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Asymmetric catalytic [1,3]- or [3,3]-sigmatropic rearrangement of 3-allyloxy-4*H*-chromenones and their analogues†

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A highly efficient asymmetric [1,3]- and [3,3]-O-to-C sigmatropic rearrangement of 3-allyloxy-4*H*-chromenones and their analogues was developed. Chiral *N*,*N*′-dioxide complexes of **3d** late transition metal complexes enabled two mechanistically different processes, giving a series of optically active 2,2-disubstituted chromane-3,4-diones and 2-allyl-3-hydroxy-4*H*-chromen-4-ones as well as their related compounds in excellent yield and enantioselectivity. Systemic mechanistic studies and DFT calculation revealed the nature of the vinyl ether unit of the substrate, which biased regioselectivity *via* a stepwise tight ion pair pathway and a concerted pericyclic pathway, respectively. The enantioselectivity of the two processes is also disclosed.

Introduction

O-to-C-sigmatropic rearrangements represent an important method to construct sterically congested carbon stereocenters,[1] providing convenient synthetic routes to complicated natural products and related compounds. In the past two decades, Lewis-acid-catalyzed sigmatropic rearrangement developed rapidly.[2] Lewis acids accelerate the concerted Claisen rearrangement through a charge-delocalized transition state. Alternatively, a suitable Lewis acid could induce the heterolytic cleavage of the C–O bond to concomitantly form stabilized electrophilic and nucleophilic fragments, performing non-concerted [1,3] O-to-C rearrangement, which was earlier reported by Yamamoto,[3] Grieco,[4] Gansäuer,[5] and Rovis[6] (Scheme 1a). The regioselectivity of O-to-C-sigmatropic rearrangement shows bias to both acidity and steric hindrance of the Lewis acid catalysts, and the intrinsic property of the allyl vinyl ethers (Scheme 1a). Catalytic asymmetric versions of the [3,3]- and [1,3]-rearrangements have made achievements in recent years,[7,8] but the chiral catalytic system which is tolerant to both [1,3]- and [3,3]-rearrangements is elusive due to the diverse reaction pathways.

The natural-product-inspired synthesis plays an important role in enriching chemical space and exploring bioactive compounds.[9] Substituted 3-hydroxyl pyranones and benzopyranones are popular structural motifs in natural products, such as flavonol, lawsone, kojic acid, and allomaltol (Scheme 1b). Rearrangements of 3-allyloxyflavone or *O*-allyl kojic acid have been designed for the synthesis of sanggenon-type natural products by Porco[10] and Hou,[11] and the tricyclic core of 1α-alkyldaphnanes by Wender and co-workers.[12] There are rare examples related to the asymmetric catalytic C2-functionalization of 3-hydroxychromenones: one is a chiral Pybox-Sc(III)-complex-catalyzed formal [3,3]-rearrangement to construct 3,4-chromanediones by Porco and co-workers,[13] and another is the chiral NHC-initiated formation of an α,β-unsaturated acyl azolium intermediate to perform Coates–Claisen rearrangement by Bode's group[14] and Rafiński's group.[15] Based on the above-mentioned studies, as well as Rovis's and Ishihara's[16] vigorous work on asymmetric catalytic [1,3]-rearrangement, we envision that suitable chiral Lewis acids and substitution on allyl vinyl ethers would enable [1,3]- and [3,3]-rearrangements of allyloxyflavones to construct C2-functionalized 3-hydroxychromenones and their analogues. As a continuation of the project of asymmetric rearrangements by chiral *N*,*N*′-dioxide-metal complexes,[17] we herein disclose both rearrangement processes *via* substrate and catalyst modification under mild reaction conditions. A series of optically active 2,2-disubstituted chromane-3,4-diones were obtained efficiently *via* cobalt-complex-catalyzed asymmetric [1,3]-rearrangement, while a 2-allyl-3-hydroxy-4*H*-chromen-4-one series could be afforded *via* nickel-complex-catalyzed asymmetric [3,3]-rearrangement. The key structure could be extended to kojic acid, allomaltol and lawsone varieties. DFT calculation revealed the regioselectivity tendency in the two cases, and demonstrated the enantioselectivity profile in the rearrangements.

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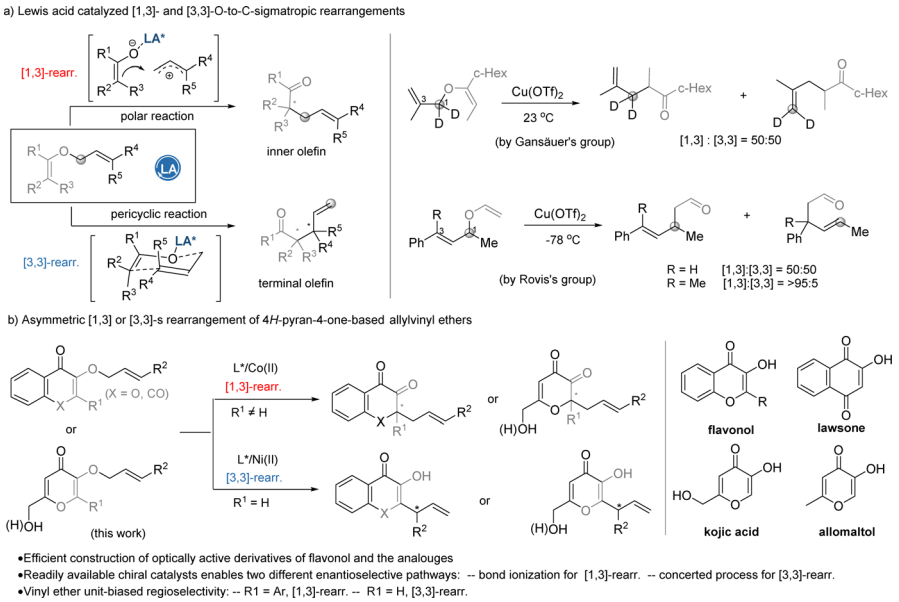
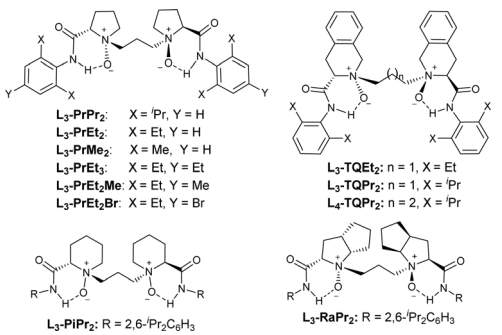


Scheme 1 Lewis-acid-catalyzed regioselective [1,3]- and [3,3]-O-to-C rearrangement.

Table 1 Structures of the chiral ligands

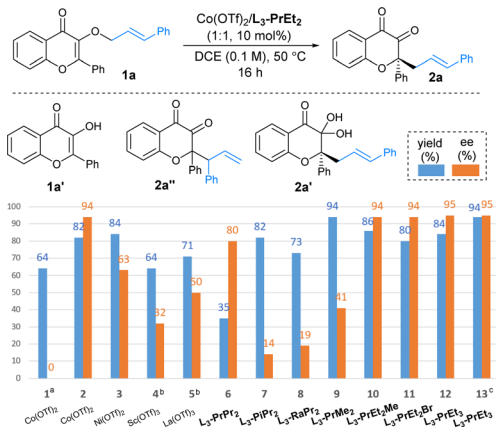


Results and discussion

To develop an enantioselective [*n*,3]-O-to-C sigmatropic rearrangement of a 3-allyloxy-flavonol derivative, we began by searching for the reaction conditions of the rearrangement of *E*-cinnamyl flavonol ether **1a** (Table 2). We found that the reaction in the presence of 10 mol% of $Co(OTf)_2$ in DCE at 50 °C led to the generation of a [1,3]-rearrangement product diketone **2a** in 64% yield after 16 hours. Additionally, high regioselectivity was observed and none of the [3,3]-rearrangement product **2a**″ was formed. At the same time, flavonol **1a**′ was detected *via* deallylation, which indicates that the [1,3]-rearrangement probably takes place *via* a non-concerted route. It was also found that there is an equilibrium between diketone **2a** and ketal **2a**′ in solvent;[18] thus the total yield of **2a** and **2a**′ was determined by ^1H NMR experiments using $CHBr_2CHBr_2$ as an internal standard. Employing chiral *N*,*N*′-dioxide-metal complexes to induce enantioselectivity manifested that both metal salts and the substructures of the ligands had a dramatic influence on the reactivity and the presence of **L_3-PrEt$_2$** (entry 2). L-Proline-based ligands resulted in better ee values than L-pipecolic acid or L-ramipril (entries 6–8); while 2,6-diethyl substitutions at the anilines of the ligand are beneficial to enantioselectivity in comparison with methyl or isopropyl groups (entries 2, 6, and 9). An array of **L_3-PrEt$_2$** analogues produced by installing a *para*-substitution could give good yield with high enantioselectivity (entries 10–12), and 1,3-rearrangement product **2a** could be obtained in 94% yield and 95% ee after 24 hours in the presence of a **L_3-PrEt$_3$**/$Co(OTf)_2$ complex catalyst (entry 13).

The scope of enantioselective [1,3]-rearrangement is reasonably broad with respect to flavonol ethers bearing different substitutions at the aryl backbone (Table 3). For the convenience of characterization, the products were treated with benzene-1,2-diamine to form quinoxaline **3** in one pot after the standard catalytic reaction. Highly efficient [1,3]-rearrangement products (**3a–3q**) were afforded in good yields (71–98%) and enantioselectivities (81 to >99% ee). Generally, electron-withdrawing and electron-donating groups at the 6-, 7- or 8-positions (**3b–3i**) did not significantly affect the outcomes. Benzo[*h*]chromen-4-one derivative **3j** was formed in 86% yield with >99% ee. An array of flavones bearing a substituted aryl group at the C2-position served as suitable reactants in the [1,3]-rearrangement, and the desired quinoxalines (**3k–3q**) were delivered smoothly in good yield (71–98%) with 81–97% ee. The absolute configuration of product **3k** was determined to be *S* according to an X-ray crystallographic analysis.[19] Subsequently, we turned our attention to different allyl substitutions (**3r–3y**). Noteworthily, the reactions of these substrates are electron-sensitive, and *para*-halo-substituted cinnamyl groups (**3r–3u**) undermined the reactivity and enantioselectivity in comparison with *para*- and *meta*-methyl substituted ones (**3v–3w**) or a heteroaromatic ring substituted one (**3x**). The reaction of phenylbut-2-enyl substituted ether also worked to give the product **3y** in medium yield (43%) with 94% ee, accompanied by

Table 2 Optimization of the reaction conditions of [1,3]-rearrangement[a]

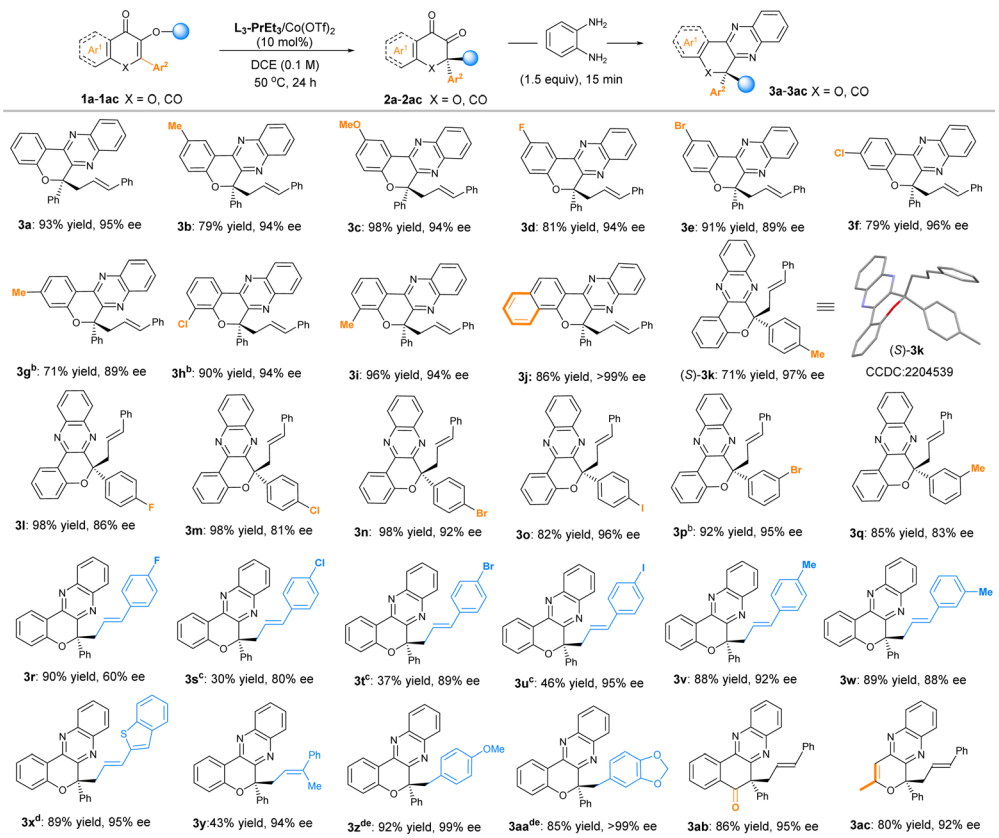


[a] Unless otherwise noted, all reactions were carried out with $Co(OTf)_2$/ligand (1 : 1, 10 mol%), **1a** (0.1 mmol) in DCE (0.1 M) at 50 °C; the yield of the mixture **2a**/**2a′** was determined by ^1H NMR spectra using $CHBr_2CHBr_2$ as internal standard; ee determined by UPC[2] analysis. [b] Without ligand. [c] At 35 °C. [d] 24 h.

byproduct flavonol **1a′**. In addition, benzyl flavonol ethers with electron-donating substituents underwent [1,3]-rearrangement smoothly, giving the corresponding products **3z** and **3aa** in the presence of $\mathbf{L_3}$-$\mathbf{PrPr_2}$/$Co(OTf)_2$ catalyst. Moreover, not only lawsone but also allomaltol-derived allylic ethers performed the rearrangement well, giving important derivatives (**3ab** and **3ac**) with excellent results.

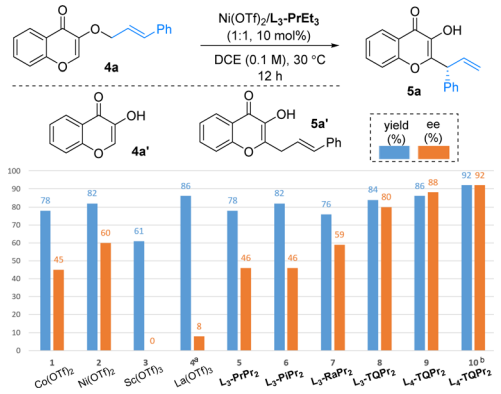
By switching the flavonol-derived ether **1a** into 3-hydroxychromone derivative *E*-**4a** in the presence of an $\mathbf{L_3}$-$\mathbf{PrEt_3}$/$Co(OTf)_2$ complex, the [3,3]-rearrangement product **5a** was formed in 78% yield with 45% ee (Table 4, entry 1) instead of [1,3]-rearrangement product **5a′**. Further optimizing the reaction conditions showed that the results with a complex of $Ni(OTf)_2$ were superior to those of other classic Lewis acids, such as $Sc(OTf)_3$ or $La(OTf)_3$ (Table 4, entries 1–4). Reinvestigation of the *N*,*N′*-dioxide (Table 1) confirmed that $\mathbf{L_3}$-$\mathbf{TQPr_2}$ gave better enantioselectivity and yield than the ligands bearing other amino acid backbones (Table 4, entries 5–8). When the alkyl chain between the two amine-oxides changed from three carbons ($\mathbf{L_3}$-$\mathbf{TQPr_2}$) to four carbons ($\mathbf{L_4}$-$\mathbf{TQPr_2}$), the enantioselectivity increased to 88% ee (entry 9). Finally, the combination of $\mathbf{L_4}$-$\mathbf{TQPr_2}$ with $Ni(NTf_2)_2$ well promoted the [3,3]-

Table 3 Substrate scope for indanonecarbonyl compounds bearing substituted styrene derivatives[a]



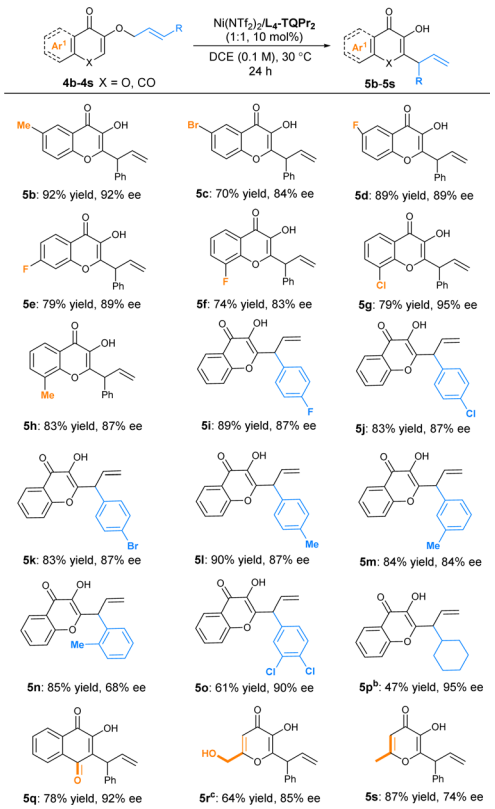
[a] Unless otherwise noted, all reactions were carried out with $Co(OTf)_2$/$\mathbf{L_3}$-$\mathbf{PrEt_3}$ (1 : 1, 10 mol%), **1** (0.1 mmol) in DCE (0.1 M) at 50 °C for 24 h; then *o*-phenylenedianmine (1.5 equiv.) at 30 °C for 15 min. Isolated yield of **3**. ee determined by UPC[2] analysis. [b] 72 h. [c] At 40 °C. [d] At 30 °C. [e] $\mathbf{L_3}$-$\mathbf{PrPr_2}$ as the ligand.

Table 4 Optimization of the reaction conditions of [3,3]-rearrangement[a]



[a] Unless otherwise noted, all reactions were carried out with M/L (1 : 1, 10 mol%), **4a** (0.1 mmol) in DCE (0.1 M) at 30 °C for 12 h; isolated yield of the product **5a**. ee determined by HPLC analysis. [b] *ent*-**5a** was the major. [c] $Ni(NTf_2)_2$ was used.

Table 5 Scope of allylic ethers of 3-hydroxychromones for [3,3]-rearrangement[a,b]



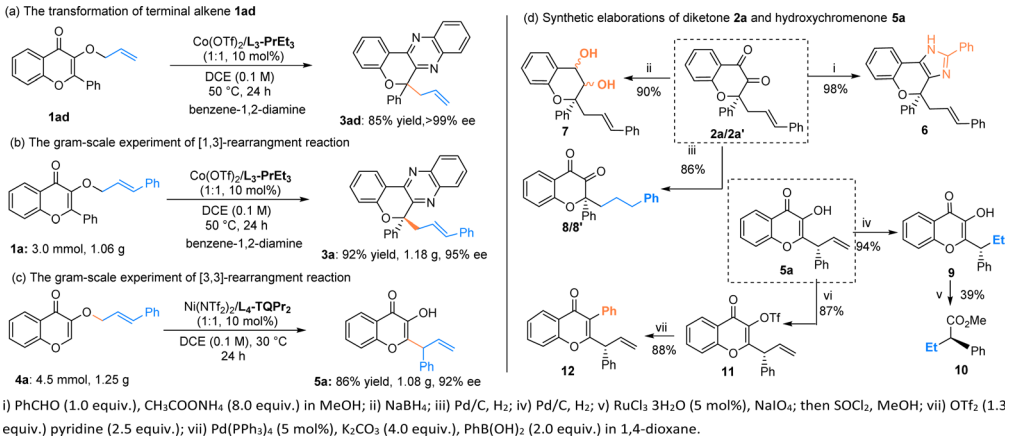
[a] Unless otherwise noted, all reactions were carried out with $Ni(NTf_2)_2$/**L_4-TQPr$_2$** (1 : 1, 10 mol%), **4** (0.1 mmol) in DCE (0.1 M) at 30 °C for 24 h. Isolated yield of product **5**. ee determined by HPLC analysis. [b] 72 h. [c] At 40 °C.

rearrangement at 30 °C, affording 2-substituted 3-hydroxychromone **5a** in 92% yield, with 92% ee (entry 10).

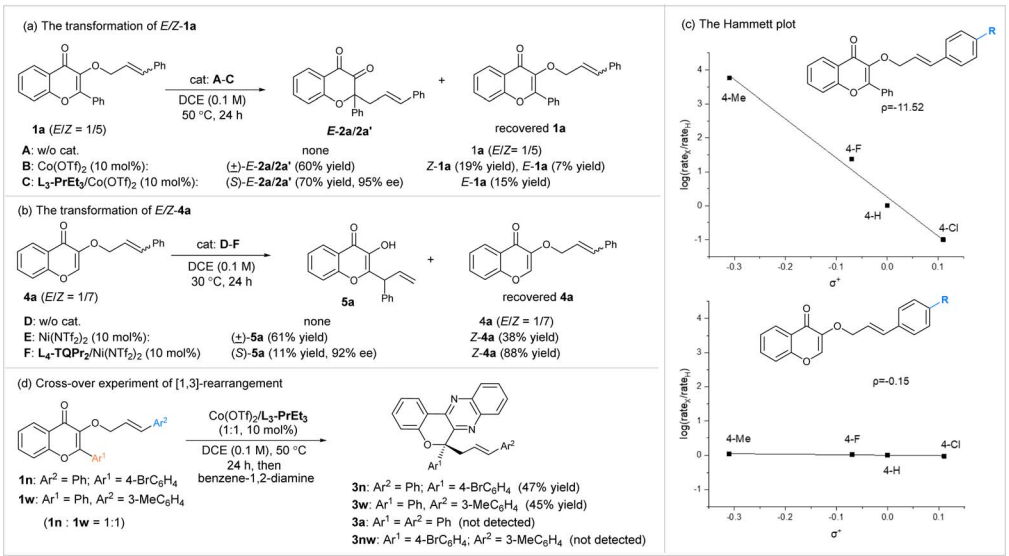
Subsequently, the scope of enantioselective [3,3]-rearrangement was systematically investigated (Table 5). It gave access to a wide range of 2-(1-phenylallyl)-substituted 3-hydroxyl-4*H*-chromen-4-ones (**5b–5h**) in good yields (70–92%) with good enantioselectivities (83–92% ee). Unlike [1,3]-rearrangement, the different substituents at the cinnamyl groups had little influence on yield or ee value in [3,3]-rearrangement. Good yields (83–90%) and enantioselectivities (84–87% ee) were obtained when cinnamyl groups were used bearing different substituents at the *para*- and *meta*-positions of the aryl group (**5i–5m**). The *ortho*-methyl substituted ether **4n** reacted smoothly to afford **5n** in 85% yield with medium enantioselectivity (68% ee). A 3,4-dichlorophenyl-containing substrate was also compatible to give **5o** in 61% yield with 90% ee. We also tested 3-cyclohexylallyl ether **4o**, which showed a lower reactivity (47% yield) but good enantioselectivity (95% ee) after a longer reaction time. Furthermore, other important compounds derived from kojic acid (**5q**), allomaltol (**5r**) and lawsone (**5s**) could be efficiently constructed in good yields (64–87%) and enantioselectivities (74–92% ee).

The allyl flavonol ether **1ad** which has been studied by Porco's group[10] was also tested, and the desired product **3ad** was obtained with excellent yield (85%) and enantioselectivity (>99% ee) (Scheme 2a). The two kinds of rearrangement can be easily scaled up, as demonstrated for **1a** (3.0 mmol) in Scheme 2b and 4a (4.5 mmol) in Scheme 2c. Other chromone derivatives could be obtained through synthetic elaboration (Scheme 2d). Besides transformation into quinoxaline, a mixture of diketone **2a** and ketal **2a**′ could also be smoothly converted to imidazole **6** in 98% yield, and to diol **7** *via* selective reduction with $NaBH_4$, as well as 2-phenyl-2-alkyl substituted diketone **8** and its ketal form upon reduction. 1-Phenylpropanyl substituted 3-hydroxychromone **9** could be obtained after reduction by H_2 and Pd/C, which was converted to known methyl 2-phenylbutanoate **10** by successive oxidative fragmentation ($RuCl_3$/$NaIO_4$) and esterification reactions. The absolute configuration of **10** was assigned by comparison of the optical rotation with known data;[20] thus the absolute configuration of product **5a** was assigned as R. Additionally, 2,3-disubstituted 4*H*-chromen-4-one **12** could be readily obtained *via* Suzuki coupling, forming the triflate derivative **11**.

In order to understand the mechanistic profile of the regioselective rearrangement, we set out control experiments (Scheme 3). First, the effect of *E*/*Z* cinnamyl substitution on the performance was investigated. It was found that without a catalyst, *Z*-dominated **1a** (*E*/*Z* = 1/5) did not undergo the rearrangement (Scheme 3a condition A). While the same [1,3]-rearrangement *E*-products, which are the thermodynamically stable isomers, were found from *Z*-dominated **1a** (*E*/*Z* = 1/5) with comparable yield and enantioselectivity by the use of a $Co(OTf)_2$ or chiral **L_3-PrEt$_3$**/$Co(OTf)_2$ catalyst (Scheme 3a, conditions B and C). It is notable that the *E*/*Z* configuration of the cinnamyl unit changed during the [1,3]-rearrangement, which is consistent with a non-concerted step. In contrast, [3,3]-rearrangement product **5a** was observed from *Z*-dominated **4a** (*E*/*Z* = 1/7), but with decreased conversion, especially in the presence of a chiral **L_4-TQPr$_2$**/$Ni(NTf_2)_2$ catalyst (Scheme 3b,



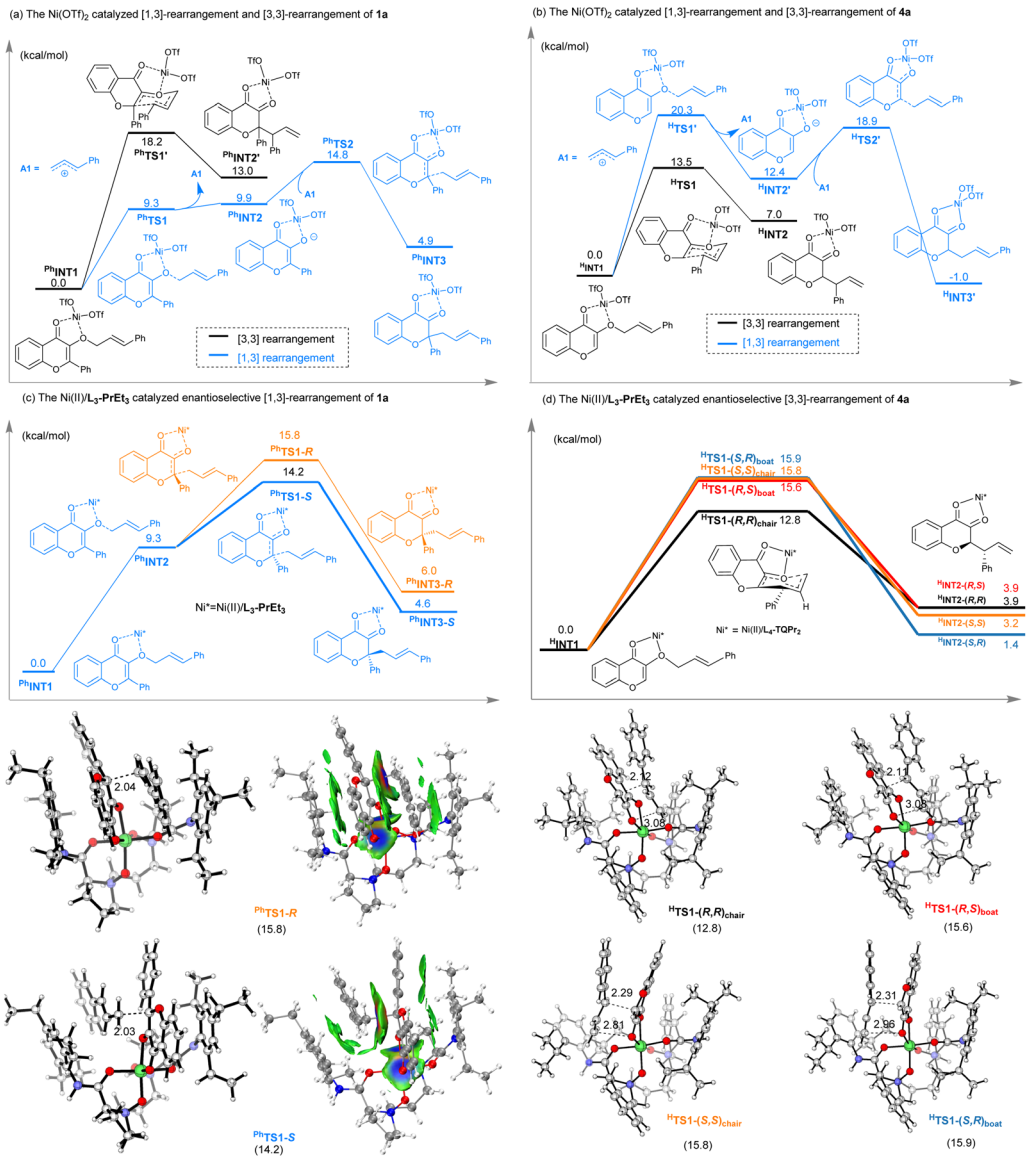
Scheme 2 The gram-scale experiment and synthetic elaborations.



Scheme 3 Control experiments for mechanism study.

conditions E and F). *Z*/*E* selectivity of the recovered reactant revealed the configuration preference for *E*-**4a** over *Z*-**4a** in the rearrangement, and in the presence of the chiral catalyst *Z*-**4a** was fully recovered. This indicates that the [3,3]-rearrangement likely undergoes a concerted pathway, and the cyclic transition states are under the influence of the interaction of the subunits of the reactants, as well as with the chiral catalysts. Next, Hammett plots were carried out to probe into the electronic effect of substitution on the cinnamyl group on the reactivity (Scheme 3c). For the [1,3]-rearrangement reaction, the Hammett plot of $\log(k_X/k_H)$ against substituent constant σ_p^+ for the reaction of *para*-substituted cinnamyl flavonol ethers **1** gave a straight line with good correlation. The negative slope ($\rho = -11.52$) strongly suggests that the [1,3]-rearrangement is more likely to proceed through an ion-pair mechanism, and an electron-donating group accelerates the reaction, probably due to stabilizing the allyl cation intermediate. Instead, a relatively smaller slope ($\rho = -0.15$) was observed in Hammett studies of [3,3]-rearrangement,[21] indicting concerted Claisen rearrangement. Furthermore, a crossover reaction was conducted with two different cinnamyl flavonol ethers for [1,3]-rearrangement (Scheme 3d), and no crossover products were detected, supporting a tight pair pathway.

DFT calculations were carried out to elucidate the substrate-dependent regioselective [1,3]- and [3,3]-rearrangement. The discussion here is based on the data calculated on the B3LYP-D3/def2-TZVP(SMD)//B3LYP-D3/6-31G(d)~SDD(Co) level of theory (see the ESI† for more details). Firstly, we performed computations on [1,3]- and [3,3]-rearrangements catalyzed by $Ni(OTf)_2$. For 2-phenyl substituted **1a** (Scheme 4a), in the proposed chair-like transition state (^{Ph}**TS1**′), the steric repulsion between 2-aryl substituent and cinnamyl group caused the energy barrier of [3,3]-rearrangement to be much higher. However, a 2-aryl substituent could stabilize the negative charge of enolate ^{Ph}**INT2**; the energy barrier for the [1,3]-rearrangement is lower than that of [3,3]-rearrangement (14.8 kcal mol^{-1} *vs.* 18.2 kcal mol^{-1}). Furthermore, the free energy profile of the enantioselective version in the case of the Ni(II)/**L$_3$-PrEt$_3$**-



Scheme 4 The possible catalytic cycle and asymmetric catalytic modes.

catalyzed [1,3]-rearrangement reaction of **1a** is shown in Scheme 4c. The energy barrier for the formation of the *S*-product is 1.6 kcal mol^{-1} lower than that of the *R*-product due to the stronger π–π interaction between the Lewis-acid-stabilized enolate and an allyl cation pair intermediate. The expected ee value is 87%, consistent with the experimental results.

Conversely, for 2-unsubstituted reactant **4a** (Scheme 4b), the energy barrier for the [3,3]-rearrangement is lower than that of [1,3]-rearrangement (13.5 kcal mol^{-1} *vs.* 20.3 kcal mol^{-1}). In the case of the Ni(II)/**L$_4$-TQPr$_2$**-catalyzed enantioselective [3,3]-rearrangement reaction of **4a**, four possible transition states to give the final product with one stereocenter are compared (Scheme 4d). The energy barrier for the formation of the *R* configuration *via* a chair-type transition state (^{Ph}**TS1-(*R*,*R*)$_{chair}$**) is 2.8 kcal mol^{-1} lower than that of the *S*-configuration-based boat-type transition state (^{Ph}**TS1-(*R*,*S*)$_{boat}$**).

Conclusions

In summary, we have achieved a regioselective asymmetric O-to-C-rearrangement of 3-allyloxy-4*H*-chromenones and their analogues. The [1,3]- and [3,3]-rearrangements are affected by substitution on the substrates, which resulted in biased steric hindrance and stability of the intermediates. Nonetheless, both processes could be realized in good yield and enantioselectivity after the chiral *N*,*N*′-dioxide/metal complex catalysts were adjusted slightly, meeting the requirements of the different mechanisms. The protocol enabled access to a number of 3-hydroxyl pyranone and benzopyranone derivatives. Systematic mechanistic studies and DFT calculation revealed the reasons for the regioselectivity and stereoselectivity, which provided guidance and reference for regioselective asymmetric O-to-C [1,3] and [3,3]-rearrangement of allyl vinyl ether. Further

investigations on other types of asymmetric rearrangements are currently underway.

Data availability

Further details of the experimental procedure, ^{1}H, $^{13}C\{^{1}H\}$ and $^{19}F\{^{1}H\}$ NMR, HPLC spectra, X-ray crystallographic data and details of the computational studies are available in the ESI.†

Author contributions

Y. L., Q. T., K. X. L. and Q. C. L. preformed the experiments. L. C. N. conducted the DFT calculation. B. Q. Y. reproduced the data. X. M. F. and X. H. L. supervised the project. Y. L. and X. H. L. co-wrote the manuscript.

Conflicts of interest

There are no conflicts to declare.

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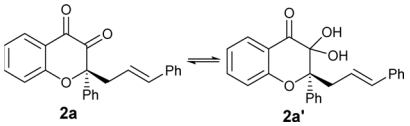
Notes and references

1 (*a*) C. M. Rojas, *Molecular Rearrangement in Organic Synthesis*, Wiley, Hoboken, 2015; (*b*) J. P. Zhu, *Eur. J. Org Chem.*, 2019, 1964.
2 Y. B. Liu, X. H. Liu and X. M. Feng, *Chem. Sci.*, 2022, 12290.
3 K. Nonoshita, H. Banno, K. Maruoka and H. Yamamoto, *J. Am. Chem. Soc.*, 1990, **112**, 316.
4 P. A. Grieco, J. D. Clark and C. T. Jagoe, *J. Am. Chem. Soc.*, 1991, **113**, 5488.
5 (*a*) A. Gansäuer, D. Fielenbach and C. Stock, *Adv. Synth. Catal.*, 2002, **344**, 845; (*b*) A. Gansäuer, D. Fielenbach, C. Stock and D. Geich-Gimbel, *Adv. Synth. Catal.*, 2003, **345**, 1017.
6 C. G. Nasveschuk and T. Rovis, *Org. Lett.*, 2005, **7**, 2173.
7 For asymmetric 3,3-rearrangement reaction examples: (*a*) L. Abraham, R. Czerwonka and M. Hiersemann, *Angew. Chem., Int. Ed.*, 2001, **40**, 4700; (*b*) M. Rueping and A. P. Antonchick, *Angew. Chem., Int. Ed.*, 2008, **47**, 10090; (*c*) M. Rueping and A. P. Antonchick, *Angew. Chem.*, 2008, **120**, 10244; (*d*) H. Ren and W. D. Wulff, *J. Am. Chem. Soc.*, 2011, **133**, 5656. For asymmetric 1,3-rearrangement reaction examples: (*e*) M. Terada and Y. Toda, *J. Am. Chem. Soc.*, 2009, **131**, 6354; (*f*) M. Terada, T. Komuro, Y. Toda and T. Korenaga, *J. Am. Chem. Soc.*, 2014, **136**, 7044; (*g*) A. B. Gade, P. N. Bagle, P. S. Shinde, V. Bhardwaj, S. Banerjee, A. Chande and N. T. Patil, *Angew. Chem., Int. Ed.*, 2018, **57**, 5735.
8 Y. L. Zhang and Y. S. Chen, *Org. Chem. Front.*, 2022, **9**, 4744.
9 T. Rodrigues, D. Reker, P. Schneider and G. Schneider, *Nat. Chem.*, 2016, **8**, 531.
10 C. Qi, Y. Xiong, V. Eschenbrenner-Lux, H. Cong and J. A. Porco Jr, *J. Am. Chem. Soc.*, 2016, **138**, 798.
11 X. Sheng, X. Y. Jia, F. Tang, Y. Wang and A. J. Hou, *Tetrahedron*, 2017, **73**, 3485.
12 P. A. Wender, N. D'Angelo, V. I. Elitzin, M. Ernst, E. E. Jackson-Ugueto, J. A. Kowalski, S. McKendry, M. Rehfeuter, R. Sun and D. Voigtlaender, *Org. Lett.*, 2007, **9**, 1829.
13 J. Marié, Y. Xiong, K. Min, A. R. Yeager, T. Taniguchi, N. Berova, S. E. Schaus and J. A. Porco Jr, *J. Org. Chem.*, 2010, **75**, 4584.
14 (*a*) J. Kaeobamrung, J. Mahatthananchai, P. Zheng and J. W. Bode, *J. Am. Chem. Soc.*, 2010, **132**, 8810; (*b*) J. Mahatthananchai, P. Zheng and J. W. Bode, *Angew. Chem., Int. Ed.*, 2011, **50**, 1673; (*c*) J. Mahatthananchai, J. Kaeobamrung and J. W. Bode, *ACS Catal.*, 2012, **2**, 494; (*d*) J. Mahatthananchai and J. W. Bode, *Acc. Chem. Res.*, 2014, **47**, 696.
15 K. Dzieszkowski, M. Słotwiński, K. Rafińska, T. M. Muzioł and Z. Rafiński, *Chem. Commun.*, 2021, **57**, 9999.
16 L. Yao and K. Ishihara, *Chem. Sci.*, 2019, **10**, 2259.
17 For related examples: (*a*) Y. B. Liu, H. P. Hu, H. F. Zheng, Y. Xia, X. H. Liu, L. L. Lin and X. M. Feng, *Angew. Chem., Int. Ed.*, 2014, **53**, 11579; (*b*) Y. B. Liu, X. H. Liu, H. P. Hu, J. Guo, Y. Xia, L. L. Lin and X. M. Feng, *Angew. Chem., Int. Ed.*, 2016, **55**, 4054; (*c*) J. Li, L. L. Lin, B. W. Hu, P. F. Zhou, T. Y. Huang, X. H. Liu and X. M. Feng, *Angew. Chem., Int. Ed.*, 2017, **56**, 885; (*d*) H. F. Zheng, Y. Wang, C. R. Xu, X. Xu, L. L. Lin, X. H. Liu and X. M. Feng, *Nat. Commun.*, 2018, **9**, 1968; (*e*) Y. S. Chen, S. X. Dong, X. Xu, X. H. Liu and X. M. Feng, *Angew. Chem., Int. Ed.*, 2018, **57**, 16554; (*f*) L. Wang, P. F. Zhou, Q. C. Lin, S. X. Dong, X. H. Liu and X. M. Feng, *Chem. Sci.*, 2020, **11**, 10101; (*g*) X. B. Lin, Z. Tan, W. K. Yang, W. Yang, X. H. Liu and X. M. Feng, *CCS Chem.*, 2021, **3**, 1423; (*h*) L. Wang, Y. Q. Zhou, Z. S. Su, F. C. Zhang, W. D. Cao, X. H. Liu and X. M. Feng, *Angew. Chem., Int. Ed.*, 2022, **61**, e202211785; (*i*) Y. Liu, Y. S. Chen, A. Y. Yihuo, Y. Zhou, X. H. Liu, L. L. Lin and X. M. Feng, *ACS Catal.*, 2022, **12**, 1784; (*j*) L. F. Hu, J. Z. Li, Y. Y. Zhang, X. M. Feng and X. H. Liu, *Chem. Sci.*, 2022, **13**, 4103. For reviews on chiral *N*,*N*′-dioxides: (*k*) X. H. Liu, L. L. Lin and X. M. Feng, *Acc. Chem. Res.*, 2011, **44**, 574; (*l*) X. H. Liu, L. L. Lin and X. M. Feng, *Org. Chem. Front.*, 2014, **1**, 298; (*m*) X. H. Liu, H. F. Zheng, Y. Xia, L. L. Lin and X. M. Feng, *Acc. Chem. Res.*, 2017, **50**, 2621; (*n*) X. H. Liu, S. X. Dong, L. L. Lin and X. M. Feng, *Chin. J. Chem.*, 2018, **36**, 791; (*o*) Z. Wang, X. H. Liu and X. M. Feng, *Aldrichimica Acta*, 2020, **53**, 3; (*p*) M. Y. Wang and W. Li, *Chin. J. Chem.*, 2021, **39**, 969.
18 The equilibrium between **2a** and **2a′**, for detail see ESI†.



19 CCDC 2204539 (for **3k**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre.†
20 (*a*) G. Sarakinos and E. J. Corey, *Org. Lett.*, 1999, **11**, 1741; (*b*) Y. Zhang, Z. B. Han, F. Y. Li, K. L. Ding and A. Zhang, *Chem. Commun.*, 2010, **46**, 156; (*c*) J. Y. Mao, F. P. Liu, M. Wang, L. Wu, B. Zheng, S. Z. Liu, J. C. Zhong, Q. H. Bian and W. J. Patrick, *J. Am. Chem. Soc.*, 2014, **136**, 17662; (*d*) F. Malmedy and T. Wirth, *Chem.–Eur. J.*, 2016, **22**, 16072.
21 N. F. O'Rourke and J. E. Wulff, *Org. Biomol. Chem.*, 2014, **12**, 1292.