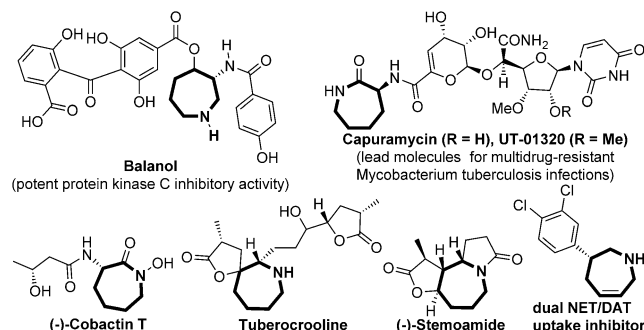


Cycloaddition Reactions

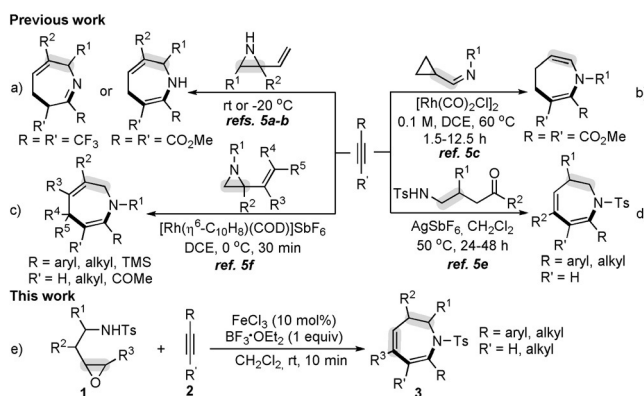
Deutsche Ausgabe: DOI: 10.1002/ange.201604679
Internationale Ausgabe: DOI: 10.1002/anie.201604679**[5+2] Cycloaddition of 2-(2-Aminoethyl)oxiranes with Alkynes via Epoxide Ring-Opening: A Facile Access to Azepines**Chao Hu⁺, Ren-Jie Song⁺, Ming Hu, Yuan Yang, Jin-Heng Li,* and Shenglian Luo*

Abstract: A new FeCl_3 and $\text{BF}_3\cdot\text{OEt}_2$ co-catalyzed tandem hetero-[5+2] cycloaddition of 2-(2-aminoethyl)oxiranes with a wide range of alkynes, including terminal alkynes and alkyl-substituted internal alkynes is presented. This is the first example of rapid and facile production of diverse 2,3-dihydro-1*H*-azepines through a sequence of epoxide ring-opening, annulation, and dehydroxylation with broad substrate scope and exquisite selectivity control.

Access to seven-membered ring systems, especially seven-membered *N*-heterocyclic systems, have gained growing interest among the synthetic community owing to the continuing identification of the seven-membered-ring-containing natural products with the appealing pharmacological and pesticidal activities.^[1,2] Attractive *N*-heterocyclic systems include azepine derivatives,^[3] which are unique structural motifs presented in many biologically active natural products and pharmaceuticals, such as balanol,^[3e,f] capuramycin and its derivatives,^[3g] (–)-cobactin T,^[3h–i] tuberocrooline,^[3j,k] (–)-stemoamide,^[3l–n] and (S)-3-(3,4-dichlorophenyl)-2,3,4,7-tetrahydro-1*H*-azepine^[3o] (Scheme 1). Accordingly, considerable efforts have been devoted to the development of new efficient methods for assembling azepines.^[4–6] Among them, cycloaddition reactions,^[1,2,4] including the hetero-[5+2] cycloaddition reactions with alkynes,^[5] are particularly fascinating for straightforward building the azepine frameworks. Despite the obvious synthetic utility, approaches through the hetero-[5+2] cycloaddition reactions with alkynes are less abundant and remain limited to the substrate scope with regard to both the five-atom units and the alkynes.^[5] Pioneering work of the [5+2] cycloaddition reaction relied on the use of 2,3-divinylaziridine as a five-atom unit under metal-free conditions, but only two electron-poor alkynes were investigated for the synthesis of two azepines (Scheme 2a).^[5a,b] To access



Scheme 1. Examples of important azepine derivatives.



Scheme 2. [5+2] Cycloaddition for the synthesis of azepines.

more azepines, Wender and co-workers first developed a rhodium-catalyzed hetero-[5+2] cycloaddition of cyclopropyl imines with dimethyl acetylenedicarboxylate (Scheme 2b).^[5c] Recently, we reported a new silver-catalyzed tandem [5+2] cycloaddition of γ -amino ketones with simple terminal alkynes, which provided a practical access to 2,3-dihydro-1*H*-azepines (Scheme 2d).^[5e] Interestingly, Zhang and co-workers recently documented a new rhodium catalysis to extend the [5+2] cycloaddition to various vinylaziridines and alkynes leading to 2,5-dihydro-1*H*-azepines (Scheme 2c).^[5f] Thus, new efficient strategies, especially involving the use of new readily available five-atom units, for the intermolecular [5+2] cycloaddition with alkynes would be warmly welcomed.

Herein, we report a new iron and $\text{BF}_3\cdot\text{OEt}_2$ co-catalyzed intermolecular [5+2] cycloaddition of 2-(2-aminoethyl)oxiranes with alkynes for producing diverse 2,3-dihydro-1*H*-azepines (Scheme 2e); this reaction proceeds via epoxide ring-opening by C–O bond cleavage,^[7,8] annulation and dehydroxylation cascades, and represents the first example

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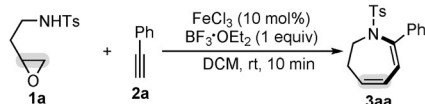
[†] These authors contributed equally to this work.

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of utilizing oxiranes for the [5+2] intermolecular cycloaddition with alkynes.

We started our studies to explore optimal reaction conditions for the [5+2] cycloaddition between 4-methyl-*N*-(2-(oxiran-2-yl)ethyl)benzenesulfonamide (**1a**) and phenylacetylene (**2a**) (Table 1). We were pleased to find that

Table 1: Screening of optimal reaction conditions.^[a]

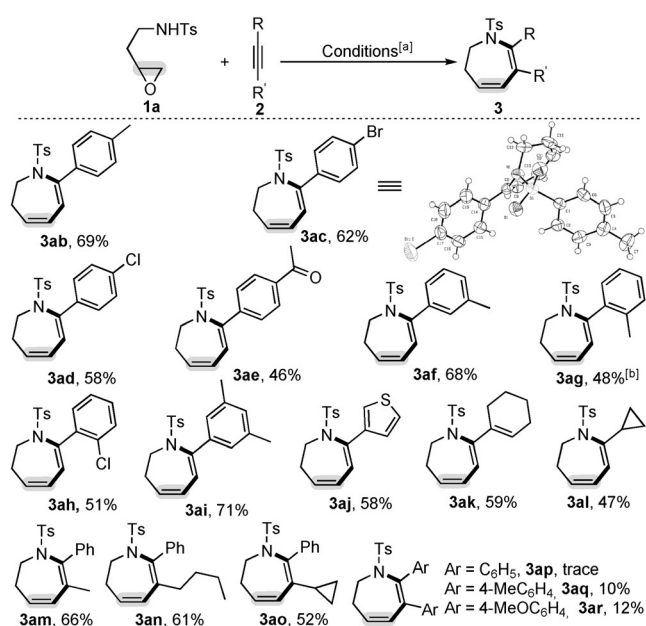


Entry	Variation from the standard conditions	Yield ^[d] [%]
1 ^[b]	none	74
2	without BF ₃ ·OEt ₂	51
3	without FeCl ₃	60
4	FeCl ₃ (5 mol %)	68
5	FeCl ₃ (15 mol %)	61
6	BF ₃ ·OEt ₂ (0.8 equiv)	69
7	BF ₃ ·OEt ₂ (1.2 equiv)	68
8	FeCl ₂ instead of FeCl ₃	57
9	Fe(OTf) ₃ instead of FeCl ₃	67
10	CuCl ₂ instead of FeCl ₃	54
11	InCl ₃ or YbCl ₃ instead of FeCl ₃	49
12	at 0 °C	71
13	CH ₂ ClCH ₂ Cl instead of CH ₂ Cl ₂	70
14	MeCN instead of CH ₂ Cl ₂	< 5
15 ^[c]	none	60

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), FeCl₃ (10 mol %), BF₃·OEt₂ (1 equiv), CH₂Cl₂ (2 mL), room temperature, 10 min. [b] The reaction gave the same yield under air or argon atmosphere. [c] **1a** (1 mmol) and 30 min. A side-product, 2-(phenylethynyl)-1-tosylpyrrolidine (**4aa**), was obtained in 15 % yield. [d] Yield of isolated product.

treatment of oxirane **1a** with alkyne **2a**, 10 mol % of FeCl₃ and 1 equiv of BF₃·OEt₂ in CH₂Cl₂ at room temperature for 10 min was preferred to furnish the desired product **3aa** in 74% yield (entry 1). The reaction was successful when using FeCl₃ or BF₃·OEt₂ alone, albeit giving diminishing yields (entries 2 and 3). A screen of the amount of both FeCl₃ and BF₃·OEt₂ revealed a combination of 10 mol % of FeCl₃ and 1 equiv of BF₃·OEt₂ as the best option (entries 1 and 4–7). A series of other Lewis acids, such as FeCl₂, Fe(OTf)₃, CuCl₂, InCl₃ and YbCl₃, were subsequently examined: each of which exhibited catalytic activity, but was less efficient than FeCl₃ (entries 1 and 8–11). A lower reaction temperature (0°C) slightly affected the reaction in terms of yield (entry 12). While CH₂ClCH₂Cl was proved to be a highly reactive medium (entry 13), MeCN had a rather lower reactivity (entry 14). Gratifyingly, the reaction scale up to 1 mmol of oxirane **1a** was successfully performed, providing **3aa** in moderate yield (entry 15).

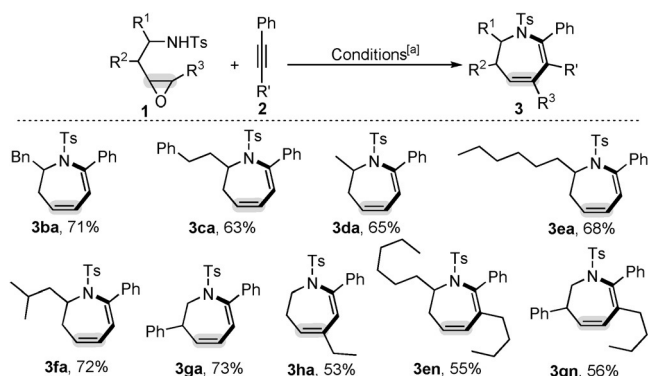
With the optimal reaction conditions in hand, we set out to investigate the scope of this intermolecular [5+2] cycloaddition protocol with respect to alkenes (**2**) (Scheme 3). Initial screening revealed that the optimal conditions were compatible with a wide range of terminal alkynes, namely arylalkynes (**2b-i**), heteroarylalkyne (**2j**), 3-enyne (**2k**) and aliphatic alkyne (**2l**). In the presence of oxirane **1a**, FeCl₃, and



Scheme 3. Variation of the alkynes (**2**). [a] Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), FeCl₃ (10 mol %), BF₃·OEt₂ (1 equiv; 0.2 mmol), CH₂Cl₂ (2 mL), room temperature and 10 min. [b] A side product, 1-(*o*-tolyl)-2-(1-tosylpyrrolidin-2-yl)ethan-1-one (**5ag**), was obtained in 23 % yield.

BF₃·OEt₂, several substituents, including Me, Br, Cl, and MeCO groups, on the aryl ring were well tolerated, and their nature of electron and position had an obviously effect on the yields (**3ab–ah**). While alkyne **2b** with an electron-donating Me group on the phenyl ring delivered **3ab** in 69% yield, alkyne **2e** having an electron-withdrawing MeCO group led a decrease in the yield (46%; **3ae**). Alkyne **2b** with a high active Br group was also converted to **3ab** in 62% yield.^[9] In the case of methyl-substituted arylalkynes **2b**, **2f** and **2g**, the reactivity decreased from *para* to *meta* to *ortho* substitution in terms of yields (**3ab**, **3af** and **3ag**). Gratifyingly, diMe-substituted arylalkyne **2i** or 3-ethynylthiophene **2j** were viable for producing the corresponding products **3ai** and **3aj**. The optimal conditions were found to be tolerated the alkene and the cyclopropyl ring, thus giving products **3ak** and **3al** in moderate yields. Encouraged by the resulted described above, a number of internal alkynes were examined (**3am–ar**). Alkyl-substituted internal alkynes **2m–o** were viable substrates for the reaction, but 1,2-diaryllkynes **2p–r** showed lower reactivity: 1,2-Diphyllalkyne **2p** had no reactivity, and other alkynes, 1,2-di-*p*-tolylethyne **2q** and 1,2-bis(4-methoxyphenyl)ethyne **2r**, delivered **3aq** and **3ar** in lower yields.

We next turned our attention to explore the generality of 2-(2-aminoethyl)oxiranes **1** in the presence of alkyne **2a**, FeCl₃ and BF₃·OEt₂ (Scheme 4). The optimal conditions were applicable to a wide range of 2-(2-aminoethyl)oxiranes (**1**) bearing diverse substituents at the different position (**3ba-ha**). 2-Benzyl-substituted 2-(2-aminoethyl)oxirane **1b** could be smoothly converted into the desired product **3ba** in 71 % yield. PhCH₂CH₂-substituted 2-(2-aminoethyl)oxirane **1c** and Me-substituted 2-(2-aminoethyl)oxirane **1d** were suitable for the synthesis of **3ca** and **3da** in moderate yields. Using other



Scheme 4. Variation of the 2-(2-aminoethyl)oxiranes **1**. [a] Reaction conditions: see Table 1 and Scheme 3.

2-alkyl-substituted oxirane **1e** and **1f** successfully assembled **3ea** and **3fa**. For 2-(2-aminoethyl)oxirane **1g** having a Ph group on the 2-position of the ethyl moiety, the reaction generated **3ga** in 73 % yield. Pleasingly, 2-(2-aminoethyl)oxirane **1h** with an ethyl group on the 3-position of the oxirane moiety was a suitable substrate for the cycloaddition (**3ha**). Substrates **1e** and **1g** also exhibited high reactivity with internal alkyne **1n**, thus building **3en** and **3gn** in 55 % and 56 % yield, respectively.

Gratifyingly, (*R*)-**1d** with 1.3:1 d.r. could be smoothly converted into the desired product (*R*)-**3da** in 64 % yield with > 99 % *ee* [Eq. (1); Scheme 5]. Notably, two five-membered-ring side-products **4aa** [Eq. (2); Scheme 5] and **5ag** [Eq. (3); Scheme 5] were obtained (Table 1 and Scheme 3).

Consequently, the possible mechanisms outlined in Scheme 5 were proposed to understand the current tandem [5+2] cycloaddition reaction.^[7,8] Both FeCl₃ and BF₃·OEt₂ act

as Lewis acids to form the carbocation intermediate **B** by coordinating with the oxygen atom in 2-(2-aminoethyl)oxirane **1a**,^[8] which then undergoes ring-opening of the intermediate **B** and complex with alkyne **2a** afford the oxocarbenium ion intermediate **C** (Pathway I). Electrophilic *anti*-addition of the intermediate **C** across the C–C triple bond in alkyne **2a** selectively gives the vinyl cation intermediate **D**, followed by annulation to produce the seven-membered ring intermediate **E**, which is supported by the formation of the five-membered-ring side-products **4aa** [Eq. (2)] and **5ag** [Eq. (3)]. Finally, elimination of the intermediate **E** assembles the desired product **3aa** and releases H₂O.

Although it is difficult to synthesize the five-membered-ring side-products **4aa** [Eq. (2)] and **5ag** [Eq. (3)] from intermediate **D'**, we cannot rule out the possible Pathway II. Notably, the results show that using a combination of FeCl₃ and BF₃·OEt₂ as Lewis acids is necessary to offer the desired products **3** with high yields, and it might be because FeCl₃ can promote the ring-opening process in this tandem cycloaddition process, and a stoichiometric amount of BF₃·OEt₂ can make the reaction faster and promoted the final elimination process.

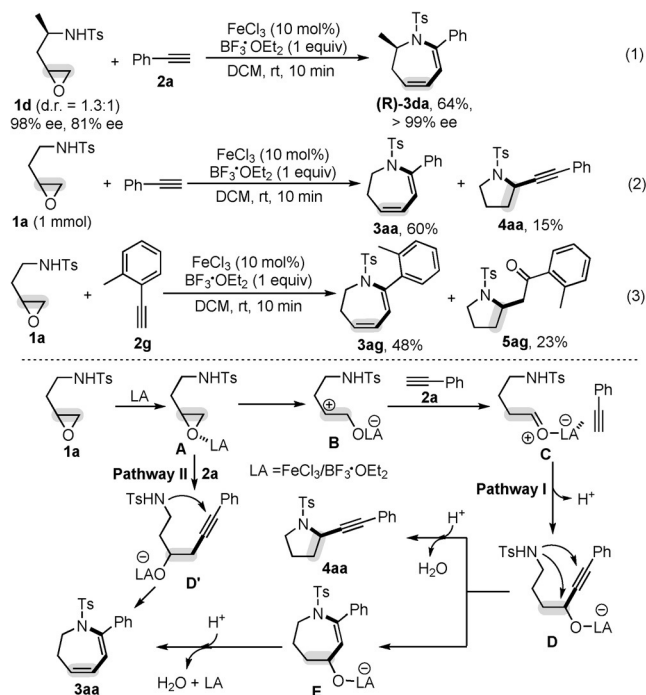
In summary, we have developed a novel tandem hetero-[5+2] cycloaddition of 2-(2-aminoethyl)oxiranes with alkynes for the synthesis of 2,3-dihydro-1*H*-azepines by means of the FeCl₃ and BF₃·OEt₂ co-catalysis. The reaction features a broad scope with respect to a wide range of both substituted 2-(2-aminoethyl)oxirane and alkynes. Importantly, the reaction employs two simple and inexpensive Lewis acids, FeCl₃ and BF₃·OEt₂, as co-catalysts to achieve exquisite regio- and chemocontrol, thus provides a new utilization of oxiranes in the intermolecular cycloaddition reaction for the rapid and practical construction of diverse 2,3-dihydro-1*H*-azepines. Further studies on the applications of this tandem cycloaddition strategy in heterocycle synthesis are currently underway in our laboratory.

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Keywords: azepines · cycloaddition · Lewis acids · oxiranes · ring opening

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Scheme 5. Control experiments and possible reaction mechanisms.

- J.* **2011**, *17*, 3812; h) K. Tanaka, *Heterocycles* **2012**, *85*, 1017; i) C. M. Schienebeck, X. Li, X. — z. Shu, W. Tang, *Pure Appl. Chem.* **2014**, *86*, 409; j) L. Jiao, Z.-X. Yu, *J. Org. Chem.* **2013**, *78*, 6842; k) Y. Wang, Z.-X. Yu, *Acc. Chem. Res.* **2015**, *48*, 2288; l) *Modern Rhodium-Catalyzed Organic Reactions* (Ed.: P. A. Evans), Wiley-VCH, Weinheim, **2005**.
- [2] For special reviews on the [5+2] cycloaddition reaction, see: a) H. Pellissier, *Adv. Synth. Catal.* **2011**, *353*, 189; b) K. E. O. Ylijoki, J. M. Stryker, *Chem. Rev.* **2013**, *113*, 2244.
- [3] For selected reviews and papers, see: a) T. Kametani, K. Fukumoto, *Heterocycles* **1975**, *3*, 931; b) B. Renfro, C. Harrington, G. R. Proctor, *Heterocyclic Compounds: Azepines*, Wiley & Interscience, New York, **1984**; c) C. R. Ganellin, D. J. Triggle, *Dictionary of Pharmacological Agents*, Chapman & Hall/CRC, London, **1996**; d) J. J. Vaquero, A. M. Cuadro, B. Herradyn, *Modern Heterocyclic Chemistry*, Wiley-VCH, Weinheim, **2011**; balanol: e) P. Kulanthavel, Y. F. Hallock, C. Boros, S. M. Hamilton, W. P. Janzen, L. M. Ballas, C. R. Loomis, J. B. Jiang, B. Katz, J. R. Steiner, J. Clardy, *J. Am. Chem. Soc.* **1993**, *115*, 6452; f) S. Ohshima, M. Yanagisawa, A. Katoh, T. Fujii, T. Sano, S. Matsukuma, T. Furumai, M. Fujii, K. Watanabe, K. Yokose, M. Arisawa, T. Okuda, *J. Antibiot.* **1994**, *47*, 639; capuramycin and its derivatives: g) H. Yamaguchi, S. Sato, S. Yoshida, K. Takada, M. Itoh, H. Seto, N. Otake, *J. Antibiot.* **1986**, *39*, 1047; (–)-cobactin T: h) J. Hu, M. J. Miller, *Tetrahedron Lett.* **1995**, *36*, 6379; i) Y.-F. Song, Y. Qu, X.-P. Cao, W. Zhang, *Mar. Biotechnol.* **2011**, *13*, 868; tubercrooline: j) R.-W. Jiang, P.-M. Hon, Y. Zhou, Y.-M. Chan, Y.-T. Xu, H.-X. Xu, H. Greger, P.-C. Shaw, P. P.-H. But, *J. Nat. Prod.* **2006**, *69*, 749; k) W.-H. Lin, H.-Z. Fu, *J. Chin. Pharm. Sci.* **1999**, *8*, 1; stemoamide: l) M. Götz, O. E. Edwards, In *The Alkaloids*, Vol. 9 (Ed.: R. H. F. Manske), Academic Press, New York, **1967**, pp. 545–551; m) K. Sakata, K. Aoki, C.-F. Chang, A. Sakurai, S. Tamura, S. Murakoshi, *Agric. Biol. Chem.* **1978**, *42*, 457; n) Y. Ye, G.-W. Qin, R.-S. Xu, *Phytochemistry* **1994**, *37*, 1205; (S)-3-(3,4-dichlorophenyl)-2,3,4,7-tetrahydro-1H-azepine: o) D. G. Brown, P. R. Bernstein, Y. Wu, R. A. Urbanek, C. W. Becker, S. R. Throner, B. T. Dembofsky, G. B. Steelman, L. A. Lazor, C. W. Scott, M. W. Wood, S. S. Wesolowski, D. A. Nugiel, S. Koch, J. Yu, D. E. Pivonka, S. Li, C. Thompson, A. Zacco, C. S. Elmore, P. Schroeder, J. Liu, C. A. Hurley, S. Ward, H. J. Hunt, K. Williams, J. McLaughlin, V. Hoesch, S. Sydserff, D. Maier, D. Aharon, *ACS Med. Chem. Lett.* **2013**, *4*, 46.
- [4] For representative papers on the synthesis of azepine derivatives via the cycloaddition reactions, see: a) D. J. Anderson, A. Fiasner, *J. Am. Chem. Soc.* **1971**, *93*, 4339; b) N. D. Shapiro, F. D. Toste, *J. Am. Chem. Soc.* **2008**, *130*, 9244; c) Y. Bai, J. Fang, J. Ren, Z. Wang, *Chem. Eur. J.* **2009**, *15*, 8975; d) H. Liu, X. Li, Z. Chen, W.-X. Hu, *J. Org. Chem.* **2012**, *77*, 5184; e) Y. Karibe, H. Kusama, N. Iwasawa, *Angew. Chem. Int. Ed.* **2012**, *51*, 6214; *Angew. Chem.* **2012**, *124*, 6318; f) L. Wang, J. Huang, S. Peng, H. Liu, X. Jiang, J. Wang, *Angew. Chem. Int. Ed.* **2013**, *52*, 1768; *Angew. Chem.* **2013**, *125*, 1812; g) N. Iqbal, A. Fiksdahl, *J. Org. Chem.* **2013**, *78*, 7885; h) M.-B. Zhou, R.-J. Song, J.-H. Li, *Angew. Chem. Int. Ed.* **2014**, *53*, 4196; *Angew. Chem.* **2014**, *126*, 4280; i) R. Shenje, M. C. Martin, S. France, *Angew. Chem. Int. Ed.* **2014**, *53*, 13907; *Angew. Chem.* **2014**, *126*, 14127; j) A. Seoane, N. Casanova, N. Quiñones, J. L. Mascareñas, M. Gullías, *J. Am. Chem. Soc.* **2014**, *136*, 834; k) D. J. Lee, H. S. Han, J. Shin, E. J. Yoo, *J. Am. Chem. Soc.* **2014**, *136*, 11606; l) Y. Yang, M.-B. Zhou, X.-H. Ouyang, R. Pi, R.-J. Song, J.-H. Li, *Angew. Chem. Int. Ed.* **2015**, *54*, 6595; *Angew. Chem.* **2015**, *127*, 6695; m) J.-J. Feng, T.-Y. Lin, H.-H. Wu, J. Zhang, *Angew. Chem. Int. Ed.* **2015**, *54*, 15854; *Angew. Chem.* **2015**, *127*, 16080.
- [5] For special papers on the synthesis of azepine derivatives via the hetero-[5+2] cycloaddition reactions with alkynes, see: a) E. L. Stogryn, S. J. Brois, *J. Am. Chem. Soc.* **1967**, *89*, 605; b) A. Hassner, R. D'Costa, A. T. McPhail, W. Butler, *Tetrahedron Lett.* **1981**, *22*, 3691; c) P. A. Wender, T. M. Pedersen, M. J. C. Scanio, *J. Am. Chem. Soc.* **2002**, *124*, 15154; d) M. M. Montero-Campillo, E. M. Cabaleiro-Lago, J. Rodríguez-Otero, *J. Phys. Chem. A* **2008**, *112*, 9068; e) M.-B. Zhou, R.-J. Song, C.-Y. Wang, J.-H. Li, *Angew. Chem. Int. Ed.* **2013**, *52*, 10805; *Angew. Chem.* **2013**, *125*, 11005; f) J.-J. Feng, T.-Y. Lin, C.-Z. Zhu, H. Wang, H.-H. Wu, J. Zhang, *J. Am. Chem. Soc.* **2016**, *138*, 2178; g) J.-J. Feng, T.-Y. Lin, H.-H. Wu, J. Zhang, *J. Am. Chem. Soc.* **2015**, *137*, 3787; h) L. Zhu, X. Qi, Y. Lan, *Organometallics* **2016**, *35*, 771.
- [6] For selected papers on the classical methods for azepine synthesis, radical: a) L. Yet, *Tetrahedron* **1999**, *55*, 9349; b) R. Guo, J. Huang, H. Huang, X. Zhao, *Org. Lett.* **2016**, *18*, 504, and references therein; ring-expansion: c) T. J. V. Bergen, R. M. Kellogg, *J. Org. Chem.* **1971**, *36*, 978; d) H. F. Motiwala, M. Charaschanya, V. W. Day, J. Aubé, *J. Org. Chem.* **2016**, *81*, 1593, and references therein; ring-closing metathesis: e) M. E. Maier, *Angew. Chem. Int. Ed.* **2000**, *39*, 2073; *Angew. Chem.* **2000**, *112*, 2153; f) P. Jakubec, A. Hawkins, W. Felzmann, D. J. Dixon, *J. Am. Chem. Soc.* **2012**, *134*, 17482; nitrone insertion or diene-conjugated nitrile ylide cyclization: g) *Comprehensive Heterocyclic Chemistry*, Vol. 9 (Ed.: A. R. Katritzky II), Pergamon, New York, **1996**, p. 21; metal-catalyzed cyclization: h) L. F. Tietze, R. Schimpf, *Synthesis* **1993**, 876; i) H. Ohno, H. Hamaguchi, M. Ohata, S. Kosaka, T. Tanaka, *J. Am. Chem. Soc.* **2004**, *126*, 8744; j) T. O. Vieira, H. Alper, *Org. Lett.* **2008**, *10*, 485; k) I. Nakamura, M. Okamoto, Y. Sato, M. Terada, *Angew. Chem. Int. Ed.* **2012**, *51*, 10816; *Angew. Chem.* **2012**, *124*, 10974; l) Z. Shi, C. Grohmann, F. Glorius, *Angew. Chem. Int. Ed.* **2013**, *52*, 5393; *Angew. Chem.* **2013**, *125*, 5503; m) W. Zhu, L. Zhao, M.-X. Wang, *J. Org. Chem.* **2015**, *80*, 12047; n) Z. Zuo, J. Liu, J. Nan, L. Fan, W. Sun, Y. Wang, X. Luan, *Angew. Chem. Int. Ed.* **2015**, *54*, 15385; *Angew. Chem.* **2015**, *127*, 15605; o) Y.-P. Han, X.-R. Song, Y.-F. Qiu, H.-R. Zhang, L.-H. Li, D.-P. Jin, X.-Q. Sun, X.-Y. Liu, Y.-M. Liang, *Org. Lett.* **2016**, *18*, 940, and references therein; others: p) G. Yin, Y. Zhu, P. Lu, Y. Wang, *J. Org. Chem.* **2011**, *76*, 8922.
- [7] For selected reviews on the epoxide ring-opening reactions, see: a) R. N. Armstrong in *Comprehensive Natural Products Chemistry*, Vol. 5 (Ed.: D. C. Poulter), Elsevier, Amsterdam, **1999**, p. 51; b) *Aziridines and Epoxides in Organic Synthesis* (Ed.: A. K. Yudin), Wiley-VCH, Weinheim, **2006**; c) A. Gansäuer, C.-A. Fan, F. Keller, P. Karbaum, *Chem. Eur. J.* **2007**, *13*, 8084; d) I. Vilotijevic, T. F. Jamison, *Angew. Chem. Int. Ed.* **2009**, *48*, 5250; *Angew. Chem.* **2009**, *121*, 5352; e) C. J. Morten, J. A. Byers, A. R. V. Dyke, I. Vilotijevic, T. F. Jamison, *Chem. Soc. Rev.* **2009**, *38*, 3175; f) J. He, J. Ling, P. Chiu, *Chem. Rev.* **2014**, *114*, 8037; g) C. Wang, L. Luo, H. Yamamoto, *Acc. Chem. Res.* **2016**, *49*, 193.
- [8] For papers on the ring-opening/annulation of epoxides with alkynes, see: a) M. Pineschi, F. Bertolini, V. Di Bussolo, P. Crotti, *Adv. Org. Synth.* **2013**, *5*, 101; b) P. Ghosh, P. Saha, S. Bondalapati, K. Indukuri, A. K. Saikia, *J. Org. Chem.* **2014**, *79*, 4119; c) J. M. Fraile, J. A. Mayoral, L. Salvatella, *J. Org. Chem.* **2014**, *79*, 5993; d) E. Hasegawa, S. Arai, E. Tayama, H. Iwamoto, *J. Org. Chem.* **2015**, *80*, 1593; e) R. Liu, M. Zhang, J. Zhang, *Chem. Commun.* **2011**, *47*, 12870; f) W. Chen, X. Fu, L. Lin, X. Yuan, W. Luo, J. Feng, X. Liu, X. Feng, *Chem. Commun.* **2014**, *50*, 11480; g) T. Boningari, A. Olmos, M. B. Reddy, J. Sommer, P. Pale, *Eur. J. Org. Chem.* **2010**, 6338.
- [9] CCDC 1479587 (**3ac**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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