



Cite this: *Chem. Sci.*, 2017, 8, 4130

Received 12th January 2017  
Accepted 20th March 2017

DOI: 10.1039/c7sc00161d  
rsc.li/chemical-science

# Total synthesis of aristolactam alkaloids via synergistic C–H bond activation and dehydro-Diels–Alder reactions†

Mallu Chenna Reddy <sup>a</sup> and Masilamani Jeganmohan <sup>\*ab</sup>

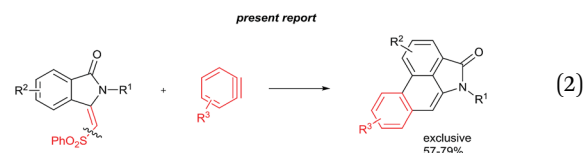
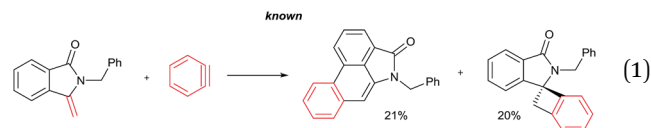
A concise total synthesis of aristolactam alkaloids by a synergistic combination of C–H bond activation and dehydro-Diels–Alder reactions is described. To achieve the synthesis two new synthetic methodologies, namely the oxidative cyclization of benzamides with vinyl sulfone leading to 3-methyleneisindolin-1-ones via a ruthenium-catalyzed C–H bond activation, and a dehydro-Diels–Alder reaction followed by the fluoride ion mediated desulfonylation of 3-methyleneisindolin-1-ones with benzynes, were developed. The method presented allows the opportunity for the construction of all the rings of aristolactams from easily available starting materials.

## Introduction

Aristolactams are naturally occurring phenanthrene lactam alkaloids. These alkaloids are isolated from *Aristolochiaceae*, *Annonaceae*, *Piper Piperaceae*, and *Saururaceae* plant species.<sup>1–3</sup> Aristolactams are frequently used as folk medicines in several countries.<sup>2d–f</sup> Meanwhile, these molecules show an interesting array of biological properties such as anti-inflammatory, anti-platelet, anti-mycobacterial, neuroprotective and anti-cancer activities.<sup>2,3</sup> Due to their unique structural features and potential biological activities, a considerable amount of effort has been devoted to synthesizing these molecules by several research groups.<sup>4</sup> After surveying all these elegant contributions, we understood that a general and easily approachable method for synthesizing these alkaloids with a minimum number of steps from easily affordable starting materials is needed. Meanwhile, the new method should be general for the preparation of numerous aristolactam derivatives in order to explore the utility of these molecules in various areas. Particularly, the utility of these alkaloids in various biological applications has been extensively increased in the past two decades.

Herein, we wish to report an efficient two step synthesis of aristolactam alkaloids from easily available and affordable starting materials such as aromatic acids, alkyl amines and alkenes. To execute the synthesis two new synthetic methodologies, namely the preparation of 3-methyleneisindolin-1-ones

via a ruthenium-catalyzed oxidative cyclization of aromatic amides with vinyl sulfone, and a dehydro-Diels–Alder reaction followed by SO<sub>2</sub>Ph cleavage of 3-methyleneisindolin-1-ones with benzynes, were developed. The present method is compatible for the preparation of various aristolactam derivatives including sensitive I, Br, Cl, F and CF<sub>3</sub> functional groups. The combination of C–H bond activation and dehydro-Diels–Alder reactions allows a short and efficient synthesis of several aristolactam alkaloids in good yields.



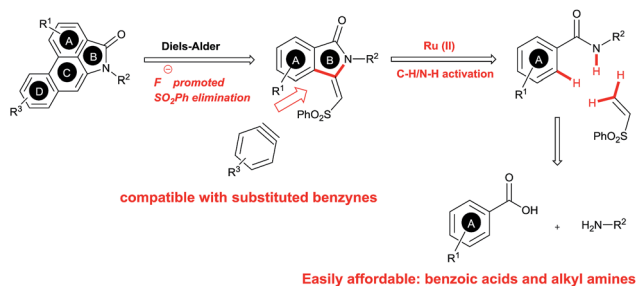
The goal of this work is to construct aristolactam cyclic rings A–D in a simple manner from easily affordable starting materials (Scheme 1). Rings A and B having 3-methyleneisindolinone can be constructed via a metal-catalyzed C–H/N–H annulation of substituted benzamides with alkenes in one pot.<sup>5–7</sup> Substituted benzamides can be easily prepared from benzoic acids and amines. Rings C and D can be constructed in one pot via the dehydro-Diels–Alder reaction of 3-methyleneisindolin-1-ones with benzynes.<sup>8,9</sup> However, this type of cycloaddition reaction is not very effective, because it provides competing side products along with the expected product (eqn (1)).<sup>4i</sup> To

<sup>a</sup>Department of Chemistry, Indian Institute of Science Education and Research, Pune 411021, India. E-mail: mjeganmohan@iiserpune.ac.in

<sup>b</sup>Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, Tamil Nadu, India. E-mail: mjeganmohan@iitm.ac.in

† Electronic supplementary information (ESI) available: Detailed experimental procedures and spectroscopic data. CCDC 1526825. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7sc00161d





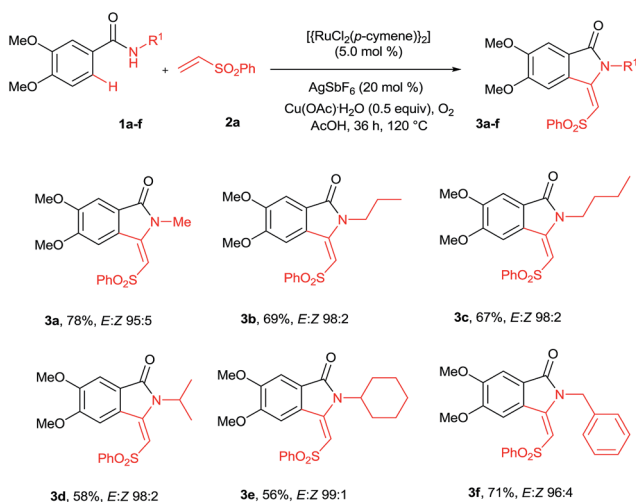
Scheme 1 Retrosynthetic analysis.

overcome this problem, we engineered a molecule that has a cleavable  $\text{SO}_2\text{Ph}$  group at the  $\beta$ -carbon of alkene of 3-methyleneisindolin-1-one. After the cycloaddition reaction, the sulfonyl group can be easily cleaved by a fluoride source in the same step (eqn (2)). Thus, the cycloaddition reaction can be done in a highly selective manner.

## Results and discussion

Our continuous interest in ruthenium-catalyzed C–H bond activation reaction prompted us to explore the possibility of developing a new synthetic route for the synthesis of key intermediates 3-methyleneisindolin-1-ones *via* the ruthenium-catalyzed oxidative cyclization of benzamides with vinyl phenyl sulfone.<sup>6c,d,7f</sup> The oxidative cyclization of *N*-methyl benzamide **1a** with phenyl vinyl sulfone (**2a**) in the presence of  $[\{\text{RuCl}_2(p\text{-cymene})\}_2]$  (5 mol%),  $\text{AgSbF}_6$  (20 mol%) and  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  (0.5 equiv.) under oxygen at 120 °C for 36 h provided 3-methyleneisindolin-1-one **3a** in 78% yield in an 95 : 5 *E/Z* ratio (Scheme 2).

Initially, the cyclization reaction was examined with various solvents such as 1,2-dichloroethane, THF, 1,4-dioxane, DMF, toluene,  $\text{CF}_3\text{COOH}$  and  $\text{CH}_3\text{COOH}$  (Table 1). Among them, acetic acid was effective yielding product **3a** in 78% yield (entry 7). Other solvents such as toluene and THF were less effective,

Scheme 2 Cyclization of *N*-substituted benzamides.Table 1 Optimization studies<sup>a</sup>

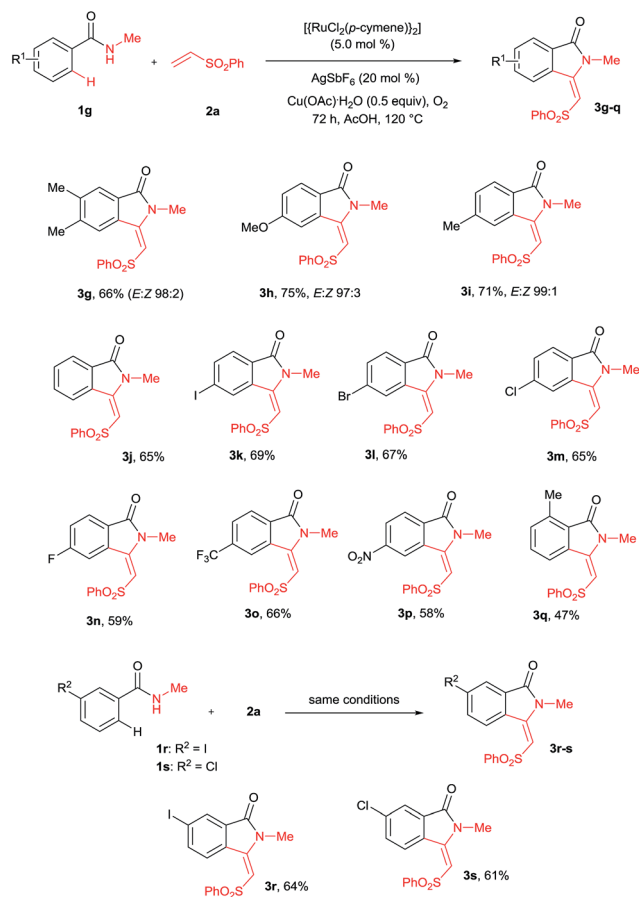
Entry	Solvent	Additive	Yield of <b>3a</b> <sup>b</sup> (%)
1	$\text{ClCH}_2\text{CH}_2\text{Cl}$	$\text{AgSbF}_6$	—
2	THF	$\text{AgSbF}_6$	15
3	1,4-Dioxane	$\text{AgSbF}_6$	—
4	DMF	$\text{AgSbF}_6$	—
5	Toluene	$\text{AgSbF}_6$	20
6	$\text{CF}_3\text{COOH}$	$\text{AgSbF}_6$	—
7	$\text{CH}_3\text{COOH}$	$\text{AgSbF}_6$	78
8	$\text{CH}_3\text{COOH}$	$\text{AgBF}_4$	42
9	$\text{CH}_3\text{COOH}$	$\text{AgOTf}$	46
10	$\text{CH}_3\text{COOH}$	$\text{KPF}_6$	15
11	$\text{CH}_3\text{COOH}$	—	NR

<sup>a</sup> All reactions were carried out under the following conditions: **1a** (75 mg), **2a** (1.5 equiv.),  $[\{\text{RuCl}_2(p\text{-cymene})\}_2]$  (5 mol%), additive (20 mol%) and  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  (50 mol%) in solvent at 120 °C for 36 h under an oxygen atmosphere. <sup>b</sup> Isolated yield.

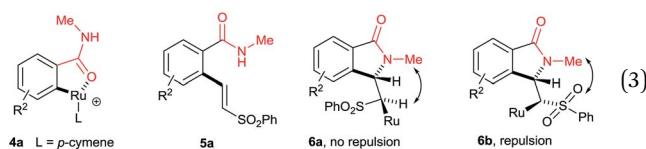
affording product **3a** in 20% and 15% yields, respectively (entries 2 and 5). The remaining solvents were not effective. The cyclization reaction was further examined with additives  $\text{AgSbF}_6$ ,  $\text{AgBF}_4$ ,  $\text{AgOTf}$  and  $\text{KPF}_6$ . Among them,  $\text{AgSbF}_6$  was effective, providing product **3a** in 78% yield (entry 7). The remaining additives were less effective for the cyclization reaction (entries 8–10). The cyclization reaction did not proceed without  $\text{AgSbF}_6$  (entry 11).  $\text{AgSbF}_6$  is used to generate a cationic ruthenium species for activating weak amide group assisted C–H bonds.<sup>5c,d</sup>  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  has been widely used as an oxidant for weak chelating group assisted C–H bond activation.<sup>5c</sup> Usually, a 2.0 equiv. amount of copper source is needed for this type of reaction. However, in the present reaction, a 0.5 equiv. amount of copper source was used and the remaining amount of the copper source was regenerated under oxygen. The cyclization reaction was examined with various substrates such as methyl, propyl, butyl, isopropyl, cyclohexyl and benzyl substituted benzamides **1b–f** (Scheme 2). These reactions worked very well, providing the expected cyclization products **3b–f** in 69%, 67%, 58%, 56% and 71% yields, respectively, in 96 : 4 to 99 : 1 *E/Z* ratios.

A variety of substituted benzamides **1g–s** were compatible for the cyclization reaction (Scheme 3). Electron-releasing (OMe and Me) and halogen (I, Br, Cl and F) substituted benzamides **1g–n** efficiently reacted with **2a** affording isindolin-1-ones **3g–n** in good yields. The less reactive electron withdrawing ( $\text{CF}_3$  and  $\text{NO}_2$ ) substituted benzamides **1o–p** also efficiently reacted with **2a** providing products **3o** and **3p** in good yields. Similarly, *ortho* and *meta* substituted benzamides **1q–s** also efficiently participated in the reaction, giving products **3q–s** in 47%, 64% and 61% yields, respectively. Particularly, in the *meta* substituted benzamides **1r–s**, C–H bond activation takes place at a less hindered  $\text{C}_6\text{–H}$ .





Scheme 3 Scope of substituted benzamides.



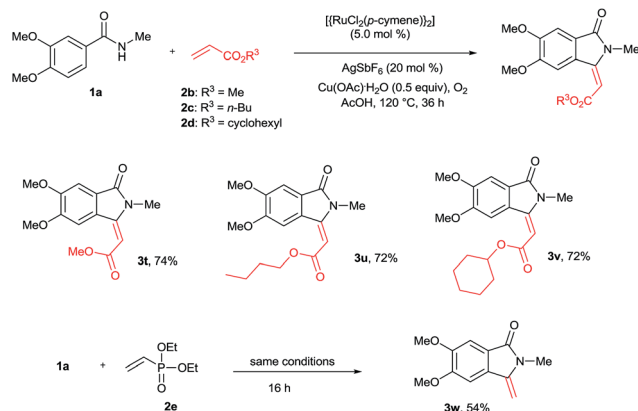
The cyclization reaction proceeds *via* a cationic ruthenium(II) catalyzed *ortho* alkenylation of benzamide **1a** with alkene **2a** *via* intermediate **4a**, providing *ortho* alkenylated benzamide **5a**.<sup>7i</sup> Intramolecular addition of the amide N-H bond of **5a** into an alkene moiety affords product **3** (eqn (1), for the detailed mechanism see the ESI<sup>†</sup>). It is important to note that a minor amount of *Z* stereoisomer was observed in the cyclization of electron-rich OMe and Me substituted benzamides. Intermediate **6b** accounts for the formation of the *Z* stereoisomer. Presently, the exact reason for the observation of a minor amount of the *Z* stereoisomer is unclear. However, in halogen and electron-withdrawing substituted benzamides, the *E* stereoisomer was observed exclusively. The observation of high *E* stereoselectivity for product **3** is mainly due to the formation of intermediate **6a** in which the sulfonyl moiety of the alkene and the cyclic tertiary C-N-Me bond are anti to each other (eqn (3)). Syn coplanarity is avoided due to the steric hindrance of the methyl and  $SO_2Ph$  groups of intermediate **6b**.<sup>7i</sup>

The cyclization reaction was further examined with various alkenes (Scheme 4). Methyl, *n*-butyl and cyclohexyl acrylates **2b–d** efficiently reacted with **1a** yielding cyclization products **3t–v** in good yields. In these reactions, only *E* stereoselectivity was observed. Diethyl vinylphosphonate (**2e**) was also efficiently involved in the reaction, giving product **3w** in 54% yield with a free exo double bond. In the product **3w**, phosphonate ( $P=O(OEt)_2$ ) was cleaved under the present reaction conditions. The cyclization reaction was not compatible with acrylonitrile, methyl vinyl ketone and styrene.

To explore the possibility of the preparation of aristolactam derivatives, the dehydro-Diels–Alder reaction of **3** with benzyne was examined (Scheme 5). The cycloaddition of **3g** with benzyne precursor **7a** in the presence of CsF in  $CH_3CN$  at  $30\text{ }^\circ C$  for 24 h gave aristolactam derivative **9a** in 66% yield. It is believed that after cycloaddition reaction, intermediate **8a** is formed in which  $SO_2Ph$  is cleaved by a fluoride ion. The formation of intermediate **8a** was confirmed by MALDI-TOF experiment (for the detailed mechanism, see the ESI<sup>†</sup>).<sup>8</sup> However, in the cycloaddition reaction of **3w** with **7a**, no product was observed. In the cycloaddition of **3t** in which an ester substituent is present at the  $\beta$ -carbon of the alkene with **7a**, a mixture of heterocyclic molecules **9b** and **9b'** was observed in a 4 : 1 diastereoselective ratio. In the reaction, the  $CO_2Me$  group did not eliminate like  $SO_2Ph$ . This result clearly reveals that the  $SO_2Ph$  group is crucial in order to obtain aristolactams in greater yield with high selectivity.

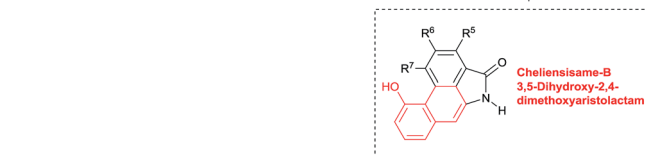
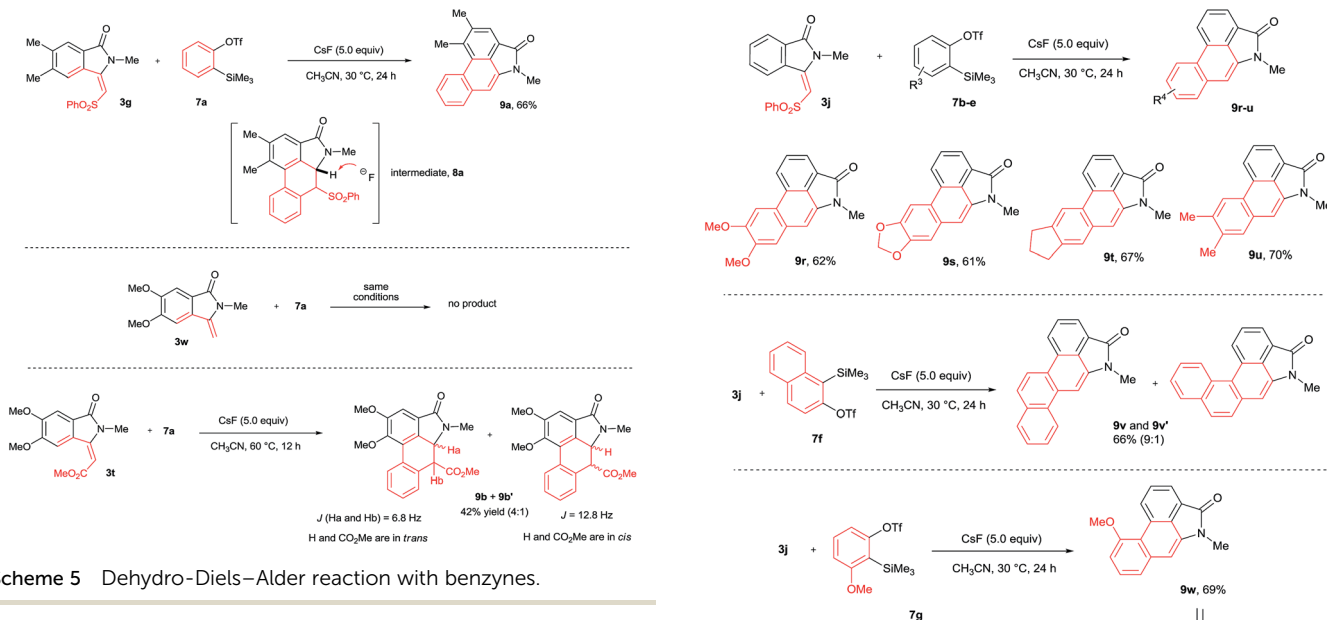
The cycloaddition reaction was examined with various *N*-substituted indolin-1-one derivatives **3b–f** (Scheme 6). *N*-propyl, butyl, iso-propyl, cyclohexyl and benzyl substituted isoindolin-1-ones **3b–f** underwent cycloaddition with **7a** providing aristolactam derivatives **9c–g** in good yields. Meanwhile, OMe, Me, I, Br, Cl, F and  $CF_3$  substituted isoindolin-1-ones **3h–s** also efficiently participated in the reaction yielding products **9h–q** in good yields.

The scope of the cycloaddition reaction was further examined with substituted benzynes **7b–g** (Scheme 7). Symmetrical benzynes such as 3,4-dimethoxy benzyne, 3,4-dimethyl benzyne, indene derivative and 1,3-benzodioxole reacted with **3j**, providing cyclization products **9r–u** in good yields. When



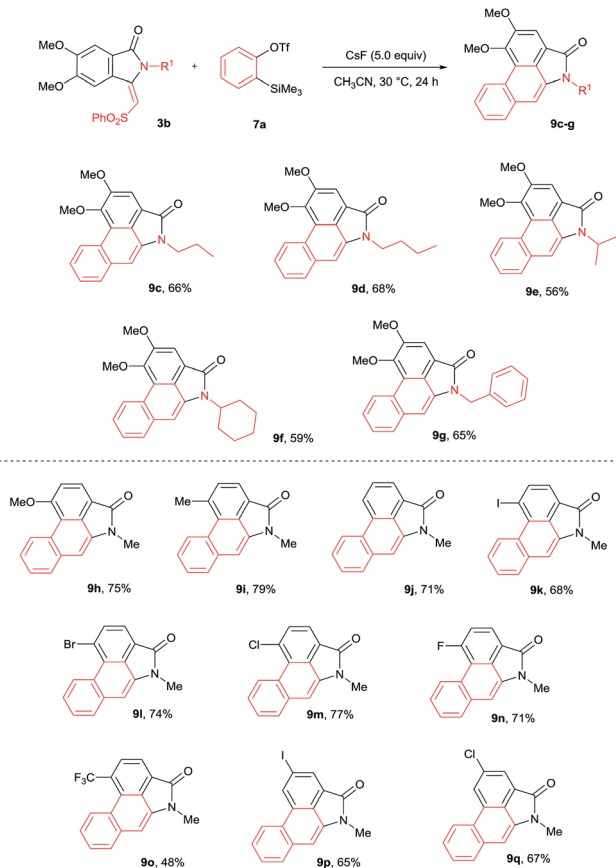
Scheme 4 Scope of alkenes.





diffraction analysis. It is important to note that by using benzyne precursor **7g**, several natural products can be prepared by changing the substituent on the benzamides.

This result prompted us to explore the possibility of preparing *N*-methyl aristolactam alkaloids (Scheme 8). Treatment of compound **3a** with benzyne precursors **7a** or **7b** in the presence of CsF in CH<sub>3</sub>CN at 30 °C for 24 h gave caldensine **10a** and **10b** in 63% and 55% yields, respectively. Caldensine exhibited an IC<sub>50</sub> value of 25 mM against chloroquine-sensitive and also showed antiplasmodial activity.<sup>3a</sup> Compound **10b** is equally potent towards multidrug-resistant cell lines compared with the commercially available drug etoposide.<sup>2a</sup> In a similar fashion, other alkaloids such as 2,3-dimethoxy-*N*-methyl-aristolactam **10c** and 2,3,4-trimethoxy-*N*-methyl-aristolactam **10d** were prepared in good yields. It is important to note that the alkaloids **10c-d** were prepared for the first time in the literature. A highly useful sauristolactam (**10e**) and *N*-methyl piperolactam A (**10f**) were prepared in three steps. The reaction of 3-hydroxy-4-methoxy (**1v**) and 3-methoxy-4-hydroxy (**1w**) benzamides with **2a** provided products **3z** and **3wa** in good yields. Later, a free hydroxy group of **3z** and **3wa** was protected with benzyl bromide followed by a cycloaddition reaction with **7a** affording products **12a-b**. Later, the benzyl group was deprotected by a palladium-catalyzed hydrogenation reaction, yielding alkaloids **10e-f** in excellent yields. Sauristolactam (**10e**) and *N*-methyl piperolactam A (**10f**) have



unsymmetrical benzyne **7f** was used, regioisomeric products **9v** and **9v'** were observed in 66% yield in a 9 : 1 ratio. Interestingly, the unsymmetrical benzyne precursor **7g** provided aristolactam **9w** in 69% yield in a highly regioselective manner. The structure of compound **9w** was supported by single crystal X-ray





- 2006, **23**, 444; (c) J. Michle, M. J. Ingrouille, M. S. J. Simmonds and M. Heinrich, *Nat. Prod. Rep.*, 2014, **31**, 676.
- 2 (a) Y. L. Choi, J. K. Kim, S.-U. Choi, Y.-K. Min, M.-A. Bae, B. T. Kim and J.-N. Heo, *Bioorg. Med. Chem. Lett.*, 2009, **19**, 3036; (b) S. J. Desai, B. R. Prabhu and N. B. Mulchandani, *Phytochemistry*, 1988, **27**, 1511; (c) Y.-N. Zhang, X.-G. Zhong, Z.-P. Zheng, X.-D. Hu, J.-P. Zuo and L. H. Hu, *Bioorg. Med. Chem.*, 2007, **15**, 988; (d) P. J. Houghton and M. Ogutveren, *Phytochemistry*, 1991, **30**, 253; (e) B. S. Vishwanath and T. V. Gowda, *Toxicon*, 1987, **25**, 929; (f) H. A. Priestap, *Phytochemistry*, 1987, **26**, 519.
- 3 (a) F. Martin, V. Choomuenwai and R. A. Davis, *Phytochemistry*, 2013, **86**, 121; (b) S. R. Kim, S. H. Sung, S. Y. Kang, K. A. Koo, S. H. King, C. J. Ma, H.-S. Lee, M. J. Park and Y. C. Kim, *Planta Med.*, 2004, **70**, 391; (c) K. Likhitwitayawuid, L. Wiasathien, V. Jongboonprasert, J. Krungkrai, N. Aimi, H. Takayama and M. Kitajima, *Pharm. Pharmacol. Lett.*, 1997, **7**, 99; (d) S. K. Kim, S. Ryu, Y. J. No, S. U. Choi and Y. S. Kim, *Arch. Pharmacol. Res.*, 2001, **24**, 518; (e) I. L. Tsai, F. P. Lee, C. C. Wu, C. Y. Duh, T. Ishikawa, J. J. Chen, Y. C. Chen, H. Seki and I. S. Chen, *Planta Med.*, 2005, **71**, 535.
- 4 (a) J. C. Estevez, M. C. Villaverde, R. J. Estevez and L. Castedo, *Tetrahedron*, 1995, **51**, 4075; (b) J. C. Estevez, R. J. Estevez and L. Castedo, *Tetrahedron*, 1995, **51**, 10801; (c) B. Gomez, E. Guitian and L. Castedo, *Synlett*, 1992, 903; (d) V. Rys, A. Couture, E. Deniau and P. Grandclaoudon, *Eur. J. Org. Chem.*, 2003, 1231; (e) C. Hoarau, A. Couture, H. Cornet, E. Deniau and P. Grandclaoudon, *J. Org. Chem.*, 2001, **66**, 8064; (f) A. Couture, E. Deniau, P. Grandclaoudon and C. Hoarau, *J. Org. Chem.*, 1998, **63**, 3128; (g) A. Couture, E. Deniau, P. Grandclaoudon and S. Lebrun, *Synlett*, 1997, 1475; (h) J. I. Levin and S. M. Weinreb, *J. Am. Chem. Soc.*, 1983, **105**, 1397; (i) N. Atanes, L. Castedo, E. Guitian, C. Saa, J. M. Saa and R. Suau, *J. Org. Chem.*, 1991, **56**, 2984; (j) J. K. Kim, Y. H. Kim, H. T. Nam, B. T. Kim and J.-N. Heo, *Org. Lett.*, 2008, **10**, 3543; (k) J.-N. Heo, T. J. Kim and J. K. Kim, *Bull. Korean Chem. Soc.*, 2011, **32**, 4431; (l) K. Sakthivel and K. Srinivasan, *Eur. J. Org. Chem.*, 2013, 3386; (m) L. Benesch, P. Bury, D. Guillaneux, S. Houldsworth, X. Wang and V. Snieckus, *Tetrahedron Lett.*, 1998, **39**, 961; (n) T. Yao and R. C. Larock, *J. Org. Chem.*, 2005, **70**, 1432; (o) J. C. Estevez, R. J. Estevez, E. Guitian, M. C. Villaverde and L. Castedo, *Tetrahedron Lett.*, 1989, **30**, 5786.
- 5 C-H activation: (a) T. Satoh and M. Miura, *Chem.-Eur. J.*, 2010, **16**, 11212; (b) D. A. Colby, R. G. Bermann and J. A. Ellman, *Chem. Rev.*, 2010, **110**, 624; (c) C. Zhu, R. Wang and J. R. Flack, *Chem.-Asian J.*, 2012, **7**, 1502; (d) P. B. Arokiam, C. Bruneau and P. H. Dixneuf, *Chem. Rev.*, 2012, **112**, 5879; (e) L. Ackermann, *Acc. Chem. Res.*, 2014, **47**, 281; (f) T. W. Lyons and M. S. Sanford, *Chem. Rev.*, 2010, **110**, 1147; (g) K. M. Engle, T.-S. Mei, M. Wasa and J.-Q. Yu, *Acc. Chem. Res.*, 2012, **45**, 788; (h) J. L. Bras and J. Muzart, *Chem. Rev.*, 2011, **111**, 1170; (i) P. Gandeepan and C.-H. Cheng, *Chem. Asian J.*, 2015, **10**, 824; (j) R. Y. Zhu, M. E. Farmer, Y.-Q. Chen and J.-Q. Yu, *Angew. Chem., Int. Ed.*, 2016, **55**, 10578.
- 6 Ruthenium papers: (a) E. F. Flegeau, C. Bruneau, P. H. Dixneuf and A. Jutand, *J. Am. Chem. Soc.*, 2011, **133**, 10161; (b) T. Ueyama, S. Mochida, T. Fukutani, K. Hirano, T. Satoh and M. Miura, *Org. Lett.*, 2011, **13**, 706; (c) K. Padala and M. Jeganmohan, *Org. Lett.*, 2011, **13**, 6144; (d) R. Manikandan, P. Madasamy and M. Jeganmohan, *ACS Catal.*, 2016, **6**, 230; (e) K. Muralirajan, K. Parthasarathy and C.-H. Cheng, *Org. Lett.*, 2012, **14**, 4262; (f) A. Bechtoldt, C. Tirler, K. Raghuvanshi, S. Warratz, C. Kornhaab and L. Ackermann, *Angew. Chem., Int. Ed.*, 2016, **55**, 264.
- 7 Isoindolinone synthesis: (a) J. W. Wrigglesworth, B. Cox, G. C. Lloyd-Jones and K. I. Booker-Millburn, *Org. Lett.*, 2011, **13**, 5326; (b) D.-D. Li, T.-T. Yuan and G.-W. Wang, *Chem. Commun.*, 2011, 47, 12789; (c) F. W. Patureau, T. Besset and F. Glorius, *Angew. Chem., Int. Ed.*, 2011, **50**, 1064; (d) X. Wei, F. Wang, G. Song, Z. Dub and X. Li, *Org. Biomol. Chem.*, 2012, **10**, 5521; (e) A. M. Martínez, N. Rodríguez, R. G. Arrayás and J. C. Carretero, *Chem. Commun.*, 2014, **50**, 6105; (f) C. Shangjun, C. Chao, S. Peng and X. Chanjuan, *Org. Lett.*, 2014, **16**, 3142; (g) B. Zhou, W. Hou, Y. Yang and Y. Li, *Chem.-Eur. J.*, 2013, **19**, 4701; (h) Y. Lu, D.-H. Wang, K. M. Engle and J.-Q. Yu, *J. Am. Chem. Soc.*, 2010, **132**, 5916; (i) J. Li, M. John and L. Ackermann, *Chem.-Eur. J.*, 2014, **20**, 5403; (j) J. Zhou, B. Li, Z.-C. Qian and B.-F. Shi, *Adv. Synth. Catal.*, 2014, **356**, 1038; (k) R. Manoharan and M. Jeganmohan, *Chem. Commun.*, 2015, **51**, 2929; (l) M. C. Reddy and M. Jeganmohan, *Org. Lett.*, 2014, **16**, 4866, references therein.
- 8 SO<sub>2</sub>R cleavage: (a) L. Li, Y. Liu, Y. Peng, L. Yu, X. Wu and H. Yan, *Angew. Chem., Int. Ed.*, 2016, **55**, 331; (b) V. Sikervar, J. C. Fleet and P. L. Fuchs, *Chem. Commun.*, 2012, **48**, 9077.
- 9 Selected benzyne reviews and papers: (a) P. M. Tadross and B. M. Stoltz, *Chem. Rev.*, 2012, **112**, 3550; (b) A. Bhunia, S. R. Yetra and A. T. Biju, *Chem. Soc. Rev.*, 2012, **41**, 3140; (c) K. M. Allan and B. M. Stoltz, *J. Am. Chem. Soc.*, 2008, **130**, 17270; (d) J. Li, N. Wang, C. Li and X. Jia, *Org. Lett.*, 2012, **14**, 4994; (e) S. S. Bhojgude, A. Bhunia, R. G. Gonnade and A. T. Biju, *Org. Lett.*, 2014, **16**, 676; (f) H. X. Siyang, X. R. Wu, H. L. Liu, X. Y. Wu and P. N. Liu, *J. Org. Chem.*, 2014, **79**, 1505; (g) A. F. C. Rossini, A. C. A. Muraca, G. A. Casagrande and C. Raminelli, *J. Org. Chem.*, 2015, **80**, 10033; (h) G. P. Perecim, A. Rodrigues and C. Raminelli, *Tetrahedron Lett.*, 2015, **56**, 6848; (i) J. M. Medina, J. L. Mackey, N. K. Garg and K. N. Houk, *J. Am. Chem. Soc.*, 2014, **136**, 15798; (j) S.-E. Suh, S. A. Barros and D. M. Chenoweth, *Chem. Sci.*, 2015, **6**, 5128; (k) T. R. Hoye, B. Baire, D. Niu, P. H. Willoughby and B. P. Woods, *Nature*, 2012, **490**, 208; (l) A. E. Goetz and N. K. Garg, *Nat. Chem.*, 2013, **5**, 54; (m) C. M. Gampe and E. M. Carreira, *Angew. Chem., Int. Ed.*, 2012, **51**, 3766; (n) S. S. Bhojgude, A. Bhunia and A. T. Biju, *Acc. Chem. Res.*, 2016, **49**, 1658; (o) S. S. Bhojgude, A. Bhunia, R. G. Gonnade and A. T. Biju, *Org. Lett.*, 2014, **16**, 676; (p) H. X. Siyang, X. R. Wu, H. L. Liu, X. Y. Wu and P. N. Liu, *J. Org. Chem.*, 2014, **79**, 1505; (q) J.-C. Castillo, J. Quiroga, R. Abonia, J. Rodriguez and Y. Coquerel, *Org. Lett.*, 2015, **17**, 3374.

