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Asymmetric Inverse-Electron-Demand Oxa-Diels–Alder Reaction of Allylic Ketones through Dienamine Catalysis

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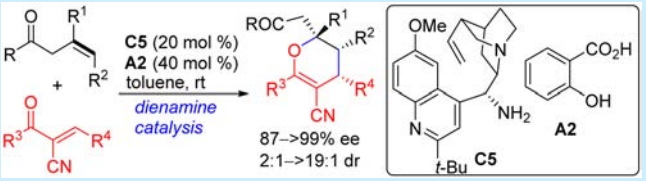
Supporting Information

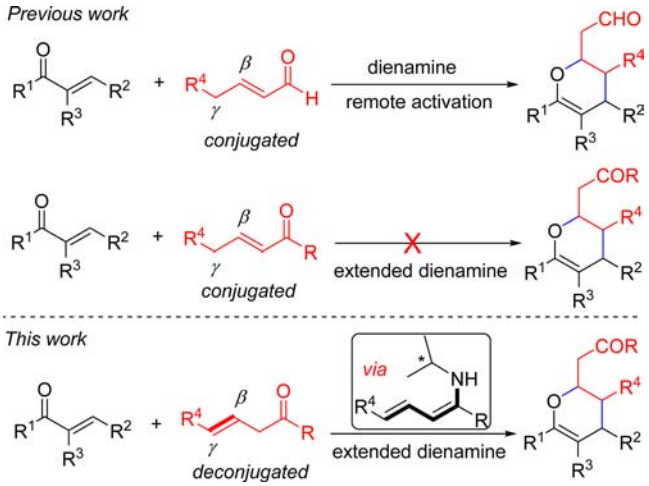
ABSTRACT: A remote β,γ-regioselective asymmetric inverse-electron-demand oxa-Diels–Alder reaction between allylic ketones and α-cyano-α,β-unsaturated ketones has been developed through induced extended dienamine catalysis of a cinchona-derived primary amine. A spectrum of densely substituted dihydropyran frameworks were efficiently produced with excellent enantioselectivity and fair to exclusive diastereoselectivity.



Dihydropyran and tetrahydropyran skeletons are widely encountered in numerous natural products.[1] They also constitute important structural motifs in biologically active synthetic compounds and medicines.[2] Therefore, a variety of strategies have been explored for constructing such frameworks.[3] Among them, the oxa-Diels–Alder (DA) cycloaddition has evolved as the most straightforward protocol, either in a normal-electron-demand (with carbonyl substances and dienes)[4] or an inverse-electron-demand (IED, with alkenes and oxadienes) manner.[5] For the latter strategy, a variety of electron-rich dienophiles, such as alkenes, enol ethers, enamines, and enolates, or aldehydes, ketones, and acyl chlorides as the precursors were successfully utilized in IED-oxa-DA reactions through asymmetric Lewis acid catalysis or organocatalysis.[6] The Jørgensen group developed a remote β,γ-regioselective IED-oxa-DA reaction with α,β-unsaturated aldehydes and β,γ-unsaturated-α-ketoesters through dienamine catalysis assisted by a H-bond-directing strategy.[7] Subsequently, Pericàs and Albrecht expanded this tool by using alkylidene pyrazolones and 2-alkylidenebenzothiophene-3(2*H*)-ones as the oxadiene partners, respectively.[8] In spite of such progress, one of the long-standing challenges of the asymmetric IED-oxa-DA reaction is the lack of more appropriate and effective electron-rich alkene dienophiles. In comparison with α,β-unsaturated aldehydes, the analogous α,β-unsaturated ketones also can potentially provide the extended carbon moiety. However, to the best of our knowledge, there is still no successful example involving linear enones as HOMO-raised 2C dienophile synthons in cycloaddition reactions via amino-catalysis,[9] probably due to the lack of effective protocols for generating the required extended dienamine species (Scheme 1).

Recently, we presented a γ-regioselective direct vinylogous Michael addition of allyl alkyl ketones to maleimides catalyzed by a chiral primary amine.[10] The deconjugated β,γ-C=C bond[11] is crucial for formation of the desired dienamine species since the conjugated enone substrates were inert under the same catalytic conditions. As a result, we speculated that such an inducing strategy would be applicable for the development of the previously unreported IED-oxa-DA reaction between β,γ-unsaturated ketone substrates and proper oxadiene components (Scheme 1).

Scheme 1. Application of Dienamine Catalysis in Oxa-Diels–Alder Reactions with Diverse Unsaturated Carbonyl Compounds



α-Cyano-α,β-unsaturated ketones are readily available electrophiles,[12] but they have been seldom applied as oxadiene components in oxa-DA-type reactions.[13] Our initial investigation with allyl ketone **1a** and enone substance **2a** was encouraging under the catalysis of amine **C1** and benzoic acid **A1**.[10] The desired β,γ-regioselective IED-oxa-DA cycloadduct

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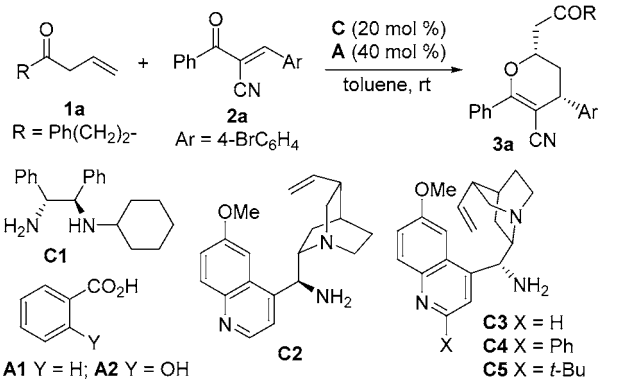
3a was produced efficiently in remarkable enantioselectivity, albeit in fair diastereoselectivity (Table 1, entry 1). The

Table 1. Screening Conditions of Asymmetric IED−Oxa-Diels−Alder Reaction[a]



entry	cat.	acid	time (h)	yield[b] (%)	dr[c]	ee[d] (%)
1	**C1**	**A1**	24	91	3.4:1	98
2	**C2**	**A1**	30	66	6.5:1	−98
3	**C3**	**A1**	18	82	9.8:1	93
4	**C4**	**A1**	18	82	13.0:1	97
5	**C5**	**A1**	18	92	>19:1	98
6	**C5**	**A2**	20	92	>19:1	>99

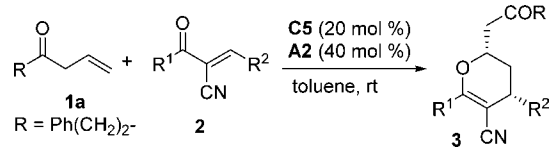
[a]Unless noted otherwise, reactions were performed with **1a** (0.15 mmol), **2a** (0.1 mmol), amine **C** (20 mol %), and acid (40 mol %) in toluene (1.0 mL) at rt. [b]Isolated yield of inseparable diastereomers. [c]Determined by ^{1}H NMR analysis. [d]Determined by HPLC analysis on a chiral stationary phase.

diastereocontrol was moderate when 9-amino-9-deoxyepiquinine **C2** was used as the catalyst (entry 2), and even better data were obtained with 9-amino-9-deoxyepiquinidine **C3** (entry 3). Pleasingly, both diastereo- and enantioselectivity were improved in the presence of the 2′-phenyl-substituted amine **C4** (entry 4), and almost exclusive diastereoselectivity (>19:1) was attained by the 2′-*tert*-butyl-substituted amine **C5** (entry 5).[14] In addition, excellent yield and outstanding stereoselectivity were furnished with the combination of amine **C5** and salicylic acid **A2** (entry 6).[15]

Consequently, we explored the substrate scope and limitations of this new oxa-DA reaction. At first, an array of *α*-cyano-*α*,*β*-unsaturated ketones **2** were investigated in the reactions with allyl ketone **1a** in toluene under the catalysis of **C5** (20 mol %) and acid **A2** (40 mol %) at room temperature. As summarized in Table 2, oxadienes **2** with diverse *β*-aryl, heteroaryl, and 2-styryl groups were well tolerated, and excellent data were generally produced (Table 2, entries 1−7). On the other hand, oxadienes **2** with various *α*′-substitutions, including a methyl group, were compatible partners in combination with ketone **1a**, while modest diastereoselectivity was observed in a few cases (entries 8−13). It is noteworthy that a CF_3- or even H-substituted substrate showed comparable reactivity, but low diastereoselectivity with high enantiocontrol was attained, probably due to electronic and steric reasons (entries 15 and 16). Moreover, when we conducted a gram-scale reaction under the optimized conditions, the product **3c** could be efficiently obtained with similar good results (entry 17).

Next, an array of allylic ketones were investigated in the reactions with oxadiene **2c**. As summarized in Table 3, the allyl

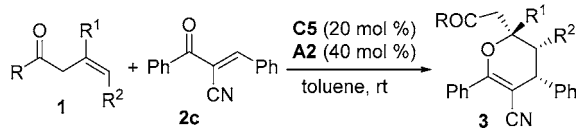
Table 2. Scope of Oxadiene Substrates 2[a]



entry	R^1, R^2	time (h)	yield[b] (%)	dr[c]	ee[d] (%)
1	Ph, 4-BrC_6H_4	20	**3a**, 92	>19:1	>99
2	Ph, 3-ClC_6H_4	20	**3b**, 91	>19:1	>99
3	Ph, Ph	20	**3c**, 91	>19:1	>99
4	Ph, 4-MeC_6H_4	24	**3d**, 81	>19:1	>99
5	Ph, 4-MeOC_6H_4	36	**3e**, 89	>19:1	>99
6	Ph, 2-furyl	60	**3f**, 95	19:1	94
7	Ph, 2-styryl	36	**3g**, 89	14:1	99
8	2-BrC_6H_4, Ph	18	**3h**, 64	15:1	98
9	3-BrC_6H_4, Ph	18	**3i**, 89	17:1	99[e]
10	4-BrC_6H_4, Ph	18	**3j**, 91	>19:1	>99
11	4-MeOC_6H_4, Ph	30	**3k**, 82	6:1	>99
12	1-naphthyl, Ph	40	**3l**, 72	6:1	87
13	2-furyl, Ph	24	**3m**, 83	6:1	98
14	Me, Ph	36	**3n**, 61	10:1	>99
15	CF_3, Ph	36	**3o**, 72	2:1	90 (96)[f]
16	H, Ph	60	**3p**, 67	3:1	87 (64)[f]
17[g]	Ph, Ph	20	**3c**, 82	19:1	98

[a]Unless noted otherwise, reactions were performed with **1a** (0.15 mmol), **2** (0.1 mmol), amine **C5** (20 mol %), and acid **A2** (40 mol %) in toluene (1.0 mL) at rt. [b]Isolated yield of diastereomers. [c]Determined by ^{1}H NMR analysis. [d]Determined by HPLC analysis on a chiral stationary phase. [e]The absolute configuration of enantiopure **3i** was determined by X-ray analysis. The other products were assigned by analogy. [f]Ee of minor diastereomer. [g]With 3.0 mmol of oxadiene substrate.

Table 3. Scope of Allylic Ketones 1[a]



entry	R, R^1, R^2	*t* (h)	yield[b] (%)	dr[c]	ee[d] (%)
1	*n*Pent, H, H	20	**3q**, 80	>19:1	>99
2	*n*Hept, H, H	20	**3r**, 82	18:1	99
3	*c*Hex, H, H	48	**3s**, 64	8:1	91
4	1-naphthyl-CH_2-, H, H	48	**3t**, 61	9:1	98
5	3-indolyl-CH_2-, H, H	48	**3u**, 79	14:1	>99
6	3-indolyl-$(CH_2)_2$-, H, H	36	**3v**, 83	17:1	>99
7	 , H, H	48	**3w**, 79	14:1	98
8	Ph, H, H	56	**3x**, 54	>19:1	95
9	Ph$(CH_2)_2$-, H, Me	28	**3y**, 66	>19:1	>99
10	Ph$(CH_2)_2$-, Me, H	60	**3z**, 86	19:1	97

[a]Unless noted otherwise, reactions were performed with **1** (0.15 mmol), **2c** (0.1 mmol), amine **C5** (20 mol %), and acid **A2** (40 mol %) in toluene (1.0 mL) at rt. [b]Isolated yield of diastereomers. [c]Determined by ^{1}H NMR analysis. [d]Determined by HPLC analysis on a chiral stationary phase.

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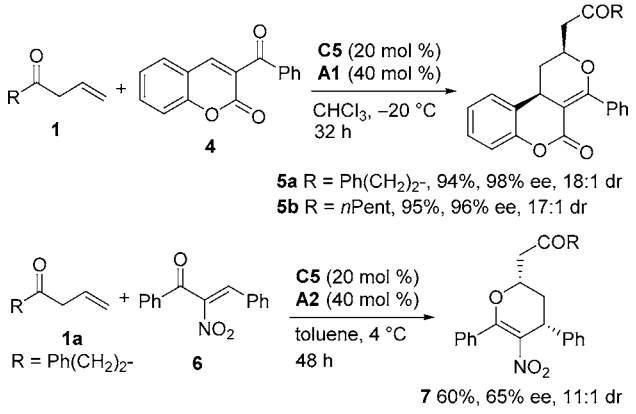
ketones bearing diverse α'-alkyl groups showed similar reactivity, and the corresponding cycloadducts **3q**–**w** were obtained with excellent enantioselectivity and moderate to high diastereoselectivity (Table 3, entries 1–7). An allyl phenyl ketone exhibited lower reactivity, still affording the product **3x** with outstanding stereocontrol (entry 8). Importantly, a deconjugated enone bearing a γ-methyl group could be smoothly utilized (entry 9). Furthermore, introducing a methyl group at the β-site also did not affect the reaction, with the product **3z** bearing a quaternary stereogenic center being produced in excellent diastereo- and enantioselectivity (entry 10).

Although inert reactions were unfortunately observed when conventional β,γ-unsaturated-α-ketoesters were applied, it was found that 3-benzoyl-2*H*-chromen-2-one **4** exhibited high reactivity with allyl ketones in $CHCl_3$ even at −20 °C. As outlined in Scheme 2, the corresponding tricyclic products **5a** and **5b** were produced in excellent yields with outstanding stereoselectivity. In addition, α-nitro-α,β-unsaturated ketone **6** also could be assembled with allyl ketone **1a** under similar catalytic conditions, while a moderate ee value with high diastereoselectivity for product **7** was obtained at 4 °C.

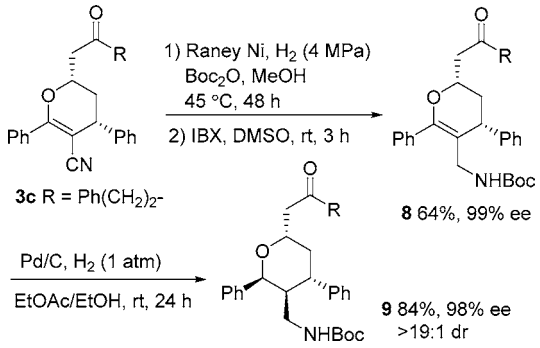
Scheme 2. Exploration of Other Oxadiene Partners



We further conducted some synthetic transformations with product **3c**. The cyano group was smoothly hydrogenated and subsequently protected as an *N*-Boc derivative in the presence of Raney Ni and $(Boc)_2O$. Since the ketone group also was reduced to the alcohol in low diastereoselectivity, reoxidation of the intermediate with IBX could effectively afford the compound **8** as a ketone form in a moderate yield. Moreover, the alkene moiety of **8** could be chemoselectively hydrogenated under the mild catalytic conditions of Pd/C and H_2, directly delivering the pure tetrahydropyran derivative **9** with four stereogenic centers in a high yield (Scheme 3).

In summary, we have investigated the asymmetric inverse-electron-demand oxa-Diels–Alder cycloaddition reactions of allylic ketones and α-cyano-α,β-unsaturated ketones under the induced dienamine catalysis of a cinchona-derived primary amine. The reactions exhibited remote β,γ-regioselectivity, and a spectrum of densely substituted dihydropyran derivatives were produced with excellent enantioselectivity and fair to outstanding diastereoselectivity, which could be further converted to useful functionalized tetrahydropyran substances. This catalytic strategy could be expanded to enone substrates bearing an α-ester or -nitro group, further enriching the multiple functionalities of the heterocyclic products, which might be valuable in medicinal chemistry. Currently, additional applications of allylic ketones via dienamine catalysis are being studied, and the results will be reported in due course.

Scheme 3. Transformations of Multifunctional Product 3c



■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b03384.

Complete experimental procedures and characterization of new products; NMR spectra and HPLC chromatograms (PDF)

Crystallographic file of enantiopure product **3i** (CIF)

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Notes

The authors declare no competing financial interest.

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