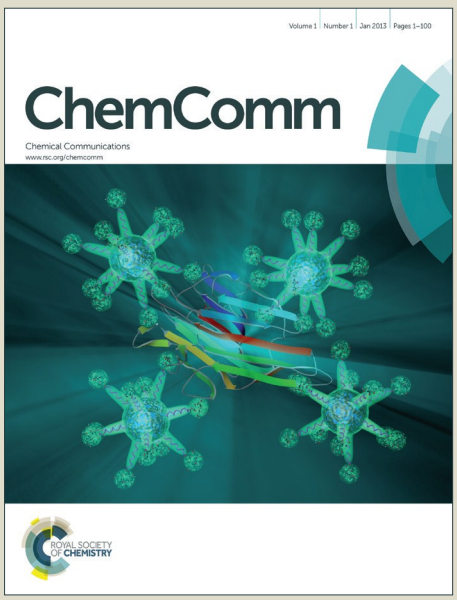
ChemComm

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

Journal Name

COMMUNICATION

Thermal Induced Formal [3+2] Cyclization of *Ortho*-Aminoaryl-Tethered Alkylidenecyclopropanes: Facile Synthesis of Furoquinoline and Thienoquinoline Derivatives†

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Liu-Zhu Yu,[a] Xu-Bo Hu,[a] Qin Xu,[a] and Min Shi*[a,b]

A facile synthetic method to access furoquinoline and thienoquinoline derivatives has been disclosed via a thermal induced ring-opening and cyclization reaction from *ortho*-aminoaryl-tethered alkylidenecyclopropanes with in situ generated isocyanates or isothiocyanates. These reactions exhibited excellent yields and functional group tolerance under metal free conditions.

Quinoline scaffolds are probably the most ubiquitous heterocycles that widely existed in natural products,[1] medicinal agents[2] and functional materials.[3] Notably, furoquinoline alkaloids, which represent diverse pharmacological and biological properties including antimicrobial, antitumor and antiemetic activities,[4] are widely distributed among plants of *Rutaceae* and *Solanaceae* family.[5] However, until now, most existing accesses to furoquinoline were linear and involved harsh reaction conditions. Therefore, new synthetic methods to furoquinoline derivatives have been extensively pursued during the recent years.[6] On the other hand, thienoquinoline derivatives are also known to possess antibacterial, antifungal, antiviral, anti-inflammatory and antiparasitic activities.[7] Last several years have witnessed vigorous synthetic methods for the construction of thienoquinolines.[8] However, such procedures are often accompanied by poor yields, undesired side products, vigorous reaction conditions, expensive or toxic reagents and tedious work-up. Therefore, we are urgent to develop simpler, general, and convenient processes using easily available starting materials for the synthesis of such useful substances.

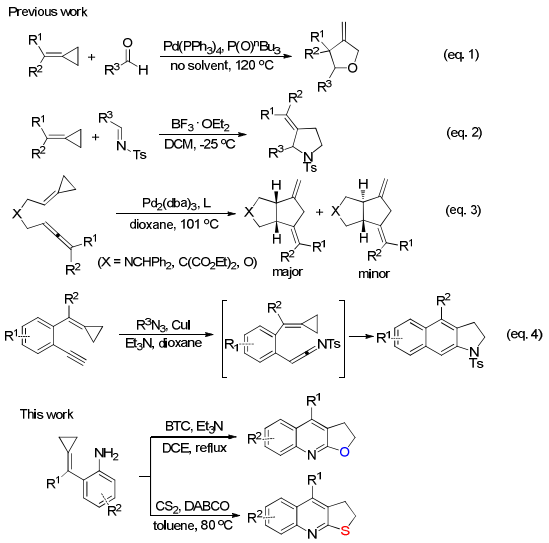
Alkylidenecyclopropanes (ACPs), as highly strained but readily accessible molecules, are useful building block in organic synthesis.[9] In the past decades, numerous outstanding works to rapidly access complex polycyclic frameworks by cyclization of ACPs have been achieved in the presence of transition metals or Lewis acids.[10] As an important C_3 synthon, [3+2] cyclization reactions of ACPs have attracted intensive attention.[11] For example, in 2001, Yamamoto's group has developed a palladium-catalyzed [3+2] cycloaddition of ACPs and aldehydes for synthesis of exo-methylene tetrahydrofuran derivatives (Scheme 1, eq. 1).[11a] Thereafter, our group has also reported that ACPs can undergo [3+2] cycloaddition with aldimines to afford corresponding pyrrolidine skeletons in the presence of $BF_3{\cdot}OEt_2$ in good yields (Scheme 1, eq. 2).[11d] Moreover, Mascareñas's group disclosed the first palladium-catalyzed intramolecular [3+2] cycloaddition of ACPs with allenes in high efficiency (Scheme 1, eq. 3).[11h] More recently, Zhang's group developed a nickel-catalyzed intramolecular cycloaddition of ACPs with arylalkynes[11l] and Wu's group discovered a novel cascade formal [3+2] cycloaddition of ACPs with ketenimine intermediate to generate fused indolines (Scheme 1, eq. 4).[11m] Herein we wish to report an unprecedented thermal induced formal [3+2] cyclization reaction of ACPs with in situ generated isocyanates or isothiocyanates for convenient synthesis of furoquinoline and thienoquinoline derivatives with excellent yields and functional group tolerance under metal free conditions.

We initially investigated the formal [3+2] cyclization reaction of *ortho*-aminoaryl-tethered alkylidenecyclopropane **1a** with in situ generated isocyanate. As shown in Table 1, we proceeded with a simplified optimization study by initially varying the amount of triethylamine while maintaining one third equiv of triphosgene (BTC).[12] To our delight, when the reaction was conducted under reflux in DCE (1,2-dichloroethane) with 1.0 equiv of triethylamine, tricyclic furoquinoline derivative **2a** was predominantly produced along with quinolinone derivative **4a** formation (Table 1, entry 1). According to our hypothesis, increasing the amount of triethylamine would inhibit the formation of undesired quinolinone derivative. Increasing the loading of triethylamine to 2.0 equiv afforded **2a** and **4a** in 81% and 17% yields (Table 1, entry 2). Gratifyingly, **2a** could be

[a] *Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, Meilong Road No. 130, Shanghai, 200237 (China).*
[b] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032 China. E-mail: mshi@mail.sioc.ac.cn*

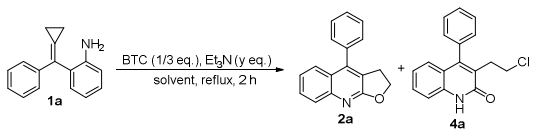
† Electronic Supplementary Information (ESI) available: Experimental procedures, characterization data of new compounds, and CCDC 1430177, 1430157 and 1058933. See DOI: 10.1039/b000000x

isolated in up to 99% yield and **4a** was totally suppressed when 3.0 equiv of triethylamine was added (Table 1, entry 3). Indeed, when **4a** was treated with 1.0 equiv of triethylamine, **4a** could be transformed into **2a** in 99% yield. The solvent effect and the temperature were also examined and no better results could be realized (Table 1, entries 4-6).



Scheme 1 [3+2] cyclization reactions of ACPs

Table 1 Optimization of the reaction conditions for the synthesis of furoquinoline **2a**

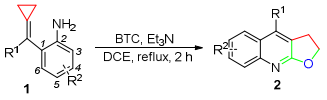


entry[a]	y	solvent	yield[b] 2a	4a
1	1.0	DCE	66	33
2	2.0	DCE	81	17
3	3.0	DCE	99	-
4	3.0	$CHCl_3$	96	-
5	3.0	acetone	90	-
6[c]	3.0	DCE	92	-

[a] Reaction conditions: **1a** (0.30 mmol), BTC (1/3 eq.), Et_3N (y eq.), solvent (3.0 mL), air atmosphere, reflux, 2 h. [b] Isolated yield. [c] At 70 °C.

Under the optimized conditions (3.0 equiv of triethylamine, 1/3 equiv of BTC in DCE under reflux for 2 h), we next surveyed the substrate scope of this reaction and the results are shown in Table 2. When R^1 is an aryl group, we firstly examined the electronic effect at the *para*-position of the benzene ring: as for substrates **1b**-**1f**, the reactions could all proceed smoothly to furnish the desired products **2b**-**2f** in 92-96% yields regardless of whether they have electron-rich or electron-poor aromatic ring (Table 2, entries 2-6). For the *meta*-substituted and *ortho*-substituted substrates, the reactions were also well tolerated under the reaction conditions, providing the desired products **2g**-**2j** in excellent yields (Table 2, entries 7-10). Furthermore, when R^2 was substituted by OMe group and Cl atom, the desired products **2k**-**2m** were isolated in excellent yields ranging from 90% to 98% (Table 2, entries 11-13). As for both phenyl rings substituted substrates **1n** and **1o**, the reactions also proceeded efficiently, giving the corresponding products **2n** and **2o** in 84% and 95% yields, respectively (Table 2, entries 14 and 15). Substrate **1p**, replacing aryl group with a methyl group, could also afford the corresponding product **2p** in 97% yield (Table 2, entry 16). **2q** could also be isolated in 77% yield when R^1 was substituted by hydrogen atom (Table 2, entry 17). The structure of **2c** and **4c** were determined by X-ray analysis.[13]

Table 2 Reaction Scope: Synthesis of furoqinolines **2**



Entry[a]	**1** (R^1/R^2)	Yield [%][b]
1	**1a**, (Ph/H)	**2a**, 99
2	**1b**, (4-FC_6H_4/H)	**2b**, 92
3	**1c**, (4-ClC_6H_4/H)	**2c**, 95
4	**1d**, (4-BrC_6H_4/H)	**2d**, 96
5	**1e**, (4-$^tBuC_6H_4$/H)	**2e**, 94
6	**1f**, (4-MeC_6H_4/H)	**2f**, 95
7	**1g**, (3-MeC_6H_4/H)	**2g**, 95
8	**1h**, (2-MeC_6H_4/H)	**2h**, 99
9	**1i**, (2-EtC_6H_4/H)	**2i**, 99
10	**1j**, (2-$MeOC_6H_4$/H)	**2j**, 94
11	**1k**, (Ph/5-Cl)	**2k**, 90
12	**1l**, (Ph/5-OMe)	**2l**, 96
13	**1m**, (Ph/4-Cl)	**2m**, 98
14	**1n**, (2-ClC_6H_4/5-Cl)	**2n**, 84
15	**1o**, (4-$^tBuC_6H_4$/5-Cl)	**2o**, 95
16	**1p**, (Me/H)	**2p**, 97
17	**1q**, (H/H)	**2q**, 77

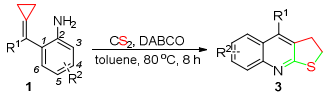
[a] Reaction conditions: **1** (0.60 mmol, 1.0 eq.), BTC (0.20 mmol, 1/3 eq.), Et_3N (1.80 mmol, 3.0 eq.), DCE (6.0 mL), reflux, 2 h. [b] Isolated yield.

We then turned our attention to investigate the formal [3+2] cyclization reaction of *ortho*-aminoaryl-tethered alkylidenecycloproane with in situ generated isothiocyanate. We were also delighted to discover that the corresponding desired thienoquinoline **3a** was achieved in excellent yield in up to 99% yield when **1a** was treated with 4.0 equiv of CS_2 and 4.0 equiv of DABCO in toluene at 80 °C for 8 h. Then the optimized reaction conditions were employed to investigate the substrate scope for the synthesis of thienoquinoline and the results are shown in Table 3. As for aryl substituted R^1 with different substituents on the aromatic ring, the reactions could all proceed smoothly to furnish the desired products **3b**-**3j** in excellent yields ranging from 87% to 97% which revealed that electronic effect and substituent position had no obvious impact to the reaction outcomes (Table 3, entries 2-10). Changing R^2 to OMe group or Cl atom, the reaction proceeded smoothly, furnishing the desired products **3k**-**3m** in 90%-93% yields (Table 3, entries 11-13). Both phenyl ring substituted substrates **1n** and **1o** were also tolerable, giving the corresponding products **3n** and **3o** in 85% and 88% yields, respectively (Table 3, entries 14 and 15). Similarly, when R^1 was replaced by methyl group or hydrogen atom, the reactions still proceeded efficiently to afford the desired products **3p** and **3q** in 75% and 98% yields, respectively (Table 3, entries 16 and 17). The structure of **3a** was confirmed by single crystal X-ray analysis.[14]

To further illustrate the synthetic value of this protocol, the obtained product **2a** was conducted with 1.5 equiv of 2,3,5,6-dichlorodicyanoquinone (DDQ) in chlorobenzene under reflux

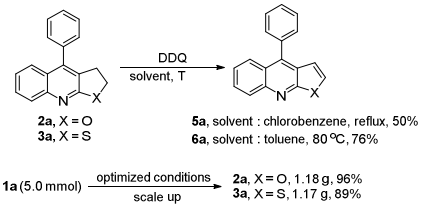
and we found that the corresponding dehydrogenative product **5a** could be isolated in 50% yield. **6a** was also obtained in 76% yield when **3a** was used to react with 1.5 equiv of DDQ in toluene at 80 °C. Furthermore, a gram-scale synthesis of **2a** and **3a** was carried out to test the practicality of this new methodology. We were delighted to find that 5.0 mmol scale reaction produced 1.18 grams of **2a** in 96% yield and 1.17 grams **3a** in 89% yield, thus indicating that this transformation is easy to scale-up to gram scale without loss of reaction efficiency (Scheme 2 and more information is included in Schemes S1 and S2, ESI†).

Table 3 Reaction Scope: Synthesis of thienoquinoline **3**



Entry[a]	**1** (R^1/R^2)	**3** Yield (%)[b]
1	**1a**, (Ph/H)	**3a**, 99
2	**1b**, (4-FC_6H_4/H)	**3b**, 87
3	**1c**, (4-ClC_6H_4/H)	**3c**, 92
4	**1d**, (4-BrC_6H_4/H)	**3d**, 90
5	**1e**, (4-$^tBuC_6H_4$/H)	**3e**, 91
6	**1f**, (4-MeC_6H_4/H)	**3f**, 90
7	**1g**, (3-MeC_6H_4/H)	**3g**, 97
8	**1h**, (2-MeC_6H_4/H)	**3h**, 95
9	**1i**, (2-EtC_6H_4/H)	**3i**, 93
10	**1j**, (2-$OMeC_6H_4$/H)	**3j**, 94
11	**1k**, (Ph/5-Cl)	**3k**, 92
12	**1l**, (Ph/5-OMe)	**3l**, 90
13	**1m**, (Ph/4-Cl)	**3m**, 93
14	**1n**, (2-ClC_6H_4/5-Cl)	**3n**, 85
15	**1o**, (4-$^tBuC_6H_4$/5-Cl)	**3o**, 88
16	**1p**, (Me/H)	**3p**, 75
17	**1q**, (H/H)	**3q**, 98

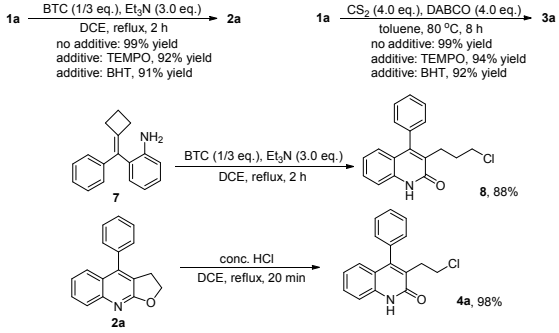
[a] Reaction conditions: **1** (0.50 mmol, 1.0 eq.), CS_2 (2.0 mmol, 4.0 eq.), DABCO (2.0 mmol, 4.0 eq.), toluene (5.0 mL), 80 °C, 8 h. [b] Isolated yield.



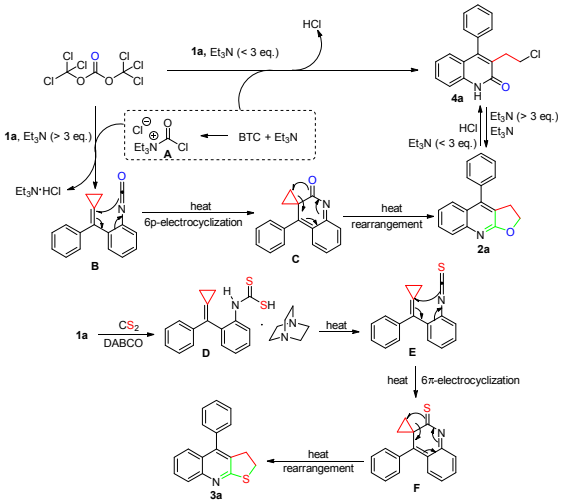
Scheme 2 Transformations and gram-scale synthesis of **2a** and **3a**.

To gain more insights into the reaction mechanism for the formal [3+2] cyclization of *ortho*-aminoaryl-tethered alkylidenecyclopropane with in situ generated isocyanates or isothiocyanates. A well-known radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was used to react with **1a** under the above optimized reaction conditions respectively and the reaction outcomes were unaffected. Moreover, the other conventional radical scavenger, 2,6-di-tert-butyl-4-methylphenol (BHT), also did not inhibit the formation of **2a** and **3a**, thus excluding the intervention of a radical reaction pathway. Furthermore, *ortho*-aminoaryl-tethered alkylidenecyclobutane **7** was also performed under the optimization reaction conditions. However, only non-cyclic product **8** was formed instead of pyran-fused quinoline. Moreover, upon heating with conc. hydrochloric acid, **2a** was transformed into **4a** almost in quantitative yield, which indicated that the reaction preferentially produced **2a**, and **4a** was obtained owing to the released hydrochloric acid originated from the reaction system (Scheme 3 and more information is included in Schemes S3, S4, S5 and S6, ESI†).

Based on the above results and the previously reported literature,[11m, 11n, 12, 15] a plausible mechanism of formal [3+2] cyclization of *ortho*-aminoaryl-tethered alkylidenecyclopropane has been proposed in Scheme 4. As for the synthesis of furoquinoline, it is a common sense that intermediate **A** is formed when Et_3N is treated with triphosgene. Then isocyanate-tethered alkylidenecyclopropane **B** is formed when **1a** reacts with intermediate **A**, followed by a thermal induced 6π-electrocyclization to produce intermediate **C**,[16] which subsequently undergoes a rearrangement to produce the corresponding furoquinoline **2a**. At this stage, **4a** would be produced if triethylamine was not excess, because **2a** could react with released hydrochloric acid from the reaction system. As for the synthesis of thienoquinoline, we believe that the reaction begins with a rapid formation of dithiocarbamate salt **D**. Subsequently isothiocyanate-tethered alkylidenecyclopropane **E** is formed upon heating, followed by a consecutive 6π-electrocyclization and rearrangement to produce the corresponding thienoquinoline **3a**.



Scheme 3 Control experiments.



Scheme 4 A plausible reaction mechanism.

In summary, we have developed a novel and efficient synthetic protocol to easily access furoquinoline and thienoquinoline derivatives via thermal induced formal [3+2]

cyclization reaction of *ortho*-aminoaryl-tethered alkylidenecyclopropanes with in situ generated isocyanates and isothiocyanates. The reaction exhibits easily available starting materials, scalable production and a broad substrate scope with excellent yield and functional group tolerance under metal free conditions. The potential utilization and extension of the scope of this new synthetic methodology are currently under investigation.

We are grateful for the financial support from the National Basic Research Program of China (973)-2015CB856603, and the National Natural Science Foundation of China (20472096, 21372241, 21361140350, 20672127, 21102166, 21121062, 21302203, 20732008 and 21572052).

Notes and references

1 a) J. P. Michael, *Nat. Prod. Rep.*, 1997, **14**, 605; b) V. V. Kouznetsov, L. Y. V. Mendez and C. M. M. Gomez, *Curr. Org. Chem.,* 2005, **9**, 141.

2 a) C. H. Kaschula, T. J. Egan, R. Hunter, N. Basilico, S. Parapini, D. Taramelli, E. Pasini and D. Monti, *J. Med. Chem.,* 2002, **45**, 3531; b) J. P. Michael, *Nat. Prod. Rep.*, 2008, **25**, 166;

3 a) G. Jégou and S. A. Jenekhe, *Macromolecules*, 2001, **34**, 7926; b) H. Tong, L. Wang, X. Jing and F. Wang, *Macromolecules*, 2003, **36**, 2584.

4 M. Anzini, A. Cappelli, S. Vomero, G. Giorgi, T. Langer, M. Hamon, N. Merahi, B. M. Emerit, A. Cagnotto, M. Skorupska, T. Mennini and J. C. Pinto, *J. Med. Chem.*, 1995, **38**, 2692.

5 a) C. Ito, M. Itoigawa, A. Sato, C. M. Hasan, M. A. Rashid, H. Tokuda, T. Mukainaka, H. Nishino and H. Furukawa, *J. Nat. Prod.*, 2004, **67**, 1488; b) R. Grougnet, P. Magiatis, N. Fokialakis, S. Mitaku, A.-L. Skaltsounis, F. Tillequin, T. Sévenet and M. Litaudon, *J. Nat. Prod.*, 2005, **68**, 1083.

6 a) A. Fayol and J. Zhu, *Angew. Chem., Int. Ed.*, 2002, **41**, 3633; b) W. Du and D. P. Curran, *Org. Lett.*, 2003, **5**, 1765; c) U. Bhoga, R. S. Mali and S. R. Adapa, *Tetrahedron Lett.*, 2004, **45**, 9483; d) I. Aillaud, E. Bossharth, D. Conreaux, P. Desbordes, N. Monteiro and G. Balme, *Org. Lett.*, 2006, **8**, 1113; e) Z. Zhang, Q. Zhang, S. Sun, T. Xiong and Q. Liu, *Angew. Chem., Int. Ed.*, 2007, **46**, 1726.

7 a) J. Bompart, L. Giral, G. Malicorne and M. Puygrenier, *Eur. J. Med. Chem.*, 1987, **22**, 139; b) M. M. El-Abadelah, M. Z. Nazer, S. F. Okasha, M. Calas, J. Bompart and P. Mion, *Eur. J. Med. Chem.*, 1998, **33**, 33; c) N. Cho, M. Harada, T. Imaeda, T. Imada, H. Matsumoto, Y. Hayase, S. Sasaki, S. Furuya, N. Suzuki, S. Okubo, K. Ogi, S. Endo, H. Onda and M. Fujino, *J. Med. Chem.*, 1998, **41**, 4190.

8 a) B. Bhat and A. P. Bhaduri, *Synthesis*, 1984, 673; b) L. Benati, R. Leardini, M. Minozzi, D. Nanni, P. Spagnolo and G. Zanardi, *J. Org. Chem.*, 2000, **65**, 8669; c) C. N. S. S. P. Kumar, E. Srihari, M. Ravinder, K. P. Kumar, U. S. N. Murthy and V. J. Rao, *J. Heterocycl. Chem.*, 2013, **50**, E131; d) P. Zhao, X. Yan, H. Yin and C. Xi, *Org. Lett.*, 2014, **16**, 1120.

9 For selected review: a) I. Nakamura and Y. Yamamoto, *Adv. Synth. Catal.*, 2002, **344**, 111; b) E. Nakamura and S. Yamago, *Acc. Chem. Res.*, 2002, **35**, 867; c) A. Brandi, S. Cicchi, F. M. Cordero and A. Goti, *Chem. Rev.*, 2003, **103**, 1213; d) M. Rubin, M. Rubina and V. Gevorgyan, *Chem. Rev.*, 2007, **107**, 3117; e) M. Shi, L.-X. Shao, J.-M. Lu, Y. Wei, K. Mizuno and H. Maeda, *Chem. Rev.*, 2010, **110**, 5883; f) G. Audran and H. Pellissier, *Adv. Synth. Catal.*, 2010, **352**, 575; g) M. Shi, J.-M. Lu, Y. Wei and L.-X. Shao, *Acc. Chem. Res.*, 2012, **45**, 641; h) L. Yu and R. Guo, *Org. Prep. Proc. Int.*, 2011, **43**, 209; i) A. Brandi, S. Cicchi, F. M. Cordero and A. Goti, *Chem. Rev.*, 2014, **114**, 7317; j) H. Pellissier, *Tetrahedron*, 2014, **70**, 4991; k) D.-H. Zhang, X.-Y. Tang and M. Shi, *Acc. Chem. Res.*, 2014, **47**, 913.

10 For recent contributions from our group and others, see: a) M. Lautens and W. Han, *J. Am. Chem. Soc.*, 2002, **124**, 6312; b) M. Lautens, W. Han and J. H. Liu, *J. Am. Chem. Soc.*, 2003, **125**, 4028; c) S. Simaan, A. Masarwa, P. Bertus and I. Marek, *Angew. Chem., Int. Ed.,* 2006, **45**, 3963; d) A. Fürstner and C. Aïssa, *J. Am. Chem. Soc.*, 2006, **128**, 6306; e) M. Shi, L.-P. Liu and J. Tang, *J. Am. Chem. Soc.*, 2006, **128**, 7430; f) M. E. Scott, Y. Bethuel and M. Lautens, *J. Am. Chem. Soc.*, 2007, **129**, 1482; g) C. Aïssa and A. Fürstner, *J. Am. Chem. Soc*., 2007, **129**, 14836; h) R. J. Felix, D. Weber, O. Gutierrez, D. J. Tantillo and M. R. Gagné, *Nat. Chem.*, 2012, **4**, 405; i) P. A. Evans and P. A. Inglesby, *J. Am. Chem. Soc.*, 2012, **134**, 3635; j) D.-H. Zhang, X.-Y. Tang, Y. Wei and M. Shi, *Chem. - Eur. J.*, 2013, **19**, 13668; k) P. A. Inglesby, J. Bacsa, D. E. Negru and P. A. Evans, *Angew. Chem., Int. Ed.*, 2014, **53**, 3952; l) K. Chen, Z.-Z. Zhu, Y.-S. Zhang, X.-Y. Tang and M. Shi, *Angew. Chem., Int. Ed.*, 2014, **53**, 6645.

11 For representative examples of [3+2] cycloaddition reactions of ACPs, see: a) I. Nakamura, B.-H. Oh, S. Saito and Y. Yamamoto, *Angew. Chem., Int. Ed.*, 2001, **40**, 1298; b) B.-H. Oh, I. Nakamura, S. Saito and Y. Yamamoto, *Tetrahedron Lett.*, 2001, **42**, 6203; c) T. Kawasaki, S. Saito and Y. Yamamoto, *J. Org. Chem.*, 2002, **67**, 4911; d) M. Shi, B. Xu and J.-W. Huang, *Org. Lett.*, 2004, **6**, 1175; e) S. Saito, M. Masuda and S. Komagawa, *J. Am. Chem. Soc.*, 2004, **126**, 10540; f) T. Kurahashi and A. de Meijere, *Angew. Chem., Int. Ed.*, 2005, **44**, 7881; g) L.-X. Shao, B. Xu, J.-W. Huang and M. Shi, *Chem. - Eur. J.*, 2006, **12**, 510; h) B. Trillo, M. Gulías, F. López, L. Castedo and J. L. Mascareñas, *Adv. Synth. Catal.*, 2006, **348**, 2381; i) M. Murakami, N. Ishida and T. Miura, *Chem. Commun.*, 2006, 643; j) M. Gulías, J. Durán, F. López, L. Castedo and J. L. Mascareñas, *J. Am. Chem. Soc.*, 2007, **129**, 11026; k) G. Bhargava, B. Trillo, M. Araya, F. López, L. Castedo and J. L. Mascareñas, *Chem. Commun.*, 2010, **46**, 270; l) B. Yao, Y. Li, Z. Liang and Y. Zhang, *Org. Lett.*, 2011, **13**, 640; m) S. Li, Y. Luo and J. Wu, *Org. Lett.*, 2011, **13**, 3190; n) K. Chen, Z. Zhang, Y. Wei and M. Shi, *Chem. Commun.*, 2012, **48**, 7696.

12 a) C. E. Ayala, A. Villalpando, A. L. Nguyen, G. T. McCandless and R. Kartika, *Org. Lett.*, 2012, **14**, 3676; b) A. Villalpando, C. E. Ayala, C. B. Watson and R. Kartika, *J. Org. Chem.*, 2013, **78**, 3989; c) A. Villalpando, M. A. Saputra, T. H. Tugwell and R. Kartika, *Chem. Commun.*, 2015, **51**, 15075.

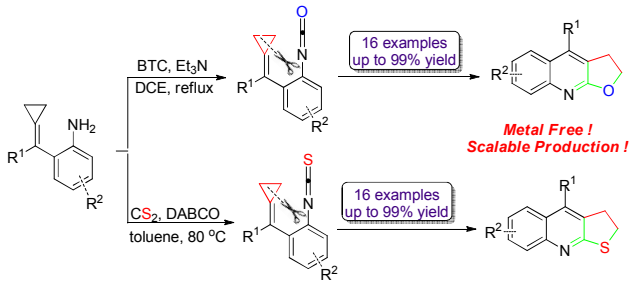
13 The crystal data of **2c** and **4c** have been deposited in CCDC with number 1430177 and 1430157.

14 The crystal data of **3a** have been deposited in CCDC with number 1058933.

15 a) P. Molina, M. Alajarín, A. Vidal and P. Sánchez-Andrada, *J. Org. Chem.*, 1992, **57**, 929; b) T. Saito, H. Ohmori, E. Furuno and S. Motoki, *J. Chem. Soc., Chem. Commun.*, 1992, 22.

16 a) E. E. Schweizer and C. M. Kopay, *J. Org. Chem.*, 1971, **36**, 1489; b) H. N. C. Wong, M. Y. Hon, C. W. Tse, Y. C. Yip, J. Tanko and T. Hudlicky, *Chem. Rev.*, 1989, **89**, 165. c) D. L. Boger, R. M. Garbaccio and Q. Jin, *J. Org. Chem.*, 1997, **62**, 8875.

Thermal Induced Formal [3+2] Cyclization of *Ortho*-Aminoaryl-Tethered Alkylidenecyclopropanes: Facile Synthesis of Furoquinoline and Thienoquinoline Derivatives



Thermal induced formal [3+2] cycloaddition reactions of ACPs and in situ generated isocyanates and isothiocyanates were disclosed respectively.

*Liu-Zhu Yu, Xu-Bo Hu, Qin Xu, and Min Shi**