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Construction of pyrroles, furans and thiophenes via intramolecular cascade desulfonylative/dehydrogenative cyclization of vinylidenecyclopropanes induced by NXS (X = I or Br)[†]

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Pyrroles, furans, and thiophenes are important structural motifs in biologically active substances, pharmaceuticals and functional materials. In this paper, we disclose an efficient synthetic strategy for the rapid construction of multisubstituted pyrroles, furans, and thiophenes via NXS mediated desulfonylative/dehydrogenative cyclization of vinylidenecyclopropanes (VDCPs). The advantages of this method include wide substrate range, high efficiency and synthetic usefulness of the heterocyclic products under metal-free and mild conditions. The derivatization of pyrrole products and the preparation of functional molecules successfully demonstrated the synthetic potential of the products as platform molecules. The reaction mechanism has been investigated on the basis of control experiments and DFT calculations.

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Introduction

Five-membered heterocycles including pyrroles, furans and thiophenes are widely found in a variety of bioactive molecules, functional and polymeric materials.¹ Moreover, they are also core structural motifs in many natural products and pharmaceuticals. For example, the pyrrole fragment is the key structural unit in licofelone, which possesses significant analgesic, anti-inflammatory, and antiasthmatic activities.^{1b} Lophotoxin is a novel neuromuscular toxin that has been isolated from several Pacific gorgonians and contains a furan fragment in its molecular structure.^{1c} In addition, thiophene fragment exists in a commercial drug known as duloxetine, which possesses effective antihypertensive activity (Scheme 1a). The synthetic methods of these heterocyclic compounds have been widely reported and are of great concern.² To date, the traditional synthetic methods for these heterocycles, including Paal–Knorr condensation,³ Hantzsch reaction,⁴ Feist–Benary reaction,⁵ Hinsberg reaction,⁶ transition metal-catalyzed cyclizations,⁷ and photochemical

reactions,⁸ have been developed for many years. However, the above reactions frequently employ different synthetic protocols to obtain the starting substrates depending on the required heteroatoms such as N, O, and S. Thus, the development of new strategies that facilitate rapid construction of each of these heterocycles by a single method and provide functionalized pyrroles, furans, and thiophenes in a one-pot manner would be extremely useful and highly desirable. Nonetheless, thus far, only a few methods to access each of these heterocycles by changing the heteroatoms of substrates have been developed (Scheme 1b).⁹ For example, Shishido's group reported an efficient strategy for the synthesis of pyrroles, furans and thiophenes utilizing ynolates.^{9a} In addition, Marques's group developed the preparation of pyrroles, furans and thiophenes by the gold-catalyzed dehydration and cyclization of heteroatom-substituted propargylic alcohols.^{9b} Nevertheless, these synthetic methods usually need harsh reaction conditions, metal catalysts, and prolonged reaction time.

In view of the aforementioned research circumstances, we attempted to introduce heteroatoms into vinylidenecyclopropanes (VDCPs)¹⁰ and assumed that these heteroatomic VDCPs could be excellent candidates for exploiting new methods in cyclization for the rapid construction of heteroaromatics due to their multiple reaction sites. Herein, we describe an intramolecular desulfonylative/dehydrogenative cyclization reaction that proceeds effectively under mild and metal-free conditions, providing functionalized pyrroles, furans, and thiophenes in good yields (Scheme 1c).

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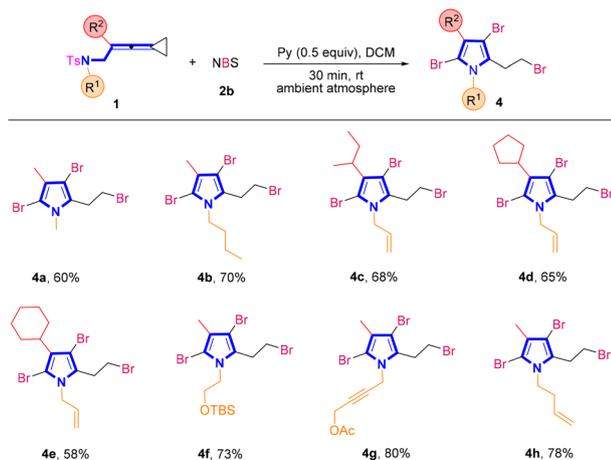
[†] Electronic supplementary information (ESI) available: Experimental procedures, characterization data of new compounds. CCDC 2083431 and 2142800. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d3sc01542d>



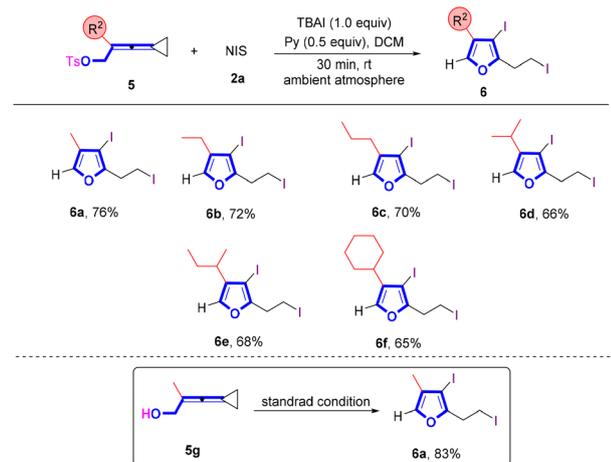
the reaction and the desired pyrrole product was not obtained. Moreover, we observed that the reactions did not proceed when **1ah** and **1ai** were employed as substrates (see Fig. S1 on page S14 in the ESI†).

In order to further demonstrate the generality of this synthetic strategy, we then turned our attention to examining the substrate scope of brominated pyrroles **4** in the presence of NBS **2b** (Scheme 3). Similarly, using VDCPs **1** as the substrates, the desired brominated pyrrole products **4a–4h** were produced in moderate to good yields ranging from 58% to 80%. In VDCPs **1**, R^1 could be an alkyl, an allyl, an alkyl group bearing a protected hydroxy group, a propargyl group or a homoallyl group and R^2 could be an alkyl or a cycloalkyl group, smoothly delivering the desired products **4** under the standard conditions.

When VDCPs **5**, in which the VDCP moiety is connected with a tosylated oxygen atom, were utilized as substrates to react with NIS under the standard conditions, the corresponding iodinated

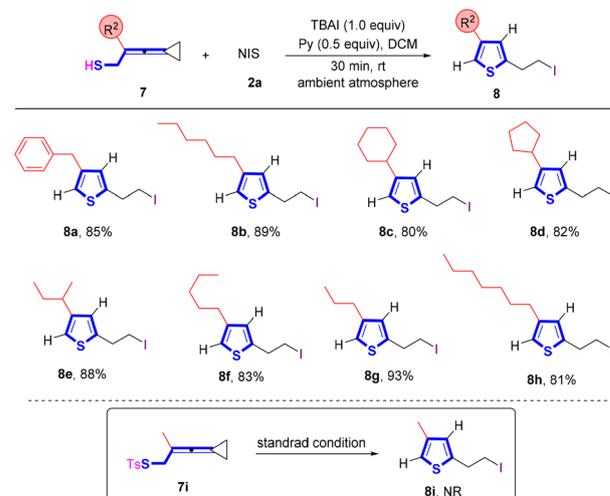


Scheme 3 Standard conditions: substrate **1** (0.2 mmol, 1.0 equiv.), **2b** (3.5 equiv.) and pyridine (0.5 equiv.) in DCM (2 mL), ambient atmosphere, 30 min, rt.

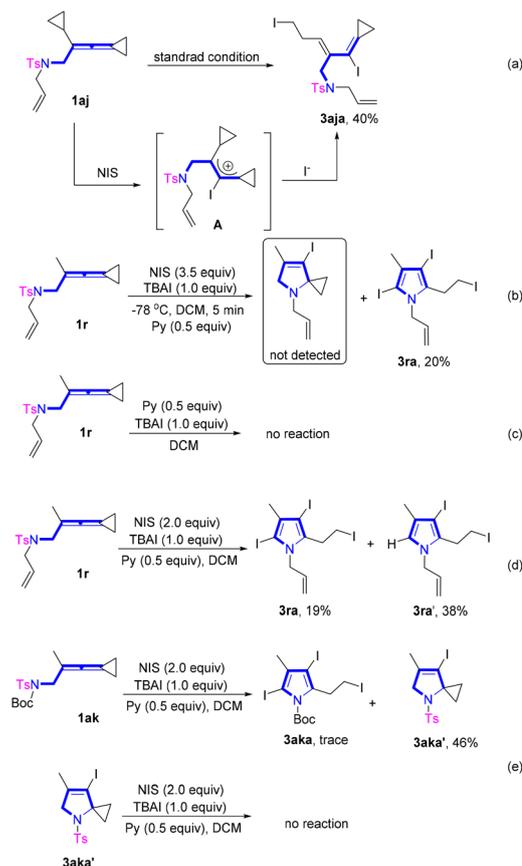


Scheme 4 Standard conditions: substrate **5** (0.2 mmol, 1.0 equiv.), **2a** (3.5 equiv.) and pyridine (0.5 equiv.) in DCM (2 mL), ambient atmosphere, 30 min, rt.

furan products **6** were obtained in moderate yields (Scheme 4). A variety of VDCPs **5a–5f** bearing an alkyl or a cycloalkyl group were tolerated, giving furans **6a–6f** in 65–76% yields. Substrate **5g**, replacing the OT moiety with the hydroxy group, could also afford the desired product **6a** in 83% yield.



Scheme 5 Standard conditions: substrate **7** (0.2 mmol, 1.0 equiv.), **2a** (1.0 equiv.) and pyridine (0.5 equiv.) in DCM (2 mL), ambient atmosphere, 30 min, rt.



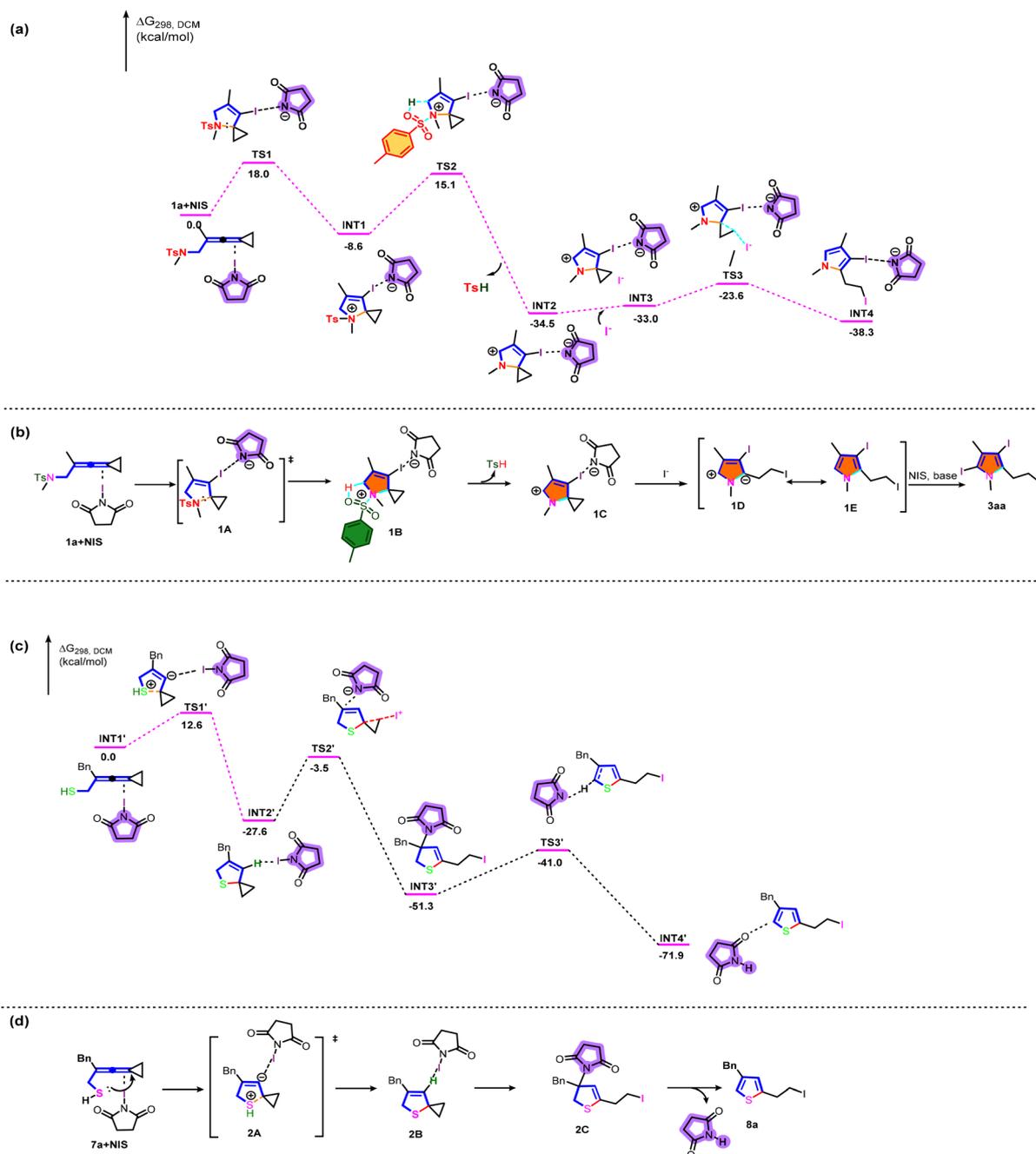
Scheme 6 Control experiments.



To synthesize thiophene derivatives, we further prepared VDCP **7i**, in which the VDCP moiety is connected with a tosylated sulfur atom (Scheme 5). However, no reaction occurred and the starting materials were fully recovered upon conducting the reaction under the standard protocol, probably because the nucleophilicity of the sulfur atom was weakened by the tosyl group and its steric effect hampered the cyclization. Afterwards, we utilized VDCP substrates **7** having a free thiol group to conduct the reaction and found that the cyclization smoothly took place, affording the desired thiophenes **8** in good yields. As shown in Scheme 5, R² substituents as a broad range of alkyl or

cycloalkyl groups were all suitable for this reaction, affording the corresponding thiophenes **8a–8h** in 80–93% yields.

To further unveil the reaction mechanism, we carried out a series of control experiments (Scheme 6) and density functional theory (DFT) calculations (Scheme 7). When VDCP **1aj** was utilized as the substrate for the reaction under the standard conditions, instead of the desired pyrrole product, a cyclopropane ring-opened product **3aja** was obtained in 40% yield, suggesting that during the reaction of **1aj** with NIS, I⁺ tended to add to the middle carbon atom of the allene moiety to generate an allyl cationic intermediate **A** (Scheme 6a). Afterwards, the cyclopropane in **1aj**



Scheme 7 (a) DFT calculation of **3aa**. (b) Proposed reaction mechanism of **3aa**. (c) DFT calculation of **8a**. (d) Proposed reaction mechanism of **8a**.



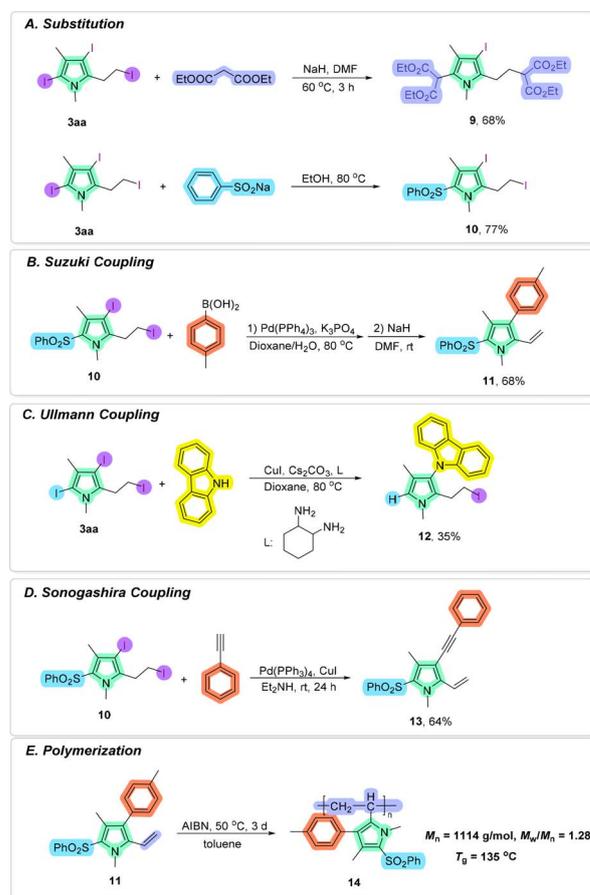
was attacked by iodine anion to afford the cyclopropane ring-opened product **3aja**. Subsequently, we attempted to trap the reaction intermediates in the system at $-78\text{ }^{\circ}\text{C}$ with VDCP **1r** as the substrate to verify the possible reaction pathway (Scheme 6b). Unfortunately, we did not trap any useful intermediate presumably due to the very fast reaction rate of this transformation. In addition, it was found that using **1r** as the substrate, no reaction occurred in the absence of NIS (Scheme 6c). Moreover, when the employed amount of NIS was reduced to 2.0 equiv., a large amount of diiodinated product **3ra'** was afforded under the standard conditions, indicating that the triiodosubstituted product was forged by the iodination of the diiodosubstituted product (Scheme 6d). In addition, when **1ak** was used as a substrate, we isolated a by-product **3aka'** in 46% yield. However, **3aka'** was unable to convert to the desired product under standard conditions (Scheme 6e). Therefore, **3aka'** was not an active intermediate for this reaction, thus we exclude the possible halocyclization and deprotection pathway (see page S17 in the ESI†).

We subsequently embarked on DFT calculations to gain insight into the reaction mechanism. All calculations have been performed at the SMD(DCM)/B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level with the Gaussian 16 program.¹¹ The solvation Gibbs free energy profile in dichloromethane for the suggested reaction pathway is shown in Scheme 7a (see Table S7 in the ESI† for more information). We investigated the reaction pathway starting from the complex **1a+NIS** shown in Scheme 7a. Firstly, **1a+NIS** undergoes cyclization *via* **TS1** with an energy barrier of $18.0\text{ kcal mol}^{-1}$ to form a cationic intermediate **INT1**. The Ts moiety in **INT1** promotes subsequent dehydrogenation to generate **INT2** and release TsH through an activation barrier of $23.7\text{ kcal mol}^{-1}$, which is a highly exothermic process and indicates that the process shown in Scheme 7a is thermodynamically favorable and has a possibility to take place. In addition, the intermediate **INT3** is obtained by adding iodine anion to the system. Then, the intermediate **INT3** undergoes a cyclopropane ring-opening step to give the pyrrole intermediate **INT4** *via* **TS3** with an energy barrier of 9.4 kcal mol^{-1} , which is also an exothermic process.

Based on the aforementioned experimental results and the detailed DFT calculations, we propose a plausible reaction mechanistic paradigm (Scheme 7b). Initially, in the presence of NIS, the intramolecular nucleophilic attack of the nitrogen atom to the allylic cation moiety *via* transition state **1A** affords cyclized cationic intermediate **1B**. Then, the Ts moiety in **1B** promotes subsequent dehydrogenation to give another cyclized cationic intermediate **1C** and release TsH. Subsequently, the iodine anion attacks cyclopropane and undergoes a ring-opening reaction of cyclopropane to yield the zwitterionic intermediate **1D** (see Fig. S5 in the ESI† for more information), which undergoes a subsequent aromatization to furnish the desired pyrrole intermediate **1E**. Finally, the halogenation reaction of **1E** in the presence of base and NIS gives the desired triiodosubstituted product **3aa**. Furan derivatives **6** were generated by a similar mechanism. However, the low reactivity of furans made it difficult to perform further halogenation

reactions under the standard conditions, only furnishing diiodosubstituted products.

Next, we investigated the mechanistic details for the generation of thiophene derivatives through computational studies (Scheme 7c). The intermediate **INT1'** undergoes cyclization and intramolecular hydrogen transfer *via* **TS1'** with an energy barrier of $12.6\text{ kcal mol}^{-1}$ to generate a stable spirocyclic intermediate **INT2'**. The transition state **TS1'** is probably stabilized by *N*-iodosuccinimide in the system. Subsequently, the intermediate **INT3'** is generated through a cyclopropane ring opening reaction in the presence of NIS, passing through **TS2'** with an energy barrier of $24.1\text{ kcal mol}^{-1}$. The following deprotonation takes place to afford the product complex **INT3'** *via* **TS3'** with an energy barrier of $10.3\text{ kcal mol}^{-1}$. On the basis of DFT calculations shown in Scheme 7c, the plausible reaction mechanism for the production of **8a** is depicted in Scheme 7d. Initially, **7a** is cyclized by intramolecular nucleophilic attack to yield intermediate **2B** *via* the transition state **2A**. Subsequently, **8a** is produced through cyclopropane ring opening and deprotonation induced by *N*-iodosuccinimide.



Scheme 8 Synthetic transformations. (A) **3aa** (0.5 mmol), NaH (2.5 equiv.), DMF (5.0 mL), $60\text{ }^{\circ}\text{C}$; **3aa** (0.5 mmol), PhSO₂Na (2.0 equiv.), EtOH; (B) **10** (0.2 mmol), 4-MeC₆H₄B(OH)₂ (2.5 equiv.), Pd(PPh₃)₄ (10 mol%), K₃PO₄ (3.0 equiv.); (C) **3aa** (0.2 mmol), carbazole (1.5 equiv.), CuI (20 mol%), Cs₂CO₃ (2.0 equiv.); (D) **10** (0.2 mmol), phenylacetylene (2.0 equiv.), Pd(PPh₃)₄ (5 mol%), CuI (10 mol%), (E) **11**, AIBN, toluene.



The synthetic utility of the current protocol was demonstrated by diverse derivatizations of the obtained pyrrole product **3aa**. As illustrated in Scheme 8A, substitution of **3aa** with diethyl malonate under basic conditions in DMF successfully provided functionalized pyrrole **9** in 68% yield. In addition, in the presence of sodium benzenesulfinate, **3aa** could be substituted to give pyrrole **10** in 77% yield.¹² Moreover, pyrrole **10** could be effectively transformed into the corresponding product through a Pd-catalyzed Suzuki–Miyaura cross-coupling reaction with 4-methylphenylboronic acid¹³ and a combined elimination reaction under basic conditions in DMF¹⁴ (for pyrrole **11**) (Scheme 8B). A carbazole substituted pyrrole **12** could be obtained in 35% yield through a Cu-catalyzed Ullmann reaction with carbazole (Scheme 8C). Furthermore, the Sonogashira coupling¹⁵ reaction of pyrrole **10** with phenylacetylene afforded pyrrole **13** in 64% yield (Scheme 8D). In addition, polypyrroles have been widely used in electrochemistry, and biomedical and sensor applications due to their excellent conductive properties.¹⁶ Polymerization of pyrrole **11** with AIBN as the radical initiator furnished the polymeric product **14** with a molecular weight of 1114 g mol⁻¹ ($M_w/M_n = 1.28$) and the glass transition temperature (T_g) as 135 °C¹⁷ (Scheme 8E).

Conclusions

In summary, we have established a novel and practical strategy for the rapid construction of functionalized pyrroles, furans and thiophenes under metal-free and mild conditions. This synthetic protocol is quite efficient, affording these five-membered heterocycles in moderate to excellent yields within a short reaction time (<30 min.) through NXS mediated desulfonylative/dehydrogenative cyclization of vinylidenecyclopropanes (VDCPs). Compared with traditional reaction modes that frequently employ different synthetic methods to prepare the related substrate depending on the required heteroatom (N, O, S), this reaction can easily provide these heterocycles through a single way. Furthermore, the reaction mechanism was investigated by a series of control experiments and DFT calculations. DFT calculations revealed that a desulfonylative reaction is initiated by the intramolecular nucleophilic attack of the nitrogen atom on the allylic cation moiety and the desulfonylative reaction is the rate-determining step. In addition, the dehydrogenative cyclization may involve a synergistic effect of *N*-iodosuccinimide and iodine anion. Moreover, synthetic transformations demonstrated that this strategy could realize concise synthesis of multi-substituted five-membered heterocyclic compounds and polymers. Further studies on discovering the detailed mechanism and novel reaction types to synthesize other useful compounds are underway.

Data availability

Experimental and computational data have been made available as the ESI.†

Author contributions

Z. Meng, J. Yan and C. Ning contributed to the investigation. Z. Meng and Y. Wei contributed to the calculations. Z. Meng, Y. Wei and M. Shi contributed to the conceptualization and writing-original draft.

Conflicts of interest

There are no conflicts to declare.

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References

- (a) V. Bhardwaj, D. Gumber, V. Abbot, S. Dhiman and P. Sharma, *RSC Adv.*, 2015, **5**, 15233–15266; (b) S. K. Kulkarni and V. P. Singh, *Curr. Top. Med. Chem.*, 2007, **7**, 251–263; (c) M. Ochi, K. Yamada, H. Kawakami, A. Tatsukawa, H. Kotsuki and K. Shibata, *Tetrahedron Lett.*, 1992, **33**, 7531–7534; (d) R. A. Craig and B. M. Stoltz, *Chem. Rev.*, 2017, **117**, 7878–7909; (e) E. M. Sorenson, P. Culver and V. A. Chiappinelli, *Neuroscience*, 1987, **20**, 875–884; (f) A. Mishra, C. Q. Ma and P. Bäuerle, *Chem. Rev.*, 2009, **109**, 1141.
- G. D. Yin, Z. H. Wang, A. H. Chen, M. Gao, A. X. Wu and Y. J. Pan, *J. Org. Chem.*, 2008, **73**, 3377–3383.
- (a) V. Amarnath, D. C. Anthony, K. Amarnath, W. M. Valentine, L. A. Wetterau and D. G. Graham, *J. Org. Chem.*, 1991, **56**, 6924–6931; (b) C. Paal, *Ber. Dtsch. Chem. Ges.*, 1884, **17**, 2756–2767; (c) L. Knorr, *Ber. Dtsch. Chem. Ges.*, 1884, **17**, 2863–2870.
- A. Hantzsch, *Ber. Dtsch. Chem. Ges.*, 1890, **23**, 1474.
- (a) M. A. Calter, R. M. Phillips and C. Flaschenriem, *J. Am. Chem. Soc.*, 2005, **127**, 14566–14567; (b) F. Feist, *Ber. Dtsch. Chem. Ges.*, 1902, **35**, 1537–1544; (c) E. Benary, *Ber. Dtsch. Chem. Ges.*, 1911, **44**, 489–493.
- O. Hinsberg, *Ber. Dtsch. Chem. Ges.*, 1910, **43**, 901–906.
- (a) I. Nakamura and Y. Yamamoto, *Chem. Rev.*, 2004, **104**, 2127–2198; (b) M. Gao, C. He, H. Chen, R. Bai, B. Cheng and A. Lei, *Angew. Chem., Int. Ed.*, 2013, **52**, 6958–6961; (c) Z. W. Gilbert, R. J. Hue and I. A. Tonks, *Nat. Chem.*, 2016, **8**, 63–68; (d) M. Zhang, X. Fang, H. Neumann and M. Beller, *J. Am. Chem. Soc.*, 2013, **135**, 11384–11388; (e) K. Y. Dong, A. Humeidi, W. Griffith, H. Arman, X. F. Xu and M. P. Doyle, *Angew. Chem., Int. Ed.*, 2021, **60**, 13394–13400; (f) X. M. Wang, A. Lerchen, C. G. Daniliuc and F. Glorius, *Angew. Chem., Int. Ed.*, 2018, **57**, 1712–1716; (g) V. Y. Chen and O. Kwon, *Angew. Chem., Int. Ed.*, 2021, **60**, 8874–8881; (h) H. M. Jin and A. Fürstner, *Angew. Chem.*,



- Int. Ed.*, 2020, **59**, 13618–13622; (i) D. Kurandina and V. Gevorgyan, *Org. Lett.*, 2016, **18**, 1804–1807; (j) L. Pan, B. H. Zheng, X. H. Yang, L. P. Deng, Y. F. Li and Q. Liu, *Adv. Synth. Catal.*, 2021, **363**, 234–243.
- 8 (a) W. G. Hu, Q. Q. Zhan, H. W. Zhou, S. S. Cao and Z. Y. Jiang, *Chem. Sci.*, 2021, **12**, 6543–6550; (b) Y. J. Liu, W. P. Luo, T. T. Xia, Y. W. Fang, C. Du, X. P. Jin, Y. Li, L. Zhang, W. Lei and H. Wua, *Org. Chem. Front.*, 2021, **8**, 1732–1738; (c) X. X. Gong, M. J. Wang, S. Q. Ye and J. Wu, *Org. Lett.*, 2019, **21**, 1156–1160.
- 9 (a) M. Shindo, Y. Yoshimura, M. Hayashi, H. Soejima, T. Yoshikawa, K. Matsumoto and K. Shishido, *Org. Lett.*, 2007, **9**, 1963–1966; (b) A. Aponick, C. Y. Li, J. Malinge and E. F. Marques, *Org. Lett.*, 2009, **11**, 4624–4627; (c) F. Yang, T. N. Jin, M. Bao and Y. Yamamoto, *Tetrahedron*, 2011, **67**, 10147–10155; (d) W. W. Tan and N. Yoshikai, *J. Org. Chem.*, 2016, **81**, 5566–5573.
- 10 (a) M. Shi, L. X. Shao, J. M. Lu, Y. Wei, K. Mizuno and H. Maeda, *Chem. Rev.*, 2010, **110**, 5883–5913; (b) S. Yang and M. Shi, *Acc. Chem. Res.*, 2018, **51**, 1667–1680; (c) D. H. Zhang, X. Y. Tang and M. Shi, *Acc. Chem. Res.*, 2014, **47**, 913–924; (d) K. H. Rui and M. Shi, *Org. Chem. Front.*, 2019, **6**, 1816–1820; (e) Z. Meng, X. Y. Zhang and M. Shi, *Org. Chem. Front.*, 2021, **8**, 3796–3801; (f) C. Xu, C. Ning, S. Yang, Y. Wei and M. Shi, *Adv. Synth. Catal.*, 2021, **363**, 1727–1732; (g) C. Ning, K. H. Rui, Y. Wei and M. Shi, *Chem. Sci.*, 2022, **13**, 7310–7317.
- 11 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
- 12 M. Z. Miao, X. Xu, L. J. Xu and H. J. Ren, *Eur. J. Org. Chem.*, 2014, **27**, 5896–5900.
- 13 K. Cui, M. Gao, H. Y. Zhao, D. F. Zhang, H. Yan and H. H. Huang, *Molecules*, 2019, **24**, 1594.
- 14 E. C. Taylor and W. B. Young, *J. Org. Chem.*, 1995, **24**, 7947–7952.
- 15 E. R. Wearing, D. E. Blackmun, M. R. Becker and C. S. Schindler, *J. Am. Chem. Soc.*, 2021, **39**, 16235–16242.
- 16 (a) E. N. Zarea, T. Agarwal, A. Zarepour, F. Pinelli, A. Zarrabi, F. Rossi, M. Ashrafizadeh, A. Malekif, M. A. Shahbazi, T. K. Maiti, R. S. Varma, F. R. Tayi, M. R. Hamblin, V. Mattoli and P. Makvandi, *Appl. Mater. Today*, 2021, **24**, 101117; (b) P. Pinyou, V. Blay, J. Monkrathok, P. Janphuang, K. Chansaenpak and J. P. S. Lisnund, *Microchim. Acta*, 2022, **189**, 410; (c) L. Hao, C. Y. Dong, L. F. Zhang, K. M. Zhu and D. M. Yu, *Polymers*, 2022, **14**, 5139; (d) X. T. Ding, T. Xu, J. Gao, Y. M. Qi, H. M. Zhang and L. T. Qu, *J. Mater. Chem. B*, 2017, **5**, 5733–5737; (e) M. Wysocka and K. Winkler, *Electrochim. Acta*, 2017, **258**, 1421–1434.
- 17 L. L. Liao, Z. H. Wang, K. G. Cao, G. Q. Sun, W. Zhang, C. K. Ran, Y. W. Li, L. Chen, G. M. Cao and D. G. Yu, *J. Am. Chem. Soc.*, 2022, **144**, 2062–2068.

