Heterocycle Synthesis

DOI: 10.1002/anie.201004685

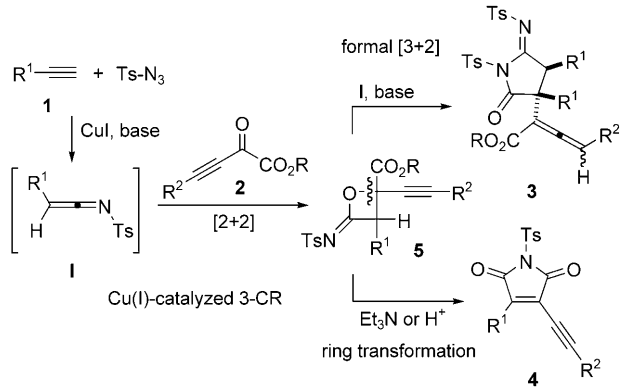
Three-Component Assembly and Divergent Ring-Expansion Cascades of Functionalized 2-Iminooxetanes**

*Weijun Yao, Lianjie Pan, Yiping Zhang, Gang Wang, Xiaoqin Wang, and Cheng Ma**

In memory of Yaozu Chen

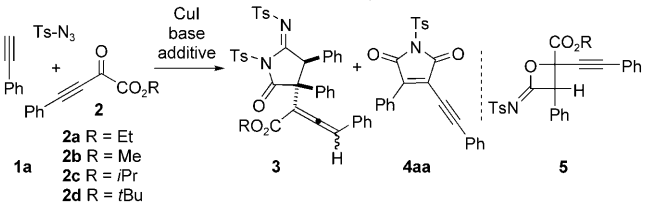
Small-ring heterocycles are of prominent importance because of their potential as bioactive compounds and synthetic building blocks. However, considerably less is known about 2-iminooxetanes, not only with respect to their formation but also in terms of their reactivity profiles. The synthesis of these compounds has previously been limited to those bearing electron-donating groups at the nitrogen atom.[1] Furthermore, we were unable to find a report of a ring-expansion reaction of this type of heterocycle, although many ring-enlargement processes of other small-ring systems have been reported to give functionalized molecules efficiently and expeditiously.[2] Intrigued by their potential synthetic applications, especially those based on a ring-opening process, we therefore focused our efforts on the construction of electron-deficient 2-iminooxetanes.[3,4] Herein, we present a novel copper(I)-catalyzed three-component reaction (3-CR) to produce functionalized *N*-sulfonyl-2-iminooxetanes **5** by a [2+2] cycloaddition of aromatic 2-oxobut-3-ynoates **2** with *N*-sulfonylketenimines **I** generated in situ.[5,6] These 2-iminooxetanes **5** are well-established substrates for selective rearrangement to functionalized pyrrolidinones **3** or maleimides **4** through a divergent ring-expansion cascade reaction (Scheme 1).

Initially, we found that, in the presence of triethylamine, CuI catalyzed the multicomponent reaction of phenylacetylene (**1a**), *p*-toluenesulfonyl azide (TsN_3), and ethyl 2-oxo-4-phenylbut-3-ynoate (**2a**)[7] to give the 5-iminopyrrolidinone **3aa** and maleimide **4aa** in 34 and 11% yield, respectively (Table 1, entry 1). However, when **2a** was replaced with methyl ester **2b**, the same product **4aa** was isolated as the major product along with a small amount of **3ab** (Table 1, entry 2). Realizing that both the structure of the ester moiety of **2** and the base used might be playing prominent roles in these processes, we then investigated the reaction of a set of esters **2a–d** under different basic conditions in CH_2Cl_2 to improve the reaction selectivity. Interestingly, the use of K_2CO_3 instead of NEt_3 almost completely suppressed the formation of **4aa** to yield products **3** cleanly (Table 1, entries 3–6). The addition of Et_4NI (10 mol%) accelerated the formation of **3** and gave the desired product in higher yield (Table 1, entries 4 and 5). However, the isopropyl ester **2c** proved to be the substrate of choice for this transformation in terms of the yield of products. In sharp contrast, reactions with cesium carbonate (Cs_2CO_3) as the base did not enable access to **3** but furnished [2+2] cycloadducts **5**, which were



Scheme 1. Assembly and divergent ring-expansion cascades of functionalized *N*-sulfonyl-2-iminooxetanes **5**. Ts = *p*-toluenesulfonyl.

Table 1: Effects of the ester moiety of **2** and the base.[a]



Entry	Base/additive	**1a** [equiv]	**2**	Yield [%][b] **3**	**4aa**
1	Et_3N	2.5	**2a**	34 (**3aa**)	11
2	Et_3N	2.5	**2b**	7 (**3ab**)	33
3	K_2CO_3/Et_4NI	3.0	**2a**	55 (**3aa**)	<5
4	K_2CO_3	3.0	**2c**	58 (**3ac**)	<2
5	K_2CO_3/Et_4NI	3.0	**2c**	73 (**3ac**)	<2
6	K_2CO_3/Et_4NI	3.0	**2d**	52 (**3ad**)	<2
7[c]	Cs_2CO_3	3.0	**2a**	<5 (**3aa**)	77
8[c]	Cs_2CO_3	1.5	**2a**	<2 (**3aa**)	75
9[c]	Cs_2CO_3	1.5	**2c**	<2 (**3ac**)	61

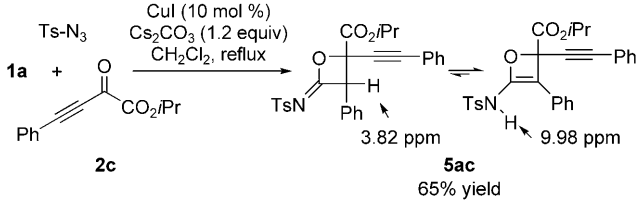
[a] Reaction conditions: **1a**/TsN_3 1:1, **2** (0.3 mmol), CuI (10 mol%), base (1.2 equiv), additive (10 mol%), CH_2Cl_2 (2 mL), reflux, N_2. [b] Yield of the isolated product. [c] After the consumption of **2**, trifluoromethanesulfonic acid (TfOH; 3 equiv) was added.

[*] W. Yao, L. Pan, Y. Zhang, G. Wang, X. Wang, Prof. C. Ma
Department of Chemistry, Zhejiang University
20 Yugu Road, Hangzhou 310027 (P.R. China)
Fax: (+86) 571-879-53-375
E-mail: mcorg@zju.edu.cn

[**] We thank the National Natural Science Foundation of China (Grant No. 20772106) and the Fundamental Research Funds for the Central Universities (2010QNA3010).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201004685.

stable in the reaction mixture and underwent smooth rearrangement to **4aa** upon treatment with TfOH (Table 1, entries 7–9). Although we expected the adduct **5** to be converted slowly into **4aa** on a silica-gel column at room temperature, careful chromatography over SiO_2 at −10 °C enabled the isolation of **5ac** in 65% yield (Scheme 2).

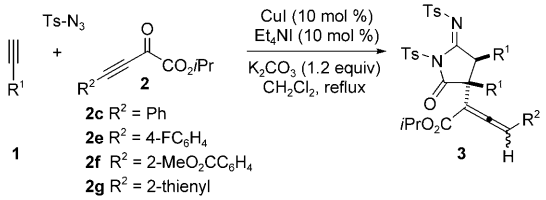


Scheme 2. Formation of 2-iminooxetane **5ac**.

^{1}H NMR spectroscopy of **5ac** revealed that the imine and enamine tautomers were present in a 1:4 ratio in acetone.[8] A possible rationale for the different reaction outcome in the presence of Cs_2CO_3 is that this base might enhance the coordination ability of the enamine form of **5ac** to give a stable complex with cesium or copper ions and thus inhibit the subsequent ring-opening cascade of **5ac**.[9]

Next, we explored the scope of the unique reaction to form 5-imino-2-pyrrolidinones (Table 2). A variety of aromatic alkynes **1** with both electron-donating (Table 2, entries 2, 3, and 5) and electron-withdrawing (Table 2, entries 4 and 6) substituents were suitable substrates for this tandem process in the presence of K_2CO_3 as the base. Electron-rich aryl alkynes displayed lower reactivity than their electron-deficient counterparts; as a result, an extended reaction time was required for the synthesis of products **3cc** and **3ec** in 31 and 41% yield, respectively (Table 2, entries 3 and 5). The alkenyl-substituted terminal alkyne **1g** did not undergo this reaction (Table 2, entry 7). Variation of the aromatic moiety of ketoesters **2** was also possible: aryl derivatives with different substitution patterns and a heterocycle-substituted substrate underwent the cycloaddition/ring-expansion cascade efficiently to give the corresponding products (Table 2, entries 8–10). The structure and relative configuration of compound **3aa** was confirmed unambiguously by single-crystal X-ray diffraction analysis, which indicated that the two adjacent R^1 groups were oriented *syn* to one another.[10] In all cases, the 5-imino-2-pyrrolidinone products **3**, which feature two contiguous stereogenic centers and a chiral allene unit, were obtained as a mixture of only two diastereomers (d.r. 1.7–1.1:1), as determined by ^{1}H NMR spectroscopy.

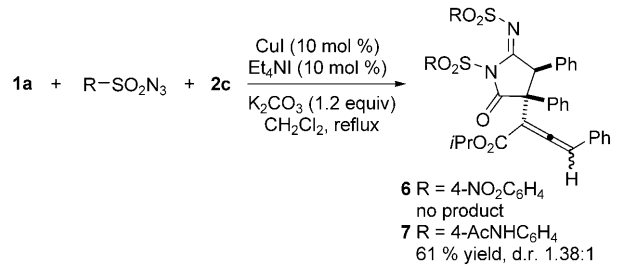
Table 2: Formation of 5-imino-2-pyrrolidinones **3**.[a]



Entry	**1**, R^1	**2**	*t* [h]	**3**	Yield [%][b] (d.r.)[c]
1	**1a**, Ph	**2c**	4	**3ac**	73 (1.5:1)
2	**1b**, 4-MeC_6H_4	**2c**	7	**3bc**	61 (1:1)
3	**1c**, 4-$MeOC_6H_4$	**2c**	12	**3cc**	31 (1.22:1)
4	**1d**, 4-ClC_6H_4	**2c**	4	**3dc**	57 (1:1)
5	**1e**, 3-$AcNHC_6H_4$	**2c**	12	**3ec**	41 (2:1)
6	**1f**, 3-$NO_2C_6H_4$	**2c**	8	**3fc**	48 (1.18:1)
7	**1g**, 1-cyclohexenyl	**2c**	24	–	–
8	**1a**, Ph	**2e**	7	**3ae**	59 (1.22:1)
9	**1a**, Ph	**2f**	4.5	**3af**	51 (1.22:1)
10	**1a**, Ph	**2g**	5.5	**3ag**	61 (1:1)

[a] Reaction conditions: **1** (3 equiv), TsN_3 (3 equiv), K_2CO_3 (1.2 equiv), **2** (0.3 mmol), CuI (10 mol%), Et_4NI (10 mol%), CH_2Cl_2 (2 mL), reflux, N_2. [b] Yield of the isolated product. [c] The diastereomeric ratio was determined by ^{1}H NMR spectroscopy.

We also examined variation of the aryl sulfonyl azide component for this transformation (Scheme 3). None of the desired product was formed when an azide with a very strongly electron withdrawing substituent (nitro group) on the aromatic ring was used. In contrast, 4-acetamidobenzenesulfonyl azide, which contains a moderately electron-donating substituent, underwent the transformation smoothly to give **7** with d.r. 1.38:1 in 61% yield.

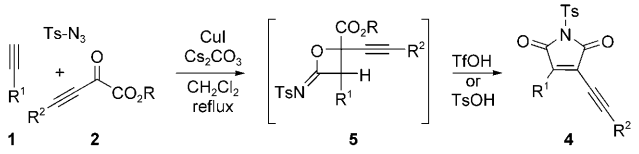


Scheme 3. Variation on the aryl sulfonyl azide component in the synthesis of pyrrolidinones.

Upon treatment with Cs_2CO_3 and CuI, a variety of ketoesters **2** reacted readily with tosyl azide and phenylacetylene (**1a**) to furnish the [2+2] cycloadducts **5**, which further rearranged to maleimides **4** in one pot in the presence of TfOH (Table 3, entries 1–5). Owing to the instability of intermediates and the product, TsOH (3.0 equiv) was used to deliver **4ag** in 55% yield (Table 3, entry 5). Variation of the substituent on terminal alkynes **1** was also tolerated (Table 3, entries 6–9). This protocol offers an alternative, conceptually new three-component synthetic route to 3,4-disubstituted maleimides: an important family of natural and synthetic compounds with valuable pharmacological and photophysical properties.[11]

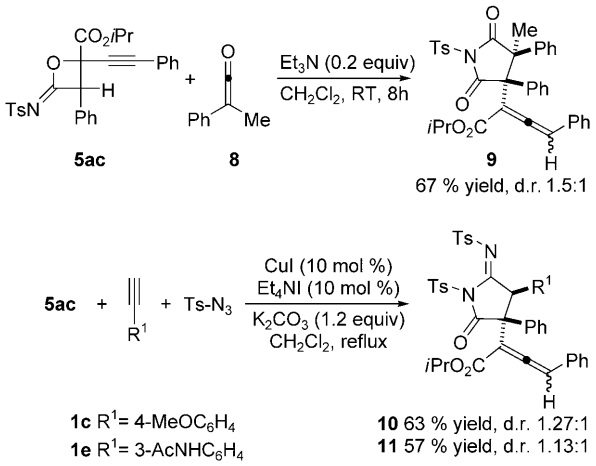
We used 2-iminooxetane **5ac** to explore the intermolecular cyclization of the unique small-ring system with an aryl ketene or another *N*-sulfonylketenimine (Scheme 4). Interestingly, Et_3N catalyzed a similar annulation of **5ac** with phenylmethylketene (**8**) to give a fully substituted succimidate derivative **9** with d.r. 1.5:1 in 67% yield in the absence of CuI; thus, a copper salt was not necessary for the ring opening and cyclization of **5ac**. 2-Iminooxetane **5ac** also reacted with

Table 3: Formation and acid-promoted ring expansion of 2-iminooxetanes **5**.[a]



Entry	**1**, R^1	**2**, R^2, R	t[b] [h]	**4**	Yield[c] [%]
1	**1a**, Ph	**2a**, Ph, Et	17	**4aa**	75
2	**1a**, Ph	**2c**, Ph, *i*Pr	12	**4ac**	61
3	**1a**, Ph	**2e**, 4-FC_6H_4, *i*Pr	12	**4ae**	72
4	**1a**, Ph	**2f**, 2-$MeO_2CC_6H_4$, *i*Pr	24	**4af**	41
5[d]	**1a**, Ph	**2g**, 2-thienyl, *i*Pr	21	**4ag**	55
6	**1c**, 4-$MeOC_6H_4$	**2a**, Ph, Et	13	**4ca**	35
7	**1d**, 4-ClC_6H_4	**2a**, Ph, Et	20	**4da**	51
8	**1f**, 3-$NO_2C_6H_4$	**2a**, Ph, Et	12	**4fa**	52
9	**1g**, 1-cyclohexenyl	**2a**, Ph, Et	12	**4ga**	57

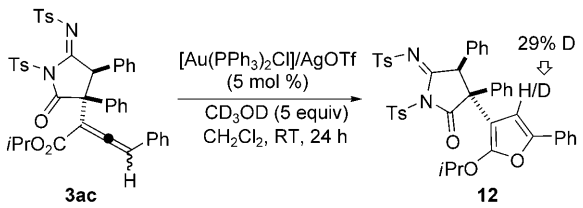
[a] Reaction conditions: **1** (1.5 equiv), TsN_3 (1.5 equiv), Cs_2CO_3 (1.2 equiv), **2** (0.3 mmol), CuI (10 mol%), CH_2Cl_2 (2 mL), reflux, N_2; after the consumption of **2**, TfOH (3.0 equiv) was added. [b] Reaction time for the consumption of **2**. [c] Yield of the isolated product. [d] TsOH (3.0 equiv) was used instead of TfOH.



Scheme 4. Cyclization of 2-iminooxetane **5ac**.

N-sulfonylketenimines generated in situ from **1c** or **1e** and *p*-toluenesulfonyl azide in the presence of CuI and K_2CO_3 to give the target products **10** (d.r. 1.27:1) and **11** (d.r. 1.13:1) in 63 and 57% yield, respectively.

The functionalized pyrrolidinone structure **3** provided a very useful handle for further structural manipulation. For example, **3ac** was readily transformed into the structurally complex furan derivative **12** in the presence of methanol by gold-catalyzed rearrangement of the allenoate moiety (Scheme 5).[12] Moreover, furan **12** was obtained as a single diastereomer from two mixtures of the two diastereomers of **3ac** with different d.r. values in similar yields. This result showed that the diastereoisomerism of **3ac** was due to the configuration of the allene group, and that the formation of the two carbon stereogenic centers in **3ac** was completely diastereoselective. Notably, the heterocyclic architecture of



Scheme 5. Gold-catalyzed rearrangement of allenoate **3ac**.

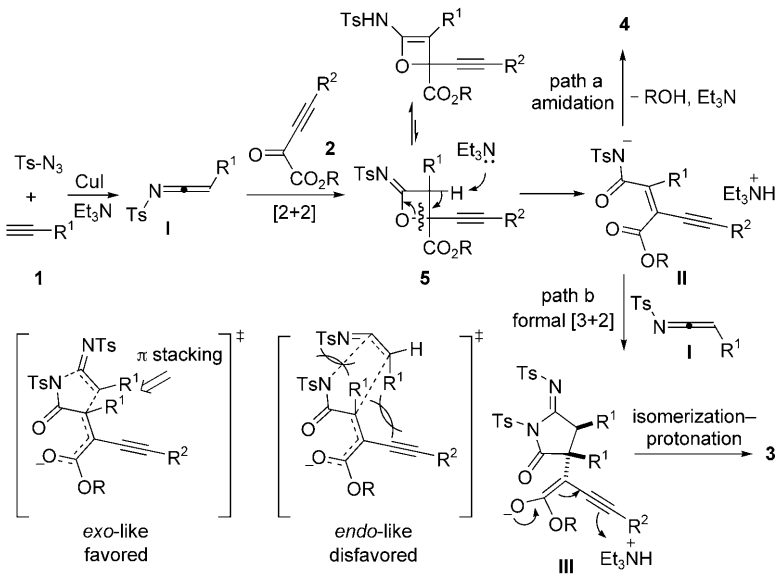
12, containing furan and pyrrolidinone units, could be assembled diastereoselectively from three simple acyclic substrates in only two operations.

A postulated mechanism for the present reaction cascade with Et_3N as the base is depicted in Scheme 6. Initially, the terminal alkyne **1** reacts with the sulfonyl azide upon treatment with CuI and Et_3N to give a ketenimine intermediate **I**,[13] which undergoes a regioselective [2+2] cycloaddition with a ketoester **2** to yield a 2-iminooxetane **5**. Upon deprotonation by Et_3N,[14] **5** is converted into a ring-opened intermediate **II**, which undergoes the subsequent cyclization cascades by two pathways. By path a, a maleimide **4** is formed through an intramolecular nucleophilic acylation along with the elimination of an alcohol. This process is sensitive to the ester moiety of **II** (Table 1, entries 1 and 2). On the other hand, when the amidate ion **II** attacks another unit of the ketenimine, a formal [3+2] cycloaddition furnishes an enolate **III** in the *trans* configuration (path b). The diastereoselectivity observed is explained by the favorable π stacking of an *exo*-like transition state in contrast to the steric repulsion in an *endo*-like transition state. Finally, the enolate **III** undergoes alkyne–allene isomerization and protonation to give the product **3** (path b).[15]

In conclusion, we have developed a novel copper(I)-catalyzed multicomponent reaction of terminal alkynes, sulfonyl azides, and aromatic 2-oxobut-3-ynoates to give functionalized 2-iminooxetanes. Divergent skeleton rearrangements of the 2-iminooxetane intermediates could be controlled well by choosing the appropriate reaction conditions. Thus, functionalized pyrrolidinone and maleimide derivatives with potential biological and synthetic utility could be synthesized highly efficiently. Experiments designed to explore the scope and asymmetric variants of this reaction as well as other synthetic applications of the unique 2-iminooxetanes are ongoing.

Experimental Section

3ac: Phenylacetylene (**1a**, 99 μL, 0.9 mmol) was added to a suspension of *p*-toluenesulfonyl azide (177.5 mg, 0.9 mmol), CuI (5.7 mg, 0.03 mmol), K_2CO_3 (49.7 mg, 0.36 mmol), Et_4NI (7.7 mg, 0.03 mmol), and isopropyl 2-oxo-4-phenylbut-3-ynoate (**2c**, 64.9 mg, 0.3 mmol) in CH_2Cl_2 (2 mL) in a Schlenk tube under N_2. The reaction mixture was stirred at reflux for 4 h and then diluted with CH_2Cl_2 (20 mL). The organic layer was washed with aqueous NH_4Cl (5 mL) and brines (5 mL) and then dried over anhydrous $MgSO_4$. The solvent was removed under vacuum, and the resulting oil was purified by column



Scheme 6. Plausible mechanism for the formation and divergent ring expansion of functionalized 2-iminooxetanes with Et_3N as the base.

chromatography (hexane/EtOAc 3:1) to give **3ac** (d.r. 1.5:1, 166.2 mg, 73%) as a white solid (m.p. 190–191 °C). The d.r. value of **3ac** could be raised to 23:1 through a single recrystallization from CH_2Cl_2/hexane, as determined by ^1H NMR spectroscopic analysis.

4aa: CuI (5.7 mg, 0.03 mmol) and Cs_2CO_3 (117.3 mg, 0.36 mmol) were added to a solution of *p*-toluenesulfonyl azide (88.7 mg, 0.45 mmol), phenylacetylene (**1a**, 50 μL, 0.45 mmol), and ethyl 2-oxo-4-phenylbut-3-ynoate (**2a**, 60.7 mg, 0.3 mmol) in CH_2Cl_2 (2 mL) under N_2. The mixture was stirred at reflux for 17 h and then cooled to 0–5 °C. TfOH (79 μL, 0.9 mmol) was then added, and the resulting mixture was stirred further at reflux for 4 h. The reaction was then quenched with saturated aqueous $NaHCO_3$ (5 mL), and the reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were washed with brine (10 mL), dried over anhydrous $MgSO_4$, and then filtered. The filtrate was concentrated under vacuum, and the resulting oil was purified by column chromatography (hexane/CH_2Cl_2 1:1) to afford **4aa** (96.2 mg, 75%) as a yellow solid (m.p. 198–199 °C).

Received: July 29, 2010
Revised: September 16, 2010
Published online: October 20, 2010

Keywords: alkynes · azides · cycloaddition · heterocycles · ring expansion

[1] For the formation of 2-iminooxetanes with alkyl groups at the nitrogen atom, see: a) G. Barbaro, A. Battaglia, P. Giorgianni, *J. Org. Chem.* **1988**, *53*, 5501; b) W. M. F. Fabian, R. Janoschek, *J. Am. Chem. Soc.* **1997**, *119*, 4253; c) L. A. Singer, G. A. Davis, R. L. Knutsen, *J. Am. Chem. Soc.* **1972**, *94*, 1188; d) F. M. Perna, V. Capriati, S. Florio, R. Luisi, *Tetrahedron Lett.* **2003**, *44*, 3477; e) R. Gandolfi, A. Gamba, M. Presutto, R. Oberti, N. Sardone, *Tetrahedron Lett.* **1996**, *37*, 917; for the ring opening of 2-iminooxetanes, see: f) G. Barbaro, A. Battaglia, P. Giorgianni, *J. Org. Chem.* **1992**, *57*, 5128; g) G. Barbaro, A. Battaglia, P. Giorgianni, *J. Org. Chem.* **1994**, *59*, 906; h) G. Barbaro, A. Battaglia, P. Giorgianni, *J. Org. Chem.* **1995**, *60*, 1020.

[2] a) B. M. Trost in *Small Ring Compounds in Organic Synthesis* (Ed.: A. de Meijere), Springer, Berlin, **1986**, p. 3; b) H. N. C. Wong, K. L. Lau, K. F. Tam in *Small Ring Compounds in Organic Synthesis* (Ed.: A. de Meijere), Springer, Berlin, **1986**, p. 83; c) A. Padwa, S. K. Bur, *Tetrahedron* **2007**, *63*, 5341; d) Y. Wang, R. L. Tennyson, D. Romo, *Heterocycles* **2004**, *64*, 605; for recent studies, see: e) Z. Zhang, Q. Zhang, S. Sun, T. Xiong, Q. Liu, *Angew. Chem.* **2007**, *119*, 1756; *Angew. Chem. Int. Ed.* **2007**, *46*, 1726; f) I. Braun, F. Rudroff, M. D. Mihovilovic, T. Bach, *Angew. Chem.* **2006**, *118*, 5667; *Angew. Chem. Int. Ed.* **2006**, *45*, 5541; g) B. M. Trost, J. Xie, N. Maulide, *J. Am. Chem. Soc.* **2008**, *130*, 17258; h) J. Barluenga, A. Gómez, J. Santamaría, M. Tomás, *Angew. Chem.* **2010**, *122*, 1328; *Angew. Chem. Int. Ed.* **2010**, *49*, 1306.

[3] For reviews of ring rearrangements, see: a) N. Vivona, S. Buscemi, V. Frenna, G. Gusmano, *Adv. Heterocycl. Chem.* **1993**, *56*, 49; b) G. Hajós, Z. Riedl, G. Kollenz, *Eur. J. Org. Chem.* **2001**, 3405; c) N. Isambert, R. Lavilla, *Chem. Eur. J.* **2008**, *14*, 8444.

[4] For our recent studies on ring transformations of heterocycles, see: a) C. Ma, H. Ding, Y. Zhang, M. Bian, *Angew. Chem.* **2006**, *118*, 7957; *Angew. Chem. Int. Ed.* **2006**, *45*, 7793; b) H. Ding, Y. Zhang, M. Bian, W. Yao, C. Ma, *J. Org. Chem.* **2008**, *73*, 578; c) H. Ding, Y. Zhang, W. Yao, D. Xu, C. Ma, *Chem. Commun.* **2008**, 5797; d) C. Ma, Y. Yang, *Org. Lett.* **2005**, *7*, 1343.

[5] For elegant [2 + 2] annulations of imines and iminophosphoranes, see: a) M. Whiting, V. V. Fokin, *Angew. Chem.* **2006**, *118*, 3229; *Angew. Chem. Int. Ed.* **2006**, *45*, 3157; b) X. Xu, D. Cheng, J. Li, H. Guo, J. Yan, *Org. Lett.* **2007**, *9*, 1585; c) Y. Shang, X. He, J. Hu, J. Wu, M. Zhang, S. Yu, Q. Zhang, *Adv. Synth. Catal.* **2009**, *351*, 2709; d) S.-L. Cui, J. Wang, Y.-G. Wang, *Org. Lett.* **2008**, *10*, 1267.

[6] For reviews on copper(I)-catalyzed multicomponent reactions that reply on the in situ generation of *N*-sulfonyl- or *N*-phosphorylketenimines, see: a) E. J. Yoo, S. Chang, *Curr. Org. Chem.* **2009**, *13*, 1766; b) P. Lu, Y. G. Wang, *Synlett* **2010**, 165.

[7] For recent references, see: a) Y. Liu, M. Liu, S. Guo, H. Tu, Y. Zhou, H. Gao, *Org. Lett.* **2006**, *8*, 3445; b) H. Li, Y.-Q. Wang, L. Deng, *Org. Lett.* **2006**, *8*, 4063; c) C. Francois-Endelmond, T. Carlin, P. Thuery, O. Loreau, F. Taran, *Org. Lett.* **2010**, *12*, 40; d) Q. Kang, Z.-A. Zhao, S.-L. You, *Org. Lett.* **2008**, *10*, 2031.

[8] For a review of tautomerism, see: A. I. Kol'tsov, G. M. Kheifets, *Russ. Chem. Rev.* **1972**, *41*, 452. According to ^1H NMR spectroscopic analysis, the isolated compound **5ac** contained **4aa** as an impurity (ca. 7%). Compound **5ac** could be stored under N_2 in a refrigerator at −20 °C for three weeks without any detectable change (see the Supporting Information for details).

[9] For a review of the synthetic application of cesium carbonate, see: a) T. Flessner, S. Doye, *J. Prakt. Chem.* **1999**, *341*, 186; for a review of the "cesium-ion effect" and macrocyclization, see: b) C. Galli, *Org. Prep. Proced. Int.* **1992**, *24*, 285.

[10] CCDC-779220(**3aa**), CCDC-779221(**4aa**), and CCDC-785681(**12**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

[11] a) C. Sánchez, C. Méndez, J. A. Salas, *Nat. Prod. Rep.* **2006**, *23*, 1007; b) H.-J. Knölker, K. R. Reddy, *Chem. Rev.* **2002**, *102*, 4303; c) T.-S. Yeh, T. J. Chow, S.-H. Tsai, C.-W. Chiu, C.-X. Zhao, *Chem. Mater.* **2006**, *18*, 832; d) B. K. Kaletas, V. N. Kozhevnikov, M. Zimine, R. M. Williams, B. Koenig, L. De Cola, *Eur. J. Org.*

Chem. **2005**, 3443; e) L. Bouissane, J. P. Sestelo, L. A. Sarandeses, *Org. Lett.* **2009**, *11*, 1285; f) Y. Li, H. Zou, J. Gong, J. Xiang, T. Luo, J. Quan, G. Wang, Z. Yang, *Org. Lett.* **2007**, *9*, 4057; g) D. Basavaiah, B. Devendar, K. Aravindu, A. Veerendhar, *Chem. Eur. J.* **2010**, *16*, 2031.

[12] For a review of metal-catalyzed allenoate cyclizations, see: a) S. Ma, *Acc. Chem. Res.* **2003**, *36*, 701; for recent references, see: b) L.-P. Liu, B. Xu, M. S. Mashuta, G. B. Hammond, *J. Am. Chem. Soc.* **2008**, *130*, 17642; c) A. S. K. Hashmi, C. Lothschütz, R. Döpp, M. Rudolph, T. D. Ramamurthi, F. Rominger, *Angew. Chem.* **2009**, *121*, 8392; *Angew. Chem. Int. Ed.* **2009**, *48*, 8243; d) Y. Shi, K. E. Roth, S. D. Ramgren, S. A. Blum, *J. Am. Chem. Soc.* **2009**, *131*, 18022.

[13] a) E. J. Yoo, M. Ahlquist, I. Bae, K. B. Sharpless, V. V. Fokin, S. Chang, *J. Org. Chem.* **2008**, *73*, 5520; b) I. Bae, H. Han, S. Chang, *J. Am. Chem. Soc.* **2005**, *127*, 2038; c) S. H. Cho, E. J. Yoo, I. Bae, S. Chang, *J. Am. Chem. Soc.* **2005**, *127*, 16046; d) M. P. Cassidy, J. Raushel, V. V. Fokin, *Angew. Chem.* **2006**, *118*, 3226; *Angew. Chem. Int. Ed.* **2006**, *45*, 3154; e) E. J. Yoo, I. Bae, S. H. Cho, H. Han, S. Chang, *Org. Lett.* **2006**, *8*, 1347; f) E. J. Yoo, S. H. Park, S. H. Lee, S. Chang, *Org. Lett.* **2009**, *11*, 1155.

[14] For the deprotonation of acyclic sulfonylimidates and their use as nucleophiles, see: a) R. Matsubara, F. Berthiol, S. Kobayashi, *J. Am. Chem. Soc.* **2008**, *130*, 1804; b) S. Kobayashi, R. Matsubara, *Chem. Eur. J.* **2009**, *15*, 10694; c) H. Van Nguyen, R. Matsubara, S. Kobayashi, *Angew. Chem.* **2009**, *121*, 6041; *Angew. Chem. Int. Ed.* **2009**, *48*, 5927.

[15] For 3-alkynoate-to-allenoate isomerizations, see: a) T. Yasokouchi, K. Kanematsu, *Tetrahedron Lett.* **1989**, *30*, 6559; b) A. K. Basak, M. A. Tius, *Org. Lett.* **2008**, *10*, 4073; c) H. Liu, D. Leow, K.-W. Huang, C.-H. Tan, *J. Am. Chem. Soc.* **2009**, *131*, 7212.

