ChemPubSoc Europe

DOI: 10.1002/chem.201304701

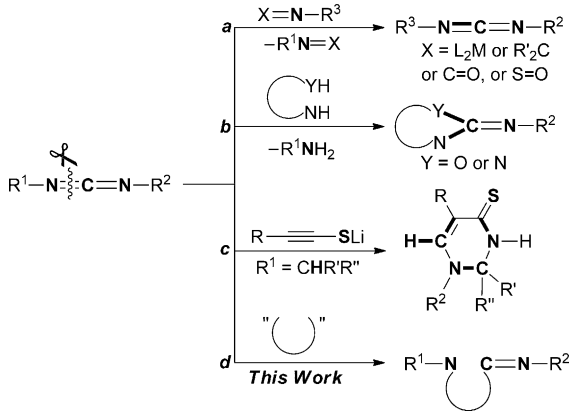
CHEMISTRY
A European Journal
Communication

Multicomponent Reactions

Cleavage of the C=N Bond in Carbodiimides via Release of High Ring Strain: A New Strategy for the Selective Synthesis of 2-Aminoaryl Alkynyl Imines

Yi Zhou,[a] Yue Chi,[a] Fei Zhao,[a] Wen-Xiong Zhang,*[a, b] and Zhenfeng Xi[a]

Abstract: A novel pattern of the cleavage and reorganization of C=N bond in the multicomponent reaction (MCR) of terminal alkynes or haloalkynes, carbodiimides, and benzynes is achieved for the first time to construct efficiently 2-aminoaryl alkynyl imines. The selective formation and ring-opening of the azetine intermediate with the high ring strain is essential for this reaction. Further transformation of 2-aminoaryl alkynyl imines via the Cu-catalyzed cycloisomerization is explored to provide steroselectively the bi-, tri-, and tetracyclic fused pyrrolines.



Scheme 1. Reconnected models of the cleaved fragments.

The cleavage of C=N double bonds is of significant synthetic interest, and is a more challenging issue than that of C–N single bonds because of the stronger bond energy.[1] In contrast to the cleavage of C–N single bonds,[1] the cleavage of C=N double bonds is much less explored.[2–5] Imines, which have the typical C=N double bonds, could undergo through acid or transition-metal mediated metathesis to cleave C=N double bonds.[2] In case of carbodiimide having the cumulative C=N double bonds,[6,7] three types of the cleavage and reorganization of C=N double bonds have been reported. At the early stage, the cleavage of C=N double bonds of carbodiimide were reported in the stoichiometric metathesis reaction of carbodiimide with transition-metal imido complexes or unsaturated substrates to reconstruct different carbodiimide derivatives (Scheme 1 a).[3] The dual nucleophilic addition/elimination could also lead to the cleavage of C=N double bonds (Scheme 1 b).[4] We reported the cleavage and reorganization of C=N and C(sp^3)–H bonds in the reaction of carbodiimide with lithium alkynethiolate to efficiently construct 2,3-dihydropyrimidinthiones (Scheme 1 c).[5] In this process, these three cleaved fragments were reconnected by the formation of two C–N single bonds, one C=C double bond, and one C–H bond. However, as far as we are aware, the reconnected pattern between "NR^1" and "$C{=}N{-}R^2$" units is not reported (Scheme 1 d).

Although recent years have witnessed a significant development of aryne chemistry, the reaction chemistry of carbodiimides with benzynes is not reported.[8,9] Herein, we wish to report a room temperature and transition-metal-free multicomponent reaction of readily available terminal alkynes or haloalkynes, carbodiimides, and two molecules of benzynes to construct 2-aminoaryl alkynyl imines. The alkynyl imines are useful synthons in organic synthesis because of their polyfunctionality,[10,11] however, such 2-aminoaryl alkynyl imines could not accessed by other methods. In this process, two fragments formed via the cleavage of C=N bond of the carbodiimide are both incorporated into 2-aminoaryl alkynyl imines by the formation of one C–H (Br and I), two C–N, and two C–C bonds. The selective formation and ring opening of the azetine intermediate with the high ring strain is essential for this reaction. Furthermore, the mechanism and application of 2-aminoaryl alkynyl imines are explored.

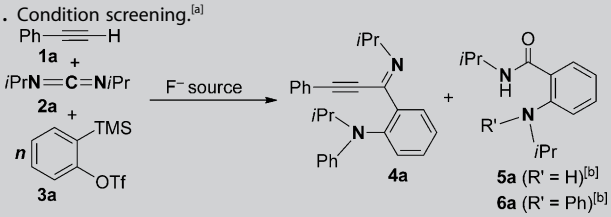
The multicomponent coupling[12] of phenylethyne (**1 a**), *N*,*N*′-diisopropylcarbodiimide (DIC, **2 a**), 2-(trimethylsilyl) phenyltriflate (**3 a**) was chosen as a model to establish the reaction conditions (Table 1). As control experiment, no reaction was observed between **1 a** and **2 a** or between **1 a** and **3 a** in the presence of CsF in MeCN at room temperature (entries 1 and 2). However, the reaction of **2 a** with **3 a** gave two hydrolysis products **5 a** and **6 a** (entries 3 and 4). Interestingly, the multicomponent coupling of **1 a**, **2 a**, and **3 a** yielded the unexpected al-

[a] *Y. Zhou, Y. Chi, Dr. F. Zhao, Prof. Dr. W.-X. Zhang, Prof. Dr. Z. Xi*
Beijing National Laboratory for Molecular Sciences (BNLMS),
Key Laboratory of Bioorganic Chemistry
and Molecular Engineering of Ministry of Education, College of Chemistry
Peking University, Beijing 100871 (P.R. China)
Fax: (+86) 10-62751708
E-mail: wx_zhang@pku.edu.cn

[b] *Prof. Dr. W.-X. Zhang*
State Key Laboratory of Elemento-Organic Chemistry
Nankai University, Tianjin 300071 (P.R. China)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201304701.

Table 1. Condition screening.[a]



Entry	Substrates	*n*	F^- source	Solvent	T [°C]	*t* [h]	Yield [%][c] 4a	5a	6a
1	**1a+2a**	0	CsF	MeCN	RT	12	–	–	–
2	**1a+3a**	1	CsF	MeCN	RT	12	–	–	–
3	**2a+3a**	1	CsF	MeCN	RT	12	0	29	33
4	**2a+3a**	2	CsF	MeCN	RT	12	0	22	48
5	**1a+2a+3a**	2	CsF	MeCN	RT	12	82	0	12
6	**1a+2a+3a**	2	TBAF	THF	RT	12	8	67	21
7	**1a+2a+3a**	2	KF, [18]crown-6	THF	RT	9	95	0	trace
8	**1a+2a+3a**	2	KF, [18]crown-6	THF[d]	RT	9	64	11	23
9	**1a+2a+3a**	3	KF, [18]crown-6	THF	RT	9	83	0	10
10	**1a+2a+3a**	1	KF, [18]crown-6	THF	RT	9	63	13	17
11	**1a+2a+3a**	2	KF, [18]crown-6	THF	0	9	0	trace	trace
12	**1a+2a+3a**	2	KF, [18]crown-6	THF	60	9	trace	trace	trace

[a] Conditions: terminal alkynes (0.5 mmol), carbodiimide (0.5 mmol), benzyne precursors, fluoride source (1.2 mmol) in solvent (3 mL), unless otherwise noted. [b] H_2O (5 mmol). [c] Isolated yields. [d] THF was not dried.

kynyl imine **4a** in 82% yield of the isolated product followed by a small amount of **6a**. After many screening experiments, the optimal condition was established. Thus, as shown in entry 7, the mixture of **1a**, **2a,** and **3a** (2 equiv) was treated with the effective fluoride source KF/[18]crown-6 (2.4 equiv) in THF at room temperature for 9 h to give **4a** in 95% yield.

Summarized in Table 2 are representative results from the MCRs among terminal alkynes, carbodiimides, and 2-(trimethylsilyl) phenyltriflate (**3a**). Carbodiimides, such as *i*PrN=C=N*i*Pr, CyN=C=NCy, *t*BuN=C=N*t*Bu could be used as suitable substrates to yield the corresponding compounds **4a–c** in moderate to high isolated yields. When the unsymmetrical carbodiimide, such as *t*BuN=C=NEt was applied, the sole regioisomer **4d** was obtained in 74% isolated yield. The exclusive formation of **4d** is ascribed to the steric hindrance of *tert*-butyl group resulting in the prior reactivity of benzyne with the C=N double bond adjoining the ethyl group of the carbodiimide. A large range of polyfunctional terminal alkynes could be used for the MCRs. The reaction was not affected by either electron-withdrawing or electron-donating substituents or their positions at the phenyl ring (**4e–k**). Naphthalenyl or thiophenyl substituted terminal alkynes were also applicable to yield the corresponding products **4l** and **4m**. In addition, a wide variety of the aliphatic alkynes also smoothly underwent this reaction to generate the corresponding products **4n–t**. The keto group in **4u** survived the present conditions. It was noted that, in addition to terminal alkynes, bromoalkyne or iodoalkyne could also act as suitable substrates under the same conditions to provide the bromo- or iodo-substituted 2-aminoaryl alkynyl imines **4a-Br, 4n-Br**, and **4a-I**.

In addition to aryne precursor **3a**, other aryne precursors have been tested under the optimized reaction conditions to provide the corresponding products **4v–x** in high yields (Table 3).

Although the 2-aminoaryl alkynyl imines could, in principle, have two possible isomers *E* or *Z*, the ^1H and ^{13}C NMR spectra of the resulting 2-aminoaryl alkynyl imine compounds (**4a–x**) suggested that only one isomer is present for each compound in solution. The X-ray structure analyses of **4h** and **4a-Br** revealed that it is *E* in the solid state (Figure 1).

In order to gain mechanistic insight into the present MCRs, a deuterium labeling experiment was conducted. When phenylacetylene-D was used under the standard conditions, the deuterated product **4a-D** was isolated in 87% yield with 95% D-incorporation on the *ortho* position of the phenyl ring (reaction 1).

Then, we aimed to isolate and characterize the possible intermediates by exploring the different substrates. When *N*-phenyl-*N*′-cyclohexyl carbodiimide was allowed to react with benzyne and phenylethyne, **4y** was formed in only 20% yield. In the above reaction, 9-imino-9,10-dihydroacridine **7** coupled by two benzynes and one carbodiimide was isolated as the major product in 58% yield (reaction 2). However, no reaction was observed between **7** and phenylethyne under the same condition. This result showed that the formation of **4y** and **7** was a competitive process, and

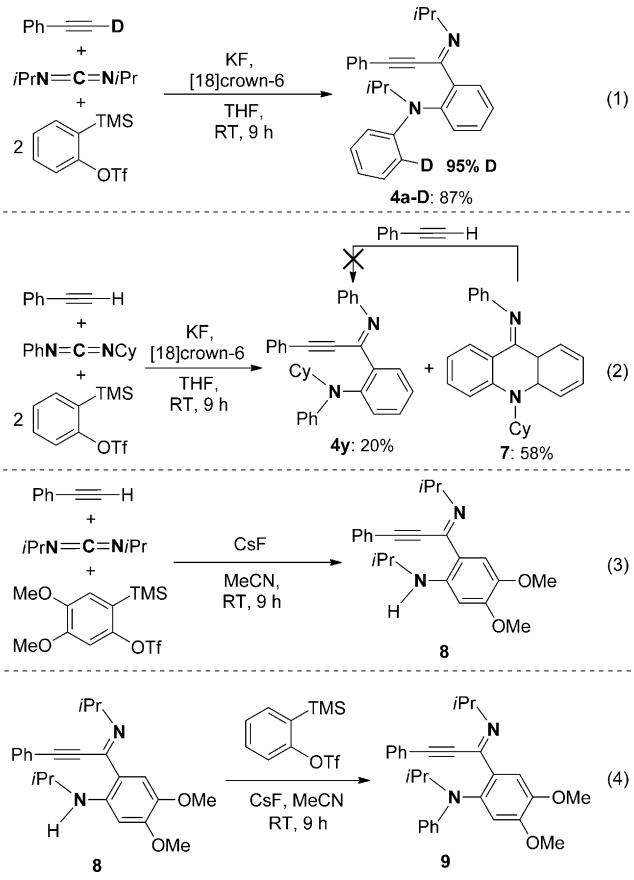
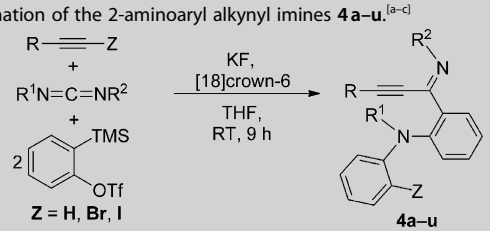
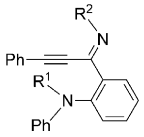


Table 2. Formation of the 2-aminoaryl alkynyl imines **4a–u**.[a–c]

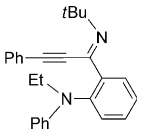


Z = H, Br, I — **4a–u**

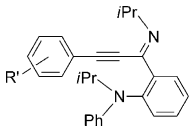
Z = H



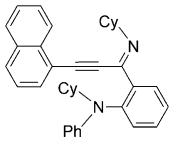
4a: $R^1 = R^2 = i$Pr, 95%
4b: $R^1 = R^2$ = Cy, 78%
4c: $R^1 = R^2 = t$Bu, 90%



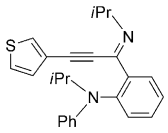
4d: 74%



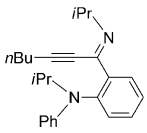
4e: R′ = 4-Me, 80%
4f: R′ = 4-MeO, 82%
4g: R′ = 4-F, 82%
4h: R′ = 3-Cl, 82%
4i: R′ = 2-Br, 93%
4j: R′ = 4-CF_3, 92%
4k: R′ = 4-CN, 79%



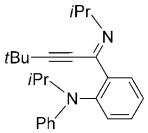
4l: 88%



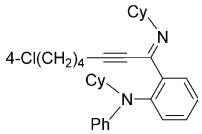
4m: 75%



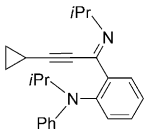
4n: 70%



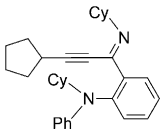
4o: 73%



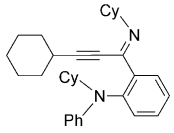
4p: 77%



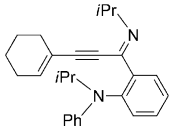
4q: 76%



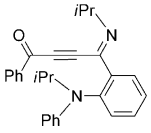
4r: 72%



4s: 80%

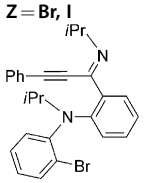


4t: 73%

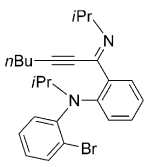


4u: 84%

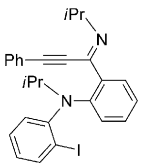
Z = Br, I



4a-Br: 71%



4n-Br: 63%



4a-I: 58%

[a] Conditions: terminal alkynes (0.5 mmol), carbodiimide (0.5 mmol), benzyne precursor (1.0 mmol, KF (1.2 mmol), and [18]crown-6 (1.2 mmol) in THF (3.0 mL) at room temperature for 9 h, unless otherwise noted. [b] Yields of isolated product. [c] THF was dried.

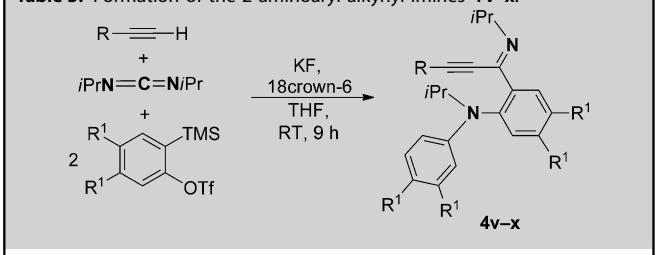
also it excluded the possibility between two benzynes and one C=N bond of carbodiimide for the present reaction process. Interestingly, when 4,5-dimethoxy aryne precursor was utilized, we successfully isolated the product **8** with the N–H moiety. Next the isolated products **8** was treated with one equivalent of arynes to give the final product **9** with the incorporation of two different arynes. Also, the formation of **9** could be achieved by one-pot sequential process from two different arynes.

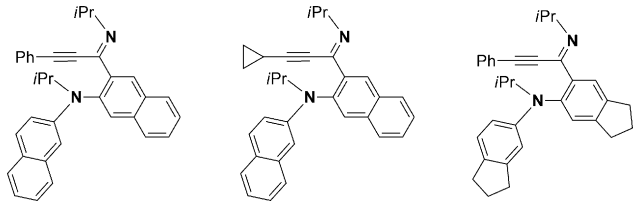
Based on the above evidence, a proposed mechanism for the formation of **4**–**6** is shown in Scheme 2 (see the Supporting Information for other possible pathways). The benzyne precursor first reacts with fluoride source to generate in situ benzyne. Then an azetine intermediate **A** is formed via [2+2]-cycloaddition between C=N double bond of the carbodiimide with benzyne.[13] Owing to the high ring strain, the regioselective ring-opening of **A** leads to the formation of **A′**. The addition of a terminal alkyne to **A′** could undergo through the six-membered ring transition state **B** to yield the intermediate **C**. The subsequent N–H bond arylation of **C** by benzyne should give the final product **4**. In the presence of the trace of water, **5** is easily observed. The subsequent reaction of **5** with benzyne gives **6**.

Further transformation of 2-aminoaryl alkynyl imines was explored (Scheme 3). When *N*-isopropyl alkynyl imine **4n** was subjected to the Cu-catalyzed cycloisomerization conditions,[10e,i] the bicyclic fused pyrroline **10a** was formed exclusively in good yield. Similarly, the Cu-catalyzed cycloisomerization of *N*-cyclohexyl alkynyl imine **4p** or *N*-cyclohexyl 2-cyclopentylethynyl imine **4r** provided the corresponding tricyclic fused pyrroline **10b** and the tetracyclic fused pyrroline **10c** in high isolated yields, respectively. The X-ray structure of **10c** revealed unambiguously the configuration of the resulting four-membered ring (Figure 2). The mechanism for the formation of **10a–c** is similar to the process proposed by Gevorgyan,[10e,i] which possibly undergoes the base-promoted propargyl-allenyl isomerization/two sequential [1,5]-H shift/CuI-catalyzed [2+2]-cycloaddition (see the Supporting Information for the detailed mechanism). These results are in striking contrast with what was observed previously for *N*-isopropyl alkynyl imines possessing an alkyl group at the propargylic position providing the mixtures of the bicyclic fused pyrrolines in low yields and pyrroles. As far as we are aware, it is the first time that tri- or tetracyclic fused pyrrolines are prepared in high yields from alkynyl imines. This is probably owing to the strong electron-donating character of the *ortho*-PhRN substituent promoting two sequential 1,5-H shifts for the formation of fused pyrrolines.

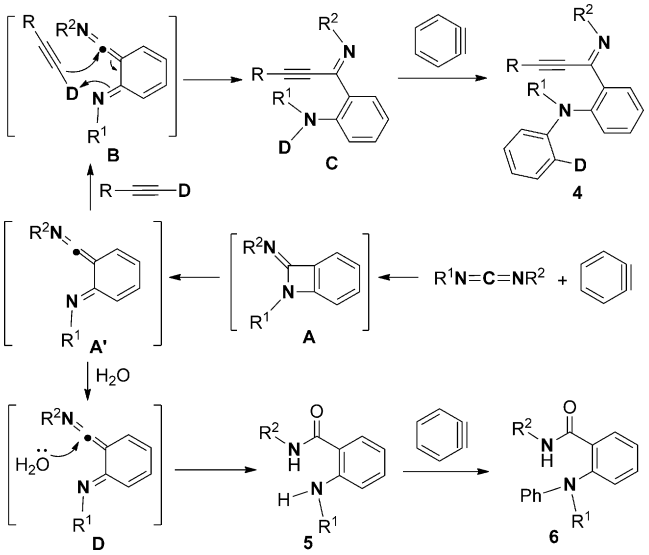
In summary, a one-pot multicomponent reaction of readily available terminal alkynes, carbodiimides, and two molecules of benzynes is achieved for the first time to afford 2-aminoaryl alkynyl imines. The reaction has the following features: 1) is transition-metal free, 2) has mild reaction conditions, 3) is highly efficient, and 4) a new reconnected pattern between "NR^1" and the "C=N–R^2" units is formed via C=N bond cleavage of the carbodiimide. The selective forma-

Table 3. Formation of the 2-aminoaryl alkynyl imines **4v–x**.[a–c]





[a] Conditions: terminal alkynes (0.5 mmol), carbodiimide (0.5 mmol), aryne precursors (1.0 mmol), KF (1.2 mmol), and [18]crown-6 (1.2 mmol) in THF (3.0 mL) at room temperature for 9 h, unless otherwise noted. [b] Yields of isolated product. [c] THF was dried.



Scheme 2. A possible mechanism for the formation of **4**–**6**.

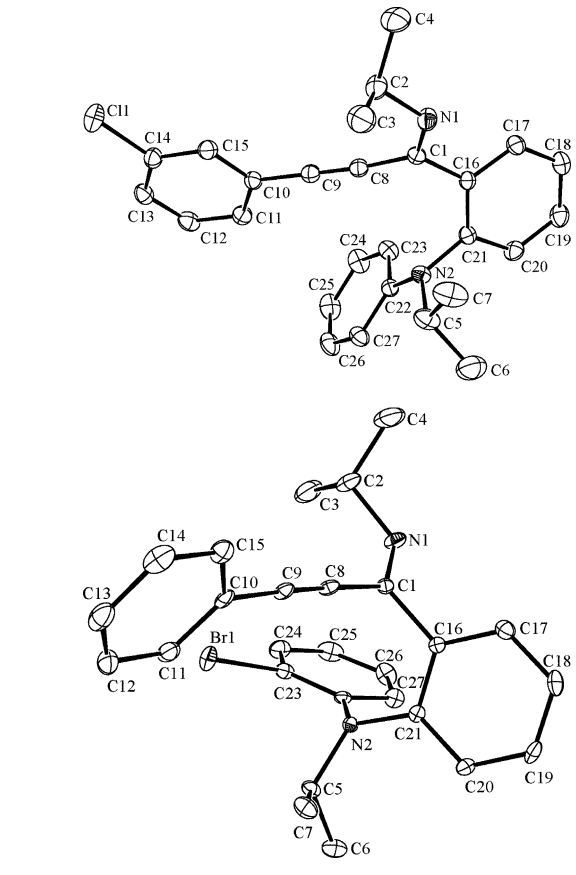
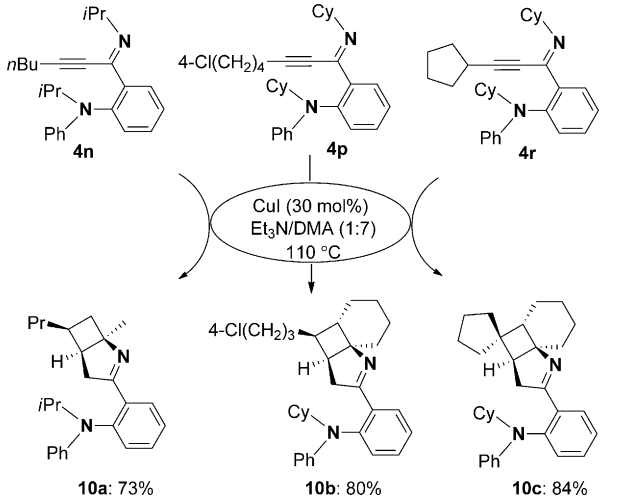


Figure 1. ORTEP drawing of **4h** (top) and **4a-Br** (bottom) with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond length (Å): **4h**: C1–C8 1.439(3), C1–C16 1.492(3), C8–C9 1.193(3), C1–N1 1.286(3), C2–N1 1.463(3), C5–N2 1.472(3), C21–N2 1.433(3), C22–N2 1.403(3), C14–Cl1 1.743(3); **4a-Br**: C1–C8 1.456(7), C1–C16 1.508(6), C8–C9 1.189(6), C1–N1 1.250(6), C2–N1 1.471(6), C5–N2 1.487(6), C21–N2 1.425(6), C22–N2 1.416(6), C23–Br1 1.901(5).



Scheme 3. Synthesis of bi-, tri-, tetracyclic fused pyrrolines **10a**–**c** via Cu-catalyzed cycloisomerization.

tion and ring opening of the azetine intermediate with the high ring strain is essential for this reaction. Further transformation of 2-aminoaryl alkynyl imines via copper-catalyzed cycloisomerization is explored to provide steroselectively the bi-, tri-, and tetracyclic fused pyrrolines.

Experimental Section

General procedure for the multicomponent coupling of terminal alkynes or haloalkynes, carbodiimides, and arynes

KF (1.2 mmol, 69.7 mg) was added to a stirred solution of terminal alkynes or haloalkynes **1** (0.5 mmol), carbodiimides **2** (0.5 mmol), 2-(trimethylsilyl)aryl triflates **3** (1.0 mmol), and [18]crown-6 (1.2 mmol, 317.2 mg) in THF (3 mL) under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 9 h, and the re-

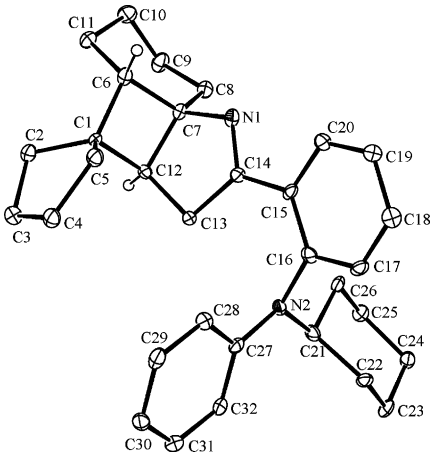


Figure 2. ORTEP drawing of **10c** with 30% thermal ellipsoids. Hydrogen atoms, except those on the C6 and C12 atoms, are omitted for clarity. Selected bond length (Å): C1–C6 1.563(5), C1–C12 1.580(5), C6–C7 1.555(5), C12–C13 1.536(5), C13–C14 1.520(5), C7–N1 1.476(5), C14–N1 1.289(5), C16–N2 1.450(5), C21–N2 1.467(4), C27–N2 1.399(5).

sulting mixture was evaporated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to give products **4**.

Synthesis of 10a–c

In a 25 mL flask, CuI (0.09 mmol, 17 mg), anhydrous DMA (1.50 mL), and 2-aminoaryl alkynyl imines **4n**, **4p**, or **4r** (0.30 mmol) were successively added. After CuI was dissolved, anhydrous Et_3N (0.22 mL) was added. The mixture was stirred at 110 °C for 12 h with protection from light. When the reaction was complete, the mixture was cooled to room temperature and H_2O (10 mL) was added. After the above mixture was extracted with hexane (3×5 mL), the combined organic phase was dried over $MgSO_4$. After the solvent was evaporated under reduced pressure, the residue was purified over a column of silica gel (petroleum ether/ethyl acetate = 10:1) to afford the pure fused pyrrolines **10a–c**.

Acknowledgements

This work was supported by the Natural Science Foundation of China, and the 973 Program (2011CB808600). We also thank Prof. Zhang-Jie Shi of Peking University and Prof. Feng Shi of Henan University for useful discussion.

Keywords: alkynes · benzynes · C=N activation · carbodiimides · multicomponent reactions

[1] For reviews on C–N bond cleavage, see: a) N. J. Turner, *Chem. Rev.* **2011**, *111*, 4073; b) A. Roglans, A. Pla-Quintana, M. Moreno-Mañas, *Chem. Rev.* **2006**, *106*, 4622; c) S.-I. Murahashi, *Angew. Chem.* **1995**, *107*, 2670; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2443; d) K. Khumtaveeporn, H. Alper, *Acc. Chem. Res.* **1995**, *28*, 414.

[2] Selected examples for C=N bond cleavage of imines, see: a) R. L. Zuckerman, S. W. Krska, R. G. Bergman, *J. Am. Chem. Soc.* **2000**, *122*, 751; b) J. M. McInnes, P. Mountford, *Chem. Commun.* **1998**, 1669; c) G. K. Cantrell, T. Y. Meyer, *J. Am. Chem. Soc.* **1998**, *120*, 8035; d) G. Tóth, I. Pintér, A. Messmer, *Tetrahedron Lett.* **1974**, *15*, 735.

[3] For examples of carbodiimide metathesis, see: a) Y. Kuninobu, T. Uesugi, A. Kawata, K. Takai, *Angew. Chem.* **2011**, *123*, 10590; *Angew. Chem. Int. Ed.* **2011**, *50*, 10406; b) T.-G. Ong, G. P. A. Yap, D. S. Richeson, *Chem. Commun.* **2003**, 2612; c) R. L. Zuckerman, R. G. Bergman, *Organometallics* **2000**, *19*, 4795; d) K. R. Birdwhistell, J. Lanza, J. Pasos, *J. Organomet. Chem.* **1999**, *584*, 200; e) M. Al-Talib, I. Jibril, J. C. Jochims, G. Huttner, *Tetrahedron* **1985**, *41*, 527; f) K. Weiss, P. Kindl, *Angew. Chem.* **1984**, *96*, 616; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 629.

[4] Selected examples for the dual nucleophilic addition/elimination, see: a) H. Shen, Y. Wang, Z. Xie, *Org. Lett.* **2011**, *13*, 4562; b) M. Ispikoudi, K. E. Litinas, K. C. Fylaktakidou, *Heterocycles* **2008**, *75*, 1321; c) P. Molina, M. Alajarín, M.-J. P. de Vega, A. López, *Heterocycles* **1989**, *29*, 1607.

[5] a) Y. Wang, F. Zhao, Y. Zhou, Y. Chi, Z. Wang, W.-X. Zhang, Z. Xi, *Chem. Eur. J.* **2013**, *19*, 10643; b) Z. Wang, Y. Wang, W.-X. Zhang, Z. Hou, Z. Xi, *J. Am. Chem. Soc.* **2009**, *131*, 15108.

[6] Selected reviews of carbodiimide chemistry, see: a) M. Nishiura, Z. Hou, *Bull. Chem. Soc. Jpn.* **2010**, *83*, 595; b) T. Suzuki, W.-X. Zhang, M. Nishiura, Z. Hou, *J. Synth. Org. Chem. Jpn.* **2009**, *67*, 451; c) H. Shen, Z. Xie, *J. Organomet. Chem.* **2009**, *694*, 1652; d) W.-X. Zhang, Z. Hou, *Org. Biomol. Chem.* **2008**, *6*, 1720; e) F. T. Edelmann, *Adv. Organomet. Chem.* **2008**, *57*, 183; f) A. Williams, I. T. Ibrahim, *Chem. Rev.* **1981**, *81*, 589.

[7] Selected examples of carbodiimide chemistry, see: a) Y. Wang, Y. Chi, W.-X. Zhang, Z. Xi, *J. Am. Chem. Soc.* **2012**, *134*, 2926; b) Y. Wang, W.-X. Zhang, Z. Wang, Z. Xi, *Angew. Chem.* **2011**, *123*, 8272; *Angew. Chem. Int. Ed.* **2011**, *50*, 8122; c) W. Yi, J. Zhang, M. Li, Z. Chen, X. Zhou, *Inorg. Chem.* **2011**, *50*, 11813; d) I. J. Casely, J. W. Ziller, W. J. Evans, *Organometallics* **2011**, *30*, 4873; e) Z. Du, W. Li, X. Zhu, F. Xu, Q. Shen, *J. Org. Chem.* **2008**, *73*, 8966; f) A. G. M. Barrett, M. R. Crimmin, M. S. Hill, P. B. Hitchcock, S. L. Lomas, M. F. Mahon, P. A. Procopiou, K. Suntharalingam, *Organometallics* **2008**, *27*, 6300; g) R. T. Yu, T. Rovis, *J. Am. Chem. Soc.* **2008**, *130*, 3262; h) X. Xu, J. Gao, D. Cheng, J. Li, G. Qiang, H. Guo, *Adv. Synth. Catal.* **2008**, *350*, 61; i) A. Volonterio, M. Zanda, *J. Org. Chem.* **2008**, *73*, 7486; j) S. Zhou, S. Wang, G. Yang, Q. Li, L. Zhang, Z. Yao, Z. Zhou, H.-B. Song, *Organometallics* **2007**, *26*, 3755; k) T.-G. Ong, J. S. O'Brien, I. Korobkov, D. S. Richeson, *Organometallics* **2006**, *25*, 4728; l) W.-X. Zhang, M. Nishiura, Z. Hou, *J. Am. Chem. Soc.* **2005**, *127*, 16788.

[8] For reviews on benzynes, see: a) C. Wu, F. Shi, *Asian J. Org. Chem.* **2013**, *2*, 116; b) A. Dubrovskiy, N. A. Markina, R. C. Larock, *Org. Biomol. Chem.* **2013**, *11*, 191; c) P. M. Tadross, B. M. Stoltz, *Chem. Rev.* **2012**, *112*, 3550; d) J. T. S. Yeoman, S. E. Reisman, *Nature* **2012**, *490*, 179; e) A. Bhunia, S. R. Yetra, A. T. Biju, *Chem. Soc. Rev.* **2012**, *41*, 3140; f) S. S. Bhojgude, A. T. Biju, *Angew. Chem.* **2012**, *124*, 1550; *Angew. Chem. Int. Ed.* **2012**, *51*, 1520; g) C. Wentrup, *Aust. J. Chem.* **2010**, *63*, 979; h) H. Butenschön, *Angew. Chem.* **2007**, *119*, 4086; *Angew. Chem. Int. Ed.* **2007**, *46*, 4012; i) W. Sander, *Acc. Chem. Res.* **1999**, *32*, 669.

[9] For an example on synthesis of benzynes, see: Y. Himeshima, Y. Sonoda, H. Kobayashi, *Chem. Lett.* **1983**, 1211.

[10] Selected examples for the synthetic application of alkynyl imines, see: a) G. Cheng, X. Cui, *Org. Lett.* **2013**, *15*, 1480; b) Z. Chen, J. Zhu, H. Xie, S. Li, Y. Wu, Y. Gong, *Org. Lett.* **2010**, *12*, 4376; c) F. Sha, X. Huang, *Angew. Chem.* **2009**, *121*, 3510; *Angew. Chem. Int. Ed.* **2009**, *48*, 3458; d) P. R. Likhar, M. S. Subhas, S. Roy, M. L. Kantam, B. Sridhar, R. K. Seth, S. Biswas, *Org. Biomol. Chem.* **2009**, *7*, 85; e) A. W. Sromek, A. L. Rheingold, D. J. Wink, V. Gevorgyan, *Synlett* **2006**, 2325; f) N. S. Josephsohn, M. L. Snapper, A. H. Hoveyda, *J. Am. Chem. Soc.* **2004**, *126*, 3734; g) H. Dube, N. Gommermann, P. Knochel, *Synthesis* **2004**, 2015; h) I. Hachiya, K. Ogura, M. Shimizu, *Org. Lett.* **2002**, *4*, 2755; i) A. V. Kel'in, A. W. Sromek, V. Gevorgyan, *J. Am. Chem. Soc.* **2001**, *123*, 2074; j) B. G. Van den Hoven, H. Alper, *J. Am. Chem. Soc.* **2001**, *123*, 10214; k) P. J. Campos, J. Arranz, M. A. Rodríguez, *Tetrahedron* **2000**, *56*, 7285; l) X.-F. Ren, E. Turos, *J. Org. Chem.* **1994**, *59*, 5858.

[11] Selected examples for the preparation of alkynyl imines, see: a) H. Yoshida, Y. Asatsu, Y. Mimura, Y. Ito, J. Ohshita, K. Takaki, *Angew. Chem.* **2011**, *123*, 9850; *Angew. Chem. Int. Ed.* **2011**, *50*, 9676; b) G. S. Kumar, C. Kurumurthy, P. S. Rao, B. Veeraswamy, P. S. Rao, B. Narsaiah, *Helv. Chim. Acta* **2011**, *94*, 1692; c) W.-X. Zhang, M. Nishiura, Z. Hou, *Angew. Chem.* **2008**, *120*, 9846; *Angew. Chem. Int. Ed.* **2008**, *47*, 9700; d) S. Mangelinckx, V. Van Speybroeck, P. Vansteenkiste, M. Waroquier, N. De Kimpe, *J. Org. Chem.* **2008**, *73*, 5481; e) Q.-L. Dong, G.-S. Liu, H.-B. Zhou, L. Chen, Z.-J. Yao, *Tetrahedron Lett.* **2008**, *49*, 1636; f) E. Barnea, T. Andrea, J.-C. Berthet, M. Ephritikhine, M. S. Eisen, *Organometallics* **2008**, *27*, 3103; g) K.

Komeyama, D. Sasayama, T. Kawabata, K. Takehira, K. Takaki, *J. Org. Chem.* **2005**, *70*, 10679; h) E. Barnea, T. Andrea, M. Kapon, J.-C. Berthet, M. Ephritikhine, M. S. Eisen, *J. Am. Chem. Soc.* **2004**, *126*, 10860; i) K. Uneyama, H. Watanabe, *Tetrahedron Lett.* **1991**, *32*, 1459.

[12] For reviews of MCRs, see: a) B. B. Touré, D. G. Hall, *Chem. Rev.* **2009**, *109*, 4439; b) *Multicomponent Reactions*; J. Zhu, H. Bienayme, Eds.; Wiley-VCH: Weinheim, Germany, **2005**; c) J. Zhu, *Eur. J. Org. Chem.* **2003**, 1133; d) A. Jacobi von Wangelin, H. Neumann, D. Gördes, S. Klaus, D. Strübing, M. Beller, *Chem. Eur. J.* **2003**, *9*, 4286.

[13] a) K. A. Tehrani, N. De Kimpe, *Curr. Org. Chem.* **2009**, *13*, 854; b) F. Couty, G. Evano, *Synlett* **2009**, 3053; c) B. Alcaide, P. Almendros, C. Aragoncillo, *Chem. Rev.* **2007**, *107*, 4437; d) Y. Dejaegher, N. M. Kuz'menok, A. M. Zvonok, N. De Kimpe, *Chem. Rev.* **2002**, *102*, 29.

Received: December 1, 2013
Published online on February 2, 2014