadditions, see: a) L. Jiao, Z.-X. Yu, *J. Org. Chem.* **2013**, *78*, 6842; b) G. Pandey, P. Banerjee, S. R. Gadre, *Chem. Rev.* **2006**, *106*, 4484; c) T. Hashimoto, K. Maruoka, *Chem. Rev.* **2015**, *115*, 5366; Selected examples, see: d) P. A. Wender, D. Strand, *J. Am. Chem. Soc.* **2009**, *131*, 7528; e) J. Fan, L. Gao, Z. Wang, *Chem. Commun.* **2009**, 5021; f) M.-B. Zhou, R.-J. Song, J.-H. Li, *Angew. Chem. Int. Ed.* **2014**, *53*, 4196; *Angew. Chem.* **2014**, *126*, 4280; g) I. Ungureanu, P. Klotz, A. Mann, *Angew. Chem. Int. Ed.* **2000**, *39*, 4615; *Angew. Chem.* **2000**, *112*, 4790; For special reviews on the [3+2] cycloadditions of aziridines, see: h) X.-L. Hou, J. Wu, R.-H. Fan, C.-H. Ding, Z.-B. Luo, L.-X. Dai, *Synlett* **2006**, 181; i) P. Dauban, G. Malik, *Angew. Chem. Int. Ed.* **2009**, *48*, 9026; *Angew. Chem.* **2009**, *121*, 9188; j) C.-Y. Huang, A. G. Doyle, *Chem. Rev.* **2014**, *114*, 8153; k) A. L. Cardoso, T. M. V. D. Pinho e Melo, *Eur. J. Org. Chem.* **2012**, 6479; For special reviews on the [3+2] cycloadditions of vinylaziridines, see: l) H. Ohno, *Chem. Rev.* **2014**, *114*, 7784.
- For special reports on the synthesis of 2-methylene- and 3-methylene-pyrrolidines, see: a) J. Yu, L. He, X.-H. Chen, J. Song, W.-J. Chen, L.-Z. Gong, *Org. Lett.* **2009**, *11*, 4946; b) Y. Ni, R. M. Kassab, M. V. Chevliakov, J. Montgomery, *J. Am. Chem. Soc.* **2009**, *131*, 17714; c) K. Liu, C. Zhu, J. Min, S. Peng, G. Xu, J. Sun, *Angew. Chem. Int. Ed.* **2015**, *54*, 12962; *Angew. Chem.* **2015**, *127*, 13154; d) M. H. Shaw, E. Y. Melikhova, D. P. Kloer, W. G. Whittingham, J. F. Bower, *J. Am. Chem. Soc.* **2013**, *135*, 4992.
- For metal-free [3+2] and formal [3+2] cycloadditions of either aryl or alkyl aziridines with allenes, see: a) L. Vo-Quang, Y. Vo-Quang, *Tetrahedron Lett.* **1980**, *21*, 939; b) F. M. R. Laia, T. M. V. D. Pinho e Melo, *Tetrahedron Lett.* **2009**, *50*, 6180; c) F. M. R. Laia, A. L. Cardoso, A. M. Beja, M. R. Silva, T. M. V. D. Pinho e Melo, *Tetrahedron* **2010**, *66*, 8815.

- [11] a) D. C. D. Butler, G. A. Inman, H. Alper, *J. Org. Chem.* **2000**, 65, 5887; b) C. Dong, H. Alper, *Tetrahedron: Asymmetry* **2004**, 15, 1537; c) B. M. Trost, D. R. Fandrick, *J. Am. Chem. Soc.* **2003**, 125, 11836; d) B. M. Trost, D. R. Fandrick, *Org. Lett.* **2005**, 7, 823; e) F. Fontana, C. C. Chen, V. K. Aggarwal, *Org. Lett.* **2011**, 13, 3454; f) K. Zhang, P. R. Chopade, J. Louie, *Tetrahedron Lett.* **2008**, 49, 4306; g) T. B. Sim, S. H. Kang, K. S. Lee, W. K. Lee, *J. Org. Chem.* **2003**, 68, 104.
- [12] K. Aoyagi, H. Nakamura, Y. Yamamoto, *J. Org. Chem.* **2002**, 67, 5977.
- [13] a) M. A. Lowe, M. Ostovar, S. Ferrini, C. C. Chen, P. G. Lawrence, F. Fontana, A. A. Calabrese, V. K. Aggarwal, *Angew. Chem. Int. Ed.* **2011**, 50, 6370; *Angew. Chem.* **2011**, 123, 6494; b) G. Arena, C. C. Chen, D. Leonori, V. K. Aggarwal, *Org. Lett.* **2013**, 15, 4250.
- [14] a) C.-F. Xu, B.-H. Zheng, J.-J. Suo, C.-H. Ding, X.-L. Hou, *Angew. Chem. Int. Ed.* **2015**, 54, 1604; *Angew. Chem.* **2015**, 127, 1624; b) T.-R. Li, B.-Y. Cheng, S.-Q. Fan, Y.-N. Wang, L.-Q. Lu, W.-J. Xiao, *Chem. Eur. J.* **2016**, 22, 6243.
- [15] J.-J. Hirner, K. E. Roth, Y. Shi, S. A. Blum, *Organometallics* **2012**, 31, 6843.
- [16] T. Hashimoto, K. Takino, K. Hato, K. Maruoka, *Angew. Chem. Int. Ed.* **2016**, 55, ASAP; *Angew. Chem.* **2016**, ASAP.
- [17] a) J.-J. Feng, T.-Y. Lin, C.-Z. Zhu, H. Wang, H.-H. Wu, J. Zhang, *J. Am. Chem. Soc.* **2016**, 138, 2178; b) L. Li, J. Zhang, *Org. Lett.* **2011**, 13, 5940; c) L. Li, X. Wu, J. Zhang, *Chem. Commun.* **2011**, 47, 5049; d) X. Wu, L. Li, J. Zhang, *Chem. Commun.* **2011**, 47, 7824; e) J.-J. Feng, T.-Y. Lin, H.-H. Wu, J. Zhang, *Angew. Chem. Int. Ed.* **2015**, 54, 15854; *Angew. Chem.* **2015**, 127, 16080.
- [18] For recent reviews, see: a) S. Ma, *Chem. Rev.* **2005**, 105, 2829; b) S. Ma, *Aldrichimica Acta* **2007**, 40, 91; c) S. Yu, S. Ma, *Angew. Chem. Int. Ed.* **2012**, 51, 3074; *Angew. Chem.* **2012**, 124, 3128; d) F. López, J. L. Mascareñas, *Chem. Soc. Rev.* **2014**, 43, 2904; e) M. P. Croatt, P. A. Wender, *Eur. J. Org. Chem.* **2010**, 19; f) R. W. Bates, V. Satcharoen, *Chem. Soc. Rev.* **2002**, 31, 12.
- [19] For general reviews on N-allenamides, see: a) L.-L. Wei, H. Xiong, R. P. Hsuang, *Acc. Chem. Res.* **2003**, 36, 773; b) T. Lu, Z. Lu, Z.-X. Ma, Y. Zhang, R. P. Hsung, *Chem. Rev.* **2013**, 113, 4862.
- [20] CCDC 1483781 [(*S,S*)-**3aa**] and 1483782 [(*R*)-**5ak**] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.
- [21] Y. Wang, P. Zhang, D. Qian, J. Zhang, *Angew. Chem. Int. Ed.* **2015**, 54, 14849; *Angew. Chem.* **2015**, 127, 15062.
- [22] For the pioneering work on the enyl ($\sigma + \pi$) rhodium species, see: P. A. Evans, J. D. Nelson, *J. Am. Chem. Soc.* **1998**, 120, 5581.
- [23] For brevity, only one mechanistic possibility is presented. The full details for the plausible mechanism is outlined in Figures S2 and S3 in the Supporting Information.

Received: June 7, 2016

Published online: August 3, 2016