nature communications

Article

https://doi.org/10.1038/s41467-025-67716-2

Enantioselective dearomative single-atom skeletal editing of benzofurans

Received: 9 September 2025

Accepted: 5 December 2025

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One-carbon ring expansion reaction of heteroarenes involving typical dearomative cyclopropanation has gained wide attention in the past decade because this method allows the facile synthesis of various valuable ring-expanded heterocycles. However, the related catalytic asymmetric exploration remains challenging with scarce reports. Herein, we disclose an enantioselective dearomative one-carbon ring expansion of benzofurans via vinyl cations formed by copper-catalyzed cyclization of diynes, leading to practical and atom-economic assembly of an array of valuable 2*H*-chromenes bearing a quaternary carbon stereocenter in generally good to excellent yields with excellent enantioselectivities (up to 96% ee). Notably, this protocol not only represents an asymmetric one-carbon ring expansion reaction of heteroarenes based on alkynes, but also constitutes an enantioselective dearomative single-atom skeletal editing of benzofurans. Additionally, this reaction also features a broad substrate scope, detailed mechanism studies strongly supported by theoretical calculations, and the biological activity of the products.

Owing to their widespread occurrence in natural products and drug molecules, as well as their demonstration of diverse and significant biological activities, such as anticancer, anti-inflammatory, and anti-HIV properties (Fig. 1)[1–6], 2-substituted 2*H*-chromenes as core scaffolds have garnered substantial interest from organic chemists and biochemists, and numerous protocols have been established to facilitate their synthesis during the past decades. However, their catalytic asymmetric synthesis, especially for the 2-substituted 2*H*-chromenes bearing a quaternary carbon stereocenter, remains highly challenging[7–11]. More importantly, the development of new strategies for constructing such chiral units from commercially available benzofurans via asymmetric single-atom skeletal editing represents an underexplored yet highly promising and urgently needed area of research.

In recent years, molecular editing has proven to be a very attractive protocol for establishing high-throughput libraries in drug discovery due to its power to modify the scaffold economically during the late-stage modification of pharmaceutical molecules[12–24]. Among numerous skeletal editing strategies, ring expansion reactions, especially the one-carbon ring expansion of heteroarenes, have unique applied potency because of their ability to construct a variety of valuable complex molecules from simple precursors. Nevertheless, the utilization of one-carbon ring expansion of these aromatic ring systems is a formidable challenge due to the high energy barriers associated with dearomatization and cleavage of carbon–carbon bonds. Although significant progress on the one-carbon ring expansion of benzofurans[25–27], indoles[28–33], benzothiophenes[34–36] and other typical heteroarenes[37–42] has been achieved (Fig. 2a), most of them are

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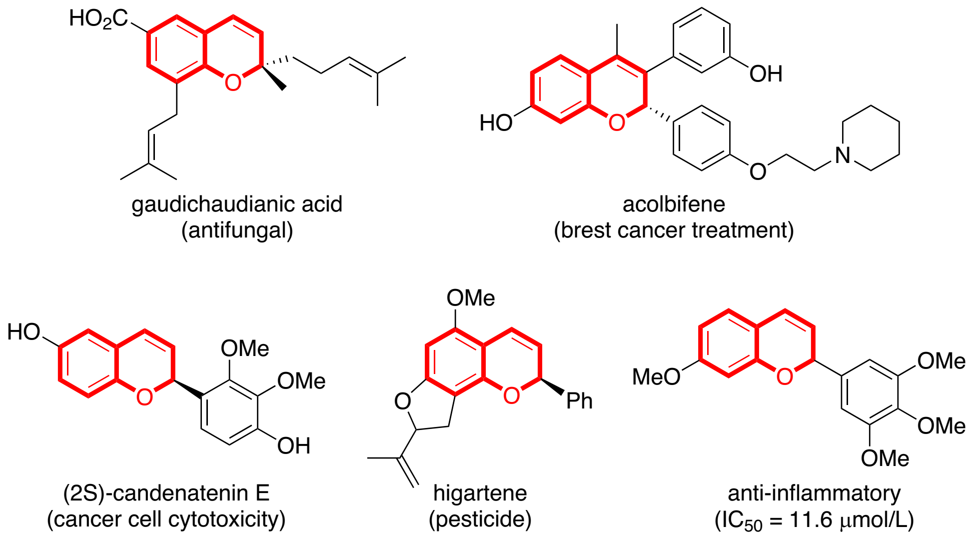


Fig. 1 | Selected examples of pharmaceuticals and bioactive compounds based on 2*H*-chromene scaffolds. Some of representative molecules are listed.

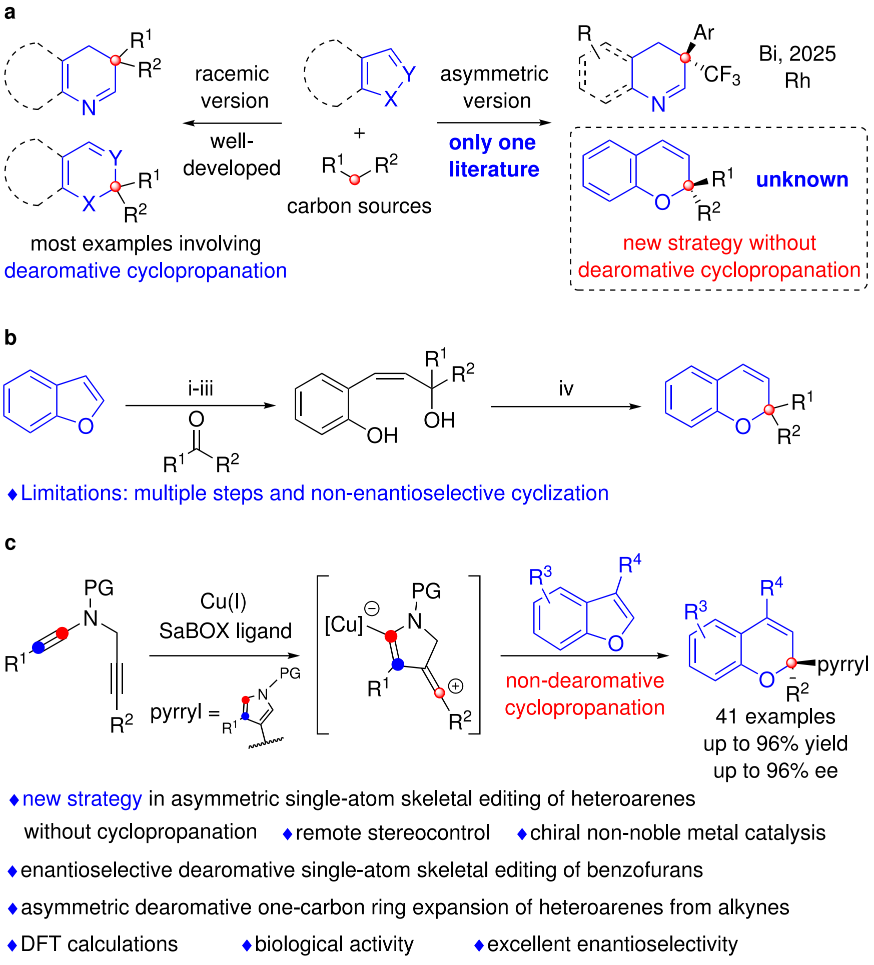


Fig. 2 | One-carbon ring expansion reactions of heteroarenes. a One-carbon ring expansion of heteroarenes via metal carbenes. **b** One-carbon ring expansion of benzofuran for synthesis of 2*H*-chromene. **c** This work: asymmetric one-carbon ring expansion of benzofurans via vinyl cations for synthesis of chiral 2*H*-chromenes.

restricted to dearomative cyclopropanation via metal carbenes by employing diazo compounds or hydrazones as one-carbon reagents, and a catalytic asymmetric version is still struggling with only one successful example[28]. Very recently, Bi and co-workers illustrated an elegant protocol of Rh-catalyzed asymmetric carbon-atom insertion involving an initial cyclopropanation step to achieve enantiodivergent dearomative skeletal editing of indoles and pyrroles by the use of trifluoromethyl *N*-triftosylhydrazones as carbene precursors, leading to chiral six-membered N-heterocycles containing a trifluoromethylated quaternary stereocenter with high efficiency and stereoselectivity[28]. Therefore, the development of novel strategies for asymmetric one-carbon ring expansion reactions of heteroarenes, particularly those involving non-dearomative cyclopropanation, utilizing alkynes as one-carbon reagents, and non-noble metal catalysis, is an underexplored yet highly desirable area (Fig. 2a).

On account of their unique carbene-like reactivity, vinyl cations have emerged as an essential reactive intermediate in organic synthesis and have attracted wide attention in recent years[43,44]. However, relevant examples of asymmetric catalysis have been rarely reported, probably due to the lack of catalytic methods for their generation and their high reactivity once formed[45]. In the past several years, we disclosed that the vinyl cations could be generated via a facile copper-catalyzed diyne cyclization, allowing the establishment of a series of asymmetric transformations of vinyl cations via a remote control of enantioselectivity[46–58]. Nevertheless, intermolecular such asymmetric transformations were still very scarce[54,57], and only one example of asymmetric one-carbon ring expansion of N-heterocycles via vinyl cations was limited to the intramolecular protocol[49]. Inspired by the above results and by our recent progress on ynamide chemistry in N-heterocycle synthesis[59–64], we envisioned that the vinyl cations generated from diyne cyclization might be intermolecularly trapped by the benzofurans, eventually furnishing the ring-expanded chiral 2*H*-chromenes. It is notable that there was only one example on the synthesis of 2*H*-chromene from benzofuran via one-carbon ring expansion to the best of our knowledge, where a multistep synthesis was involved, and its asymmetric synthesis has not been explored yet (Fig. 2b)[27]. However, realizing this dearomative one-carbon ring expansion in an orderly manner is highly challenging: (i) how to prevent the competing background hydroarylation[65,66] and cyclopropanation of the benzofurans[67–69]; (ii) due to the inherent high stability and low reactivity of the aromatic systems, whether the vinyl cation is electrophilic enough to be trapped by the heterocycles; and (iii) how to control the enantioselectivity in the context of the formation of expanded ring. Herein, we report the realization of such an intermolecular enantioselective one-carbon ring expansion reaction via vinyl cations by chiral copper-catalyzed dearomative insertion rather than previous cyclopropanation (Fig. 2c)[67–69]. This strategy enables the practical and atom-economical synthesis of a wide array of valuable chiral 2*H*-chromenes bearing a quaternary carbon stereocenter in generally good to excellent yields with excellent enantioselectivities (up to 96% ee). Importantly, this protocol not only features an asymmetric one-carbon ring expansion reaction of heteroarenes based on alkynes and an intermolecular asymmetric transformation of vinyl cations in ring expansion, but also represents an example of enantioselective dearomative single-atom skeletal editing of benzofurans.

Results

Screening of reaction conditions

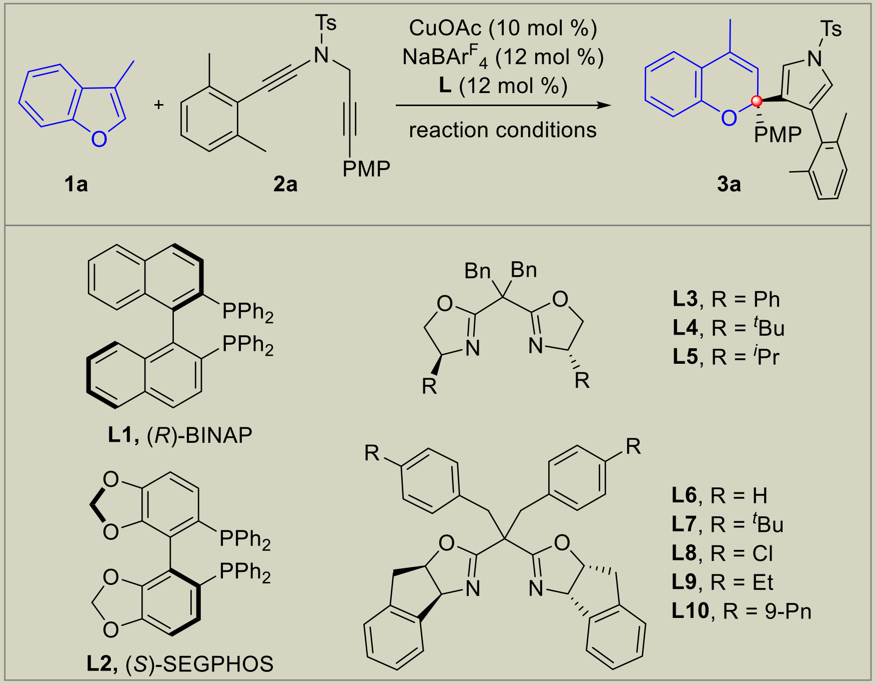
In our initial attempts, the 3-methyl-substituted benzofuran **1a** was chosen as the model substrate to react with diyne **2a** in the presence of copper(I) catalysts, and the selected results are listed in Table 1 (see the Supplementary Table 1). Of note, the 2,6-dimethylphenyl-substituted *N*-propargyl ynamide **2a** was used to prohibit the background aromatic C−H insertion reaction[58]. To our delight, the use of typical chiral bisphosphine ligands **L1**–**L2** could afford the desired 2*H*-chromene derivative **3a** in good yields, albeit with low enantioselectivities (Table 1, entries 1 and 2). Subsequently, Tang's side-armed bisoxazoline (SaBOX) ligands **L3**–**L10** were examined and led to dramatically increased enantioselectivities (Table 1, entries 3–10). Gratifyingly, the use of 9-phenanthrenyl-substituted **L10** led to the formation of the expected 2*H*-chromene **3a** in 74% yield with 88% ee (Table 1, entry 10). Next, a survey of several typical solvents failed to give better results (Table 1, entries 11–13). Finally, an apparent temperature influence was observed (Table 1, entries 14 and 15), and the desired **3a** was formed in 92% ee by decreasing the reaction temperature to 5 °C (Table 1, entry 15). The use of 15 mol % of catalyst resulted in a significantly increased reaction speed, furnishing **3a** in 75% yield with 92% ee (Table 1, entry 16).

Reaction scope study

Having established the optimized reaction conditions, we then explored the reaction scope of this asymmetric dearomative ring-expansion. As depicted in Fig. 3, various 1,5-diynes **2** with different typical *N*-protecting groups, including Ts, Mbs, SO_2Ph, 4-^{t}Bu-$C_6H_4SO_2$ and Bs groups, were well tolerated, providing the desired chiral pyrrolyl 2*H*-chromenes **3a**–**3e** bearing a chiral quaternary carbon stereocenter in 70–96% yields with 87–92% ees. In addition, different aryl-substituted diynes (R^1 = Ar) bearing both electron-withdrawing and -donating groups on the benzene ring were suitable substrates to afford the corresponding products **3f**–**3k** in moderate to good yields with 80–92% ees. Notably, the ynamide **2k** bearing a single methyl group at the phenyl ring was also compatible in this dearomative insertion, with less than 10% of C−H insertion byproduct[58]. Moreover, a wide array of mono-substituted aryl of *N*-propargyl ynamides (R^2 = Ar) were found to be suitable substrates, delivering the target products from **3l** to **3p** in good yields (50–71%) with 91–96% ees. The reaction of 4-MeC_6H_4-substituted diyne afforded the desired product **3q** in 46% yield with 90% ee, but attempts to extend the reaction to the diynes with non-electron-rich aromatic groups only led to a trace of the desired 2*H*-chromenes (see the Supplementary Fig. 1), which is similar to our previous protocols[46–58]. Besides, diynes with disubstituted aryl groups could be readily transformed into the desired products **3r**–**3t** in 64–76% yields with 92–96% ees. Of note, attempts to extend the reaction to CN-substituted diyne substrate **2v** under the related conditions only led to the formation of complicated mixtures. When the chiral ligand with opposite configuration was employed, the expected 2*H*-chromene *ent*-**3a** was also obtained smoothly in 68% yield with 93% ee. Encouraged by our previous studies on chiral copper-catalyzed atroposelective annulation[47,48,52,53], the reaction of sterically hindered diyne **2u** under optimized conditions could lead to the desired atropisomer **3u** containing central chirality in 90% yield with 90% ee and 13:1 dr. It is notable that due to the steric hindrance of the naphthyl group, compound **3u** is actually very stable and does not rotate at room temperature, which is similar to our previously reported protocol[53]. The absolute configuration of product **3 s** was confirmed by X-ray diffraction analysis (see the Supplementary Fig. 5). Thus, this strategy provides an efficient and practical route for the construction of valuable chiral 2*H*-chromenes.

Motivated by the above results, this skeleton editing reaction was also extended to other C3-substituted benzofurans, as outlined in Fig. 4. Under the optimized reaction conditions, the reaction of 3-ethyl and 3-phenyl substituted benzofurans proceeded smoothly to generate the expected products **3aa** (61%, 93% ee) and **3ab** (52%, 87% ee), respectively. In particular, this one-carbon ring expansion reaction could be applied to a wide range of diverse benzofurans with electron-donating and -withdrawing substituents, and even bearing substituents at sterically hindered positions, delivering the desired chiral 2*H*-chromenes **3ac**–**3an** in moderate to good yields with generally excellent enantioselectivities (83–95% ees). Of note, it was shown that the positions of substituents have no significant effect on the reactivity and stereoselectivity. Interestingly, the benzofuran with an unprotected hydroxy group at the C5 position was also a viable substrate, affording the target product **3ae** in 44% yield with 93% ee. In addition, it was found that the 5,6-dimethyl substituted benzofuran was also tolerated, and transformed into the expected **3ao** in 84% yield with 85% ee. To get further insight into the potential pharmaceutical utility of this skeletal editing insertion, various benzofuran derivatives from complex scaffolds, such as anti-inflammatory or antifungal drugs and

Table 1 | Optimization of reaction conditions for asymmetric dearomative single-atom skeletal editing of benzofuran 1a with diyne 2a[a]



Entry	L	Reaction conditions	Yield (%)[b]	Ee (%)[c]
1	**L1**	toluene, 35 °C, 14 h	65	16 (+)
2	**L2**	toluene, 35 °C, 14 h	79	10 (-)
3	**L3**	toluene, 35 °C, 40 h	52	71 (+)
4	**L4**	toluene, 35 °C, 15 h	57	68 (+)
5	**L5**	toluene, 35 °C, 15 h	50	44 (+)
6	**L6**	toluene, 35 °C, 14 h	54	80 (+)
7	**L7**	toluene, 35 °C, 15 h	62	72 (+)
8	**L8**	toluene, 35 °C, 18 h	70	80 (+)
9	**L9**	toluene, 35 °C, 15 h	70	76 (+)
10	**L10**	toluene, 35 °C, 19 h	74	88 (+)
11	**L10**	PhCF$_3$, 35 °C, 15 h	67	85 (+)
12	**L10**	DCE, 35 °C, 15 h	75	84 (+)
13	**L10**	THF, 35 °C, 16 h	NR	ND
14	**L10**	toluene, 15 °C, 44 h	72	90 (+)
15	**L10**	toluene, 5 °C, 72 h	62	92 (+)
16[d]	**L10**	**toluene, 5 °C, 42 h**	**75**	**92 (+)**

[a] Reaction conditions: **1a** (0.15 mmol), **2a** (0.05 mmol), CuOAc (0.005 mmol), **L** (0.006 mmol), NaBAr$^F_4$ (0.006 mmol), solvent (1 mL), in vials. [b] Measured by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. [c] Determined by HPLC analysis. [d] CuOAc (0.0075 mmol), **L** (0.009 mmol), and NaBAr$^F_4$ (0.009 mmol) were used. Ts = *p*-toluenesulfonyl, PMP = 4-methoxyphenyl, 9-Pn = 9-phenanthrenyl, DCE = 1,2-dichloroethane, NaBAr$^F_4$ = sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate.

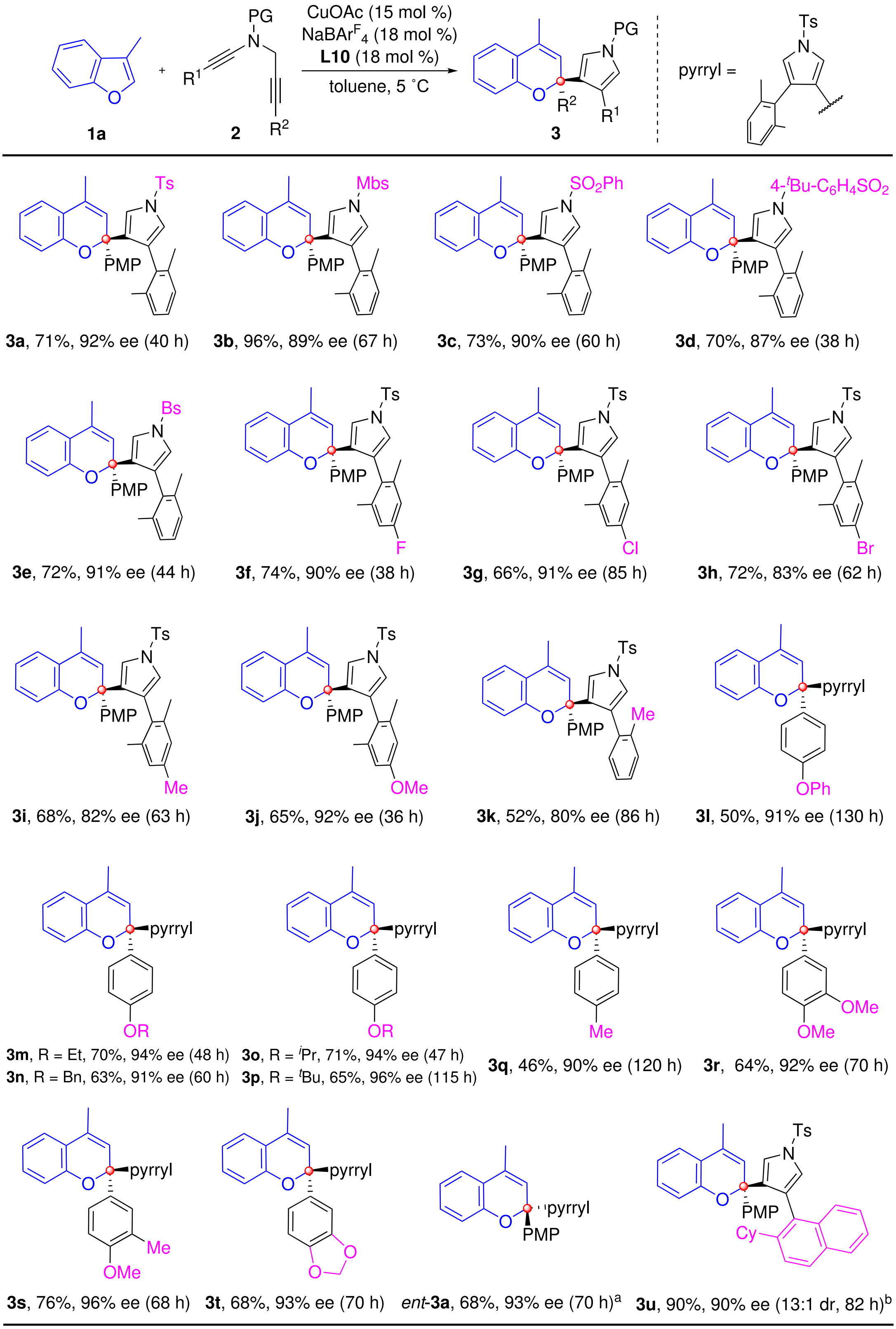


Fig. 3 | Reaction of benzofuran 1a with different *N*-propargyl ynamides 2. Reaction conditions: **1a** (0.3 mmol), **2** (0.1 mmol), CuOAc (0.015 mmol), NaBAr$^F_4$ (0.018 mmol), **L10** (0.018 mmol), toluene (2 mL), 5 °C, 36–130 h, in vials; yields were those for the isolated products; ees were determined by HPLC analysis. [a]*Ent*-**L10** was used instead of **L10**. [b](*S*)-**BINAP** was used instead of **L10**, − 20 °C. PG = protecting group, Mbs = 4-methoxybenzenesulfonyl, Bs = 4-bromobenzenesulfonyl.

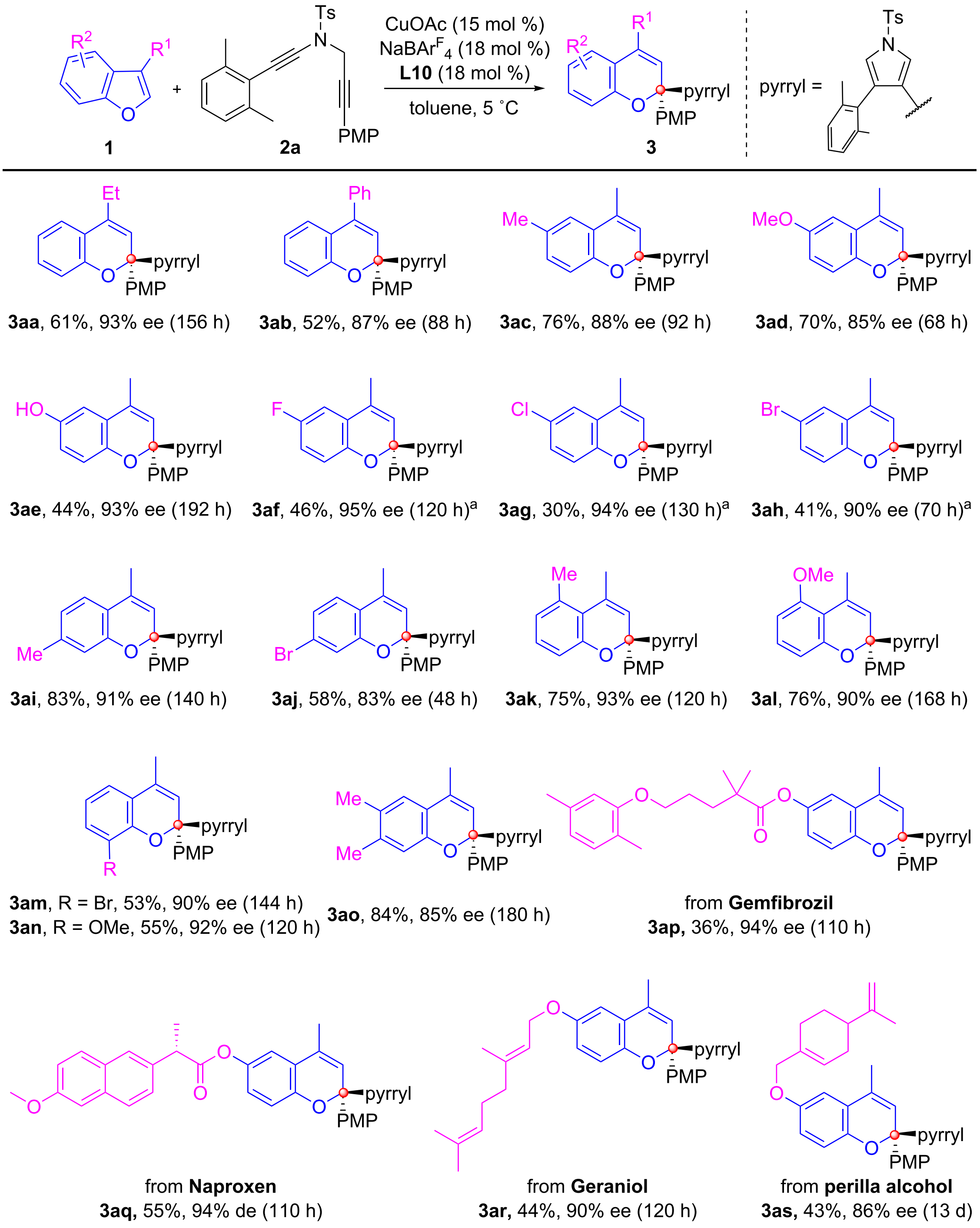


Fig. 4 | Reaction of *N*-propargyl ynamide 2a with different benzofurans 1. Reaction conditions: **1** (0.3 mmol), **2a** (0.1 mmol), CuOAc (0.015 mmol), $NaBAr^F_4$ (0.018 mmol), **L10** (0.018 mmol), toluene (2 mL), 5 °C, 48 h-13 d, in vials; yields were those for the isolated products; ees were determined by HPLC analysis. des were determined by crude ^{1}H NMR. [a]0.5 mmol of **1** was used.

natural perfume molecules, were tested, generating the corresponding products **3ap**–**3as** in 36–55% yields with high enantioselectivities, which might find potential applications in medicinal chemistry. It is notable that our attempts to extend this one-carbon ring expansion reaction to CF_3-, CN- and NO_2-substituted benzofurans **1u**–**1w** only gave a complicated mixture.

Of note, attempts to expand this chemistry to the 3-methyl-substituted benzothiophene, 2-methyl-substituted benzofuran and unsubstituted benzofuran only resulted in the formation of the corresponding cyclopropanation products (see the Supplementary Fig. 2). In the case of the indole substrates, the reaction also proceeded through the typical cyclopropanation process under the relevant conditions[70].

Synthetic applications

To demonstrate the reliability of the present protocol, a preparative scale reaction was first performed (Fig. 5a). When 1 mmol of substrate **2a** was used, 2*H*-chromene **3a** was prepared without the erosion of yield and enantiopurity. Motivated by the valuable structural motif of 2*H*-chromenes, a set of downstream transformations of **3a** was then

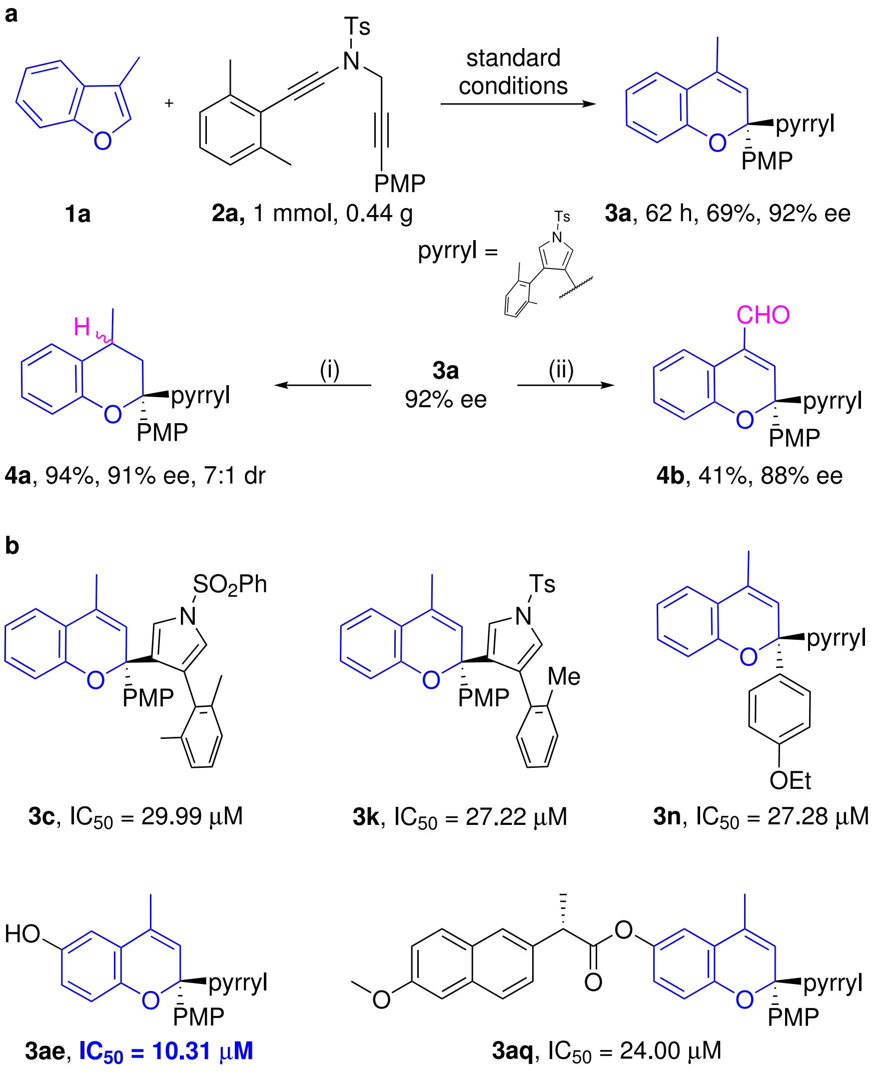


Fig. 5 | Synthetic transformations and applications. **a** Reagents and conditions: (i) H_2 (4 atm), AcOH (5 mol %), $Pd(OH)_2/C$ (20 mol %), EA:MeOH = 1:1, rt, 24 h; (ii) SeO_2 (10 equiv), 1,4-dioxane, 50 °C, 42 h. **b** Some products **3** with anti-neuroinflammatory activity against BV-2 cells.

studied. For instance, **3a** could be smoothly reduced into valuable chromane **4a** in 94% yield with 91% ee and 7:1 dr. In addition, simple Riley oxidation of **3a** led to the corresponding aldehyde **4b** in 41% yield with 88% ee.

Furthermore, to evaluate the potential biological activity of the newly prepared chiral 2*H*-chromenes, the anticancer and anti-inflammatory activities of these compounds were investigated (see the Supplementary Tables 2 and 3, the Supplementary Figs. 3 and 4), as shown in Fig. 5b. Particularly, we were pleased to find that chiral 2*H*-chromene **3ae** not only effectively inhibits the proliferation of cancer cell SK-OV-3 ($IC_{50} = 22.31 \pm 0.31$ μM)[71], but also exhibits significant anti-neuroinflammatory activity against BV-2 cells ($IC_{50} = 10.31 \pm 0.41$ μM)[72], suggesting a potential application of these chiral 2*H*-chromenes in pharmaceutically relevant realm.

Mechanistic investigations

To further understand the reaction mechanism, several control experiments were then conducted. First, the reaction of diyne **2a** with benzofuran **1a** in the presence of 10 equiv of D_2O under standard conditions led to the desired product **3a** with 30% deuterium incorporation into one of the α-position of the pyrrole moiety (Fig. 6a). In addition, when [D_2]-**2a** was subjected to the standard conditions and in the presence of 10 equiv of H_2O, it was found that only 20% deuterium and 7% deuterium were retained on one of the α-position of the formed pyrrole partner, respectively (Fig. 6b). Moreover, the reaction of **2a** with [D]-**1a** under standard conditions could afford the desired **3a** with deuterium atom completely retained (Fig. 6c). Interestingly, the Cu-catalyzed reaction of **2a** with 3-methylfuran under the standard or related conditions resulted in the formation of furan ring-opening 1,3-diene product **5**, which did not undergo further oxa-6π electrocyclization (Fig. 6d). Finally, we performed several radical control experiments and found that the addition of radical scavengers such as TEMPO (2,2,6,6-tetramethyl-1-piperinedinyloxy), BHT (butylated hydroxytoluene) and DDNU (1,1-diphenylethylene) under standard conditions almost did not affect the reaction, suggesting that the radical pathway is quite unlikely. Thus, these results are well consistent with our previous work on such a copper-catalyzed diyne cyclization[46–58], and the vinyl cation and copper carbene intermediate are presumably involved in this one-carbon ring expansion reaction.

Based on the above experimental observations, our previously published results[46–58], and detailed density functional theory (DFT) calculations, the reaction mechanism of the Cu^I-catalyzed cyclization to form the 2*H*-chromene **3a** is depicted in Fig. 7. Initially, the Cu^I catalyst, due to its distinct electronic properties, selectively activates the electron-rich C≡C bond adjacent to the amide group in *N*-propargyl ynamide **2a**, thereby forming the crucial precursor **A**. Subsequently, the C≡C bond activated by Cu^I, undergoes an intramolecular electrophilic cyclization with the alkynyl group in precursor **A**. This

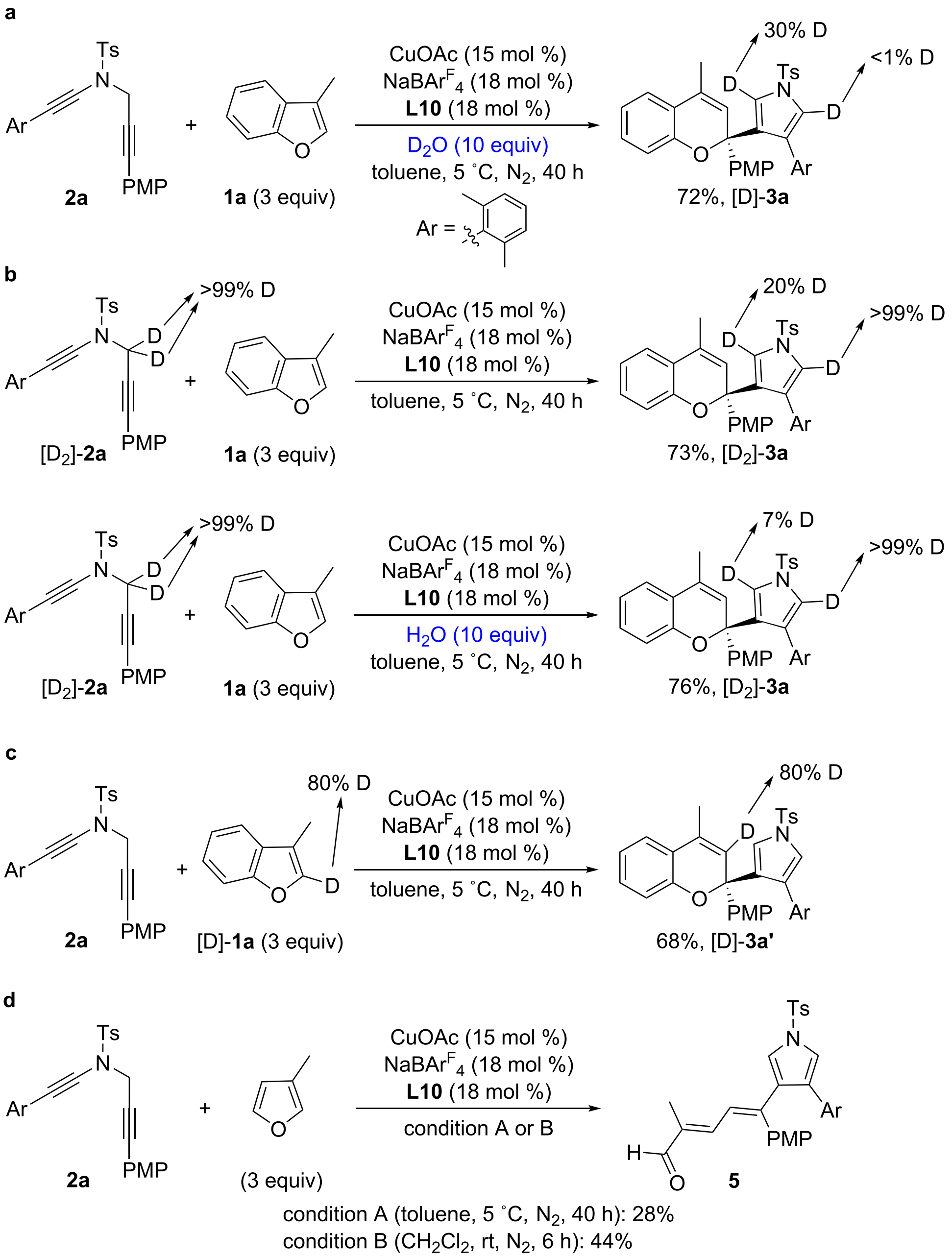


Fig. 6 | Control experiments. **a** Cu-catalyzed reaction of **2a** with **1a** in the presence of 10 equiv of D_2O. **b** Cu-catalyzed reaction of [D_2]-**2a** with **1a** under the standard conditions or in the presence of 10 equiv of H_2O. **c** Cu-catalyzed reaction of **2a** with [D]-**1a** under the standard conditions. **d** Cu-catalyzed reaction of **2a** with 2-methylfuran under the standard conditions.

step proceeds through the transition state **TS$_A$** and requires overcoming a free energy barrier of 13.8 kcal/mol to generate the vinyl cation intermediate **B**. Thereafter, the 3-methyl-substituted benzofuran **1a** attacks the vinyl cation intermediate **B**, surmounting a free energy barrier of 8.8 kcal/mol to form intermediate **C**, with a release of free energy of 9.7 kcal/mol. Intermediate **C** then undergoes a back-donation electron transfer, leading to the cleavage of the intramolecular five-membered ring and the formation of 1,3-diene intermediate **D**, releasing a free energy amounting to 12.3 kcal/mol. We speculate that this ring-opening process, instead of the direct cyclopropanation process, may be attributed to the steric hindrance of the methyl group, as the use of unsubstituted benzofuran only resulted in the formation of the cyclopropanation product (see the Supplementary Fig. 2). In addition, the fused cyclopropane can not be the intermediate on the way to the final product **3a**. Of note, a similar 1,3-diene has been isolated as **5** in the case of 3-methylfuran as substrate (Fig. 6d). Subsequently, intermediate **D** undergoes an aromatization-driven oxa-6π electrocyclization to form intermediate **E**, with a release of free energy of 16.4 kcal/mol, which is also the enantio-determining step. To our best knowledge, a successful asymmetric oxa-6π electrocyclization reaction remains unrealized[73]. Finally, formal 1,4-H shift[46–58] and demetallation yield the target product **3a**. The entire reaction process is highly exergonic, with a total free energy release of 56.3 kcal/mol, highlighting the significant thermodynamic advantage of this reaction.

The origin of the enantioselective synthesis of **3a** is also computationally investigated by utilizing the chiral ligand **L10** coordinated to the Cu^I center during the oxa-6π electrocyclization step. As shown in Fig. 8, upon further structural analysis of the two enantio-determining transition states, **[CuL10]-*R*-TS$_D$** and **[CuL10]-*S*-TS$_D$**, a significant steric repulsion is observed between the substrate and the bulky chiral

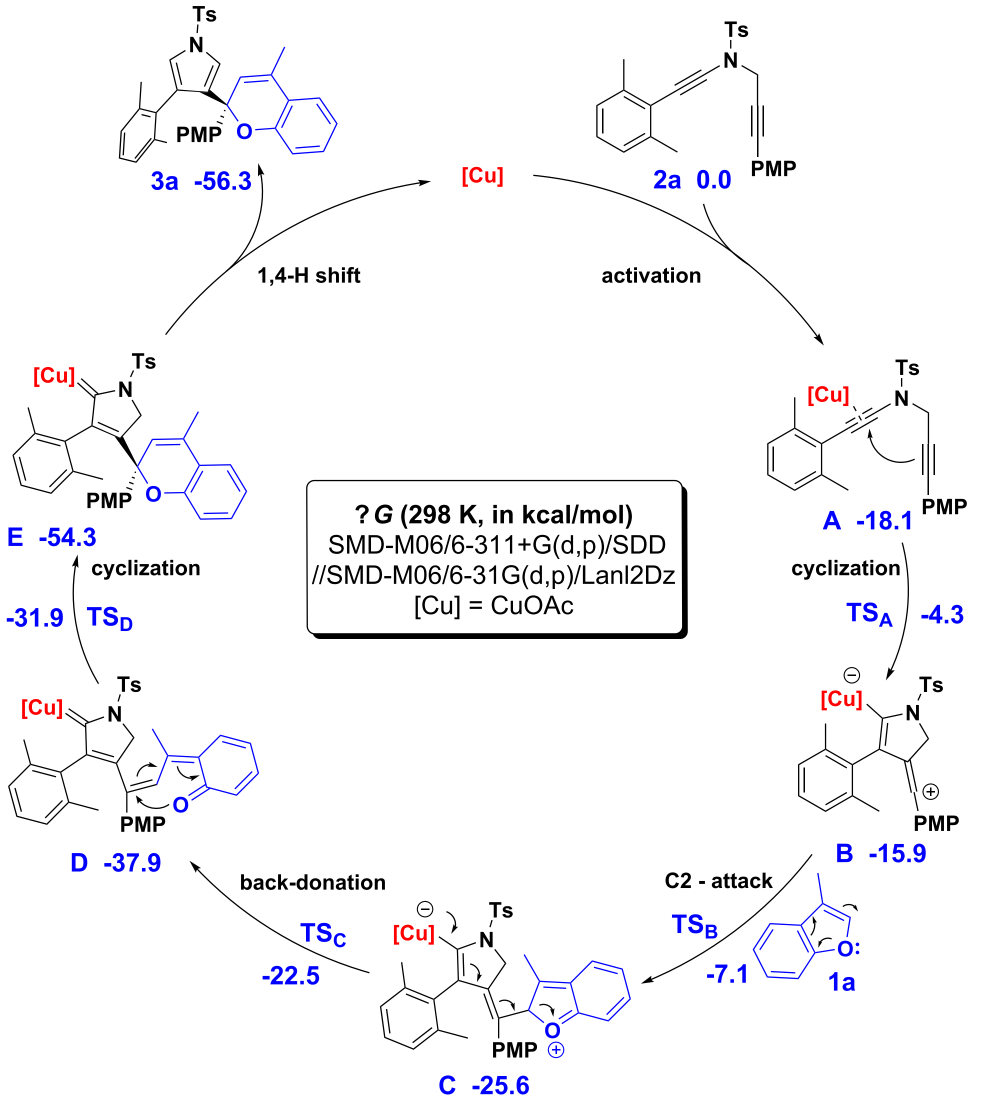


Fig. 7 | Plausible reaction mechanism. Relative free energies (Δ*G*, in kcal/mol) of all the transition states and intermediates were computed at the SMD-M06/6-311 + G(d,p)/SDD//SMD-M06/6-31 G(d,p)/Lanl2Dz.

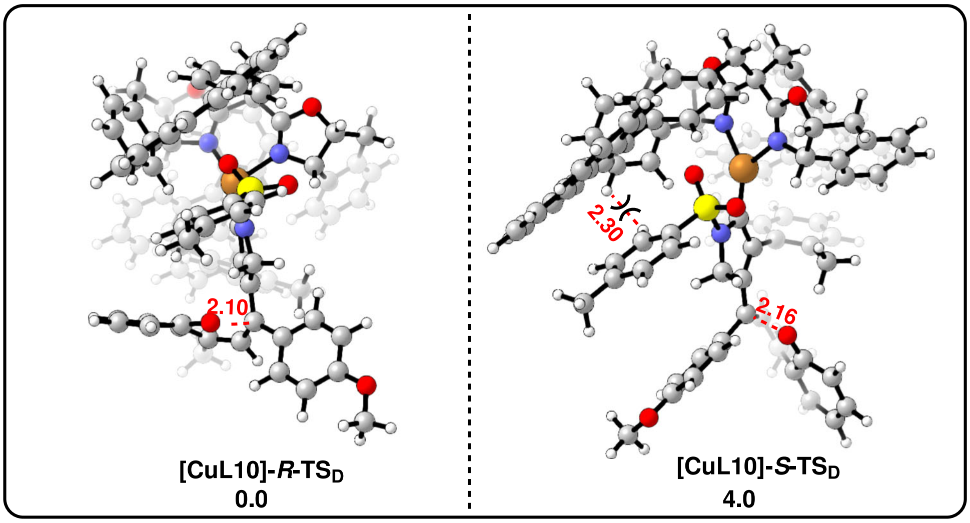


Fig. 8 | DFT calculations on the origin of enantioselectivity. The geometries, relative free energies (Δ*G*, in kcal/mol), and key bond lengths (in Å) of the transition states **[CuL10]-*R*-TS$_D$** and **[CuL10]-*S*-TS$_D$**.

ligand **L10** in **[CuL10]-*S*-TS$_\mathbf{D}$**, thereby leading to a free energy difference of 4.0 kcal/mol compared to **[CuL10]-*R*-TS$_\mathbf{D}$**. This finding aligns remarkably well with the experimentally measured enantiomeric excess (ee) value. Consequently, this unique chiral ligand plays a pivotal role in maintaining stereochemistry by remotely controlling the stereoselectivity.

Discussion

In summary, we disclose an enantioselective dearomative one-carbon ring expansion of benzofurans via copper-catalyzed cyclization of diynes, leading to the practical and atom-economic assembly of an array of valuable 2*H*-chromenes bearing a quaternary carbon stereocenter in generally good to excellent yields with excellent enantioselectivities. Further synthetic applications and biological tests demonstrate the reliability of the present protocol. Importantly, this protocol not only represents an example of asymmetric one-carbon ring expansion reaction of heteroarenes based on alkynes, but also constitutes an enantioselective dearomative single-atom skeletal editing of benzofurans and a successful asymmetric oxa-6π electrocyclization. Moreover, theoretical calculations are employed to elucidate the reaction mechanism involving non-dearomative cyclopropanation and the origin of enantioselectivity. We envision that these findings will offer a new perspective and further explorations for both one-carbon ring expansion reactions and vinyl cation chemistry, especially those based on asymmetric catalysis.

Methods

General

For ^{1}H, ^{13}C and ^{19}F nuclear magnetic resonance (NMR) spectra of compounds in this manuscript and details of the synthetic procedures, as well as more reaction conditions screening, see Supplementary Information.

General procedure for the synthesis of chiral 2*H*-chromenes 3

The powered CuOAc (1.9 mg, 0.015 mmol), **L10** (15.6 mg, 0.018 mmol) and NaBAr$^F_4$ (16.0 mg, 0.018 mmol) were introduced into a 10 mL vial. After toluene (1.0 mL) was injected into the vial, the solution was stirred at 35 °C for 2 h. Then, the mixture was cooled to 5 °C, and benzofuran **1** (0.3 mmol) and diyne **2** (0.1 mmol) in toluene (1.0 mL) was introduced into the system. The reaction mixture was stirred at 5 °C, and the progress of the reaction was monitored by TLC. Upon completion, the mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: PE/EtOAc = 15:1) to give the desired chiral 2*H*-chromene derivative **3**.

Reporting summary

Further information on research design is available in the Nature Portfolio Reporting Summary linked to this article.

Data availability

Data for the crystal structures reported in this paper have been deposited at the Cambridge Crystallographic Data Center (CCDC) under the deposition number CCDC 2448959 (**3 s**). Copies of these data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif. All other data supporting the findings of this study, including experimental procedures and compound characterization, are available within the paper and its Supplementary Information files, or from the corresponding authors on request. The coordinates of the optimized structures in this study are provided in the Source Data file. Source data are provided in this paper.

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Acknowledgements

We are grateful for financial support from MOST (2023YFA1509000, L.-W.Y.), the National Natural Science Foundation of China (22125108, 22331004 and 22121001 for L.-W.Y.; 22561033 for Q.S.), the Natural Science Foundation of Fujian Province of China (2024H6022, L.-W.Y.), Expert Workstation in Yunnan Province (202405AF140035, L.-W.Y.), the Yunnan Key Laboratory of Modern Separation Analysis and Substance Transformation (011002062503002, X.-Q.Z.), the Yunnan Fundamental Research Project (202401CF070024, X.-Q.Z.), the Jiangxi Provincial Natural Science Foundation (20242BAB25127, Q.S.), Foshan (Southern China) Institute for New Materials (2023A1515110471, Q.S.), Key Laboratory of Jiangxi Province for Persistent Pollutants Prevention Control and Resource Reuse (2023SSY02061, Q.S.), and Open Research Fund of State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University. We are very grateful to Professor Hai-Tao Tang (Guangxi Normal University) for his support in bioactivity detection.

Author contributions

X.-Q.Z., Z.-W.G., and B.Z. performed experiments. Q.S. designed DFT calculations. F.-J.M. performed DFT calculations. L.-W.Y. conceived and directed the project and wrote the paper. All authors discussed the results and commented on the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41467-025-67716-2.

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Peer review information *Nature Communications* thanks the anonymous reviewer(s) for their contribution to the peer review of this work. A peer review file is available.