Heterocycle Synthesis

Deutsche Ausgabe: DOI: 10.1002/ange.201510413
Internationale Ausgabe: DOI: 10.1002/anie.201510413

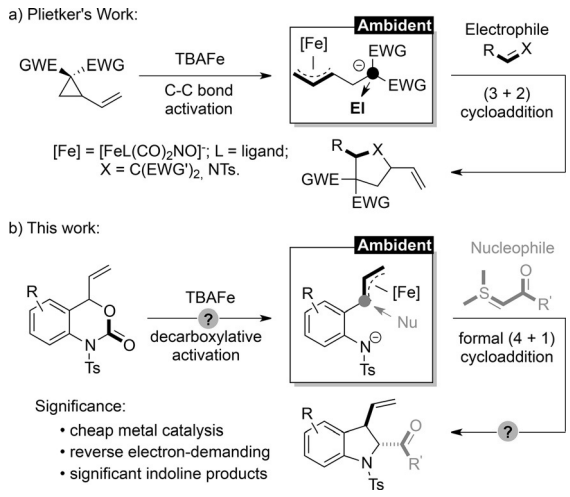
Iron-Catalyzed Decarboxylative (4 + 1) Cycloadditions: Exploiting the Reactivity of Ambident Iron-Stabilized Intermediates

Qiang Wang, Xiaotian Qi, Liang-Qiu Lu, Tian-Ren Li, Zhi-Guang Yuan, Kai Zhang, Bin-Jie Li, Yu Lan,* and Wen-Jing Xiao**

Abstract: *The first example of iron-catalyzed decarboxylative (4 + 1) cycloaddition reactions is described in this publication. By using this method, a wide range of functionalized indoline products were prepared from easily available vinyl benzoxazinanones and sulfur ylides in high yields and selectivities. A possible reaction pathway involving an allylic iron intermediate is discussed based on a series of control experiments and density-functional theory calculations.*

Transition metal catalyzed decarboxylative cycloaddition reactions enable the rapid synthesis of structurally diverse and highly functionalized cyclic molecules.[1] In 2000, Knight and co-workers first published a palladium(0)-catalyzed decarboxylative (5 + 1) cyclization reaction of 5-vinyloxazolidin-2-ones with carbon monoxide.[2a] Shortly afterward, the group of Yamamoto reported the palladium(0)-catalyzed decarboxylative (3 + 2) cycloaddition reactions of hydroxy-containing linear allylic carbonates with activated alkenes.[2b] In the following 15 years, as a result of substantial contributions from the groups of Shintani, Hayashi,[3a,b] Tunge,[3c] and many others,[3d–f] a wide range of decarboxylative cycloadditions were successfully developed by combining vinyl-substituted cyclic carbonates or carbamates with electron-deficient reagents. The use of precious-metal palladium-based catalysts is critical to the success of these processes. Despite these advances, from the perspective of green and sustainable chemistry, it is highly desirable to search for more economic and environmentally friendly metal alternatives to catalyze decarboxylative cycloaddition reactions.

Recently, homogeneous iron catalysis has undergone a great renaissance because of the attractive advantages of iron in terms of abundance, availability, and price, as well as biological and environmental tolerance.[4] In this context, ferrate $Bu_4N[Fe(CO)_3(NO)]$ (TBAFe)[5] was introduced as a versatile nucleophilic catalyst to promote the formation of diverse chemical bonds from allylic substrates.[6] For example, Plietker and co-workers successfully developed a series of iron-catalyzed decarboxylative allylation reactions of allyl carbonates with various nucleophiles, thus efficiently forging C–C,[6b,c] C–N,[6d] C–S,[6e] and C–P bonds.[6f] In 2009, the group of Tunge reported an intramolecular decarboxylative allylic etherification reaction which facile formation of C–O bonds by nucleophilic iron catalysis.[6g] However, there have been very limited applications of such catalysis in cycloaddition reactions. Recently, the group of Plietker reported an elegant example of iron-catalyzed formal (3 + 2) cycloadditions of vinyl cyclopropanes with either activated olefins or tosyl imines, where an ambident iron-stabilized intermediate is involved (Scheme 1 a).[7] Inspired by this pioneering work, we



Scheme 1. Nucleophilic iron catalysis for cycloaddition reactions. EWG = electron-withdrawing group, Ts = 4-toluenesulfonyl.

envisioned that electron-rich TBAFe might catalyze the decarboxylation process of vinyl benzoxazinanones (Tunge's reagent),[3c] thus resulting in a similar intermediate that possesses a π-allyl iron complex (electrophilic part) and a tosyl amide anion (nucleophilic part) in one molecule (Scheme 1 b). Therefore, we devised a novel nucleophilic iron-catalyzed decarboxylative (4 + 1) cycloaddition process. Theoretically, the electrophilic π-allyl iron complex on this ambident intermediate could react first with the nucleophilic sulfur ylide,[8,9] and then undergo an intramolecular S_N2 substitution of dimethyl sulfide by the tosyl amide anion to afford the 3-vinyl indoline products. It is worthy of note that the work described herein features: 1) the first exploitation of

[*] Q. Wang, Prof. Dr. L.-Q. Lu, T.-R. Li, Z.-G. Yuan, K. Zhang, B.-J. Li, Prof. Dr. W.-J. Xiao
Key Laboratory of Pesticide & Chemical Biology
Ministry of Education, College of Chemistry
Central China Normal University
152 Luoyu Road, Wuhan, Hubei 430079 (China)
E-mail: luliangqiu@mail.ccnu.edu.cn
wxiao@mail.ccnu.edu.cn
X. Qi, Prof. Dr. Y. Lan
School of Chemistry and Chemical Engineering
Chongqing University, Chongqing 400030 (China)
E-mail: lanyu@cqu.edu.cn

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201510413.

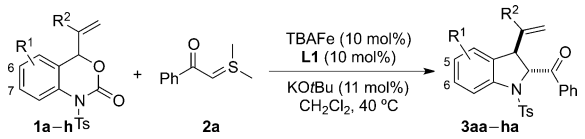
a new, reverse-electron-demand reactivity of this type of allyl/Fe species; 2) the first example of inexpensive metal iron-catalyzed cycloaddition reactions of sulfur ylides.[8–10] In addition, the resultant indolines are synthetically and pharmaceutically significant aza-heterocycles, and the reaction described herein represents a straightforward route to a wide range of functionalized indoline products.[11]

Initially, the decarboxylative (4 + 1) cycloaddition reaction of the vinyl benzoxazinanone **1a** and benzoyl sulfur ylide **2a** (for structures see Table 1) was investigated in the presence of the iron catalyst TBAFe at 40 °C in CH_2Cl_2 (see Tables S1–S3 in the Supporting Information for details and discussion). The reaction did indeed occur, and the desired product 2-benzoyl-1-tosyl-3-vinylindoline (**3aa**) was isolated in 15 % yield with greater than 95:5 diastereoselectivity (see Table S1, entry 1). Then, many reaction parameters, such as ligand, solvent, and temperature were investigated to improve the reaction efficiency. Finally, **3aa** was obtained in 88 % yield under the optimal reaction conditions (see the footnote in Table 1).

The generality of this iron-catalyzed decarboxylative (4 + 1) cycloaddition reaction was examined. As summarized in Table 1, a wide range of vinyl benzoxazinanones can be employed in this transformation. For example, vinyl benzoxazinanones bearing electron-donating groups, such as 6-Me and 6-MeO on the benzene ring can be successfully transformed into the corresponding indoline products in high yields (entries 2 and 3). Moreover, halogen atoms, such as Cl and Br, were found to be compatible with this iron catalyst system, thus providing the desired 5-Cl- or 6-Br-substituted indolines with high efficiencies and selectivities (entries 4 and 5). The introduction of a fluorine atom at either the 5- or 8-position on the benzene ring of the vinyl benzoxazinanones was also tolerated, thus providing important fluorine-containing indoline products in good yields and with excellent stereoselectivities (entry 6).[12] It was also found that isopropenyl benzoxazinanone **1h** is tolerant to this iron-catalyzed transformation, thus affording the indoline product **3ha** in 54 % yield and greater than 95:5 d.r., together with a 42 % yield of a homocyclization byproduct (3-methyl-1-tosyl-1,2-dihydroquinoline).[13] To highlight the synthetic versatility of this methodology, a gram-scale reaction of **1a** and **2a** was conducted under the standard reaction conditions, and **3aa** was obtained in good yield and high stereoselectivity (entry 1).

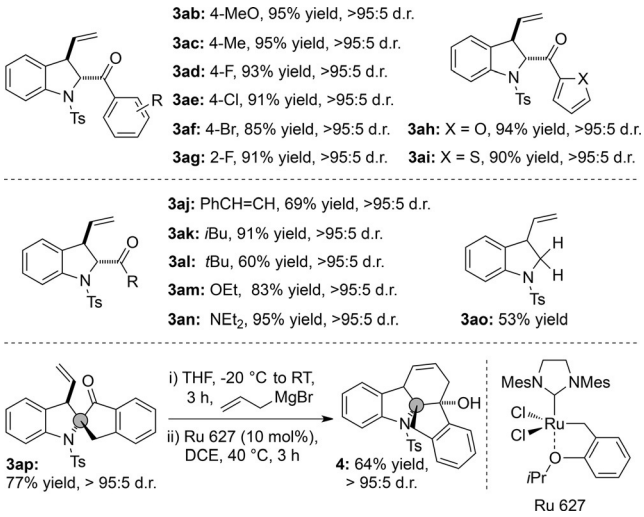
Next, experiments were performed to probe the scope with respect to the sulfur ylides for this reaction. As highlighted in Scheme 2, variation of the electronic and steric properties of the substituents on the benzene ring has no significant influence on the reaction efficiency and selectivity.

Table 1: Scope with respect to vinyl benzoxazinanone.[a,b]



Entry[a]	1: R^1	R^2	3: d.r. [b]	Yield [%][c]
1	**1a**: H	H	**3aa**: >95:5	88 (77)[d]
2	**1b**: 6-MeO	H	**3ba**: >95:5	85
3	**1c**: 6-Me	H	**3ca**: >95:5	85
4	**1d**: 6-Br	H	**3da**: >95:5	91
5	**1e**: 7-Cl	H	**3ea**: >95:5	91
6	**1f**: 5-F	H	**3fa**: >95:5	71
7	**1g**: 8-F	H	**3ga**: >95:5	63
8	**1h**: H	Me	**3ha**: >95:5	54

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), **L1** (10 mol %), and KO*t*Bu (11 mol %) in 2 mL of CH_2Cl_2 at 40 °C for 3–6 h. [b] Determined by ^{1}H NMR analysis of the reaction mixture. [c] Yield of isolated product. [d] A gram-scale reaction with 1.0 g of **1a** and 1.1 g of **2a**; results given within parentheses.

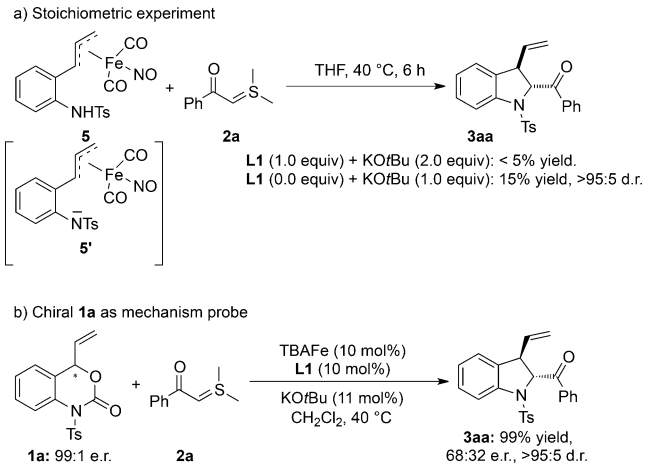


Scheme 2. Generality of sulfur ylides. DCE = 1,2-dichloroethane, THF = tetrahydrofuran.

For example, the acyl sulfur ylides with electron-rich substituents (e.g., MeO and Me) at the *para*-position of the benzene ring can be transformed into the desired products in excellent yields and diastereoselectivity (**3ab** and **3ac**). Electron-deficient substitutes, such as F, Cl, and Br, on the sulfur ylides have no major impact on the reaction efficiency and selectivity (**3ad**–**g**). Moreover, heteroaryl-substituted acyl sulfur ylides, such as 2-furyl and 2-thienyl, underwent the desired reaction smoothly to give the corresponding products with the same good results and without deleterious effects on the iron catalyst (**3ah** and **3ai**). Furthermore, the scope with respect to the sulfur ylides can be significantly extended to alkenyl- and alkyl-substituted acyl sulfur ylides, as well as ester- and amide-substituted sulfur ylides, as the corresponding polysubstituted indolines were obtained in good yields (**3aj**–**an**). Among them, even the sterically hindered *tert*-butyl acyl ylide was tolerated in the reaction, thus giving the adduct **3al** in 60 % yield and greater than 95:5 d.r. Importantly, this transformation can also tolerate dimethyloxosulfonium methylide, thus providing the 3-vinyl-substituted indoline product **3ao** in moderate yield. Furthermore, this cycloaddition reaction can be used to efficiently construct a complicated structural unit bearing an adjacent spiro-

quaternary center and a tertiary center. For example, when the in situ generated sulfur ylide was utilized, the corresponding indoline product **3ap** was obtained in 77% yield and greater than 95:5 d.r. Interestingly, a two-step operation transformed **3ap** into a tetrahydrocarbazole (**4**), containing a dihydroindene unit, in a satisfactory yield.

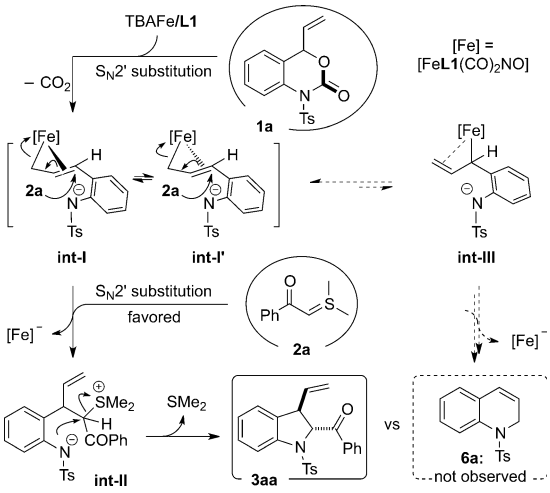
Control experiments were conducted to shed light on the reaction mechanism. Firstly, a stoichiometric experiment with the π-allyl iron complex **5**[14,15] was performed in THF at 40 °C in either the presence or absence of the ligand precursor **L1** (Scheme 3a). In the presence of 1 equivalent of **L1** only



Scheme 3. Experimental evidence.

a trace amount of **3aa** was observed, and in the absence of **L1** a very low yield of **3aa** was detected by ^{1}H NMR analysis of the reaction mixture.[16] These result indicated that, **5** and its N-deprotonated species **5′** might not be the major intermediate in the present transformation. Moreover, an enantiopure substrate **1a** (99:1 e.r.) was used under standard reaction conditions to probe the possible reaction mechanism (Scheme 3b). It was found that the chirality of the substrate was not completely transferred to **3aa** (68:32 e.r.). This result indicated that the σ-enyl-type allylic iron intermediates **int-I** and **int-I′** (Scheme 4) may exist and their slow interconversion through the coordination-dissociation process between iron and the C=C bond would result in the erosion of the enantiopurity of product.[6d]

Based on this data, a possible reaction pathway is depicted in Scheme 4. Initially, an S_N2' substitution of the allylic ester in **1a** by the iron catalyst TBAFe**/L1** affords the σ-enyl type iron intermediate **int-I**, while simultaneously releasing a molecule of CO_2. Then, the second S_N2' substitution of either **int-I** or its isomer **int-I′** by **2a** generates the new zwitterionic intermediate **int-II**. At the same time, the active iron catalyst $[Fe]^-$ is regenerated during this process. Finally, S_N2 substitution of the dimethyl sulfide by the tosyl amide anion provides the indoline products. The reaction exhibits excellent diastereoselectivity, which may be attributed to either the stereoselective attack of the sulfur ylide on the σ-allyl iron part of **int-I**, or perhaps the thermodynamic equilibration of the ketone product under the reaction conditions.



Scheme 4. Plausible reaction mechanism.

Moreover, density-functional theory (DFT) calculations were carried out to explain the good selectivity for **3aa** over the possible byproduct **6a** (Scheme 4).[17] First, the comparison of experimental and DFT computed structural parameters were performed with **5** to obtain the accurate structure. The result indicates that bond lengths and angles of **5**, calculated at B3LYP-D3(BJ)/def2-SV(P) level,[18] are consistent with experimental data derived from X-ray crystallography (see Table S4). Under this scenario, the optimized structure of **int-I** and two possible isomers of **int-III** (**int-IIIa** and **int-IIIb**; Figure 1) were identified by DFT calculations

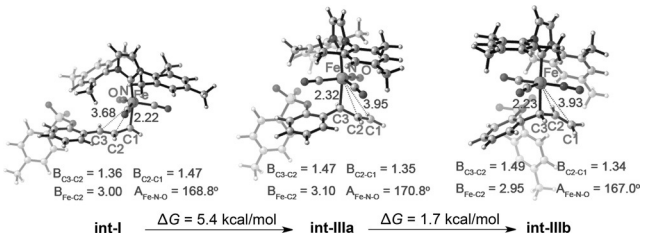


Figure 1. Optimized structures of the σ-enyl-type intermediates **int-I**, **int-IIIa**, and **int-IIIb**. The values given under each structure corresponding to bond lengths and angles.

using the same method and basis set. The data indicate that they are all σ-enyl-type iron complexes, while the π-coordination of allyl is much weak. Computed solvation single-point energies suggest that the relative free energies of **int-IIIa** and **int-IIIb** are 5.4 and 7.1 kcal mol^{-1}, respectively, higher than that of **int-I**. The instability of **int-IIIa** and **int-IIIb** can be ascribed to the steric hindrance. Consequently, **int-I** should be the main active species in this reaction, and indicates why **3aa** was produced as the sole product in this case.

In summary, this research describes the first example of an iron-catalyzed, reverse-electron-demand decarboxylative (4+1) cycloaddition reaction. A wide range of highly functionalized indoline products were isolated in good

yields and with high stereoselectivities from easily available vinyl benzoxazinanones and sulfur ylides. In addition, a possible reaction mechanism was proposed based on a series of control experiments, which were complemented by DFT calculations. The results suggest that the key to success is the selective capture of the allylic iron complexes with nucleophilic sulfur ylides. This unique reactivity of ambident iron-stabilized intermediates can facilitate a new applications for nucleophilic iron-catalyzed cycloaddition reactions.

Acknowledgments

We are grateful to the National Natural Science Foundation of China (NO. 21232003, 21202053, 21472058 and 21572074) and other financial supports (NO. 201422, CCNU15A02007 and 2015CFA033) for support of this research.

Keywords: cycloaddition · density-functional calculations · heterocycles · iron · ylides

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 2840–2844
Angew. Chem. **2016**, *128*, 2890–2894

[1] For a related review, see: J. D. Weaver, A. Recio III, A. J. Grenning, J. A. Tunge, *Chem. Rev.* **2011**, *111*, 1846–1913.

[2] For two pioneering works on decarboxylative cycloadditions, see: a) J. G. Knight, S. W. Ainge, A. M. Harm, S. J. Harwood, H. I. Maughan, D. R. Armour, D. M. Hollinshead, A. A. Jaxa-Chamiec, *J. Am. Chem. Soc.* **2000**, *122*, 2944–2945; b) M. Sekido, K. Aoyagi, H. Nakamura, C. Kabuto, Y. Yamamoto, *J. Org. Chem.* **2001**, *66*, 7142–7147.

[3] For selected examples, see: a) R. Shintani, M. Murakami, T. Hayashi, *J. Am. Chem. Soc.* **2007**, *129*, 12356–12357; b) R. Shintani, S. Park, T. Hayashi, *J. Am. Chem. Soc.* **2007**, *129*, 14866–14867; c) C. Wang, J. A. Tunge, *J. Am. Chem. Soc.* **2008**, *130*, 8118–8119; d) K. Ohmatsu, N. Imagawa, T. Ooi, *Nat. Chem.* **2014**, *6*, 47–51; e) A. Khan, R. Zheng, Y. Kan, J. Ye, J. Xing, Y. J. Zhang, *Angew. Chem. Int. Ed.* **2014**, *53*, 6439–6442; *Angew. Chem.* **2014**, *126*, 6557–6560; f) A. Khan, L. Yang, J. Xu, L. Y. Jin, Y. J. Zhang, *Angew. Chem. Int. Ed.* **2014**, *53*, 11257–11260; *Angew. Chem.* **2014**, *126*, 11439–11442.

[4] For selected reviews, see: a) E. Nakamura, T. Hatakeyama, S. Ito, K. Ishizuka, L. Ilies, M. Nakamura, *Organic Reactions*, Wiley, Hoboken, **2004**; b) S. Enthaler, K. Junge, M. Beller, *Angew. Chem. Int. Ed.* **2008**, *47*, 3317–3321; *Angew. Chem.* **2008**, *120*, 3363–3367; c) A. Correa, O. Garcia Mancheno, C. Bolm, *Chem. Soc. Rev.* **2008**, *37*, 1108–1117; d) "Iron Catalysis: Fundamentals and Applications 33": *Topics in Organometallic Chemistry, Vol. 1* (Ed.: B. Plietker), Springer, Berlin, **2011**; e) C.-L. Sun, B.-J. Li, Z.-J. Shi, *Chem. Rev.* **2011**, *111*, 1293–1314; f) I. Bauer, H. J. Knölker, *Chem. Rev.* **2015**, *115*, 3170–3387.

[5] For pioneering work on iron nucleophilic catalysis, see: a) W. Hieber, K. Z. Beutner, *Naturforsch. B* **1960**, *15*, 323–324; b) M. J. Hogsed (E.I. du Pont de Nemours), US 2865707, **1958** [*Chem. Abstr.* **1959**, 539592]; c) J. L. Roustan, J. Y. Mérour, F. Houlihan, *Tetrahedron Lett.* **1979**, *20*, 3721–3724; d) Y. Xu, B. Zhou, *J. Org. Chem.* **1987**, *52*, 974–977; e) B. Zhou, Y. Xu, *J. Org. Chem.* **1988**, *53*, 4419–4421.

[6] For a review, see: a) B. Plietker, A. Dieskau, *Eur. J. Org. Chem.* **2009**, 775–787; selected work for C–C bond formation, see: b) B. Plietker, *Angew. Chem. Int. Ed.* **2006**, *45*, 1469–1473; *Angew. Chem.* **2006**, *118*, 1497–1501; c) B. Plietker, A. Dieskau, K. Möws, A. Jatsch, *Angew. Chem. Int. Ed.* **2008**, *47*, 198–201; *Angew. Chem.* **2008**, *120*, 204–207; for C–N bond formation: d) B. Plietker, *Angew. Chem. Int. Ed.* **2006**, *45*, 6053–6056; *Angew. Chem.* **2006**, *118*, 6200–6203; for C–S bond formation: e) M. Jegelka, B. Plietker, *Org. Lett.* **2009**, *11*, 3462–3465; for C–P bond formation: f) S. Rommel, A. P. Dieskau, B. Plietker, *Eur. J. Org. Chem.* **2013**, 1790–1795; for C–O bond formation: g) R. Trivedi, J. A. Tunge, *Org. Lett.* **2009**, *11*, 5650–5652.

[7] A. P. Dieskau, M. S. Holzwarth, B. Plietker, *J. Am. Chem. Soc.* **2012**, *134*, 5048–5051.

[8] For recent reviews, see: a) E. M. McGarrigle, E. L. Myers, O. Illa, M. A. Shaw, S. L. Riches, V. K. Aggarwal, *Chem. Rev.* **2007**, *107*, 5841–5883; b) X.-L. Sun, Y. Tang, *Acc. Chem. Res.* **2008**, *41*, 937–948; c) G. Li, L. Wang, Y. Huang, *Chin. J. Org. Chem.* **2013**, *33*, 1900–1918; d) C. Zhu, Y. Ding, L.-W. Ye, *Org. Biomol. Chem.* **2015**, *13*, 2530–2536.

[9] Recent work on sulfur ylides from our group, see: a) L.-Q. Lu, J.-R. Chen, W.-J. Xiao, *Acc. Chem. Res.* **2012**, *45*, 1278–1293; b) Q.-Q. Yang, C. Xiao, L.-Q. Lu, J. An, F. Tan, B.-J. Li, W.-J. Xiao, *Angew. Chem. Int. Ed.* **2012**, *51*, 9137–9140; *Angew. Chem.* **2012**, *124*, 9271–9274; c) L.-Q. Lu, F. Li, J. An, Y. Cheng, J.-R. Chen, W.-J. Xiao, *Chem. Eur. J.* **2012**, *18*, 4073–4079; d) Q.-Q. Yang, Q. Wang, J. An, J.-R. Chen, L.-Q. Lu, W.-J. Xiao, *Chem. Eur. J.* **2013**, *19*, 8401–8404; e) T.-R. Li, F. Tan, L.-Q. Lu, Y. Wei, Y.-N. Wang, Y.-Y. Liu, Q.-Q. Yang, J.-R. Chen, D.-Q. Shi, W.-J. Xiao, *Nat. Commun.* **2014**, *5*, 5500.

[10] For precious metal gold-, palladium-, or iridium-catalyzed cyclization reactions involving sulfur ylides, see: a) X. Huang, B. Peng, M. Luparia, L. F. R. Gomes, L. F. Veiros, N. Maulide, *Angew. Chem. Int. Ed.* **2012**, *51*, 8886–8890; *Angew. Chem.* **2012**, *124*, 9016–9020; b) S. Kramer, T. Skrydstrup, *Angew. Chem. Int. Ed.* **2012**, *51*, 4681–4684; *Angew. Chem.* **2012**, *124*, 4759–4762; c) X. Huang, S. Klimczyk, L. F. Veiros, N. Maulide, *Chem. Sci.* **2013**, *4*, 1105–1110; d) S. Klimczyk, A. Misale, X. Huang, N. Maulide, *Angew. Chem. Int. Ed.* **2015**, *54*, 10365–10369; *Angew. Chem.* **2015**, *127*, 10507–10511; e) I. K. Mangion, I. K. Nwamba, M. Shevlin, M. A. Huffman, *Org. Lett.* **2009**, *11*, 3566–3569, and Ref. [9e].

[11] For biological significance of indolines and selected examples of indoline synthesis, see: a) D. Zhang, H. Song, Y. Qin, *Acc. Chem. Res.* **2011**, *44*, 447–457; b) Q. Cai, C. Zheng, J.-W. Zhang, S.-L. You, *Angew. Chem. Int. Ed.* **2011**, *50*, 8665–8669; *Angew. Chem.* **2011**, *123*, 8824–8828; c) X.-C. Xiao, C. Wang, Y. Yao, J. Sun, Y.-C. Chen, *Angew. Chem. Int. Ed.* **2011**, *50*, 10661–10664; *Angew. Chem.* **2011**, *123*, 10849–10852; d) H. Xiong, H. Xu, S. Liao, Z. Xie, Y. Tang, *J. Am. Chem. Soc.* **2013**, *135*, 7851–7854; e) Y. Duan, L. Li, M.-W. Chen, C.-B. Yu, H.-J. Fan, Y.-G. Zhou, *J. Am. Chem. Soc.* **2014**, *136*, 7688–7700; f) C. Romano, M. Jia, M. Monari, E. Manoni, M. Bandini, *Angew. Chem. Int. Ed.* **2014**, *53*, 13854–13857; *Angew. Chem.* **2014**, *126*, 14074–14077.

[12] a) S. Purser, P. R. Moore, S. Swallow, V. Gouverneur, *Chem. Soc. Rev.* **2008**, *37*, 320–330; b) V. A. Petrov, *Fluorinated Heterocyclic Compounds: Synthesis Chemistry, and Applications*, Wiley, Hoboken, **2009**.

[13] C. Wang, N. Pahadi, J. A. Tunge, *Tetrahedron* **2009**, *65*, 5102–5109.

[14] The π-allyl iron complex **5** was prepared from TBAFe and corresponding allylic bromide according to known methods. See: a) M. Holzwarth, A. Dieskau, M. Tabassam, B. Plietker, *Angew. Chem. Int. Ed.* **2009**, *48*, 7251–7255; *Angew. Chem.* **2009**, *121*, 7387–7391; b) P. Wang, S. Liao, Y. Tang, *Org. Lett.* **2013**, *15*, 3054–3057.

[15] CCDC 1048203 (**5**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

[16] Other stronger bases such as *t*BuLi and NaH were also tried and similar results were obtained.

[17] A possible byproduct, **6a**, is hypothetically generated from **int-III** through the dissociation of weak π-coordination, the rotation of single bonds, and the final intramolecular S_N2' substitution. The computational details and results are listed in the Supporting Information.

[18] a) J. E. Klein, B. Miehlich, M. S. Holzwarth, M. Bauer, M. Milek, M. M. Khusniyarov, G. Knizia, H. J. Werner, B. Plietker, *Angew. Chem. Int. Ed.* **2014**, *53*, 1790 – 1794; *Angew. Chem.* **2014**, *126*, 1820 – 1824; b) J. E. Klein, G. Knizia, B. Miehlich, J. Kastner, B. Plietker, *Chem. Eur. J.* **2014**, *20*, 7254 – 7257.

Received: November 9, 2015
Published online: January 21, 2016

