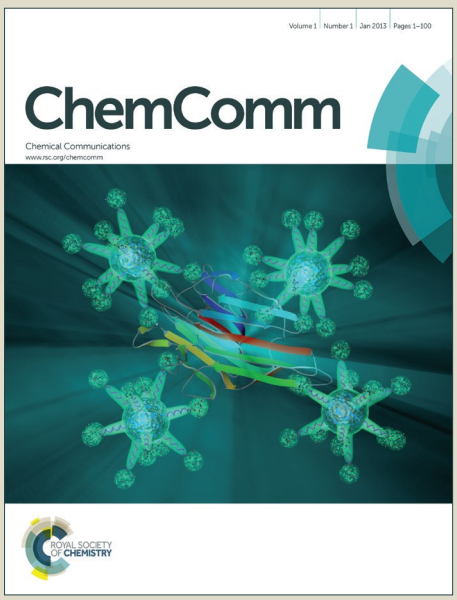
ChemComm

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

Journal Name

COMMUNICATION

Catalytic Asymmetric Sulfenylation to Structurally Diverse Dithioketals

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

DOI: 10.1039/x0xx00000x

www.rsc.org/

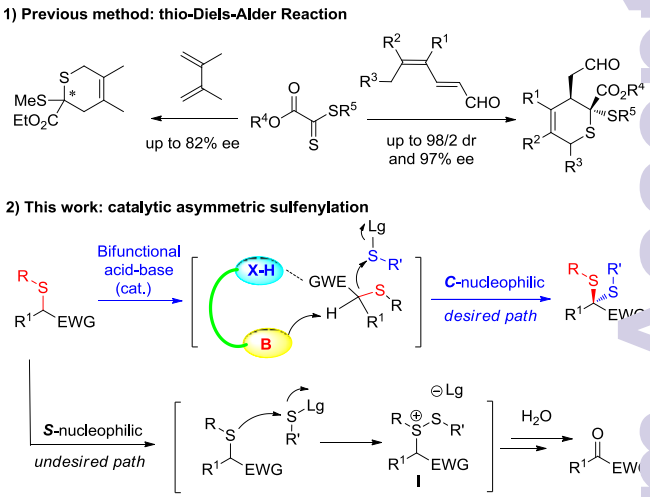
Kui Liao,[a] Feng Zhou,*[b,c] Jin-Sheng Yu,[a] Wei-Ming Gao[a] and Jian Zhou[a,d]

We report the first example of highly enantioselective synthesis of structurally diverse chiral dithioketals via asymmetric sulfenylation of various types of *S*-based nucleophiles, catalyzed by a cheap cinchona alkaloid derivative, dihydroquinine.

There is an ever-increasing interest in catalytic enantioselective synthesis of optically active organic sulfur compounds, because of their wide occurrence in natural and various biological systems.[1] Intriguingly, all of the 10 top selling drugs in 2012 contain sulfur.[2] In addition, sulfur-based compounds constitute an important class of chiral ligands, auxiliaries and synthetic intermediates in organic chemistry.[3] Despite ongoing processes in the synthesis of chiral secondary and tertiary thiol derivatives,[4] very limited attention is paid to the enantioselective synthesis of optically active dithioketals. However, besides their synthetic applications,[5] an increasing number of researches reveal that the dithioketal motifs have promising potential for the research and development of new biopharmaceutics.[6] In this context, as well as the importance of chirality in medicinal research,[7] it is highly desirable to develop efficient methods to chiral dithioketals.

Recently, along with achievements in the asymmetric synthesis of chiral ketals,[8] attention has been paid to the development of catalytic enantioselective methods to chiral dithioketals.[9] In 2010, Gulea et al pioneered thio-Diels-Alder reaction of dithioesters with dienes, catalyzed by a chiral bisoxazoline/Cu(II) complex, with up to 82% ee achieved in one example (Scheme 1).[9a] Later in 2013, Jørgensen et al made a breakthrough in this context, who developed a highly stereoselective synthesis of highly functionalized heterocycles with a chiral dithioketal moiety via trienamine catalysis mediated cycloaddition of dithioesters and unsaturated enals.[9b]

Inspired by their pioneering work, together with our efforts in enantioselective construction of *S*-containing tetrasubstituted carbon stereocenters,[10] we considered the synthesis of optically active dithioketals via chiral Brønsted base catalyzed asymmetric sulfenylation of *S*-based active methine compounds. A merit of this approach is the powerfulness in the synthesis of acyclic dithioketals with various substituents on both sulfur atoms, complementary to the thio-Diels-Alder reaction described above.



Scheme 1. Strategies to optically active dithioketals.

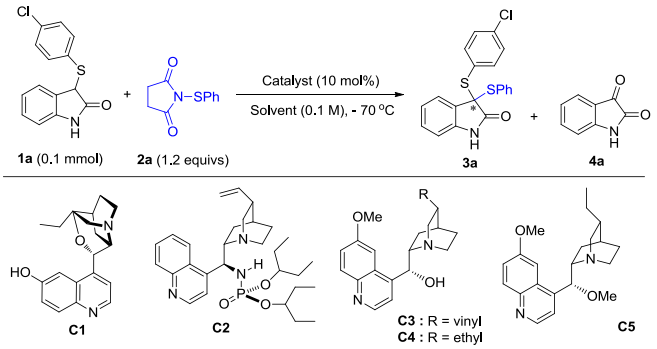
Pioneered by Jørgensen et al,[11a] asymmetric sulfenylation has been established as a powerful strategy for the enantioselective C-S bond formation.[11] *However, sulfenylation of S-containing methine reagents has not been realized, and is not so simple as it first appears.* Since the *S*-based methines are ambident nucleophiles that may attack electrophiles in a *C*- or *S*-nucleophilic way (Scheme 1). Ideally, the deprotonative activation of a methine reagent to react with an electrophilic sulfur source furnishes the desired dithioketal. However, if the sulfur of methine reagents attacks the incoming electrophilic sulfur to form a sulfonium salt **I**, side reaction may occur to form side products such as the corresponding ketone.[12] While side reaction caused by *S*-nucleophilic attack has not been mentioned in literature reports as for asymmetric reactions based on *S*-based nucleophiles,[13] we do observe severe side reaction in the reaction of 3-thiooxindoles with some highly

[a] *Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering,East China Normal University,3663N, Zhongshan Road, Shanghai 200062, China.*
[b] *Department of Chemistry, School of Chemistry and Molecular Engineering, East China Normal University. Shanghai 200062, China. E-mail: fzhou@chem.ecnu.edu.cn.*
[c] *Shanghai Engineering Research Center of Molecular Therapeutics and New Drug Development, School of Chemistry and Chemical Engineering, East China Normal University, Shanghai, 200062, China*
[d] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, CAS, Shanghai 200032, P. R. China.*
Electronic Supplementary Information (ESI) available: [experimental details and spectra data]. See DOI: 10.1039/x0xx00000x

active electrophiles.[12] Therefore, how to suppress the undesired reaction whilst achieving high yield and enantioselectivity is a conceivable challenge. Based on our efforts in bifunctional acid-base catalysis,[14] we speculated the cooperation of a H-bond donor with Brønsted base might be helpful in inhibiting the side reaction, as H-bonding interactions between a suitable H-bond donor with *S*-based methines might facilitate the deprotonative activation,[14g] which in turn favor the *C*-nucleophilic reaction path.

With this hypothesis, we first tried to develop sulfenylation of 3-thiooxindoles **1**, with our continuous efforts in enantioselective synthesis of 3,3-disubstituted oxindoles.[14,15] Noticeably, owing to the wide presence of this prominent structural motif in drugs and pharmaceutically active compounds, the diverse synthesis of 3,3-disubstituted oxindoles was of current interests.[16] During condition optimization, the undesired *S*-nucleophilic pathway indeed proved to be troublesome, when we tried to lower reaction temperature to improve enantioselectivity, as shown in Table 1 (For detail of the reaction condition optimization, please see SI).

Table 1 Reaction optimization

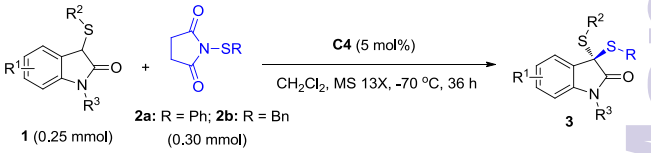


Entry	Cat.	Solvent	Time (h)	Yield of **3a**[a] (%)	Ee of **3a**[b] (%)	Yield of **4a**[a] (%)
1	**C1**	THF	84	68	3	23
2	**C2**	THF	84	20	15	71
3	**C3**	THF	12	46	43	51
4	**C3**	CH_2Cl_2	12	82	79	8
5	**C4**	CH_2Cl_2	12	88	81	7
6[c]	**C4**	CH_2Cl_2	24	82	91	7
7[d]	**C4**	CH_2Cl_2	36	78	93	trace
8[c]	**C5**	CH_2Cl_2	24	70	7	20

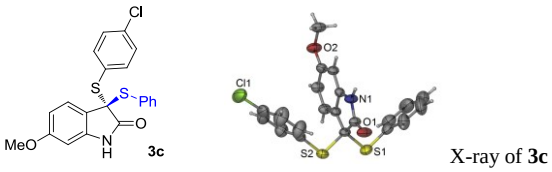
[a] Isolated yield. [b] Determined by HPLC analysis. [c] 0.05 M with 60 mg MS 13X. [d] 0.05 M with 60 mg MS 13X, 5 mol% of **C4**.

Bifunctional catalyst **C1** or **C2**, which we employed for amination[10a] and Michael addition reaction[10b] using 3-thiooxindole, respectively, all afforded side product isatin **4a** in significant amount, along with desired product **3a** in low yield and ee value (Table 1, entry 1-2). Quinine **C3** catalyzed the reaction in a much faster rate to give **3a** in 43% ee, together with isatin in 51% yield (entry 3). Afterward, the solvent effects to improve the reaction outcome, using **C3** as the catalyst were examined. Unexpectedly, the performance of quinine **C3** was significantly improved when using CH_2Cl_2 as solvent, which promote the reaction to give 82% yield and 79% ee, with the yield of isatin decreasing to 8% (entry 4). Further exploration revealed that dihydroquinine **C4** could give a better result (entry 5). When the concentration decreased from 0.1 M to 0.05 M, with the addition of MS 13X, the enantioselectivity could be further improved to 91% (entry 6). Ultimately, using 5 mol% of dihydroquinine **C4**, along with the addition of MS 13X allowed **3a** to be obtained in 78% yield with 93% ee, accompanied by trace amount of isatin (entry 7). Control experiments revealed the importance of a suitable H-bond donor in restraining the undesired *S*-nucleophilic pathway whilst achieving high enantioselectivity. For example, when the hydroxyl group of dihydroquinine **C4** was changed to methoxyl, the methylated dihydroquinine **C5** not only resulted in poor enantioselectivity, but led to the obvious increase in isatin generation (entry 8 vs 6).

Table 2 Scope of oxindole-dithioketals



Entry	R^1	R^2	R^3	**2**	**3**	Yield[a] (%)	E (%)
1	H	*p*-ClC_6H_4	H	**2a**	**3a**	78	93
2	5-OMe	*p*-ClC_6H_4	H	**2a**	**3b**	73	96
3[c]	6-OMe	*p*-ClC_6H_4	H	**2a**	**3c**	70	87
4	7-Cl	*p*-ClC_6H_4	H	**2a**	**3d**	85	91
5[d]	5,7-Me_2	*p*-ClC_6H_4	H	**2a**	**3e**	87	9
6	H	*p*-MeC_6H_4	H	**2a**	**3f**	70	88
7	H	*o*-FC_6H_4	H	**2a**	**3g**	57	90
8	H	2-Naphthyl	H	**2a**	**3h**	67	87
9	H	Bn	H	**2a**	**3i**	84	91
10	H	Allyl	H	**2a**	**3j**	56	83
11	H	*p*-ClC_6H_4	Me	**2a**	**3k**	97	90
12	H	*p*-ClC_6H_4	Bn	**2a**	**3l**	98	94
13	5-F	*p*-ClC_6H_4	Bn	**2a**	**3m**	97	91
14	5-Me	*p*-ClC_6H_4	Bn	**2a**	**3n**	99	9
15[d]	H	*p*-ClC_6H_4	Bn	**2b**	**3o**	70	81



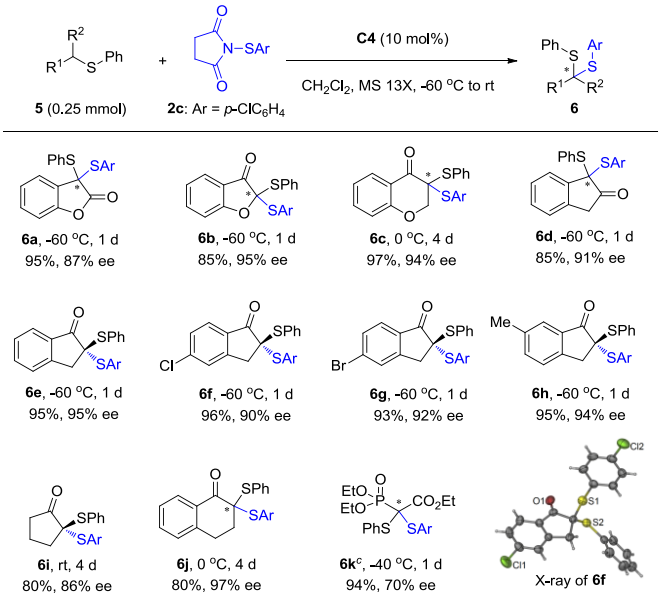
[a] Isolated yield. [b] Determined by HPLC analysis. [c] 3 d. [d] -60 °C, 3 d.

Based on these screenings, simple and cheap dihydroquinine **C4** was chosen as the optimal catalyst. Accordingly, the substrate scope with respect to differently substituted 3-thiooxindoles was examined by running the reaction in CH_2Cl_2 at -70 °C, in the presence of MS 13X. As shown in Table 2, whatever the nature of the substituent on the 5, 6 or 7-position of the oxindole framework of **1**, the reaction of both 3-alkylthiooxindoles and 3-arylthiooxindoles could all finish within 36 h, giving the corresponding products **3** in high to excellent ee value (up to 96%). When less active sulfenylating reagent *N*-benzylthiosuccinimide **2b** was used, substantial amount of side product isatin formed, so the reaction had to be conducted at elevated temperature (-60 °C), to afford the desired product **3m** in 70% yield, albeit with compromised 81%

ee value. The absolute configuration of adduct **3c** was assigned to be *S* by X-ray analysis, and that of other dithioketals were tentatively assigned.

To our delight, our protocol was not limited to the synthesis of oxindole dithioketals, other *S*-containing methine compounds with a cyclic framework all afforded desired products in high to excellent enantioselectivity, in spite of great difference in reactivity (Table 3). The 2- and 3-benzofuranone derived dithioketals **6a-b** were obtained in high enantioselectivity, and chromanone derived **6c** was prepared in 94% ee value but the reaction should be run at 0 °C. 2-Indanone and 1-indanone derived dithioketas **6d-h** were synthesized in up to 95% ee value. The absolute configuration of dithioketal **6f** was assigned to be *R* by single-crystal X-ray diffraction analysis. Cyclopentanone derivative **6i** was also provided in high ee, but the corresponding reaction should be conducted at room temperature for 4 d. Dithioketal **6j** derived from α-tetralone was furnished in 97% ee as well. Moreover, this protocol could be extended to the synthesis of acyclic dithioketals, as evidenced by the synthesis of **6k** in excellent yield, albeit with moderate enantioselectivity.

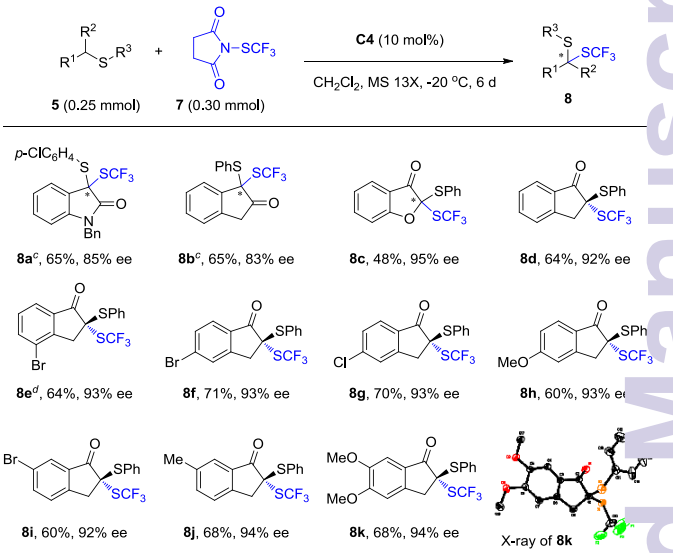
Table 3 Scope of other types of dithioketals.[a-b]



[a] Isolated yield. [b] Determined by HPLC analysis. [c] with **C7** as catalyst and THF as solvent (for detail, see SI).

Interestingly, our method could be utilized for the synthesis of dithioketals featuring an SCF_3 group, as shown in Table 4. Recently, the efficient introduction of an SCF_3 group into organic molecules had received increasing attention,[17] as the high lipophilicity and electron-withdrawing effect of the SCF_3 group might bring about beneficial effects on the pharmacokinetics of drug molecules. Inspired by the excellent work of Rueping, Shen and others in the electrophilic trifluoromethylthiolation,[18] we tried the synthesis of optically active dithioketals using *N*-SCF_3 succinimide **7** as the electrophilic SCF_3 reagent, which proved to be less reactive than non-fluorinated electrophilic *S*-source **2a-c**, so the reaction should be performed at -20 °C for six days. Under this condition, a number of structurally different dithioketals **8a-k** featuring an SCF_3 group were obtained in high to excellent ee value, albeit with mediate yield in some cases, due to the incomplete consumption of starting material. The absolute configuration of adduct **8k** was assigned to be *R* by single-crystal X-ray diffraction analysis. To the best of our knowledge, dithioketals bearing a SCF_3 group had not been reported before, which might be interesting targets for medicinal research.

Table 4 Scope of dithioketals featuring an SCF_3 group.[a-b]



[a] Isolated yield. [b] Determined by HPLC analysis. [c] 2 d. [d] With 30 mol% of catalyst **C4**, 3 d.

In summary, we have developed the first highly enantioselective synthesis of dithioketals via catalytic asymmetric sulfenylation. The use of simple and cheap dihydroquinine as catalyst, along with the broad substrate scope, makes our method attractive for the synthesis of chiral dithioketals in rich structural diversity, which may be interesting targets for medicinal research. Importantly, our work also reveals that the ambident nucleophilicity of *S*-based nucleophiles may cause severe side reactions in developing asymmetric reactions, an untrodden issue, due to the undesired *S*-nucleophilic way to form a sulfonium salt ion **I**, but bifunctional acid-base catalysis may be a good solution to tackle this issue. Further studies into the reaction mechanism and the development of new reactions to optically active dithioketals are now in progress in our laboratory.

The financial support from 973 program (2015CB856600), NSFC (21502053, 21222204, 21472049), Ministry of Education (PCSIRT), Program of SSCS (13XD1401600) and East China Normal University are highly appreciated.

Notes and references

CCDC 1413662 (**3c**), CCDC 1413670 (**6f**) and CCDC 1413672 (**8k**), contain the supplementary crystallographic data for this paper.

1 (a) L. A. Damini, *Sulphur-Containing Drugs and Related Organic Compounds*, Wiley, New York, 1989; (b) G. A. Patani and E. J. LaVoie, *Chem. Rev.*, 1996, **96**, 3147; (c) J. J. R. Fraústo da Silva and R. J. P. Williams, *The Biological Chemistry of the Elements*, Oxford University Press, New York, 2001.

2 http://www.genengnews.com/insight-and-intelligenceand153/top-200-best-selling-drugs-of-2012/77899775/?page=2.

3 (a) P. Metzner and A. Thuillier, *Sulfur Reagents in Organic Synthesis*, Academic Press, New York, 1995; (b) T. Toru and C. Bolm, *Organosulfur Chemistry in Asymmetric Synthesis*, Wiley-VCH, Weinheim, Germany, 2008.

4 For reviews: (a) P. Chauhan, S. Mahajan and D. Enders, *Chem. Rev.*, 2014, **114**, 8807; (b) D. Enders, K. Lüttgen and A. A. Narine,

Synthesis, 2007, 959; (c) J. Clayden and P. MacLellan, *Beilstein J. Org. Chem.*, 2011, **7**, 582.

5 (a) P. J. Kocieński, *Protecting Groups*, Thieme, Stuttgart, 2005; (b) T. W. Greene and P. G. M. Wuts, *Protective Groups in Organic Synthesis*, John Wiley & Sons, New York, 1999; (c) P. C. B. Page, M. B. van Niel and J. C. Prodger, *Tetrahedron*, 1989, **45**, 7643; (d) T.-Y. Luh, *J. Organomet. Chem.*, 2002, **653**, 209.

6 (a) E. M. Smith, G. F. Swiss, B. R. Neustadt, P. McNamara, E. H. Gold, E. J. Sybertz and T. Baum, *J. Med. Chem.*, 1989, **32**, 1600; (b) E. Rutenber, E. B. Fauman, R. J. Keenan, S. Fong, P. S. Furth, P. R. O. de Montellano, E. Meng, I. D. Kuntz, D. L. DeCamp, R. Salto, J. R. Rosé, C. S. Craik and R. M. Stroud, *J. Biolog. Chem.*, 1993, **268**, 15343.

7 (a) E. Francotte and W. Lindner, *Chirality in Drug Research*, Wiley-VCH, Weinheim, 2006; (b) I. K. Reddy and R. Mehvar, *Chirality in Drug Design and Development*, CRC Press, New York, 2004.

8 For reviews: (a) M. Wilsdorf and H.-U. Reissig, *Angew. Chem., Int. Ed.*, 2012, **51**, 9486; (b) L. Cala, F. J. Fañanás and F. Rodríguez, *Org. Biomol. Chem.*, 2014, **12**, 5324; For selected examples: (c) H. Audrain, J. Thorhauge, R. G. Hazell and K. A. Jørgensen, *J. Org. Chem.*, 2000, **65**, 4487; (d) I. Čorić and B. List, *Nature*, 2012, **483**, 315; (e) Z. Sun, G. A. Winschel, A. Borovika and P. Nagorny, *J. Am. Chem. Soc.*, 2012, **134**, 8074; (f) X. Wang, Z. Han, Z. Wang and K. Ding, *Angew. Chem., Int. Ed.*, 2012, **51**, 936.

9 (a) H. Dentel, I. Chataigner, F. L. Cavelier and M. Gulea, *Tetrahedron Lett.*, 2010, **51**, 6014; (b) H. Jiang, D. C. Cruz, Y. Li, V. H. Lauridsen and K. A. Jørgensen, *J. Am. Chem. Soc.*, 2013, **135**, 5200.

10 (a) F. Zhou, X.-P. Zeng, C. Wang, X.-L. Zhao and J. Zhou, *Chem. Commun.*, 2013, **49**, 2022; (b) W.-M. Gao, J.-S. Yu, Y.-L. Zhao, Y.-L. Liu, F. Zhou, H.-H. Wu and J. Zhou, *Chem. Commun.*, 2014, **50**, 15179.

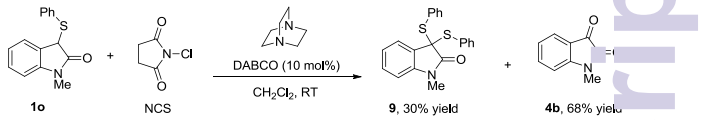
11 For review of the catalytic asymmetric α-sulfenylation, see: (a) X. Zhao, J. Shen and Z. Jiang, *Mini-Rev. Org. Chem.*, 2014, **11**, 424; For organocatalytic version: (b) M. Marigo, T. C. Wabnitz, D. Fielenbach and K. A. Jørgensen, *Angew. Chem., Int. Ed.*, 2005, **44**, 794; (c) S. Sobhani, D. Fielenbach, M. Marigo, T. C. Wabnitz and K. A. Jørgensen, *Chem. Eur. J.*, 2005, **11**, 5689; (d) L. Fang, A. Lin, H. Hu and C. Zhu, *Chem. Eur. J.*, 2009, **15**, 7039; (e) C. Wang, X. Yang, C. C. J. Loh, G. Raabe and D. Enders, *Chem. Eur. J.*, 2012, **18**, 11531; (f) Z. Han, W. Chen, S. Dong, C. Yang, H. Liu, Y. Pan, L. Yan and Z. Jiang, *Org. Lett.*, 2012, **14**, 4670; (g) X. Li, C. Liu, X.-S. Xue and J.-P. Cheng, *Org. Lett.*, 2012, **14**, 4374; (h) S. Shirakawa, T. Tokuda, A. Kasai and K. Maruoka, *Org. Lett.*, 2013, **15**, 3350; (i) B. Qiao, X. Liu, S. Duan, L. Yan and Z. Jiang, *Org. Lett.*, 2014, **16**, 672; (j) S. E. Denmark, S. Rossi, M. P. Webster and H. Wang, *J. Am. Chem. Soc.*, 2014, **136**, 13016; (k) M. Xu, B. Qiao, S. Duan, H. Liu and Z. Jiang, *Tetrahedron*, 2014, **70**, 8696; (l) L. Huang, J. Li, Y. Zhao, X. Ye, Y. Liu, L. Yan, C.-H. Tan, H. Liu and Z. Jiang, *J. Org. Chem.*, 2015, **80**, 8933; (m) Y. You, Z.-J. Wu, Z.-H. Wang, X.-Y. Xu, X.-M. Zhang and W.-C. Yuan, *J. Org. Chem.* 2015, **80**, 8470. For metal catalyzed version: (n) M. Jereb and A. Togni, *Org. Lett.*, 2005, **7**, 4041; (o) M. Jereb and A. Togni, *Chem. Eur. J.*, 2007, **13**, 9384; (p) T. Ishimaru, S. Ogawa, E. Tokunaga, S. Nakamura and N. Shibata, *J. Fluorine Chem.*, 2009, **130**, 1049; (q) Y. Cai, J. Li, W. Chen, M. Xie, X. Liu, L. Lin and X. Feng, *Org. Lett.*, 2012, **14**, 2726; (r) Q.-H. Deng, C. Rettenmeier, H. Wadepohl and L. H. Gade, *Chem. Eur. J.*, 2014, **20**, 93.

12 The speculated side reaction is based on literature report and our related studies. For details, see supporting information, SI.

First, the nucleophilic attack of a mercaptan on sulfenimides **2** was known, see: (a) K. S. Boustany and A. B. Sullivan, *Tetrahedron Lett.*, 1970, **11**, 3547. We had also observed that a mercaptan attack the sulfur atom of 3-substituted 3-alkylthiooxindole to form a disulfane, see: (b) F. Zhu, F. Zhou, Z.-Y. Cao, C. Wang, Y.-X. Zhang, C.-H. Wang and J. Zhou, *Synthesis*, 2012, **44**, 3129.

Second, in the reaction of tetrahydro-4H-thiopyran-4-one and N-chlorosuccinimide (NCS), in the presence of pyridine, Chen et al proposed that the *S*-nucleophilic attack of the sulfide to NCS led to the formation of chloro-sulfonium salt, see: (c) C. H. Chen, G. A. Reynolds and J. A. V. Allan, *J. Org. Chem.*, 1977, **42**, 2777.

Last, we found that 3-thiooxindoles reacted with NCS to give isatin **4b** and symmetric dithioketal **9**, in the presence of 10 mol% DABCO, which might be initiated from the formation of a sulfonium salt **I** the *S*-nucleophilic attack of 3-thiooxindole to NCS.



13 For metal catalyzed version: (a) S. Takechi, S. Yasuda, N. Kumagai and M. Shibasaki, *Angew. Chem., Int. Ed.*, 2012, **51**, 4218; (b) S. Takechi, N. Kumagai and M. Shibasaki, *Org. Lett.*, 2013, **15**, 2632; (c) W. Chen and J. F. Hartwig, *J. Am. Chem. Soc.*, 2014, **136**, 37[illegible]. For organocatalytic version, see: (d) Y. Fujiwara and G. C. Fu, *J. Am. Chem. Soc.*, 2011, **133**, 12293; (e) A. Sakakura, H. Yamada and K. Ishihara, *Org. Lett.*, 2012, **14**, 2972; (f) W. Wu, H. Huang, X. Yuan, K. Zhu and J. Ye, *Chem. Commun.*, 2012, **48**, 9180; (g) H. Zhang, L. Wang, L. Cui, Y. Li, J. Qu and Y. Song, *Org. Biomol. Chem.*, 2014, **12**, 9097; (h) S. Diosdado, R. López and C. Palomo, *Chem. Eur. J.*, 2014, **20**, 6526; (i) X. Dou, B. Zhou, W. Yao, F. Zhong, C. Jiang and Y. Lu, *Org. Lett.*, 2013, **15**, 4920; (j) S. Diosdado, J. Etxabe, I. Izquierdo, A. Landa, A. Mielgo, I. Olaizola, R. López and C. Palomo, *Angew. Chem., Int. Ed.*, 2013, ***52***, 11846; (k) P.-Y. Géant, M. Urban, M. Remeš, I. Císařová and J. Veselý, *Eur. J. Org. Chem.*, 2013, [illegible]; (l) E. Badiola, B. Fiser, E. Gómez-Bengoa, A. Mielgo, I. Olaizola, I. Urruzuno, J. M. García, J. M. Odriozola, J. Razkin, M. Oiarbide and C. Palomo, *J. Am. Chem. Soc.*, 2014, **136**, 17869; (m) T. Wang, Z. Yu, D. L. Hoon, K.-W. Huang, Y. Lan and Y. Lu, *Chem. Sci.*, 2015, **6**, 4912

14 (a) J. Zhou, *Multicatalyst system in asymmetric catalysis*, John Wiley & Sons, New York, 2014, chapter 3; (b) J.-S. Yu, F.-M. Liao, W.-M. Gao, K. Liao, R.-L. Zuo and J. Zhou, *Angew. Chem., Int. Ed.*, 2015, **54**, 7381; (c) X.-P. Yin, X.-P. Zeng, Y.-L. Liu, F.-M. Liao, J.-S. Yu, F. Zhou and J. Zhou, *Angew. Chem., Int. Ed.*, 2014, **53**, 13740; (d) Y.-L. Liu, B.-L. Wang, J.-J. Cao, L. Chen, Y.-X. Zhang, C. Wang and J. Zhou, *J. Am. Chem. Soc.*, 2010, **132**, 15176; (e) M. Ding, F. Zhou, Y.-L. Liu, C.-H. Wang, X.-L. Zhao and J. Zhou, *Chem. Sci.*, 2011, **2**, 2035; (f) Y.-L. Liu, T.-D. Shi, F. Zhou, X.-L. Zhao, Y. Wang and J. Zhou, *Org. Lett.*, 2011, **13**, 3826; (g) C.-B. Ji, Z.-Y. Cao, X. Wang, D.-Y. Wu and J. Zhou, *Chem. Asian. J.*, 2013, **8**, 87[illegible]; (h) Y.-H. Wang, Z.-Y. Cao, Y.-F. Niu, X.-L. Zhao and J. Zhou, *Acta Chim. Sinica.*, 2014, **72**, 867.

15 (a) Z.-Y. Cao, X. Wang, C. Tan, X.-L. Zhao, J. Zhou and K. Ding, *J. Am. Chem. Soc.*, 2013, **135**, 8197; (b) F. Zhou, C. Tan, J. Tang, Y.-Y. Zhang, W.-M. Gao, H.-H. Wu, Y.-H. Yu and J. Zhou, *J. Am. Chem. Soc.*, 2013, **135**, 10994; (c) Y.-L. Liu, X. Wang, Y.-L. Zhao, F. Zhu, X.-P. Zeng, L. Chen, C.-H. Wang, X.-L. Zhao and J. Zhou, *Angew. Chem., Int. Ed.*, 2013, **52**, 13735; (d) Z.-Y. Cao, F. Zhou, Y.-H. [illegible] and J. Zhou, *Org. Lett.*, 2013, **15**, 42; (e) Z.-Y. Cao, Y. Zhang, C.-B. Ji and J. Zhou, *Org. Lett.*, 2011, **13**, 6398; (f) Y.-L. Liu and J. Zhou, *Chem. Commun.*, 2012, **48**, 1919; (g) F. Zhou, X.-P. Zeng, C. Wang, X.-L. Zhao and J. Zhou, *Chem. Commun.*, 2013, **49**, 2022.

16 (a) C. V. Galliford and K. A. Scheidt, *Angew. Chem., Int. Ed.*, 2007, **46**, 8748; (b) B. M. Trost and M. K. Brennan, *Synthesis*, 2009, 3007; (c) F. Zhou, Y.-L. Liu and J. Zhou, *Adv. Synth. Catal.*, 2010, **352**, 1381; (d) K. Shen, X. Liu, L. Lin and X. Feng, *Chem. Sci.*, 2012, **3**, 327; (e) R. Dalpozzo, G. Bartoli and G. Bencivenni, *Chem. Soc. Rev.*, 2012, **41**, 7247.

17 For reviews: (a) X. Shao, C. Xu, L. Lu and Q. Shen, *Acc. Chem. Res.*, 2015, **48**, 1227; (b) F. Toulgoat, S. Alazet and T. Billard, *Eur. J. Org. Chem.*, 2014, 2415; (c) K. Zhang, X. Xu and F. Qing, *Chin. J. Org. Chem.*, 2015, **35**, 556.

18 (a) T. Bootwicha, X. Liu, R. Pluta, I. Atodiresei and M. Rueping, *Angew. Chem., Int. Ed.*, 2013, **52**, 12856; (b) X. Wang, T. Yang, X. Cheng and Q. Shen, *Angew. Chem., Int. Ed.*, 2013, **52**, 12860; (c) M. Rueping, X. Liu, T. Bootwicha, R. Pluta and C. Merkens, *Chem. Commun.*, 2014, **50**, 2508; (d) X.-L. Zhu, J.-H. Xu, D.-J. Cheng, L.-L. Zhao, X.-Y. Liu and B. Tan, *Org. Lett.*, 2014, **16**, 2192.