A Journal of the Gesellschaft Deutscher Chemiker

Angewandte International Edition GDCh Chemie

www.angewandte.org

Accepted Article

Title: Selective [5,5]-Sigmatropic Rearrangement via Electrophilic Assembly of Aryl Sulfoxides with Allyl Nitriles

Authors: Lei Zhang, Jia-Ni He, Yuchen Liang, Mengjie Hu, Li Shang, Xin Huang, Lichun Kong, Zhi-Xiang Wang, and Bo Peng

To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201900434
Angew. Chem. 10.1002/ange.201900434

Link to VoR: http://dx.doi.org/10.1002/anie.201900434
http://dx.doi.org/10.1002/ange.201900434

WILEY-VCH

10.1002/anie.201900434

WILEY-VCH

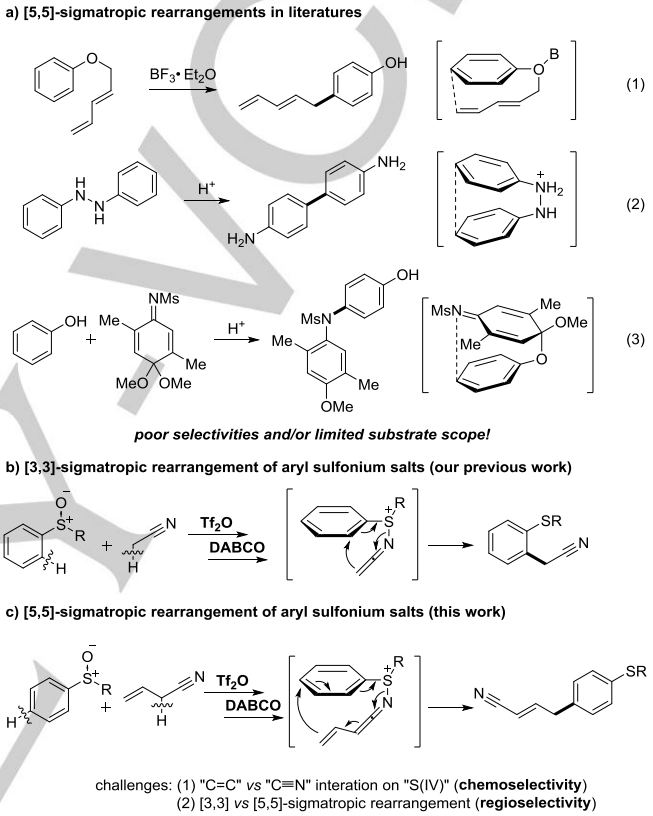
Selective [5,5]-Sigmatropic Rearrangement via Electrophilic Assembly of Aryl Sulfoxides with Allyl Nitriles

Lei Zhang,[+] Jia-Ni He,[+] Yuchen Liang,[+] Mengjie, Hu, Li Shang, Xin Huang, Lichun Kong, Zhi-Xiang Wang,[*] Bo Peng[*]

Dedication ((optional))

Abstract: Aromatic [5,5]-sigmatropic rearrangement is an appealing protocol for accessing 1,4-substituted arenes. However, such a protocol has not been well utilized in organic synthesis, because it often suffers from the difficulties in the synthesis of substrates, selectivity issues, and limited substrate scopes. Herein, we describe a new [5,5]-sigmatropic reaction by utilizing readily available aryl sulfoxides and allyl nitriles. This reaction features mild conditions, high chemo- and regioselectivity, excellent functional group compatibility and broad substrate scope. Computational studies suggested that the success of the reaction can be attributed to the selective electrophilic assembling of rearrangement precursors in which a linear -C=C=N- linkage favors [5,5]-sigmatropic rearrangement over the competitive [3,3]-sigmatropic rearrangement.

[3,3]-Sigmatropic rearrangement is a powerful process in organic synthesis, based on which a number of name reactions have been developed.[1,2] The success of this process can be mainly attributed to its inherent high chemo- and regioselectivities. In sharp contrast, [5,5]-sigmatropic rearrangement reactions, though also thermally allowed by the Woodward-Hoffmann rules, have not attracted that much attentions and were rarely reported.[3-5] The Claisen-type rearrangement of phenyl dienyl ethers to the *para*-functionalized phenols is a classic [5,5]-sigmatropic rearrangement reaction (eq 1, Scheme 1a).[3] Although the reaction was well developed with good *para*-regioselectivity by Naruta in 1986, it has not caught much attention,[3a] probably due to the limited substrate scope. The benzidine rearrangement represents another important [5,5]-sigmatropic reaction (eq 2).[4] The intriguing reaction pattern has triggered extraordinary efforts of chemists. However, in addition to the desired *para*-benzidine, the reaction also affords side products such as *ortho*-benzidine, *ortho*-semidine, *para*-semidine, and diphenyline, thus raising selectivity issues. The addition of phenol to iminoquinone acetals could also proceed via [5,5]-sigmatropic rearrangement to form a remote C-N bond (eq 3).[5] In spite of these precedents, to the best of our knowledge, there have been no reports of the protocol that could manipulate [5,5]-sigmatropic rearrangement with high chemo- and regioselectivities, and broad substrate scope.



Scheme 1. Background and this work

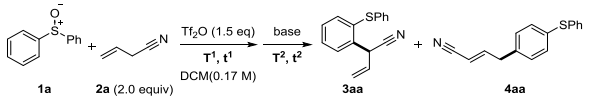
The *ortho* C-H functionalizations of aryl sulfoxides have garnered great interests in the past decades.[6-12] An array of functionalities including allyl[7], propagyl[8], carbonyl[7,9], phenolic aryl[10], and cyanoalkyl[11] groups were selectively anchored on the *ortho* position of aryl sulfoxides with electrophilic activation protocol by Kita, Procter, Maulide, Yorimitsu, Magnier and others. It's worth noting that Yorimitsu and coworkers observed *para* C-H arylation products in the development of *ortho* arylation of aryl sulfoxides with phenols.[10a] They have also reported an elegant protocol for *para* C-H sulfanylation of aryl sulfoxides using alkyl aryl sulfides as nuleophile.[13] In addition, the groups led by Hyatt and Shafir respectively reported *para* C-H benzylation of aryl iodanes via interrupted "transmetalation" process.[14]

Recently, we developed an *ortho* C-H cyanoalkylation of aryl sulfoxides (Scheme 1b).[11c] In this study, an "assembly/deprotonation" strategy, including Tf_2O initiated electrophilic assembly and DABCO promoted deprotonation,

[*] L. Zhang, J. He, M. Hu, L. Shang, X. Huang, L. Kong, Prof. B. Peng
Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Zhejiang Normal University
Jinhua 321004, China
E-mail: pengbo@zjnu.cn
Y. Liang, Prof. Z. Wang
School of Chemistry and Chemical Engineering, University of the Chinese Academy of Sciences
Beijing 100049, China
E-mail: zxwang@ucas.ac.cn
[+] These authors contributed equally to this work

10.1002/anie.201900434

Table 1. Hypothesis verification and optimization of reaction conditions[a]



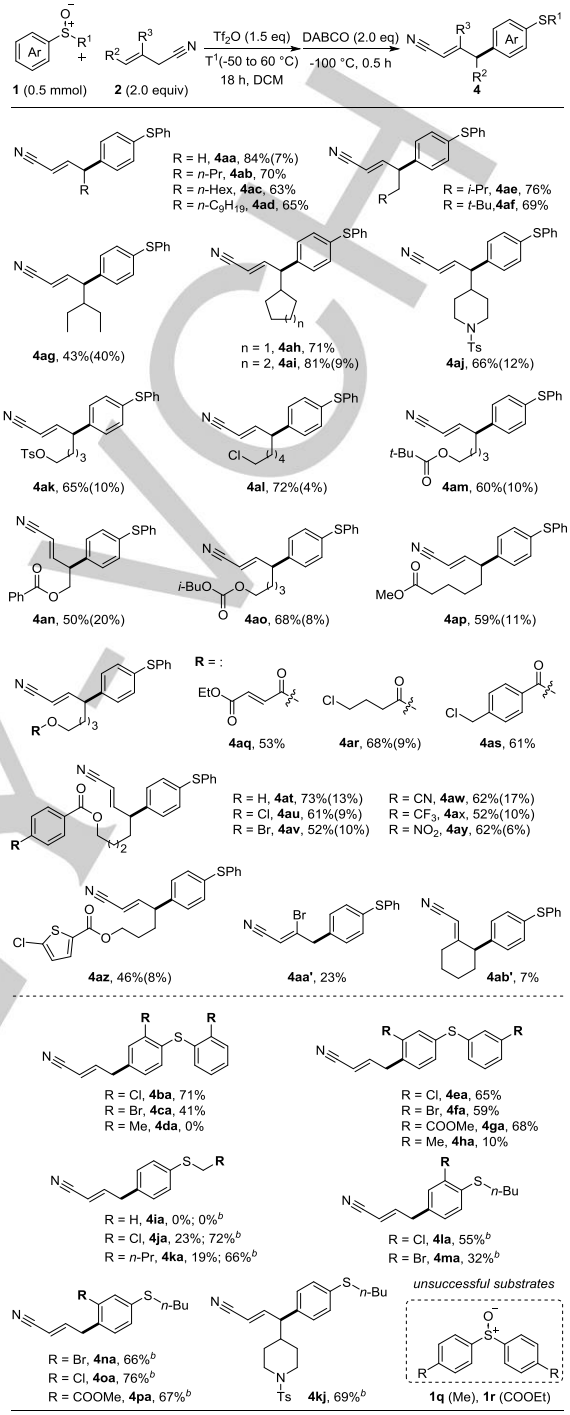
entry	T^1/t^1; T^2/t^2	base	yield(**3aa**/**4aa**)[b]
1	-30 °C/5 min; -30 °C/5 min	DABCO	12%/39%
2	-60 °C/18 h; -60 °C /0.5 h	DABCO	8%/55%
3	-60 °C/18 h; -100 °C /0.5 h	DABCO	**7%/84%**
4	-60 °C/18 h; -100 °C/0.5 h	DIPEA	38%/53%
5	-60 °C/18 h; -100 °C/0.5 h	4-methylmorpholine	37%/39%
6	-60 °C/18 h; -100 °C/0.5 h	2,6-dimethylpyridine	23%/27%

[a] Reactions were performed on 0.5 mmol scale. Tf_2O was added at -78 °C, then the mixture was warmed to T^1. DABCO (2.0 equiv) and other bases (3.0 equiv) were used. [b] Isolated yield.

was implemented to assemble a ketenimine sulfonium intermediate which can readily undergo [3,3]-sigmatropic rearrangement to give *ortho*-cyanoalkylated product. Encouraged by the success of the strategy, we sought to achieve *para* C-H functionalizations of aryl sulfoxides by assembling a vinyl ketenimine sulfonium intermediate as a precursor for [5,5]-sigmatropic rearrangement, as illustrated in Scheme 1c.[15]

To testify our hypothesis, we first investigated the reaction of allyl nitrile **2a** with diphenyl sulfoxide **1a** under the conditions for our reported *ortho*-cyanoalkylation of aryl sulfoxides (entry1, Table 1).[11c] In line with our expectation, aside from the *ortho*-cyanoalkylated product **3aa** (12%), we obtained *para*-alkylated aryl thioether **4aa** as a major product (39%). After optimization of the reaction conditions, we found that employing relatively lower temperature and prolonging reaction time (Tf_2O, -60 °C, 18 h; DABCO, -100 °C, 0.5 h) could significantly improve the yield of **4aa** from 39% to 84%. It's worth noting that the choice of base is critical for the selectivity of the reaction. DABCO proved to be better than other bases (entries 3-6). However, the influence of base on the regioselectivity is currently not clear.

To our delight, a wide range of allyl nitriles **2** proved to be suitable for the reaction as shown in Scheme 2. Varying the linear alkyl chains on γ-position of nitirles (**2b**-**2f**) had no obvious detriment to the reaction. However, nitrile **2g** bearing a larger substituent (secondary alkyl chain) at γ-position produced a modest yield of **4ag** (43%) with a significant amount of *ortho*-cyanoalkylated product **3ag** (40%). It should be noted that along with **4ah**, trace amount of o*rtho*-cyanoalkylated products **3ah** could also be observed. However, we failed to obtain this side product even after great efforts. Remarkably, the reaction could tolerate a diverse array of functional groups including alkyl/aryl halides (**4al**, **4ar**, **4as**, **4au**, **4av** and **4az**), alkyl pseudohalides (**4ak**), esters/carbonates (**4am-4az**), tertiary amines (**4aj)**, alkenes (**4aq**), aryl nitriles (**4aw**), and nitro groups (**4ay**). These functional groups tolerated in the reaction provided a versatile platform for their further derivatization. Impressively, highly electrophilic functional groups such as unsaturated ester (**4aq**)



Scheme 2. Reaction scope. [a] Yields of *ortho*-functionalized arenes **3** are given in parentheses. T^1 = -60 °C(**4aa**-**4al**, **4aa'**, **4ab'**, **4ja**, **4la**, **4ma**), -55 °C(**4am**-**4az**), -50 °C(**4ba**-**4ia**, **4ka,** **4na**-**4pa,** **4kj**). [b] Nitrile **2** (3.0 equiv) and DIPEA (2.5 equiv) instead of DABCO were used.

and benzynlic chloride (**4as**) were also nicely compatible with the reaction conditions. Nevertheless, allyl nitriles (**2a'**, **2b'**) bearing β-substituents proved to be unsuitable for the reaction as the desired products **4aa'** and **4ab'** were obtained in very low yields (Scheme 2).

Next, we examined a variety of aryl sulfoxides as shown in Scheme 2 (under dashed line). Reactions of symmetric diaryl sulfoxides (**1b**, **1c**, **1e**-**1g**) bearing electron-withdrawing groups

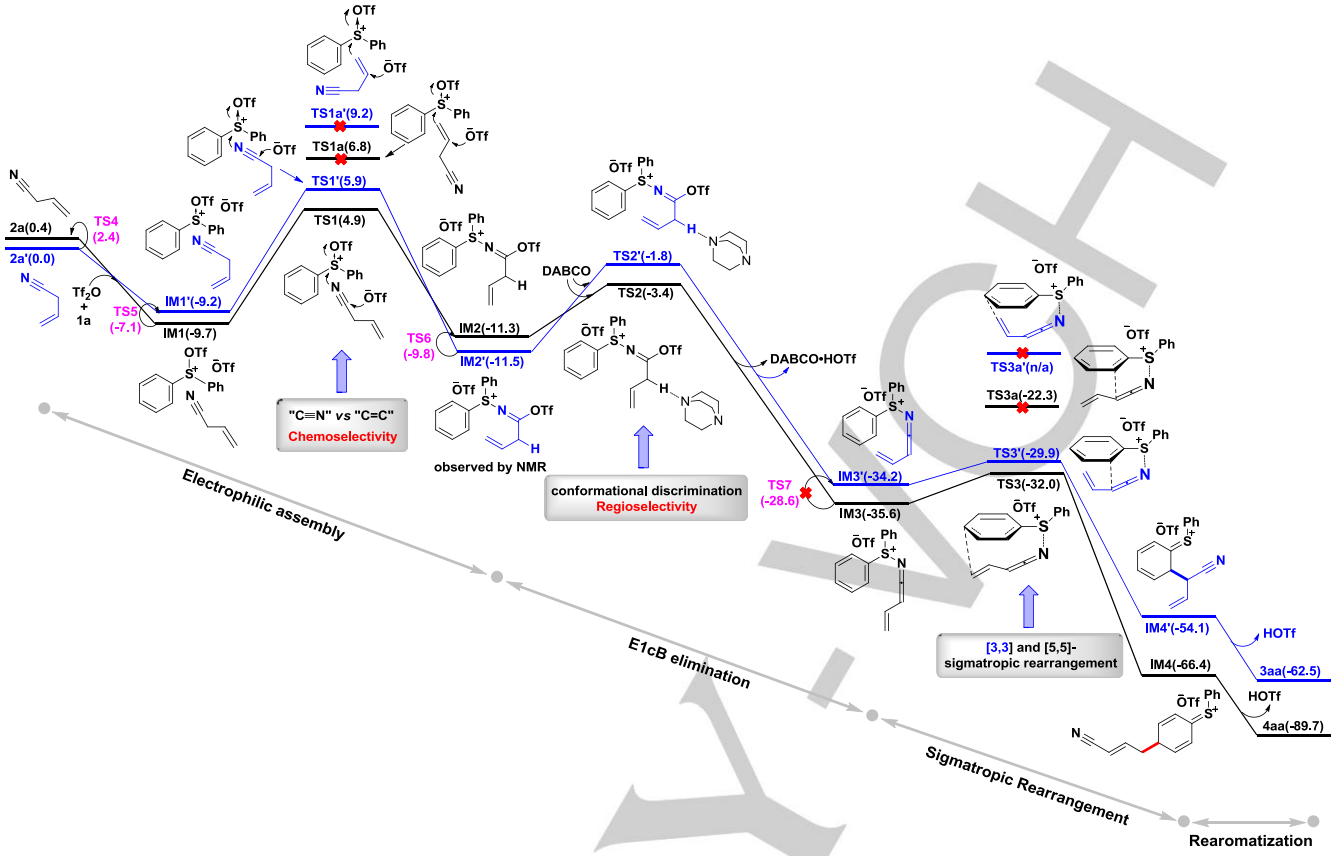
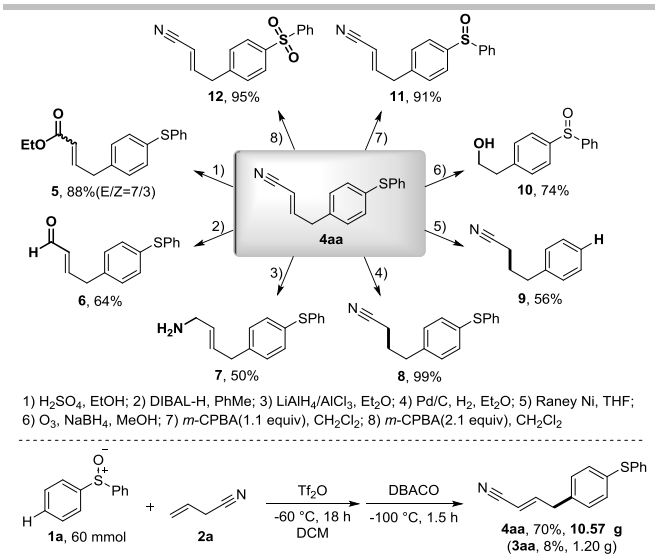


Figure 1. Simplified reaction pathways for the reaction of **1a** with **2a**. Values in the parentheses are relative free energies (in kcal mol^{-1}).

(Cl, Br, COOMe) proceeded smoothly to afford the *para*-cyanoalkylated products (**4ba**, **4ca**, and **4ea**-**4ga**) in good yields, respectively. In line with our previously reported *ortho*-cyanoalkylation of aryl sulfoxides[11c], electron-rich diaryl sulfoxide **1d** and **1h** bearing methyl groups were unsuitable for the reaction. Only 10 % of **4ha** could be obtained from sulfoxide **1h** while no desired product **4da** could be determined from **1d**. These results indicated a remarkable electronic effect in the reaction. Not surprisingly, electron-rich methyl phenyl sulfoxide**1i** was also not suitable for the reaction. To our delight, other alkyl arylsulfoxides including chloromethylated sulfoxide **1j** and *n*-butyl sulfoxide **1k** produced the desired products **4ja** and **4ka**, albeit in low yields (23% and 19%, respectively). Interestingly, changing the base from DBACO to DIPEA could significantly improve the yields of **4ja** and **4ka** (72% and 66%, respectively). However, even employing DIPEA as base, the reaction of **1i** still could not furnish any desired product. We suspect that the primary alkyl group (Me) of **1i** could be more readily deprotonated by bases after electrophilic activation which precludes the desired reaction pathway. Furthermore, alkyl aryl sulfoxides **1n**-**1p** bearing *meta* substituents (Br, Cl, COOMe) produced desired products **4na**-**4pa** in synthetically useful yields, whereas sulfoxides **1l** and **1m** bearing *ortho* substituents (Cl and Br) affording **4la** and **4ma**, respectively in slightly lower yields. In addition to **2a**, terminal substituted allyl nitriles **2j** could also react with alkyl aryl sulfoxide **1k** producing **4kj** in a good yield (69%). Unfortunately, *para*-substituted aryl sulfoxides **1q** and **1r** could merely afford complex mixtures under standard condtions.

To shed light on the reaction mechanism, we performed density functional theory (DFT) study of the reaction of **1a** with **2a** (see SI for computational details). Figure 1 describes the truncated version of the complete reaction pathways detailed in Figure S1. Proceeding along the black pathway, Tf_2O first activates **1a**, generating an ion pair ($PhSOTf^{+}\cdots OTf^{-}$, see Figure S1), which then interacts with **2a** to form a more stable ternary intermediate **IM1**. Subsequently, **IM1** undergoes C≡N nucleophilic attack via **TS1**, leading to **IM2**. The alternative terminal $C=CH_2$ attack via **TS1a** is 1.9 kcal mol^{-1} less favorable, because an alkene group is less nucleophilic than a nitrile group. In addition, the exposed C≡N, compared to $C=CH_2$, enables an electrostatic attraction between $S^{\delta+}$ and $O^{\delta-}Tf$ (attached to nitrile carbon) which is absent in **TS1a** (see Figure S2). To demonstrate the computational results we carried out *in situ* NMR study in the absence of DABCO (SI5.2), which showed the generation of **IM2**. After assembling **IM2**, the base DABCO promotes an E1cB elimination process via deprotonation illustrated by **TS2**, giving a vinyl ketenimine sulfonium intermediate **IM3** which can undergo either [5,5]- or [3,3]-sigmatropic rearrangement. The transition state (**TS3)** for [5,5]-sigmatropic rearrangement is 9.7 kcal mol^{-1} lower than **TS3a** for [3,3]-sigmatropic rearrangement. Comparing the key bond lengths given in **TS3** and **TS3a**, the strong disfavor of [3,3]-



Scheme 3. Elaboration of product **4aa** and gram-scale reactions.

sigmatropic rearrangement can be attributed to the ring strain of the six-membered ring involving alinear -C=C=N- linkage. Finally, the resulting **IM4** undergoes facile rearomatization, giving **4aa**.

The energetics of the black course well explains the production of **4aa**, but the barrier difference (9.7 kcal mol^{-1}) between **TS3a** and **TS3** is too large to explain **3aa** as a minor product. Thus, we reasoned that the conformations of the intermediates featuring an eclipsed **2a** fragment could play the role. Indeed, as depicted by the blue pathway, the pathway can afford **3aa** via [3,3]-sigmatropic rearrangement with feasible energetics. However, the transition state (labeled as **TS3a'**) for **IM3'** to undergo [5,5]-sigmatropic rearrangement could not be located, which we attributed to the bended vinyl ketenimine chain geometrically unsuitable for such a rearrangement. Compared to the course leading to **4aa**, the blue pathway is kinetically less favorable to afford **3aa**, in agreement with the experimental results. Moreover, as indicated by **TS4-TS6**, **2a'/IM1'/IM2'** can easily interconvert with its counterpart **2a/IM1/IM2**, but the conversion of **IM3** to **IM3'** is unlikely, because **TS7** is 3.4 kcal mol^{-1} higher than **TS3'**. Therefore, the regioselectivity of the reaction is determined by the kinetic preference of forming the rearrangement precursor **IM3** over **IM3'** rather than the competition of two rearrangement modes of **IM3**. It is worth noting that **IM4'** cannot further undergo [3,3]-sigmatropic rearrangement to give **4aa**, because the barrier for the second [3,3]-sigmatropic rearrangement is 13.2 kcal mol^{-1} higher than that (0.7 kcal mol^{-1}) for the facile rearomatization to give **3aa** (see Figure S1).

The utility of the reaction was exhibited by further elaboration of product **4aa**. As illustrated in Scheme 2, the nitrile group, C=C bond, and sulfide group in **4aa** could be readily converted to other functional groups by simple hydrolysis, reduction and oxidation. As a consequence, α,β-unsaturated ester **5**, α,β-unsaturated aldehyde **6**, allylic amine **7** were obtained in 88%, 64% and 50% yields, respectively. Hydrogenation of C=C bond with Pd/C catalyst quantitatively gave γ-arylated alkylnitrile **8**. Reduction of **4aa** with Raney Ni afforded γ-phenylated alkylnitrile **9** with cleavage of C-S bond. The ozone oxidation of C=C bond, followed by simple reduction, afforded β-arylethanol **10** in 74% yield. Sulfide group could be readily oxidized to give corresponding sulfoxide **11** and sulfone **12** whereas α,β-unsaturated nitrile group remained intact. Finally, the scalability of the reaction was also demonstrated by a gram-scale reaction, which produced more than 10 grams of **4aa** with high efficiency (70% yield).

In summary, we have developed a new [5,5]-sigmatropic rearrangement reaction by sequentially treating the mixture of aryl sulfoxides and β,γ-unsaturated nitriles with Tf_2O and DABCO. The reaction exhibits very high chemo- and regioselectivity, excellent functional group compatibility, and broad substrate scope, overcoming the problems often encountered in the conventional [5,5]-sigmatropic rearrangement reactions. DFT mechanistic studies unveil that the exposure and stronger nucleophilicity of C≡N site of allyl nitrile, compared to the $C=CH_2$ site, controls the chemoselectivity and the linear -C=C=N- linkage in the rearrangement precursor favors the [5,5]-sigmatropic rearrangement over the competitive [3,3]-sigmatropic rearrangement. The new strategy is expected to trigger the development of aromatic [5,5]-sigmatropic rearrangement reactions.

Acknowledgements ((optional))

B. P. thanks Zhejiang Normal University and the support of NSFC-21502171. Z.-X. W. acknowledges the support of NSFC-21573233.

Keywords: [5,5]-sigmatropic rearrangement • *para*-C-H functionalization • electrophilic activation • sulfoxide

[1] a) A. C. Jones, J. A. May, R. Sarpong, B. M. Stoltz, *Angew. Chem. Int. Ed.* **2014**, *53*, 2556; *Angew. Chem*. **2014**, *126*, 2590; b) E. A. Ilardi, C. E. Stivala, A. Zakarian, *Chem. Soc. Rev.* **2009**, *38*, 3133.

[2] a) R. Fernández de la Pradilla, M. Tortosa, A. Viso, *Top. Curr. Chem.* **2007**, *275*, 103; b) A. M. Martín Castro, *Chem. Rev.* **2004**, *104*, 2939; c) D. Tejedor, G. Méndez-Abt, L. Cotos, F. García-Tellado, *Chem. Soc. Rev.* **2013**, *42*, 458.

[3] a) K. Maruyama, N. Nagai, Y. Naruta, *J. Org. Chem.* **1986**, *51*, 5083; b) K. Maruyama, N. Nagai, Y. Naruta, *Tetrahedron Lett.* **1985**, *26*, 5149.

[4] a) M. E. Bouillon, H. H. Meyer, *Tetrahedron* **2016**, *72*, 3151; b) H. Gao, D. H. Ess, M. Yousufuddin, L. Kürti, *J. Am. Chem. Soc.* **2013**, *135*, 7086; c) H. J. Shine, H. Zmuda, K. H. Park, *J. Am. Chem. Soc.* **1981**, *103*, 955; d) L. C. Snyder, *J. Am. Chem. Soc.* **1962**, *84*, 340.

[5] a) L. Liu, K. Chen, W. Wu, P. Wang, H. Song, H. Sun, X. Wen, Q. Xu, *Org. Lett.* **2017**, *19*, 3823; b) T. Kamitanaka, K. Morimoto, K. Tsuboshima, D. Koseki, H. Takamuro, T. Dohi, Y. Kita, *Angew. Chem. Int. Ed.* **2016**, *55*, 15535; *Angew. Chem.* **2016**, *128*, 15764; c) S. Ichijima, H. Fukunaga, N. A Koga, *J. Mol. Struct.* **1999**, *461-462*, 429; d) L. K. J. Tong, M. C. Glesmann, *J. Am. Chem. Soc.* **1968**, *90*, 5164.

[6] For recent related reviews, see: a) T. Yanagi, K. Nogi, H. Yorimitsu, *Tetrahedron Lett.* **2018**, *59*, 2951; b) H. Yorimitsu, *Chem. Rec.* **2017**, *17*, 1156; c) A. P. Pulis, D. J. Procter, *Angew. Chem. Int. Ed.* **2016**, *55*, 9842; *Angew. Chem.* **2016**, *128*, 9996; d) A. Shafir, *Tetrahedron Lett.* **2016**, *57*, 2673; e) X. Huang, S. Klimczyk, N. Maulide, *Synthesis* **2012**, *2*, 175; f) Z.-Y. Tian, Y.-T. Hu, H.-B. Teng, C.-P. Zhang, *Tetrahedron Lett.* **2018**, *59*, 299.

[7] a) S. Akai, N. Kawashita, H. Satoh, Y. Wada, K. Kakiguchi, I. Kuriwaki, Y. Kita, *Org. Lett.* **2004**, *6*, 3793; b) A. Padwa, S. Nara, Q. Wang, *Tetrahedron. Lett.* **2006**, *47*, 595; c) A. J. Eberhart, J. E. Imbriglio, D. J. Procter, *Org. Lett.* **2011**, *13*, 5882; d) A. J. Eberhart, C. Cicoira, D. J. Procter, *Org. Lett.* **2013**, *15*, 3994; e) M. Šiaučiulis, S. Sapmaz, A. P. Pulis, D. J. Procter, *Chem. Sci.* **2018**, *9*, 754.

[8] a) A. J. Eberhart, D. J. Procter, *Angew. Chem. Int. Ed.* **2013**, *52*, 4008; b) A. J. Eberhart, H. J. Shrives, E. Álvarez, A. Carrër, Y. Zhang, D. J. Procter, *Chem. Eur. J.* **2015**, *21*, 7428; c) A. J. Eberhart, H. Shrives, Y. Zhang, A. Carrër, A. V. S. Parry, D. J. Tate, M. L. Turner, D. J. Procter,

Chem. Sci. **2016**, *7*, 1281; d) J. A. Fernández-Salas, A. J. Eberhart, D. J. Procter, *J. Am. Chem. Soc.* **2016**, *138*, 790; e) Z. He, H. J. Shrives, J. A. Fernández-Salas, A. Abengózar, J. Neufeld, K. Yang, A. P. Pulis, D. J. Procter, *Angew. Chem. Int. Ed.* **2018**, *57*, 5759; *Angew. Chem.* **2018**, *130*, 5861.

[9] a) X. Huang, N. Maulide, *J. Am. Chem. Soc.* **2011**, *133*, 8510; b) X. Huang, M. Patil, C. Farès, W. Thiel, N. Maulide, *J. Am. Chem. Soc.* **2013**, *135*, 7312.

[10] a) T. Yanagi, S. Otsuka, Y. Kasuga, K. Fujimoto, K. Murakami, K. Nogi, H. Yorimitsu, A. Osuka, *J. Am. Chem. Soc.* **2016**, *138*, 14582; b) H. J. Shrives, J. A. Fernández-Salas, C. Hedtke, A. P. Pulis, D. J. Procter, *Nature Commun.* **2017**, *8*, 14801; c) K. Okamoto, M. Hori, T. Yanagi, K.; Nogi, K. Murakami, H. Yorimitsu, *Angew. Chem. Int. Ed.* **2018**, *57*, 14230; *Angew. Chem*. **2018**, *130*, 14426; d) K. Yang, A. P. Pulis, G. J. P. Perry, D. J. Procter, *Org. Lett.* **2018**, *20*, 7498.

[11] a) Y. Macé, C. Urban, C. Pradet, J-C. Blazejewski, E. Magnier, *Eur. J. Org. Chem.* **2009**, 5313; b) B. Pégot, C. Urban, P. Diter, E. Magnier, *Eur. J. Org. Chem.* **2013**, 7800; c) L. Shang, Y. Chang, F. Luo, J.-N. He, X. Huang, L. Zhang, L. Kong, K. Li, B. Peng, *J. Am. Chem. Soc.* **2017**, *139*, 4211; d) F. Luo, Y. Lu, M. Hu, J. Tian, L. Zhang, W. Bao, C. Yan, X. Huang, Z.-X. Wang, B. Peng, *Org. Chem. Front.* **2018**, *5*, 1756.

[12] For other elegant examples of sulfonium-based [3,3]-sigmatropic rearrangement reactions, see: a) T. Kobatake, D. Fujino, S. Yoshida, H. Yorimitsu, K. Oshima, *J. Am. Chem. Soc.* **2010**, *132*, 11838; b) T. Kobatake, S. Yoshida, H. Yorimitsu, K. Oshima, *Angew. Chem. Int. Ed.* **2010**, *49*, 2340; Angew. Chem. 2010, 122, 2390; c) B. Lu, Y. Li, Y. Wang, D. H. Aue, Y. Luo, L. Zhang, *J. Am. Chem. Soc.* **2013**, *135*, 8512; d) B. Peng, D. Geerdink, C. Farès, N. Maulide, *Angew. Chem. Int. Ed.* **2014**, *53*, 5462; *Angew. Chem*. **2014**, *126*, 5566; (e) B. Peng, X. Huang, L.-G. Xie, N. Maulide, *Angew. Chem. Int. Ed.* **2014**, *53*, 8718; *Angew. Chem.* **2014**, *126*, 8862; f) D. Kaldre, B. Maryasin, D. Kaiser, O. Gajsek, L. González, N. Maulide, *Angew. Chem. Int. Ed.* **2017**, *56*, 2212; *Angew. Chem*. **2017**, *129*, 2248; g) D. Kaldre, I. Klose, N. Maulide, *Science* **2018**, *361*, 664. For selected examples of sulfonium-based [2,3]-sigmatropic rearrangement reactions, see: h) G. Hu, J. Xu, P. Li, *Org. Chem. Front.* **2018**, *5*, 2167; i) G. Hu, J. Xu, P. Li, *Org. Lett.* **2014**, *16*, 6036.

[13] H. Kawashima, T. Yanagi, C. C. Wu, K. Nogi, H. Yorimitsu, *Org. Lett.* **2017**, *19*, 4552.

[14] a) C. Mowdawalla, F. Ahmed, T. Li, K. Pham, L. Dave, G. Kim, I. F. D. Hyatt, *Beilstein J. Org. Chem.* **2018**, *14*, 1039; b) Y. Wu, S. Bouvet, S. Izquierdo, A. Shafir, *Angew. Chem. Int. Ed.* **2018**, DOI: 10.1002/anie.201809657.

[15] γ-Arylated alkenenitriles are typically prepared from aryl acetaldehydes by Wittig type reactions: a) T. Tomioka, Y. Takahashi, T. G. Vaughan, T. Yanase, *Org. Lett.* **2010**, *12*, 2171; b) S. Kojima, T. Fukuzaki, A. Yamakawa, Y. Murai, *Org. Lett.* **2004**, *6*, 3917.

10.1002/anie.201900434

WILEY-VCH

Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

Text for Table of Contents

((Insert TOC Graphic here))

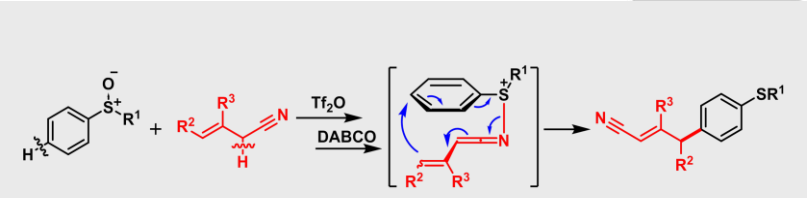
*Author(s), Corresponding Author(s)**

Page No. – Page No.

Title

Layout 2:

COMMUNICATION



A new aromatic [5,5]-sigmatropic rearrangement reaction has been achieved by simply treating the mixture of aryl sulfoxides and allyl nitriles with Tf_2O and DABCO. The reaction features high chemo- and regioselectivity which can be a great challenge for conventional [5,5]-sigmatropic rearrangement reactions.

Lei Zhang, Jia-Ni He, Yuchen Liang, Mengjie, Hu, Li Shang, Xin Huang, Lichun Kong, Zhi-Xiang Wang, Bo Peng**

Page No. – Page No.

Selective [5,5]-Sigmatropic Rearrangement via Electrophilic Assembly of Aryl Sulfoxides with Allyl Nitriles