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# Domino 1,3-dipolar cycloaddition/ring-opening/ring-cleavage: synthesis of trisubstituted pyrrole and chiral dihydropyrrole-3-carbaldehydes†

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**A unique approach has been developed to synthesize trisubstituted 1H-pyrrole-3-carbaldehydes using 4-methyl thiazolium salts,  $\alpha,\beta$ -unsaturated aldehydes, and organocatalysts via a domino 1,3-dipolar cycloaddition/ring-opening/C–S and C–N bond cleavage reaction sequence. This methodology has been successfully extended for the asymmetric synthesis of enantioenriched trisubstituted-4,5-dihydro-1H-pyrrole-3-carbaldehydes employing chiral amine organocatalysts with high efficiency (up to 98% ee, > 20 : 1 d.r.).**

Poly-substituted 1H-pyrroles are essential building blocks in many synthetic chemists because of their diverse use in organic synthesis, bioactive molecules, natural products, and catalysis.<sup>1</sup> There are several approaches to accessing diverse poly-substituted 1H-pyrroles in the literature.<sup>2</sup> Due to their privileged structure, they can be used in drug discovery, such as antitumor, antibacterial, antiviral, and anti-inflammatory agents, anticancer drugs like veliparib, and antibacterial agents like selvamycin.<sup>3</sup>

Enantioselectively synthesized, highly substituted dihydropyrrole is an essential building block in many bioactive molecules and natural products.<sup>4</sup> Various attractive methods have been designed to synthesize these heterocycles.<sup>5</sup> For instance, cyclopropane ring-opening,<sup>6a</sup> 1,3-dipolar cycloaddition reactions,<sup>6b</sup> domino ring-opening cyclization (DROC),<sup>6c,15</sup> intramolecular iminium ion cyclization,<sup>6d</sup> and intramolecular nucleophilic addition/rearrangement<sup>6e</sup> reactions have been reported in the literature. However, developing an efficient method for the synthesis of highly substituted chiral 4,5-dihydropyrroles from readily accessible starting materials using asymmetric organocatalysts in a greener and sustainable manner is highly warranted.<sup>7</sup>

Cycloaddition is an essential method for the synthesis of complex chiral molecules.<sup>8a</sup> In this regard, 1,3-dipolar cycloaddition<sup>8b,c</sup> using thiazolium azomethine ylides has been known for the past few

decades, while less attention has been paid to its development towards asymmetric transformation.<sup>9</sup> Over the past few decades, scientists have successfully developed a series of methods for synthesizing various achiral and racemic heterocyclic compounds using thiazolium salt with various unsaturated systems via 1,3-dipolar cycloaddition reactions (Scheme 1(i)).<sup>10</sup> Very recently, our group developed the organocatalytic asymmetric synthesis of chiral heterocycles using benzothiazolium azomethine ylide (Scheme 1(ii)).<sup>11</sup>

Both thiazolium and benzothiazolium azomethine ylides are expected to have the same reactivity pattern with dipolarophiles to produce a 1,3-dipolar cycloadduct as a common intermediate.<sup>11</sup> This cycloadduct further undergoes ring-opening/rearrangement, yielding various racemic and chiral N,S-heterocyclic compounds in the literature.<sup>11,12,15</sup> However, the cycloadduct experiencing ring-opening followed by unprecedented C–S/C–N bond cleavage towards synthesizing highly substituted five-membered chiral and achiral heterocyclic compounds has not been reported. We present a novel reactivity of 4-methyl thiazolium azomethine ylide with  $\alpha,\beta$ -unsaturated aldehydes, enabling the synthesis of trisubstituted 1H-pyrrole-3-carbaldehydes using amine organocatalysts. Furthermore, this approach has been extended to the enantioselective synthesis of highly enantioenriched trisubstituted 4,5-dihydro-1H-pyrrole-3-carbaldehydes using chiral amine organocatalyst (Scheme 1(iii)).

The initial reaction commenced with cinnamaldehyde **1a** (0.3 mmol), 4-methyl thiazolium salt **2a** (0.3 mmol), and racemic proline (20 mol%) with  $\text{NEt}_3$  as a base, and IPA (isopropyl alcohol) as a solvent at room temperature. This reaction provided an unexpected trisubstituted 1H-pyrrole **3a** product with a 30% yield in 48 h. The reaction conditions were varied to increase the yield **3a** with several parameters such as racemic secondary amine catalysts **C1–C5**, bases, and solvents. The results are summarized in Tables S1–S3 (ESI†).<sup>14</sup> For the complete optimization studies, refer to ESI,† Page S3–S4. From the optimization, we found the best-optimized reaction conditions with  $\alpha,\beta$ -unsaturated aldehyde **1a** (1 equiv.), 4-methyl thiazolium salt **2a** (1 equiv.), DMAP (2 equiv.), and catalyst **C5** in EtOH (0.15 M) at room temperature for 48 h.

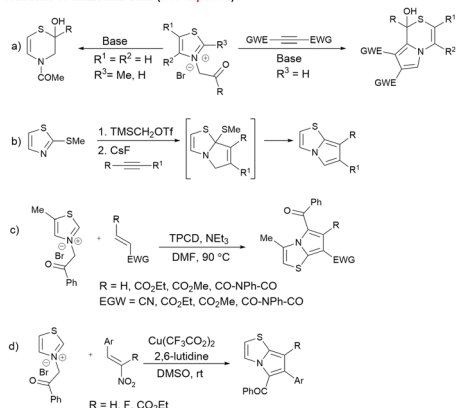
With the optimized reaction conditions in hand, the generality, and functional group tolerance of the domino reactions were

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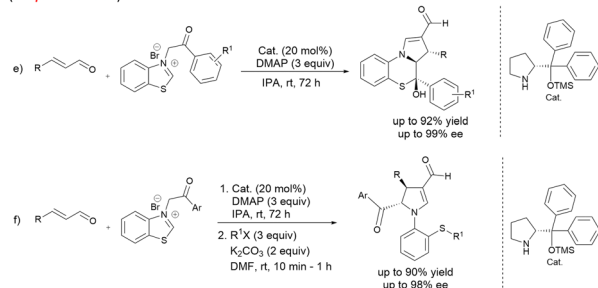
† Electronic supplementary information (ESI) available: Experimental details, <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>19</sup>F NMR spectra, and HPLC chromatogram (PDF). X-ray crystallography data for **3h**. CCDC 2354829. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d4cc06706a>

## Previous works

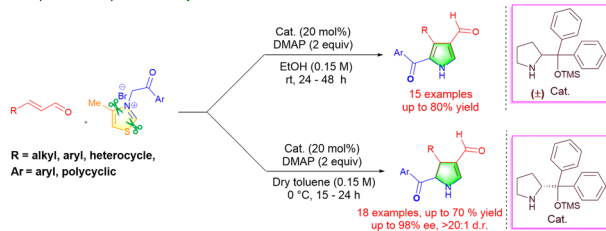
i) Base mediated 1,3-dipolar cycloaddition, nucleophilic addition/rearrangement, and aromatization reactions of thiazolium salts (*well explored*)<sup>10</sup>



ii) Organocatalytic asymmetric 1,3-dipolar cycloaddition/rearrangement/ring-opening reaction of benzothiazolium salts (*Our previous works*)<sup>11</sup>



iii) Organocatalytic asymmetric 1,3-dipolar cycloaddition/ring-opening/ring-cleavage reaction of 4-methyl thiazolium salts (*Present work*) *New reactivity*

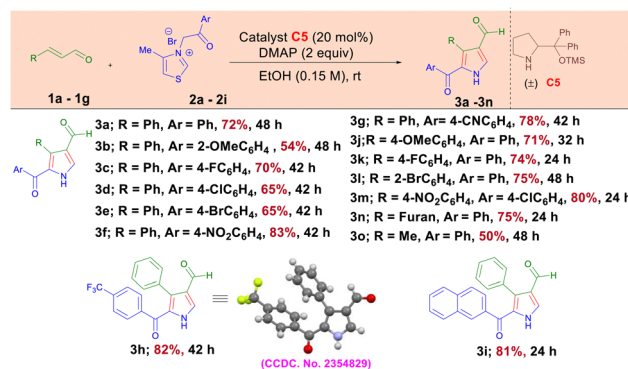


Scheme 1 1,3-Dipolar cycloaddition of thiazolium salts with  $\alpha,\beta$ -unsaturated systems.

investigated with various  $\alpha,\beta$ -unsaturated aldehydes **1** and 4-methyl thiazolium salts **2** with electron-donating and electron-withdrawing groups, halogens, and bulky substituents. All the reactions furnished the desired products **3a–3o** in good yields (Scheme 2).

The simple 4-methyl thiazolium salt gave the product **3a** in 72% yield. The 4-methyl thiazolium salt, having the electron donating methoxy group at the *ortho* position, gave product **3b** in a moderate yield of 54% compared to the unsubstituted product **3a**. The reason may be a steric hindrance to *ortho*-OMe substitution on the phenyl ring. Meanwhile, the halogen-substitution at the *para* positions of 4-methyl thiazolium salts delivered **3c–3e** in good yields (Scheme 2). The electron-withdrawing groups such as  $-\text{NO}_2$ ,  $-\text{CN}$ , and  $-\text{CF}_3$  at the *para* positions of 4-methyl thiazolium salt led to the desired trisubstituted 1*H*-pyrrole products **3f–3h** in 78–83% yields (Scheme 2). The bulky naphthyl group, well tolerated for this domino strategy, led to the product **3i** in 81% yield.

$\alpha,\beta$ -Unsaturated aldehydes **1** containing an electron-donating methoxy group at the *para* position provided the desired product **3j**

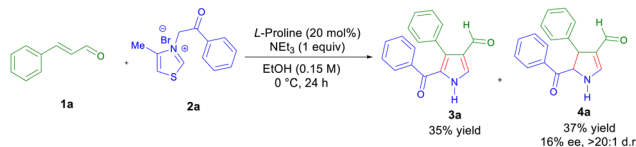


Scheme 2 Substrate scope of trisubstituted-1*H*-pyrrole-3-carbaldehydes.

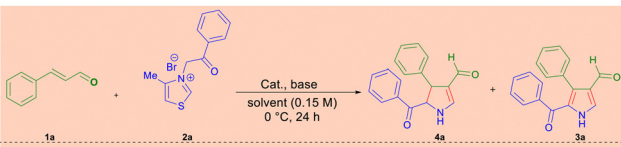
in 71% yield. The halogen substitution at the *para* position furnished the desired product **3k** in 74% yield. Surprisingly, the bromine substitution at the *ortho* position shows atropisomerism, confirmed by chiral HPLC analysis (Fig. S2 in ESI<sup>†</sup>),<sup>14</sup> and afforded the desired product **3l** in 75% yield. The electron-withdrawing group at the *para* position delivered the trisubstituted pyrrole product **3m** in 80% yield. The substitution at the 3-position of  $\alpha,\beta$ -unsaturated aldehydes such as the furan ring also offered the desired product **3n** in 75% yield. Delightfully, alkyl substitution at the 3-position of  $\alpha,\beta$ -unsaturated aldehyde also delivered the product **3o** in 50% yield. The structure of compound **3h** was unambiguously confirmed through single-crystal X-ray analysis, and a plausible reaction mechanism is provided in the ESI<sup>†</sup> (Page S13).<sup>14</sup>

We envisaged that if we could control the reaction rate of the domino synthesis of product **3**, there is a possibility of stopping the reaction at trisubstituted-4,5-dihydro-1*H*-pyrroles. In this case, if we use a chiral amine catalyst, there is a possibility of making the trisubstituted-4,5-dihydro-1*H*-pyrroles in enantioenriched form by an enantioselective domino reaction. So, to slow down the rate of the reaction, the domino reaction was performed at 0 °C, in the presence of *L*-proline (20 mol%), and NEt<sub>3</sub> (1 equiv.) in EtOH solvent, and the reaction afforded the desired product **3a** in 35% yield, along with the expected chiral trisubstituted-4,5-dihydro-1*H*-pyrrole **4a** 37% yield with 16% ee in >20:1 d.r. (Scheme 3 and Table 1, entry 1).

Notably, the domino reaction was successfully controlled at the dihydropyrrole stage by lowering the reaction temperature to 0 °C and achieving the dihydropyrrole in an enantioselective manner. Inspired by the preliminary result, further optimization was done for the enantioselective formation of **4a** and to minimize the formation of **3a**. The domino reaction was optimized with various chiral catalysts, bases, and solvents, and the results are summarized in Table 1.<sup>14</sup> Among the chiral catalysts, **C6–C12**



Scheme 3 Trail reaction for the synthesis of chiral dihydropyrrole.

Table 1 Optimization of the reaction conditions<sup>a</sup>


| Entry           | Base (equiv.)        | Cat. (mol%) | Solvent (0.15 M) | Yield of 4a <sup>b</sup> | ee <sup>c</sup> (%) | d.r. <sup>d</sup> | Yield of 3a <sup>b</sup> |
|-----------------|----------------------|-------------|------------------|--------------------------|---------------------|-------------------|--------------------------|
| 1               | Net <sub>3</sub> (1) | C6 (20)     | EtOH             | 37                       | 16                  | >20:1             | 35                       |
| 2               | Net <sub>3</sub> (1) | C7 (20)     | EtOH             | 36                       | 10                  | >20:1             | 10                       |
| 3               | Net <sub>3</sub> (1) | C8 (20)     | EtOH             | 35                       | 15                  | >20:1             | 15                       |
| 4               | Net <sub>3</sub> (1) | C9 (20)     | EtOH             | 40                       | 16                  | >20:1             | 20                       |
| 5               | Net <sub>3</sub> (1) | C10 (20)    | EtOH             | 30                       | 12                  | >20:1             | 25                       |
| 6               | DMAP (1)             | C9 (20)     | EtOH             | 50                       | 65                  | >20:1             | 25                       |
| 7               | DMAP (2)             | C9 (20)     | EtOH             | 48                       | 85                  | >20:1             | 12                       |
| 8               | DMAP (2)             | C9 (20)     | MeOH             | 48                       | 48                  | >20:1             | 12                       |
| 9               | DMAP (2)             | C9 (20)     | H <sub>2</sub> O | nr                       | —                   | —                 | —                        |
| 10              | DMAP (2)             | C9 (20)     | 1,2-DCE          | 10                       | 94                  | >20:1             | 20                       |
| 11              | DMAP (2)             | C9 (20)     | Toluene          | 25                       | 94                  | >20:1             | 20                       |
| 12              | DMAP (2)             | C9 (20)     | THF              | 30                       | 96                  | >20:1             | 30                       |
| 13              | DMAP (2)             | C9 (20)     | Dry THF          | 45                       | 96                  | >20:1             | 15                       |
| 14              | DMAP (2)             | C9 (20)     | Dry toluene      | 60                       | 96                  | >20:1             | 10                       |
| 15 <sup>e</sup> | DMAP (1)             | C9 (20)     | Dry toluene      | 45                       | 90                  | >20:1             | 25                       |
| 16 <sup>f</sup> | DMAP (2)             | C9 (10)     | Dry toluene      | 40                       | 60                  | >20:1             | 20                       |
| 17 <sup>g</sup> | DMAP (2)             | C9 (5)      | Dry toluene      | 30                       | 20                  | >20:1             | 35                       |
| 18              | DMAP (2)             | C11 (10)    | Dry toluene      | —                        | —                   | —                 | 60                       |
| 19              | DMAP (2)             | C12 (10)    | Dry toluene      | —                        | —                   | —                 | 65                       |

<sup>a</sup> Reaction conditions: **1a** (0.3 mmol), **2a** (0.3 mmol), base (1–2 equiv.), catalyst **C6**–**C12** (10–20 mol%), solvent (0.15 M). <sup>b</sup> Isolated yield. <sup>c</sup> Enantiomeric excess was determined by chiral HPLC. <sup>d</sup> d.r. ratio was determined by <sup>1</sup>H NMR using a crude reaction mixture. <sup>e</sup> The reaction was performed using 1 equivalent of DMAP base. <sup>f</sup> The reaction was performed using 10 mol% of the **C9** catalyst. <sup>g</sup> The reaction was performed using 5 mol% of the **C9** catalyst. nr = no reaction.

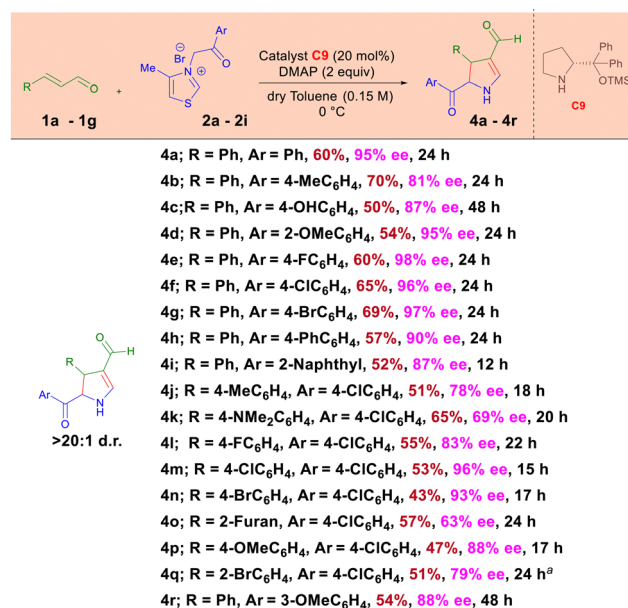
were screened to increase % ee (entries 1–5), and **C9** was the best choice (entry 4). Then, the reaction was carried out with several bases (Table S5, ESI†)<sup>14</sup> to improve the yield and % ee of **4a**.

When DMAP was used as a base, the yield and % ee of product **4a** increased to 50% and 65%, respectively (entry 6). In contrast, other bases failed to give better outcomes (Table S5, ESI†).<sup>14</sup> Increasing DMAP equivalents into two resulted in 48% with 85% ee of the product (entry 7). Notably, when dry toluene was used as a solvent, the domino reaction provided a 60% yield of **4a** with 96% ee (entry 14), and minimizing the formation of aromatic product **3a**. When the quantity of DMAP was decreased by one equivalent, the yield of product **4a** was reduced to 45% with 90% ee (entry 15). Reducing the catalyst loading to 10 mol%, the yield and % ee of product **4a** were also reduced to 40% and 60%, respectively (entry 16).<sup>14</sup> Also, the reaction was performed with other green catalysts, such as **C11** and **C12**, which produced only racemic products (entries 18 and 19).

With the optimized reaction conditions in hand, the generality of the asymmetric domino reaction was investigated with various  $\alpha,\beta$ -unsaturated aldehydes **1**, and 4-methyl thiazolium salts **2** containing electron-donating groups, heterocycles, and bulky aryl groups, and the results are summarized in Scheme 4.

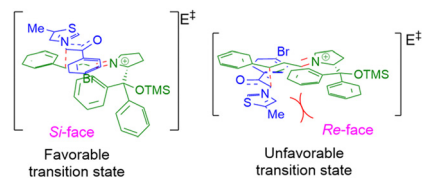
All the domino reactions took place smoothly *via* intermolecular 1,3-dipolar cycloaddition/intramolecular ring-opening/C–S/C–N bond cleavage to afford the chiral trisubstituted-4,5-dihydro-1*H*-pyrrole-3-carbaldehydes **4a–4r** in good to excellent enantioselectivity (63–98% ee). Gratifyingly, 4-methyl thiazolium salts bearing an electron-donating group at the *ortho*, *meta*, and *para* positions exhibited good reactivity and enantioselectivity (**4a–4d** and **4r**; 81–95% ee). The halogen substitution at the *para* positions provided the desired products **4e–4g** in 60–65% yields with 96–98% ee. The 4-biphenyl and bulky substitution containing naphthyl 4-methyl thiazolium salts **4h** and **4i** delivered the desired chiral products in 57% and 52% yield with 90% ee and 87% ee. The decreasing yield of **4d**, **4i**, and **4r** is due to steric hindrance with the thiazolium ring methyl group. As a result, the formation of the hydropyrrolo-thiazole cycloadduct intermediate is decreased, reducing the yield of the dihydropyrrole product.

To showcase the functional group tolerance of  $\alpha,\beta$ -unsaturated aldehyde **1**, the domino reaction proceeded with electron-donating groups, halogens, and heterocycle substituents. All the reactions underwent smoothly and yielded the enantioselective domino products **4j–4q** in 63–96% ee (Scheme 4). The cinnamaldehyde-bearing electron-donating group at the *para* position delivered the desired products **4j**, **4k**, and **4p** in good yields with 69–88% ee. The halogen substitution at cinnamaldehyde's *para* and *ortho* positions furnished **4l–4n** and **4q** in 79–96% ee. The reaction was also suitable for substituting at the 3-position of  $\alpha,\beta$ -unsaturated



Scheme 4 Substrate scope for chiral dihydro-1*H*-pyrrole-3-carbaldehydes. <sup>a</sup> When this reaction was allowed for a longer time, aromatization took place to yield the racemic atropisomeric product **3l**.





Scheme 5 Diastereomeric transition state.

aldehydes such as the furan ring and delivered the domino chiral product **4o** in 63% ee.

Gram scale synthesis was performed to check the scalability of both domino methodologies.<sup>14</sup> Also, several control experiments and mechanistic investigations were conducted to probe the reaction mechanism.<sup>14</sup>

Based on our control experiments and previous literature reports,<sup>11</sup> a plausible reaction mechanism has been proposed in the ESI† (Page No. S13).<sup>14</sup> The 4-methylthiazolium salt **2a** will initially react with DMAP to yield azomethine ylides **III**. Subsequently,  $\alpha,\beta$ -unsaturated aldehyde **1a** in the presence of chiral catalyst **C9** will provide iminium ion intermediate **I**. Intermediate **I** will react with azomethine ylide **III** to produce Michael adduct intermediate **IV** via a 1,4-addition. The formation of intermediate **IV** is a chiral induction step through the 4-methylthiazolium anion **III** approaching from the *Si*-face of iminium ion **I**, which is the favorable transition state.

The unfavorable transition state is a 4-methylthiazolium anion **III** approaching from the *Re*-face of iminium ion **I**. According to our previous report, computational study<sup>11a</sup> shows the favorable and unfavorable diastereomeric transition in Scheme 5 (for a detailed, plausible reaction mechanism, see ESI†, Page S13).<sup>14</sup>

In conclusion, we have developed a new, unusual domino methodology for the synthesis of trisubstituted 1*H*-pyrrole-3-carbaldehydes and enantioenriched dihydro-1*H*-pyrrole-3-carbaldehydes via domino 1,3-dipolar cycloaddition/ring-opening/C–S and C–N bond-cleavage reactions of  $\alpha,\beta$ -unsaturated aldehydes with 4-methylthiazolium salt utilizing organocatalysts. The enantioselective synthesis was achieved with excellent enantio- and diastereoselectivity. We have performed various control experiments and mechanistic studies to confirm the product formation. HRMS analysis confirms that the formation of 1-mercaptopropane-2-one is a by-product. However, a detailed mechanistic investigation is in progress.

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## Data availability

The data supporting this article have been included as part of the ESI.†

## Conflicts of interest

The authors declare the following competing financial interest(s): a patent is pending for both domino methodologies described herein (Indian patent application numbers: 202441067200 and 202441067175, May 05, 2024).<sup>13</sup>

## References

- 1 D. Tzankova, S. Vladimirova, L. Peikova and M. Georgieva, *J. Chem. Tech. Metall.*, 2018, **53**, 451.
- 2 (a) M. Thwin, B. Mahmoudi, O. A. Ivaschuk and Q. A. Yousif, *RSC Adv.*, 2019, **9**, 15966; (b) M. K. Hunjan, S. Panday, A. Gupta, J. Bhaumik, P. Das and J. K. Laha, *Chem. Rec.*, 2021, **21**, 715.
- 3 (a) H. Pourtaher, A. Hasaninejad and A. Iraj, *Sci. Rep.*, 2022, **12**, 15236; (b) S. Boussios, P. Karihtala, M. Moschetta, C. Abson, A. Karathanasi, N. Zakynthinakis-Kyriakou, J. E. Ryan, M. Sheriff, E. Rassy and N. Pavlidis, *Invest. New Drugs*, 2020, **38**, 181; (c) E. B. Van Arnem, A. C. Ruzzini, C. S. Sit, H. Horn, A. A. Pinto-Tomás, C. R. Currie and J. Clardy, *Proc. Natl. Acad. Sci. U. S. A.*, 2016, **113**, 12940.
- 4 (a) S. Castellano, H. D. G. Fiji, S. S. Kinderman, M. Watanabe, P. de Leon, F. Tamanoi and O. Kwon, *J. Am. Chem. Soc.*, 2007, **129**, 5843; (b) E. Fattorusso and O. Tagliatella-Scafati, *Modern Alkaloids: Structure, Isolation, Synthesis and Biology*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2008.
- 5 Studies about synthesis of dihydropyrroles: (a) A. Guðmundsson, K. P. J. Gustafson, B. K. Mai, V. Hobiger, F. Himo and J.-E. Bäckvall, *ACS Catal.*, 2019, **9**, 1733; (b) D. Wang, Y. Fan, P. Yu and L. Désaubry, *Chem. Commun.*, 2020, **56**, 5584.
- 6 (a) S. Yaragorla, R. Tangellapally and D. Arun, *Eur. J. Org. Chem.*, 2024, e202400238; (b) F.-F. Tang, W.-L. Yang, X. Yu and W.-P. Deng, *Catal. Sci. Technol.*, 2015, **5**, 3568; (c) M. K. Ghorai and D. P. Tiwari, *J. Org. Chem.*, 2013, **78**, 2617; (d) J. Xiang, H. Xie, Z. Li, Q. Dang and X. Bai, *Org. Lett.*, 2015, **17**, 3818; (e) K. M. Wen Ting and Chen Zhanguo, *Chin. J. Org. Chem.*, 2019, **39**, 3162.
- 7 Recent studies on asymmetric catalysis and sustainable methodologies: (a) A. Garg, D. Rendina, H. Bendale, T. Akiyama and I. Ojima, *Front. Chem.*, 2024, **12**, 1398397; (b) A. Chaskar and R. Darade, *Int. J. Creat. Res. Thoughts.*, 2022, **10**, 2320; (c) A. M. Koskinen, *Asymmetric synthesis of natural products*, John Wiley & Sons, 2022.
- 8 (a) X. Liu, H. Zheng, Y. Xia, L. Lin and X. Feng, *Acc. Chem. Res.*, 2017, **50**, 2621; (b) K. Wang, L. Yang, Y. Li, H. Li, Z. Liu, L. Ning, X. Liu and X. Feng, *Angew. Chem., Int. Ed.*, 2023, **62**, e202307249; (c) F. Zhang, Y. Zhou, H. Zhao, L. Chen, W. Cao and X. Feng, *Precis. Chem.*, 2023, **1**, 423.
- 9 J. L. García Ruano, A. Fraile, M. R. Martín, G. González and C. Fajardo, *J. Org. Chem.*, 2008, **73**, 8484.
- 10 (a) T. Iwamura, M. Kobayashi, T. Ichikawa, H. Shimizu and T. Kataoka, *J. Chem. Soc., Perkin Trans. 1*, 1996, 629; (b) C. R. Berry, C. A. Zificsak, A. C. Gibbs and D. J. Hlasta, *Org. Lett.*, 2007, **9**, 4099; (c) Y.-M. Shen, P.-C. Lv, M.-Z. Zhang, H.-Q. Xiao, L.-P. Deng, H.-L. Zhu and C.-Z. Qi, *Monatsh. Chem.*, 2011, **142**, 521; (d) V. A. Motornov, A. A. Tabolin and S. L. Ioffe, *New J. Chem.*, 2022, **46**, 4134.
- 11 (a) S. Pandidurai, V. S. Kumar Choutipalli, V. Subramanian and G. Sekar, *Org. Lett.*, 2024, **26**, 2971; (b) S. Pandidurai and G. Sekar, *Org. Biomol. Chem.*, 2024, **22**, 8119.
- 12 (a) O. Tsuge, S. Kanemasa and S. Takenaka, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 3320; (b) X. Zhang, X. Liu, J. Zhang, D. Zhang, L. Lin and X. Feng, *Org. Chem. Front.*, 2018, **5**, 2126; (c) Z.-H. Wang, T. Zhang, L.-W. Shen, X. Yang, Y.-P. Zhang, Y. You, J.-Q. Zhao and W.-C. Yuan, *Molecules*, 2023, **28**, 4410.
- 13 (a) S. Pandidurai, S. Kishor and G. Sekar, *Indian Pat.*, 202441067200, 2024; (b) S. Pandidurai and G. Sekar, *Indian Pat.*, 202441067175, 2024.
- 14 See the ESI† for more details.
- 15 The comparative study of ref. 6a and 12c with this study is included in the ESI,† Page 91.