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Enantioselective Synthesis of Functionalized 4-Aryl Hydrocoumarins and 4-Aryl Hydroquinolin-2-ones via Intramolecular Vinylogous Rauhut–Currier Reaction of *para*-Quinone Methides

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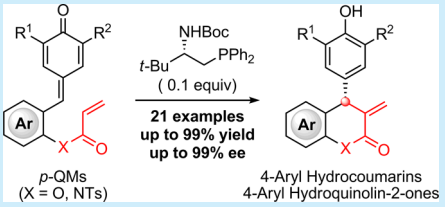
Supporting Information

ABSTRACT: A novel strategy for the asymmetric construction of functionalized 4-aryl-3,4-dihydrocoumarins and 4-aryl-3,4-dihydroquinolin-2-ones via an intramolecular vinylogous Rauhut–Currier reaction of *para*-quinone methides (*p*-QMs) under the bifunctional catalysis of chiral amine-phosphine is described. This intramolecular mode for the catalytic enantioselective 1,6-conjugate addition of *p*-QMs has been explored for the first time, delivering two types of synthetically important heterocycles in high yields and enantioselectivites.



The heterocyclic skeleton with 4-aryl-3,4-dihydrocoumarin or 4-aryl-3,4-dihydroquinolin-2-one exists in many biologically active natural products and pharmaceuticals,[1] exhibiting anticancer[1c] and antibacterial[1e] activities (Figure 1). These

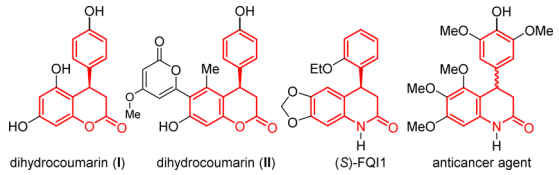
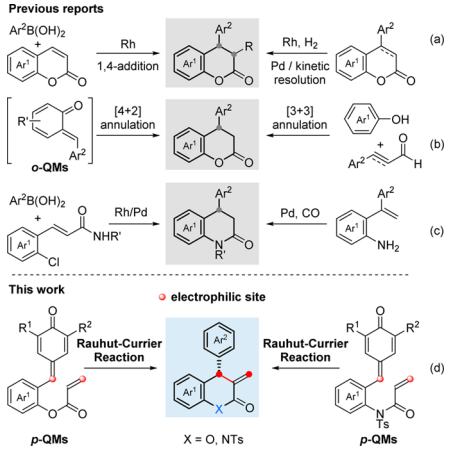


Figure 1. Selected bioactive natural products and pharmaceuticals.

structurally unique scaffolds are also common building blocks in natural product synthesis.[2] Owing to their promising biological profiles as well as synthetic utilities, numerous protocols for the assembly of 4-aryl-3,4-dihydrocoumarins and 4-aryl-3,4-dihdroquinolin-2-ones have been reported.[3,4] Among them, only a handful of approaches have been developed for the catalytic asymmetric version. For example, rhodium-catalyzed 1,4-addition of arylboronic acids with coumarins[5] or asymmetric hydrogenation of 4-aryl coumarins[6] has provided straightforward routes to such types of 4-aryl-3,4-dihydrocoumarins (Scheme 1a). Recently, the Hou group has realized the kinetic resolution of 4-substituted-3,4-dihydrocoumarins via a palladium-catalyzed allylic substitution for optically active *trans*-3,4-disubstituted-dihydrocoumarin derivatives[7] (Scheme 1a). In addition, these skeletons could be also accessed by [4 + 2] annulation of *o*-quinone methides with different two-carbon synthons in the presence of chiral organocatalysts[8] (Scheme 1b). Meanwhile, *N*-heterocyclic carbene-catalyzed annulation of phenols with enals or alkynals has been demonstrated as a valuable method for the generation of 4-substituted-3,4-dihydrocoumarins[9] (Scheme 1b). To our knowledge, however, only two reports have achieved the catalytic asymmetric synthesis of 4-aryl-3,4-dihydroquinolin-2-ones through rhodium/palladium-catalyzed reaction of arylboronic acids with acrylamides[10a] and palladium-catalyzed cyclocarbonylation of 2-vinylanilines,[10b] respectively (Scheme 1c). Thus, it is highly desirable to explore alternative catalytic enantioselective methodologies to construct both 4-aryl-3,4-dihydrocoumarins and 4-aryl-3,4-dihydroquinolin-2-ones.

Scheme 1. Catalytic Enantioselective Approaches



para-Quinone methides (*p*-QMs)[11,12] as vinylogous Michael acceptors have attracted much attention in the synthetic community. To date, 1,6-conjugate addition,[13,14] [2 + 1]-annulation,[15] [3 + 2]-annulation,[16] [4 + 1]-annulation,[17] and [4

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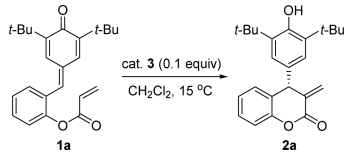
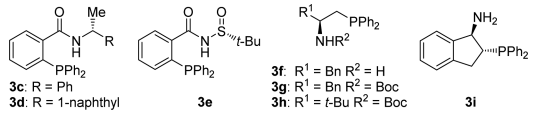
+ 2]-annulation[18] constitute the main context of the methodological studies on *p*-QMs. With our continuing interest in the chemistry of *p*-QMs,[14a,j,k,15c,17a] the installation of an electrophilic allyl ester or allyl amide group at the ortho position on the aromatic ring of *p*-QMs might render the possibility of a new intramolecular Rauhut−Currier reaction,[19,20] which would lead to access to the synthetically important, optically active heterocycles (Scheme 1d). Recently, two reports involving intermolecular Rauhut−Currier-type 1,6-conjugate addition of *p*-QMs with vinyl ketones have been presented by Liu and Zhang[21a] and Wu.[21b] Herein, we described an enantioselective synthesis of functionalized 4-aryl-3,4-dihydrocoumarins and 4-aryl-3,4-dihydroquinolin-2-ones through an unprecedented intramolecular vinylogous Rauhut−Currier reaction of *p*-QMs under the catalysis of nucleophilic chiral phosphines.

We initially conducted the model reaction using *p*-QM ester **1a** in the presence of various chiral phosphine catalysts **3a**−**3i** (Table 1). The *C*2-symmetric chiral catalysts (*R*)-BINAP **3a** and

Table 1. Optimization of Reaction Conditions[a]



entry	catalyst	time (h)	yield (%)[b]	ee (%)[c]
1	**3a** ((*R*)-BINAP)	24	NR	ND
2	**3b** ((*R*,*R*)-DIOP)	12	71	−24
3	**3c**	24	85	24
4	**3d**	24	80	24
5	**3e**	24	NR	ND
6	**3f**	10	85	72
7	**3g**	2.5	98	92
8	**3h**	1	98	98
9	**3i**	24	NR	ND

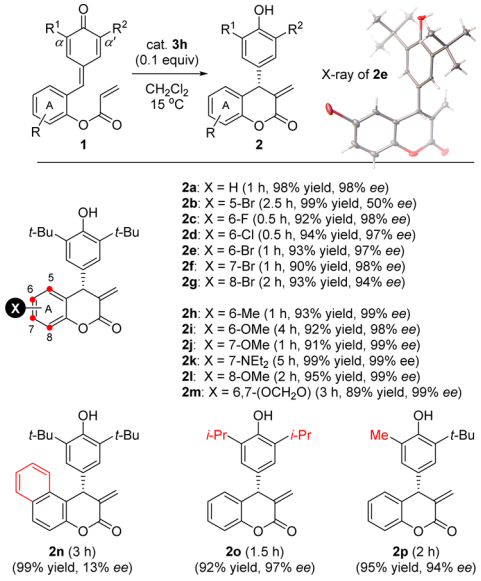


[a]Performed with **1a** (0.1 mmol) and catalyst **3** (0.01 mmol) in CH_2Cl_2 (2.0 mL) at 15 °C. [b]Yield of isolated products. [c]Determined by HPLC.

(*R*,*R*)-DIOP **3b** were first tested in this reaction (entries 1 and 2). Despite no reactivity observed using atropisomeric chiral bis(triaryl)phosphine **3a**, the desired hydrocoumarin **2a** could be obtained in 71% yield, albeit with 24% ee, under the catalysis of centrally chiral phosphine **3b**. To improve the enantioselectivity, we then examined a series of bifunctional amine-phosphine catalysts **3c**−**3i** (entries 3−9). As compared with negative results in the cases employing 1,3-amine-phosphines **3c**−**3e** (entries 3−5), amino acid-derived 1,2-amine-phosphine catalyst **3f** gave dramatically improved enantiocontrol with 72% ee (entry 6). Encouraged by this promising result, two *N*-Boc-1,2-amine-phosphines **3g** and **3h**[22] were further investigated (entries 7 and 8). To our delight, catalyst **3h** with increasing size of the substituent on the chiral center delivered the optimal result (98% yield, 98% ee, entry 8). Notably, cyclic *trans*-1,2-amine-phosphine catalyst **3i** was also surveyed (entry 9), but surprisingly, there was no reaction observed in this case.

With the optimized conditions in hand, we then explored the substrate scope (Scheme 2). A series of *p*-QM esters **1a**−**1m** with

Scheme 2. Substrate Scope of *p*-QM Esters



electronically different substituents on aromatic ring A were first examined, giving the corresponding 4-aryl hydrocoumarins **2a**−**2m** in high yields (89−99% yield) with moderate-to-excellent enantioselectivities (50−99% ee). Notably, while using *p*-QM esters **1b** and **1n** with sterically bulky *ortho*-substituents, the reaction proceeded smoothly to afford **2b** (99% yield) and **2n** (99% yield), respectively, but with a dramatic decrease of enantioselectivities (low to 13% ee). The absolute configuration of **2e** was unambiguously assigned by X-ray crystallographic analysis.[23] In addition, *p*-QM ester **1o** with a less bulky isopropyl group at the α,α'-position could afford desired product **2o** in high yield and enantioselectivity (92% yield, 97% ee). Moreover, a stereoisomeric mixture of **1p** (R^1 = Me, R^2 = *t*-Bu, *E*/*Z* = 1.5:1) was also examined, and product **2p** was readily obtained without a negative influence on both reactivity and enantioselectivity (95% yield, 94% ee).

To further expand the substrate scope of this methodology, various *p*-QM amides **4a**−**4e** were then probed (Scheme 3). Compared with cases using *p*-QM esters (Scheme 2), the reaction of *p*-QM amides with the electron withdrawing *N*-Ts group could generally be completed in 15 min, showing a significant increase in reactivity. *p*-QM amides containing electron-neutral (R = H), electron-withdrawing (R = F), or electron-donating substituents (R = Me, OMe) at the C6 position of aromatic ring A could afford the desired 4-aryl-3,4-dihydroquinolin-2-ones **5a**−**5d** in high yields (up to 98% yield) and excellent enantioselectivities (up to 94% ee). The absolute stereochemsitry of **5a** was clearly determined by X-ray crystallographic analysis.[23] Moreover, when *p*-QM amide **4e** bearing a C7−CF_3 group was exposed to the optimized conditions, product **5e** could be furnished with a satisfactory result (91% yield, 94% ee). It should be noted that substrate **4f** with an electron-donating *N*-methyl group did not undergo the expected intramolecular cyclization, mostly due to the highly decreased electrophilicity of the corresponding *N*-methylated acrylamide moiety.

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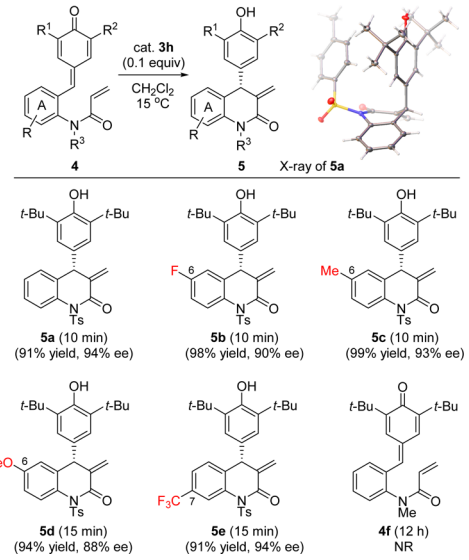
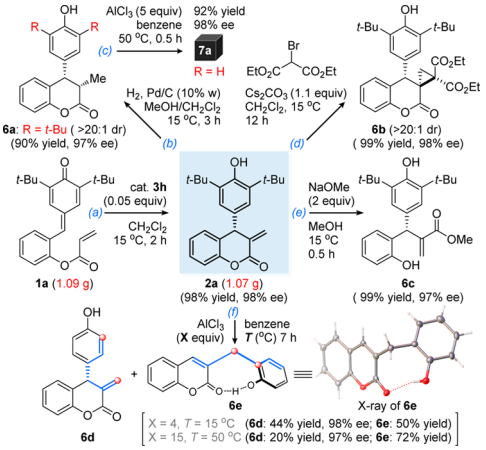
Scheme 3. Substrate Scope of *p*-QM Amides



For the synthetic utility of this protocol to be demonstrated, a gram-scale reaction of **1a** was performed with a lower catalyst loading of **3h** (0.05 equiv) (Scheme 4, route a), and the

Scheme 4. Gram-Scale Synthesis and Its Transformations



hydrocoumarin **2a** was readily obtained (98% yield, 98% ee). With **2a** in hand, its transformations were then explored. A facially selective hydrogenation of **2a** (route b) led to the formation of desired dihydrocoumarin **6a** with vicinal stereocenters (90% yield, >20:1 dr, 98% ee),[24] and pleasingly, $AlCl_3$-mediated de-*tert*-butylation of **6a** (route c) could smoothly give **7a** (92% yield, 98% ee). Moreover, a diastereoselective cyclopropanation of **2a** with 2-bromomalonic ester (route d) proceeded to deliver the spirocycle **6b** (99% yield, >20:1 dr, 98% ee).[24] Furthermore, when **2a** was subjected to NaOMe-promoted alcoholysis (route e), the resulting acyclic product **6c** could be obtained in 99% yield without detectable racemization (97% ee) at the diarylmethine stereocenter. Upon treating **2a** with 4 equiv of $AlCl_3$ at 15 °C (route f), the expected de-*tert*-butylation product **6d** was formed in 44% yield and 98% ee, but interestingly, an unexpected product **6e** resulting from a [3.3] sigmatropic rearrangement was isolated in 50% yield. The structure of **6e** was further assigned by X-ray crystallographic analysis.[23] Notably, while this de-*tert*-butylation was conducted in the presence of an increased amount of $AlCl_3$ (15 equiv) at an enhanced temperature (50 °C), the formation of unusual rearrangement product **6e** could be improved to 72% yield, to some extent demonstrating the positive influence of reaction temperature on such [3.3] sigmatropic rearrangement.

On the basis of the crystallographically determined absolute configurations of products **2e** and **5a**, a tentative model was proposed for the enantiocontrol observed in this reaction (Figure 2). Mechanistically, initial nucleophilic attack of 1,2-amine-

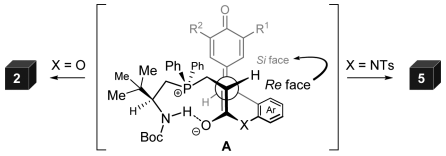


Figure 2. Proposed model for the enantioselectivity.

phosphine catalyst **3h** on the acrylate moiety of *p*-QMs provided the zwitterionic intermediates **A** stabilized by hydrogen bonding interaction, and subsequently, a stereoselective 1,6-addition of less hindered *Re* face of enolate motif to *Si* face of *p*-QM unit could predominantly occur to give desired chiral products **2** and **5**.

In conclusion, a highly catalytic enantioselective method for the effective synthesis of chiral-functionalized coumarins and quinolinones has been developed via an intramolecular vinylogous Rauhut−Currier reaction of *p*-QMs under the bifunctional catalysis of nucleophilic chiral amine-phosphines. A series of synthetically useful, optically active 4-aryl-3,4-dihydrocoumarins and 4-aryl-3,4-dihydroquinolin-2-ones were achieved in high yields (up to 99% yield) and excellent enantioselectivities (up to 99% ee). This is the first example of a catalytic enantioselective 1,6-addition reaction of *p*-QMs in an intramolecular fashion, the utility of which has been manifested by the practicability of scale-up and the diverse transformations of heterocyclic products. The current exploration of introducing additional electrophilic sites provides a new perspective for methodological design concerning the chemistry of *p*-QMs.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b01331.

Experimental procedures and spectral data (PDF)
X-ray data for compounds **2a** (CIF), **5a** (CIF), and **6e** (CIF)

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Notes

The authors declare no competing financial interest.

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(24) The relative configurations of **6a** and **6b** were determined by NOE.

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