Heterocycles

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Exploiting Distal Reactivity of Coumarins: A Rhodium-Catalyzed Vinylogous Asymmetric Ring-Opening Reaction

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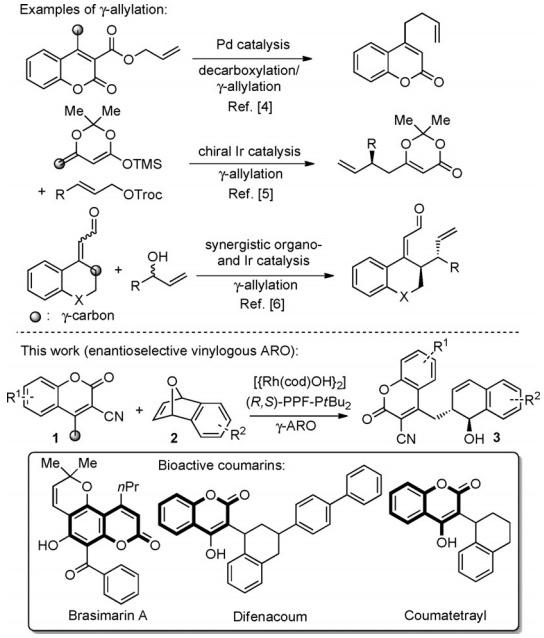
Abstract: *While the utility of vinylogous enolates is well established in the setting of vinylogous aldol, Mannich, and Michael chemistries, literature reports concerning γ-reactivity are scarce for other reaction classes. Presented herein is an unprecedented example of vinylogous reactivity exemplified by the rhodium-catalyzed asymmetric ring-opening reaction of oxabicycles. This strategy also provides a powerful route to incorporate the biologically useful coumarin motif into the hydronapthalene scaffold.*

Herein, we report a vinylogous asymmetric ring-opening (ARO) reaction, thus demonstrating a rare instance of a remote γ-functionalization utilizing oxabicyclic alkenes as a ring-strained electrophile. Despite the widespread usage of vinylogous nucleophiles with classical electrophiles such as carbonyl-based and Michael systems,[1–3] there is a general paucity of methodologies which exploit γ-reactivity in constructing other systems.

A broad application of γ-nucleophiles to less well studied electrophiles would particularly be fruitful. One area that has gained significant momentum is the transition metal catalyzed γ-allylation reaction (Scheme 1). In 2011, Tunge and co-workers reported their seminal studies in the palladium-catalyzed migratory decarboxylative γ-allylation of coumarins.[4] Subsequently, Hartwig and co-workers established the first asymmetric iridium-catalyzed γ-allylation utilizing a dioxinone-derived silyl-enol dienolate in 2014.[5] Very recently, Jørgenson and co-workers disclosed a synergistic approach by combining chiral amine organocatalysis and iridium catalysis to effect γ-allylation of α,β-unsaturated aldehydes.[6]

Other noteworthy contributions include that from Nishibayashi and co-workers, who reported a racemic γ-propargylation reaction by the combination of achiral amine catalysis and ruthenium catalysis.[7] Lindhardt, Skrydstrup, and co-workers also realized a palladium-catalyzed γ-carbonylation reaction of dioxinone with aryl and vinyl halides.[8] In 2008,



Scheme 1. Literature precedence and known bioactive coumarins. cod = 1,5-cyclooctadiene, TMS = trimethylsilyl, Troc = 2,2,2-trichloroethoxycarbonyl.

Buchwald and co-workers pioneered the seminal usage of palladium catalysis in γ-arylation reactions.[9a] This reaction was subsequently extended to silyl dienolates in 2010 by Hartwig and co-workers,[9b–c] and utilized in multicomponent reactions by Helquist and co-workers in 2015.[9d] These studies established protocols that demonstrate the versatility of transition metal catalyzed γ-functionalizations in γ-allylation, γ-carbonylation, and γ-arylation reactions. Despite these recent developments, there are no reports on γ-ring-opening reactions on any strained cyclic systems.

Furthermore, we were interested in incorporating a well-validated bioactive scaffold into our methodology and were particularly intrigued by the coumarin motif,[10] since this privileged structure is estimated to be present in over 1000 natural products. The utility of coumarins spans from biology to polymeric materials, and also provided us the practical motivation to develop effective asymmetric methodologies to γ-functionalize coumarins.

We initiated our investigation by utilizing the cyanocoumarin **1a** as the γ-nucleophile (Table 1).[11] When **1a** is subjected to the ARO reaction with **2a** utilizing the fourth-generation $[Rh(cod)OH]_2$/(*R*,*S*)-PPF-P*t*Bu_2 system,[12,13] we observed the formation of the γ-ARO product **3a** in moderate

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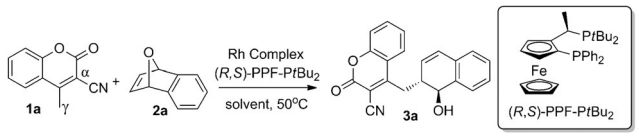
Table 1: Optimization of the γ-ARO reaction.[a]

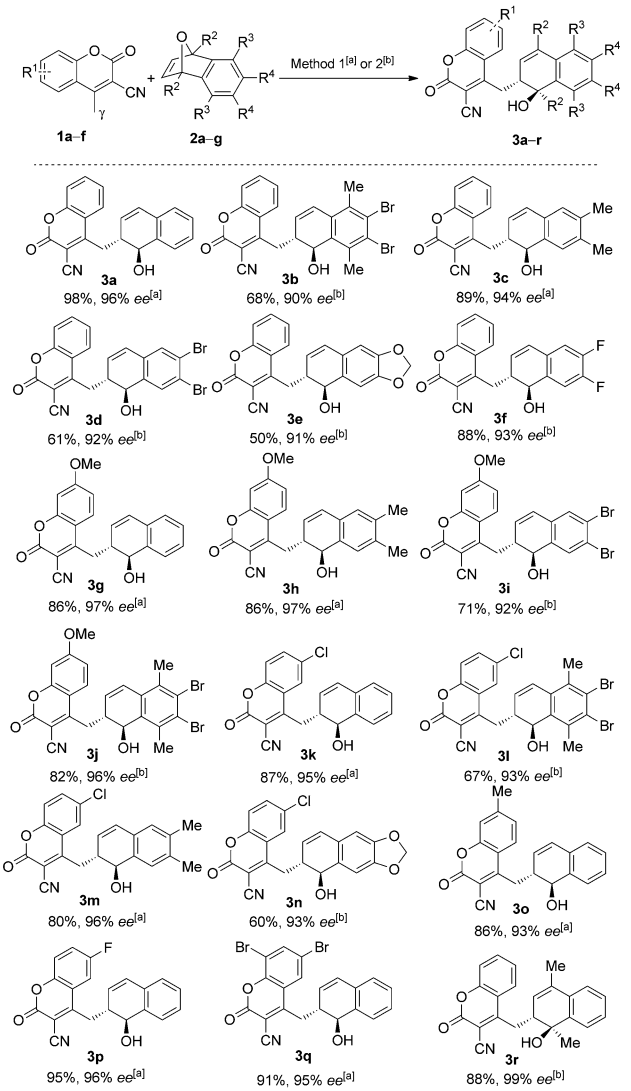


Entry	[Rh]	Cat./ Ligand[b]	Solvent	*t* [h]	Yield [%][c]	*ee* [%][d]
1	$[\{Rh(cod)OH\}_2]$	4:8	MeCN	2	56	96
2	$[\{Rh(cod)OH\}_2]$	4:8	MeCN	6	97	97
3	$[\{Rh(cod)Cl\}_2]$	4:8	MeCN	6	>99	93
4	$[\{Rh(cod)Cl\}_2]$ AgOTf, TBAI	4:8	THF	6	21[d]	n.d.
5	$[Rh(cod)_2]OTf$	5:6	THF	6	81	99
6	$[Rh(cod)_2]BF_4$	5:6	THF	6	<5[e]	n.d.
7	$[\{Rh(cod)OH\}_2]$	2:4	MeCN	15	98	96

[a] All reactions were conducted on **2a** (0.2 mmol) and **1a** (0.5 mmol). [b] Reported as mol%. [c] Yield of product isolated after flash column chromatography. [d] Determined by HPLC analysis using chiral stationary phases. [e] NMR yield using 1,3,5-trimethoxybenzene as an internal standard. TBAI = tetra-*n*-butylammonium iodide, Tf = trifluoromethylsulfonyl, THF = tetrahydrofuran.

yield and excellent enantioselectivity (entry 1). Encouraged by the initial validation of the vinylogous reactivity hypothesis, we proceeded to further optimize the γ-ARO reaction. Prolonging the reaction time to 6 hours (entry 2) afforded almost quantitative yield of **3a**. Other rhodium(I) complexes were screened as catalysts for this γ-ARO reaction. Even though the first generation dimeric $[\{Rh(cod)Cl\}_2]$ catalyst also provided quantitative yields, there was a slight decrease in enantioselectivity (entry 3).[12a] The rhodium iodide species resulted in greatly diminished yields in this protocol (entry 4).[12b] While the cationic $[Rh(cod)_2]OTf$ gave the γ-functionalized product **3a** (entry 5), a significant decrease in yield is observed.[12c] The cationic $[Rh(cod)_2]BF_4$ resulted in decomposition of the oxabicycle. The catalyst screening revealed $[\{Rh(cod)OH\}_2]$ to be the optimal catalyst.[12f] Furthermore, we managed to arrive at the optimized reaction conditions by decreasing the catalyst loading to 2 mol% (entry 7) and prolonging the reaction time to 15 hours.

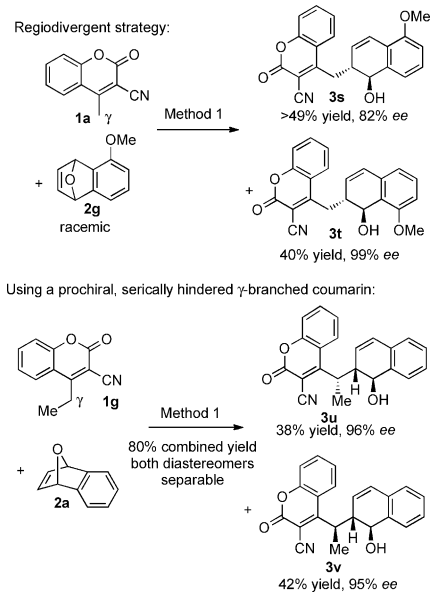
Subsequently, we proceeded to examine the substrate scope of this vinylogous ARO reaction (Scheme 2). In general, this protocol tolerates a wide spectrum of substrates with varying electronic and steric properties. Symmetric oxabicyclic alkenes bearing electron-donating groups (**3c**, **3e**, **3h**, **3m**, and **3n**) and electron-withdrawing groups (**3b**, **3d**, **3f**, **3i**, **3j**, and **3l**) proceeded smoothly in this reaction to generate the corresponding ring-opened products (**3**). In addition, this protocol also tolerates (**1**) bearing both electron-donating groups, such as OMe (**3g–j**), as well as electron-withdrawing groups, such F, Cl, and Br (**3k–q**). Generally, yields ranged from good to excellent and enantioselectivities were almost always excellent. Moreover, this methodology can be extended to bridgehead-substituted oxabicycles (**3r**). X-ray crystal structures of **3k** and **3r** also confirmed the absolute configuration of the γ-ARO products **3a–r** and the mechanistic consistency of the vinylogous ARO for various oxabicycles.[14]



Scheme 2. Scope of the γ-ARO reaction: [a] Method 1: **1** (0.5 mmol), **2** (0.2 mmol), $[\{Rh(cod)OH\}_2]$ (2 mol%), and (*R*,*S*)-PPF-P*t*Bu$_2$ (4 mol%) in MeCN (0.1 M) at 50°C for 15 h. [b] Method 2: **1** (0.5 mmol), **2** (0.2 mmol), $[\{Rh(cod)OH\}_2]$ (4 mol%), and (*R*,*S*)-PPF-P*t*Bu$_2$ (8 mol%) in MeCN (0.1 M) at 80°C for 15 h. For all reactions: Yields of products isolated after flash column chromatography are given and the *ee* values were determined by HPLC analysis using chiral stationary phases.

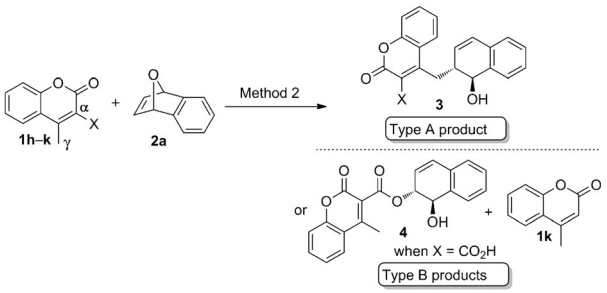
Furthermore, we also investigated the γ-ARO protocol on the racemic oxabicyclic alkene **2g** (Scheme 3) which allowed us to access **3s** and **3t** by a regiodivergent resolution. We sought to better understand the steric influence of the γ-substituent by subjecting **1g** to the vinylogous ARO conditions (Method 1). While previous reports noted that similar substrates failed to react in palladium-catalyzed allylation reactions,[4] our protocol accommodates the γ-branched **1g** to generate an 80% combined yield of two diastereomers (1.1:1 d.r.) which are separable.[14] Both diastereomers were generated in this γ-ARO reaction with excellent enantioselectivities, and the relative and absolute configurations were elucidated by X-ray crystallography for **3u**.[15]

To gain further insight into α-electronic effects on the protocol, the reactivities of the coumarins **1h–k**, having



Scheme 3. Extended scope using racemic oxabicycles and γ-branched cyanocoumarins.

Table 2: Investigation into the influence of the coumarin α-substituent.[a]

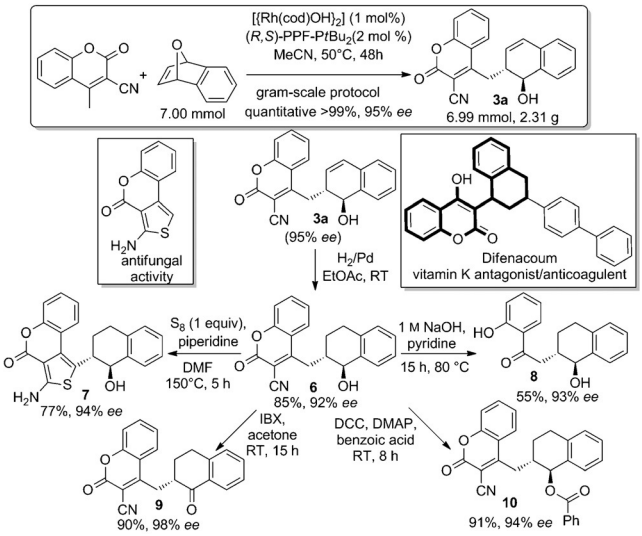


Entry	X	Product type	Yield [%][b]	*ee* [%][c]
1	CN	A	98	96
2	$CONH_2$	A	60	95
3	CO_2Et	A	43	95
4[d]	CO_2H	B	40	92
5	H	decomp.	–	–

[a] Conducted on a 0.2 mmol scale of **2a** and 0.5 mmol of cyanocoumarin (**1**). [b] Yield of isolated product. [c] Determined by HPLC analysis using chiral stationary phases. [d] **1k** was isolated in 72% yield with respect to **1i**.

different α-functional groups, were compared (Table 2). When the cyano group was replaced with an amide (entry 2), we observed that the γ-ARO product was formed with an excellent *ee* value, albeit with diminished yield. A switch to an ester group (entry 3) further diminished the yield to 43%, although still retaining the excellent enantioselectivity. We observed an interesting reactivity switch from γ-reactivity (Type A ARO products) to oxygen reactivity (Type B ARO products) when the α-substituent is a carboxylic acid (entry 4). In this case, apart from generating the ARO product **4**, the rhodium(I) catalyst also catalyzes a decarboxylation reaction yielding **1k**.[16] When no α-substituent is present on the coumarin, γ-reactivity is switched off and the oxabicycle substrate **2a** decomposes under the reaction conditions (entry 5).

In addition, a gram-scale experiment was performed efficiently where the catalyst loading was further decreased to 1 mol% (Scheme 4), and **3a** was then subjected to a Pd/C-



Scheme 4. Gram-scale reaction and further transformations. DCC = 1,3-dicyclohexylcarbodiimide, DMAP = 4-(*N*,*N*-dimethyl)pyridine, DMF = *N*,*N*-dimethylformamide, IBX = *o*-iodoxybenzoic acid.

catalyzed hydrogenation to generate **6**, which is structurally similar to a diverse range of anticoagulants and rodenticides such as Difenacoum.[17] A base-catalyzed cyclization of **6** with sulfur provided the tricyclic thiophenocoumarin **7**, which is a motif present in antifungal agents.[18] Interestingly, **6** can also subjected to a base-catalyzed retro-Knoevanagel/hydrolysis reaction, which showcases an interesting transformation towards an α-functionalized product **8**. Other transformations such as an IBX oxidation of **6** to the ketone **9**, as well as a Steglich esterification to **10** could be achieved with excellent yields and enantioselectivities.

In conclusion, a rhodium-catalyzed enantioselective vinylogous ARO reaction was developed, where the concept of vinylogy was demonstrated, for the first time, to be effective in the release of ring strain in polycyclic systems. The choice of the cyanocoumarin as our nucleophile was motivated by the widespread prevalence of coumarin in natural products and it's utility in different fields. Moreover, this versatile protocol tolerates substrates which are sterically hindered at the γ-position, thus further expanding the utility of the methodology. We have also shown that the cyanocoumarin ARO products can be further functionalized into tricyclic thiophenocoumarins or fragmented into *o*-acetophenone derivatives, thus yielding a diverse range of products which are structurally distinct from the parent coumarin scaffold. Further investigations are currently ongoing to determine the biological activities of our ARO products.

Acknowledgments

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Keywords: enantioselectivity · heterocycles · ring-opening reactions · rhodium · synthetic methods

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[14] CCDC 1446936 (**3k**), 1446937 (**3r**), and 1446938 (**3u**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

[15] We also attempted a highly sterically hindered substrate bearing a phenyl group on the γ-position (see the Supporting Information). While extensive decomposition was observed in a complex mixture, we still managed to isolate and characterize one of the diastereomers with 28% yield and 96% *ee*, thus further augmenting the tolerance of our protocol towards γ-sterically hindered cyanocoumarins.

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