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Transfer-catalyst-free biomimetic asymmetric reduction of 3-sulfonyl coumarins with a regenerable NAD(P)H model†

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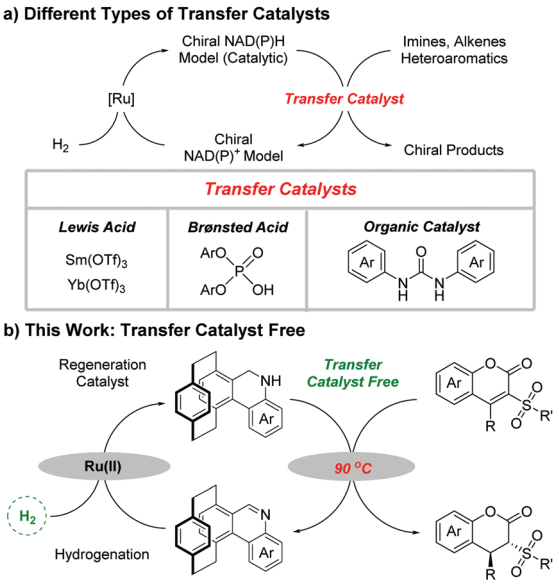
A novel transfer-catalyst-free biomimetic reduction of the tetrasubstituted olefins 3-sulfonyl coumarins with the chiral and regenerable [2.2]paracyclophane-based NAD(P)H model CYNAM has been developed, affording chiral 3-sulfonyl dihydrocoumarins with excellent enantioselectivities.

The biomimetic asymmetric reduction (BMAR) based on NAD(P)H models stands out owing to its combination of the advantages of enzyme catalysis and chemical catalysis, making the synthesis more accurate, efficient and mild. This synthesis plays an important role in the development of novel agrochemicals, pharmaceuticals and materials.[1] In the past few decades, three generations of BMAR reactions with NAD(P)H models as the core have been developed, and here the selection of transfer catalyst is very important according to the NAD(P)H model with different structures. In the first generation of stoichiometric NAD(P)H models, such as Hantzsch esters (HEH)[2] and chiral nicotinamide derivatives,[3] *in situ* regeneration of these models was not achieved, and the main transfer catalysts used were the chiral organocatalysts[4] and metal catalysts or reagents.[5] After realizing the *in situ* regeneration of NAD(P)H models,[6] the second generation based on achiral dihydrophenanthridine (DHPD) was developed. Chiral Brønsted acids such as phosphoric acids[7] have been selected as the transfer catalyst to realize the BMAR of imines and heteroaromatics. For the third generation, in 2019, Zhou and coworkers reported the BMAR of alkenes, imines and heteroaromatics with the regenerable and chiral ferrocene-based NAD(P)H model FENAM, an achiral Lewis acid containing rare-earth metal or an achiral Brønsted acid (phosphoric acid) as the transfer catalyst.[8a–c] Meanwhile, using the organic catalyst urea as the transfer catalyst can also effectively realize the BMAR of heteroaromatics.[8d] With the help of the more efficient [2.2]paracyclophane-based NAD(P)H model (abbreviated as CYNAM), Zhou and coworkers realized the BMAR of flavonoids and 2,3-disubstituted inden-1-ones using, respectively, a Lewis acid[8e] ($Sm(OTf)_3$) and Brønsted acid[8f] (*p*-toluenesulfonic acid monohydrate) as the transfer catalyst (Scheme 1a). Thus, properly choosing the transfer catalyst is essential for extending the substrate scope of the BMAR.

Optically active 3,4-dihydrocoumarins and their derivatives constitute an important structural motif and are widely found in various natural products, bioactive molecules and drugs[9] and exhibit various significant bioactivities such as anti-HIV,[10a] antiherpetic,[10b] protein kinase[10c] and aldose reductase inhibition,[10d] anti-cancer,[10e] and anti-inflammatory activities.[10f] Sulfonyl groups in organic compounds constitute another class of intriguing functional groups and play a key role in changing physical and chemical properties



Scheme 1 The transfer catalysts in biomimetic asymmetric reductions based on chiral and regenerable NAD(P)H models.

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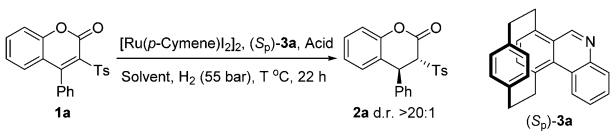
of biological targets due to their strong binding to these targets.[11] Therefore, the BMAR of 3-sulfonyl coumarins through the regulation of the transfer catalyst has great potential for achieving efficient syntheses of chiral 3,4-disubstituted dihydrocoumarins. In the work described in this article, we realized the first transfer-catalyst-free BMAR of tetrasubstituted olefins, 3-sulfonyl coumarins, with the chiral and regenerable NAD(P)H model CYNAM (Scheme 1b).

At the outset, we chose the tetrasubstituted olefin 3-sulfonyl coumarin **1a** as a model substrate. As described in the previous work of our group, in the presence of the Lewis acid or Brønsted acid as the transfer catalyst, the reduction was carried out in ethyl acetate (entries 1 and 2, Table 1). Surprisingly, there was no desired product obtained when the Brønsted acid PTSA was used as the transfer catalyst (<5% conv., entry 1, Table 1). When PTSA was replaced with the Lewis acid $Sm(OTf)_3$, the target product was obtained, but with an unsatisfactory enantioselectivity (29% conv., 63% ee, entry 2, Table 1). Subsequently, further optimization of solvent was conducted; the results suggested that benzotrifluoride was optimal (entries 2–6, Table 1). To further improve the activity and enantioselectivity, a variety of Lewis acids were investigated (entries 6–9, Table 1). Generally, low conversions were observed. An excellent 96% ee was obtained using $Mg(OTf)_2$, albeit with a low 14% conversion. Next, we decided to raise the reaction temperature to solve the problem of poor activity, albeit with the risk of lowering the enantioselectivity. It was fortunate that as the temperature was increased, the activity increased while good enantioselectivity was also maintained (entries 9–12, Table 1). Then, the investigation of the background reaction was initiated. To our surprise, without the transfer catalyst $Mg(OTf)_2$, the biomimetic asymmetric reduction could proceed smoothly with only a slight decrease in activity (70% conversion) and even an increase in enantioselectivity (97% ee, entry 13, Table 1). Increasing the amount of the ruthenium complex regeneration catalyst was found to improve the activity (up to 73% conv.), and a dosage of 1.5 mol% provided the best results (entries 13–16, Table 1). Additionally, in the absence of the NAD(P)H model CYNAM, the reduction did not occur (entry 17, Table 1), indicating that the reaction did not undergo the direct ruthenium-catalyzed hydrogenation process.

To further improve the activity, we investigated the effect of using different NAD(P)H CYNAM models on enantioselectivity and activity (entries 1–3, Table 2). Although excellent enantioselectivity was achieved while the activity was further improved, the substrate apparently could still not be fully converted. Subsequently, we found that the more electron rich the CYNAM, the higher the activity. Thus, the more electron-rich CYNAM (S_p)-**3d** containing two electron-donating methoxy groups was designed and synthesized (for details, see ESI†). As expected, the activity in this case was significantly increased (entry 4, Table 2). Finally, testing various temperatures suggested that 90 °C was optimal with regards to enantioselectivity and activity (entries 4–6, Table 2). An excellent isolated yield of **2a** (0.15 mmol) was achieved by increasing the reaction time from 22 h to 28 h (99% yield, entry 7, Table 2). Thus, the optimal reaction conditions were determined to involve the use of 3-sulfonyl coumarin **1** (0.15 mmol), $[Ru(p\text{-cymene})I_2]_2$ (1.5 mol%), CYNAM (S_p)-**3d** (10 mol%), H_2 (55 bar),and benzotrifluoride (3 mL) at 90 °C for 28 h.

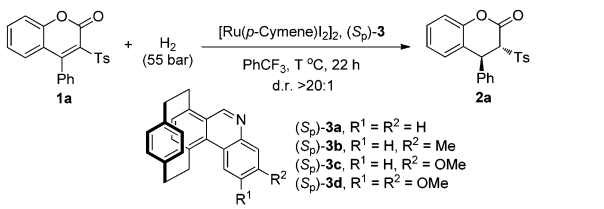
Table 1 Optimization of the reaction conditions



Entry[a]	Acid	Solvent	T (°C)	Conv.[b] (%)	ee[c] (%)
1	PTSA	EA	50	<5	—
2	$Sm(OTf)_3$	EA	50	29	63
3	$Sm(OTf)_3$	DCM	50	11	73
4	$Sm(OTf)_3$	THF	50	22	50
5	$Sm(OTf)_3$	Toluene	50	16	57
6	$Sm(OTf)_3$	$PhCF_3$	50	61	74
7	$Er(OTf)_3$	$PhCF_3$	50	64	73
8	$La(OTf)_3$	$PhCF_3$	50	12	91
9	$Mg(OTf)_2$	$PhCF_3$	50	14	96
10	$Mg(OTf)_2$	$PhCF_3$	70	32	96
11	$Mg(OTf)_2$	$PhCF_3$	90	39	96
12	$Mg(OTf)_2$	$PhCF_3$	110	78	95
13	—	$PhCF_3$	110	70	97
14[d]	—	$PhCF_3$	110	71	97
15[e]	—	$PhCF_3$	110	73	97
16[f]	—	$PhCF_3$	110	73	97
17[eg]	—	$PhCF_3$	110	<5	—

[a] Reactions were carried with **1a** (0.10 mmol), $[Ru(p\text{-cymene})I_2]_2$ (0.5 mol%), (S_p)-**3a** (10 mol%), Lewis acid (20 mol%), Brønsted acid (4 mol%), solvent (2 mL), and H_2 (55 bar), at the indicated temperature for 22 h. [b] Conversion and diastereoselectivity were determined from analysis of ^1H NMR spectra. [c] Determined using chiral HPLC. [d] $[Ru(p\text{-cymene})I_2]_2$ (1.0 mol%). [e] $[Ru(p\text{-cymene})I_2]_2$ (1.5 mol%). [f] $[Ru(p\text{-cymene})I_2]_2$ (2.0 mol%). [g] Without (S_p)-**3a**. PTSA denotes *p*-toluenesulfonic acid monohydrate. EA denotes ethyl acetate. DCM denotes dichloromethane. THF denotes tetrahydrofuran. $PhCF_3$ denotes benzotrifluoride.

Table 2 Optimization of the NAD(P)H models and temperature

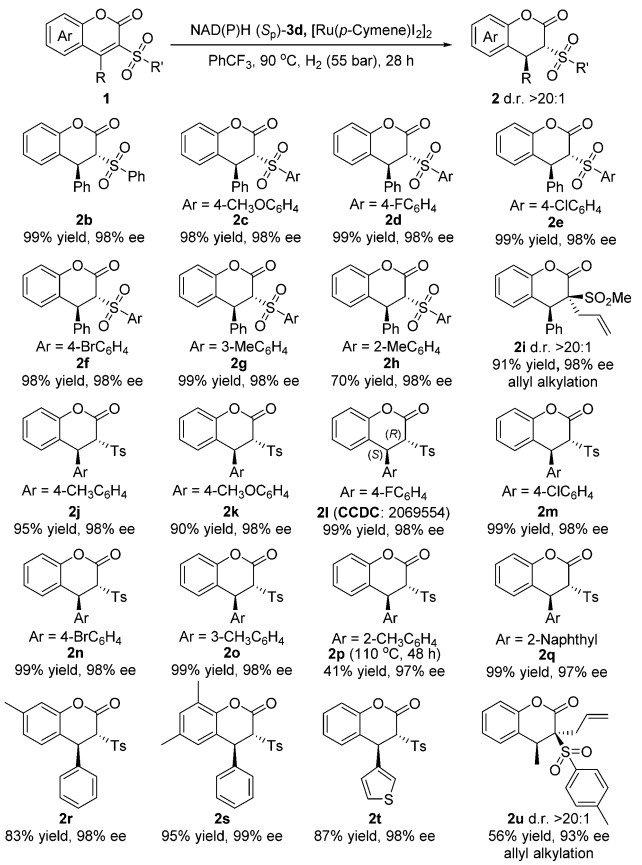


Entry[a]	Model	T (°C)	Conv.[b] (%)	ee[c] (%)
1	(S_p)-**3a**	110	73	97
2	(S_p)-**3b**	110	82	97
3	(S_p)-**3c**	110	93	98
4	(S_p)-**3d**	110	>95	98
5	(S_p)-**3d**	90	96	98
6	(S_p)-**3d**	70	78	98
7	(S_p)-**3d**	90	99[d]	98

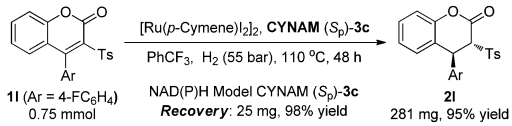
[a] Reactions were carried with **1a** (0.10 mmol), (S_p)-**3** (10 mol%), $[Ru(p\text{-cymene})I_2]_2$ (1.5 mol%), benzotrifluoride (2 mL), and H_2 (55 bar) at the indicated temperature for 22 h. [b] Conversion and diastereoselectivity were determined from ^1H NMR analysis. [c] Determined using chiral HPLC. [d] Isolated yield on 0.15 mmol scale and 28 h.

With the optimal conditions in hand, the substrate scope of the transfer-catalyst-free biomimetic asymmetric reduction of 3-sulfonyl coumarins **1** was investigated (Scheme 2). First, various sulfonyl groups were examined. High yields and enantio- and diastereoselectivities were obtained (**2a–2h**). However, due to the low steric hindrance of methane sulfonyl, the diastereoselectivity when using this group was reduced to 10 : 1, the diastereomers apparently could not be not isolated using column chromatography, and the optical purity apparently could not be determined accurately. Fortunately, after performing allyl alkylation, the single chiral product **2i** was obtained in good yield, enantioselectivity and diastereoselectivity. Single chiral products can be obtained.

Furthermore, the reaction was found to tolerate an array of functional groups on the aromatic ring (**2j–2q**), including both electron-donating and electron-withdrawing substituents. Note that the *o*-tolyl substituent (**2p**) showed a relatively obvious steric effect, in turn decreasing the yield to 24%. We tested increasing the temperature to 110 °C and increasing the reaction time to 48 h. Unfortunately, the yield here only increased to 41% and the enantioselectivity decreased to 97% ee. Examples of different substituents on the fused aromatic ring were also tested, and they all yielded excellent results (**2r–2s**). Meanwhile, this methodology was also compatible with heteroaryl-substituted substrates (**2t**). The reaction with a substrate containing a methyl group substituted at the 4-position showed only a moderate yield (72%) and diastereoselectivity (10 : 1) with a little loss of enantioselectivity (94% ee). After allyl alkylation, the single chiral product **2u** was obtained in 56% yield and 93% ee. The absolute configuration of **2l** was assigned as (3*R*,4*S*) according to its X-ray diffraction analysis (see ESI† and note deposition of X-ray results at the CCDC with the identification number 2069554†).



Scheme 2 Substrate scope.



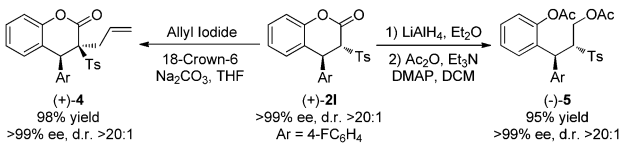
Scheme 3 Recovery of the NAD(P)H model CYNAM.

Owing to the absence of transfer catalyst, the recycling of the NAD(P)H model became much easier. The result was illustrated by the example of the biomimetic asymmetric reduction of **1l** catalyzed by CYNAM (S_p)-**3c** (Scheme 3). The NAD(P)H model CYNAM (S_p)-**3c** was recovered with 98% yield.

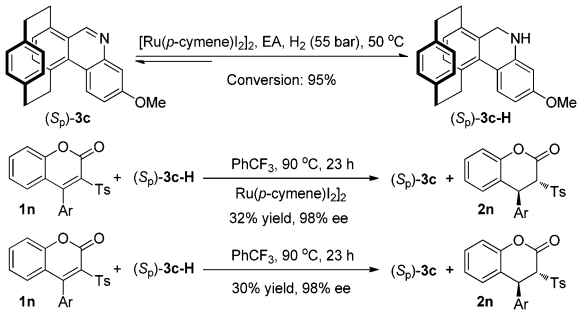
To investigate the utility of this methodology, **2l** was further modified (Scheme 4). First, a quaternary stereocenter was constructed by alkylating **2l** in 98% yield with high diastereoselectivity and enantioselectivity. Additionally, reduction of the lactone of **2l** produced the corresponding diol, and protection of this diol with an acetyl group delivered **5** in 95% yield.

To investigate the role of the ruthenium complex, control experiments were carried out, as summarized in Scheme 5. The NAD(P)H model (CYNAM (S_p)-**3c**) was regenerated by using H_2 and $[Ru(p\text{-cymene})I_2]_2$. Generally, the ruthenium complex was a Lewis acid, which might have acted as a transfer catalyst to accelerate the reduction process. To shed light on the function of the ruthenium complex, two control experiments were conducted using a stoichiometric amount of (S_p)-**3c-H** as the hydrogen source (Scheme 5). The experimental results indicated that inclusion of the ruthenium complex was not necessary for the hydride transfer process to proceed, and the enantiocontrol derived from NAD(P)H model. The low yield was mainly ascribed to the instability of (S_p)-**3c-H**, which could be directly dehydroaromatized to (S_p)-**3c**. All in all, the ruthenium complex played a critical role in the regeneration of the NAD(P)H model, but it did not act as a Lewis acid to participate in the transfer process. Based on the above experimental results and our previous work,[8] a plausible mechanism was derived and is illustrated in ESI.†

In conclusion, without the participation of a transfer catalyst, the biomimetic asymmetric reduction of the tetrasubstituted olefins 3-sulfonyl coumarins was successfully realized with chiral and regenerable CYNAM. A broad range of highly diastereo-enriched and enantiomerically enriched 3-sulfonyl



Scheme 4 Transformations of (+)-**2l**.



Scheme 5 Control experiments for determining the role of the Ru complex.

dihydrocoumarins were conveniently prepared with up to yields of 99%, >20 : 1 d.r. and 99% ee. Moreover, due to the absence of transfer catalyst, the NAD(P)H model CYNAM could be completely recovered in a convenient manner, indicating its good application prospects. In addition, successful derivatizations of the product showed its good synthetic multifunctionality. Efforts are underway in our laboratory to expand the applications of the BMAR to other transformations.

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Conflicts of interest

There are no conflicts to declare.

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