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Application of recyclable ionic liquid-supported imidazolidinone catalyst in enantioselective Diels-Alder reaction[†]

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The application of ionic liquid-supported imidazolidinone catalyst **I** in enantioselective Diels-Alder reaction was investigated. The Diels-Alder reactions involving α,β -unsaturated aldehydes and cyclopentadiene proceeded efficiently in the presence of catalyst **I** to provide the desired products in moderate to good yields with good to excellent enantioselectivities. Especially noteworthy, the catalyst **I** to can be recovered and reused for up to five runs while maintaining its high catalytic activity.

Introduction

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Asymmetric Diels-Alder reaction is one of the most powerful organic transformations for the synthesis of enantiomerically enriched cyclohexene moiety in organic synthesis.¹ Despite a ¹⁵ wide range of reports on metal-mediated asymmetric Diels-Alder

reactions, MacMillan and co-workers have firstly reported the use of imidazolidinone² as an efficient organocatalyst³ for mediating enantioselective Diels-Alder reaction^{2c-e} via a LUMO-lowering activation mechanism. Thereafter, considerable attention have

- ²⁰ been focused on achieving enantioselective Diels-Alder reaction by using metal-free organocatalysts.³ Several organocatalysts, such as hydrazide, chiral diamine, and diarylprolinol silyl ether, have been developed to realize asymmetric Diels-Alder reactions.⁴
- 25 Despite the remarkable success accomplished in the enantioselective Diels-Alder reaction by employing different organocatalysts, one of the significant challenges remains: the organocatalyst gets lost after the first run and it is difficult to recover and recycle them in further reactions. This limitation
- ³⁰ inevitably results in increased economic cost by using these expensive catalysts which are normally accessed by tedious multi-step syntheses. As a result, if the organocatalysts can be developed to recycle in subsequent reactions, it will greatly improve the overall catalytic efficiency of the organocatalysts and
- ³⁵ meet the requirement of modern Green Chemistry for sustainability.⁵ For this purpose, recently several modified methods which allowed the recycling of the imidazolidinone catalyst in Diels-Alder reaction by using polymer-, solid-, or silica gel-supported MacMillan's catalyst have been developed

by Pihko, Cozzi, Benaglia, Hagiwara, Ying, Haraguchi, Wang, ⁵⁰ and others.⁶ In addition, an imidazolidinone-catalyzed Diels-Alder reaction in an ionic liquid solvent media [bmim]PF₆/H₂O has also been reported by Kim and co-workers;^{6k} however, though the catalytic system can be recycled several times in reactions involving cinnamaldehyde and cyclopentadiene, a ⁵⁵ considerable erosion of product enantioselectivity was observed in the 4th run which might be due to the gradual loss of catalyst during repeated extraction by ether after every cycle.^{6k}

On the other hand, recent surge of using ionic liquid as catalyst supporter,⁷⁻⁸ instead of as reaction medium,⁹ has also 60 demonstrated the feasibility of enabling the recycling of organocatalyst in organic transformations by attaching it to an ionic liquid unit. With this idea in mind, very recently our group has developed an efficient synthetic route to the preparation of ionic liquid-supported imidazolidinone catalysts I-III and their 65 applications as recyclable organocatalysts in enantioselective 1,3dipolar cycloaddition.¹⁰ In continuation of our efforts in exploring the synthetic utility of the catalysts I-III in organic synthesis as well as developing practical organic transformations,¹¹ herein we describe an enantioselective Diels-Alder reaction catalyzed by 70 ionic liquid-supported imidazolidinone catalyst I. The reactions proceeded efficiently to give the desired products in moderate to good yields with good to excellent enantioselectivities. In addition, the ionic liquid-supported imidazolidinone catalyst I can be recovered and recycled up to five runs without significant loss 75 of its high catalytic activity.

Results and discussion

As illustrated in Figure 1, three chiral ionic liquid-supported imidazolidinone catalysts **I-III** with different anions were conveniently synthesized in our group.⁹ Application of the ionic ⁸⁰ liquid-supported imidazolidinone catalysts **I-III** to the Diels-Alder reaction was initially examined by choosing *trans*-cinnamaldehyde and cyclopentadiene as model substrates. In order to find an optimal conditions for the Diels-Alder reaction,

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we first explored the catalytic activities of the three catalysts I-III (10 mol%) by using CF₃COOH (10 mol%) as reaction cocatalyst.



5 Figure 1 Ionic liquid-supported imidazolidinone catalysts I-III with different anions.

Table 1 Optimization of reaction conditions by using different catalysts^a

Ph \rightarrow						
			enao		exo	
Entry	Catalyst	Yield ^b	ero endo ^c	<i>ee^d</i> (%)		
		(%)	exo.enuo	exo	endo	
1	Ι	97	1.3:1	88	93	
2	II	98	1.3:1	88	90	
3	III	96	1.3:1	87	91	

^{*a*} The reactions were carried out at room temperature for 21 h using catalyst (0.1 mmol), CF₃COOH (0.1 mmol), *trans*-cinnamaldehyde (1.0 mmol), cyclopentadiene (5.0 mmol), CH₃NO₂ (0.95 mL), H₂O (0.05 mL). ^{*b*} Isolated yield. ^{*c*} *Exo/endo* selectivity was determined by ¹H NMR analysis of crude reaction mixture. ^{*d*} Enantioselectivity was determined by GC using chiral cyclodex B column.

As shown in Table 1, the Diels-Alder reactions involving *trans*-cinnamaldehyde and cyclopentadiene proceeded efficiently at room temperature in the presence of catalysts **I-III** (10 mol%) and CF₃COOH (10 mol%) in CH₃NO₂/H₂O, affording the desired products in almost quantitative yields (96-98%) with excellent enantioselectivities (87-88% *ee* for *exo* isomer, 90-93% *ee* for *sendo* isomer). Among them, catalyst **I** exhibited a better capacity for stimulating a slightly higher enantioselectivity for *exo* isomer as compared to catalysts **II** and **III**. Therefore, catalyst **I** was selected to further optimize the reaction conditions by screening different acids as reaction co-catalysts.

²⁰ **Table 2** Optimization of reaction conditions by using different acid cocatalysts^{*a*}



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3	TfOH	95	1.3:1	87	93
4	p-TSA	95	1.3:1	88	91
5	Cl ₃ CCOOH	17	1.2:1	83	⁸ view Online
6	HBF_4	79	1.3:1	84	82
7	HPF ₆	96	1.3:1	84	89
8	HCl	75	1.3:1	87	91

^{*a*} The reactions were carried out at room temperature for 21 h using catalyst **I** (0.1 mmol), acid co-catalyst (0.1 mmol), *trans*-cinnamaldehyde (1.0 mmol), cyclopentadiene (5.0 mmol), CH₃NO₂ (0.95 mL), H₂O (0.05 mL). ^{*b*} Isolated yield. ^{*c*} *Exo/endo* selectivity was determined by ¹H NMR analysis of crude reaction mixture. ^{*d*} Enantioselectivity was determined by GC using chiral cyclodex B column.

As outlined in Table 2, among the various acids investigated, the utilization of CF₃COOH, TfOH, *p*-TSA and HPF₆ (entries 1, 3, 4 and 7) led to relatively good yields and good ²⁵ enantioselectivities of the desired Diels-Alder adduct. In contrast, relatively high yield (97%) and excellent *ee* in both *exo* and *endo* isomers were produced when CF₃COOH was selected (88% and 93%, entry 1). Thus, CF₃COOH was identified as the optimal acidic co-catalyst and we continued the optimization of the ³⁰ reaction conditions by surveying a range of solvents in an effort to further enhance the enantioselectivity of the target product. The results are depicted in Table 3.

Table 3 Optimization of reaction conditions by using different solvents^a

Ph +	Catalyst I (10 n CF ₃ COOH (10 solvent, r.t., 2	nol%) mol%) 21 h	Ph + CHO endo	e.	Дсно Ph xo
Entry	Solvent	Yield ^b (%)	exo:endo ^c	ee^d (%)	
	Solvent			exo	endo
1	CH ₃ NO ₂ /H ₂ O	97	1.3:1	88	93
2	THF/H ₂ O	17	1.1:1	89	92
3 ^e	MeOH/H ₂ O	9	1:1	42	30
4	CH ₃ CN/H ₂ O	98	1.2:1	90	94
5	CH ₂ Cl ₂ /H ₂ O	60	1.2:1	87	89
6	DMSO/H ₂ O	60	1.1:1	89	93
7	DMF/H ₂ O	33	1.1:1	87	92

^{*a*} The reactions were carried out at room temperature for 21 h using catalyst **I** (0.1 mmol), CF₃COOH (0.1 mmol), *trans*-cinnamaldehyde (1.0 mmol), cyclopentadiene (5.0 mmol), organic solvent (0.95 mL), H_2O (0.05 mL). ^{*b*} Isolated yield. ^{*c*} *Exo/endo* selectivity was determined by ¹H NMR analysis of crude reaction mixture. ^{*d*} Enantioselectivity was determined by GC using chiral cyclodex B column. ^{*e*} An 82% yield of the corresponding dimethyl acetal product was obtained and the chemoselectivity was tested as 1.3:1 *exo:endo* ratio, 92% *ee* for *exo* isomer and 96% *ee* for *endo* isomer, after hydrolysis by TFA:H₂O:CHCl₃ (1:1:2) for 2 h at room temperature.

As can be seen from Table 3, comparatively high yields were

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achieved when the reactions were performed in solvents such as CH₃NO₂ and CH₃CN, in conjunction with H₂O (entries 1 and 4). The yields obtained by using these two solvents were comparable, whereas CH₃CN gave a slightly higher *ee* for both *s exo* and *endo* isomers (entry 4). Therefore CH₃CN/H₂O was chosen as the optimal solvent system in further reactions. Notably, an 82% yield of the corresponding dimethyl acetal product was obtained when MeOH/H₂O was used as reaction media and the product should be hydrolyzed by TFA:H₂O:CHCl₃ ¹⁰ (1:1:2) before releasing the desired product in an aldehyde form.

- Thus, MeOH/H₂O solvent system, which was previously employed in the analogous reaction system by MacMillan and co-workers,^{2c} was not selected as the solvent for the present reaction.
- Having optimized the reaction conditions for the Diels-Alder reaction by utilizing the catalyst **I**, CF₃COOH as acidic cocatalyst, and CH₃CN/H₂O as the reaction solvent, we subsequently applied the optimized reaction conditions to various substrates to explore the generality of the reaction system.

Table 4 Application of catalyst I to Diels-Alder reaction^a

R ← +	Catalyst I (1 CF ₃ COOH (CH ₃ CN/H ₂ O	0 mol%) 10 mol%) , r.t., 21 h	R CHO endo	+	СНО R ехо	
Entry	R	Yield ^b	ero:endo ^c	ee^d (%)	<i>ee</i> ^d (%)	
Lifti y		(%)	exo.enuo	exo	endo	
1^e	$4\text{-BrC}_6\text{H}_4$	99	1.1:1	71	73	
2^{e}	$4-ClC_6H_4$	85	1.1:1	85	84	
3	C_6H_5	98	1.2:1	90	94	
4	2-OMeC ₆ H ₄	95	1:1	87	93	
5^e	2-naphthyl	83	1.2:1	89	92	
6	<i>n</i> -Bu	89	1:1	84	93	
7	<i>n</i> -Pr	78	1:1.1	84	91	
8	Et	45	1:1	f	94	

²⁰ ^a Unless otherwise noted, the reactions were carried out at room temperature for 21 h using catalyst I (0.1 mmol), CF₃COOH (0.1 mmol), aldehyde (1.0 mmol), cyclopentadiene (5.0 mmol), CH₃CN (0.95 mL), H₂O (0.05 mL). ^b Isolated yield. ^c *Exo/endo* selectivity was determined by ¹H NMR analysis of crude reaction mixture. ^d Enantioselectivity was 25 determined by chiral HPLC or GC analysis. ^e CH₃NO₂ was used in place of CH₃CN, due to poor solubility of the aldehyde in CH₃CN. ^f Not determined because of the inseparable *exo* enantiomers.

As summarized in Table 4, the Diels-Alder reaction involving ³⁰ various α,β -unsaturated aldehydes and cyclopentadiene proceeded efficiently in the presence of catalyst I and CF₃COOH in CH₃CN/H₂O, leading to the corresponding products in moderate to good yields with good to excellent enantioselectivities. It should be noted that, in three cases (entries ³⁵ 1, 2 and 5), owing to the poor solubility of α,β -unsaturated aldehydes in CH₃CN/H₂O, poor yields of the desired products

were obtained. Thus, in these special cases, a more polar solvent system of CH_3NO_2/H_2O was employed, furnishing good to excellent yields of the target products while maintaining their

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⁴⁰ excellent enantioselectivities. Both aryl and alkyl substituted α,β-unsaturated aldehydes were proven to be suitable candidates for the present enantioselective organic transformations. Comparable enantioselectivities were obtained in contrast to the use of imidazolidinone as reaction catalyst which were previously
 ⁴⁵ reported by MacMillan and co-workers.^{2c} For example, when *trans*-cinnamaldehyde was used as substrate, the utilization of MacMillan's imidazolidinone catalyst afforded the desired product in 93% *exo ee* and 93% *endo ee*;^{2c} Likewise, by employing ionic liquid-supported imodazolidinone catalyst I in so the reaction, similar results with 90% *exo ee* and 94% *endo ee* was achieved as well (entry 3).

With the success of above reactions, we embarked on studying the recyclability of the ionic liquid-supported imidazolidinone catalyst I in Diels-Alder reaction. It should be mentioned that the 55 catalyst I containing an ionic liquid unit is viscous liquid at room temperature and shows typical characteristics of an ionic liquid: soluble in polar solvents such as THF, CH₂Cl₂ and MeOH, while insoluble in less polar solvents such as Et₂O and hexane.⁷⁻⁹ This unique property of ionic liquid makes the recovery and recycling 60 of the catalyst I in subsequent reaction possible, which can be exemplified as follows: after reaction, the polar reaction solvent of either CH₃CN or CH₃NO₂ was removed under reduced pressure; then the residue in the flask was extracted for five times by directly adding Et₂O (5 mL per time) into the flask with 65 stirring on a magnetic stirrer; the extracted crude product in Et₂O was purified by routine silica gel column chromatography, while the imidazolidinone catalyst I still remained intact in the flask because of its poor solubility in Et₂O. Therefore, the catalyst I remained in the flask can be directly reused in further reactions 70 by adding the substrates, acid co-catalyst, and solvent into the same flask to start another run.

Table 5 Recycling of catalyst I in Diels-Alder reaction

Ph \rightarrow 0 + CF ₃ COOH (20 mol%) CH ₃ CN/H ₂ O, r.t., 21 h			Ph + Acho CHO + Ph		
			endo	exo	
Cruala	Yield ^a (%)	ana an dab	ee (%)		
Cycle		exo.enao	exo	endo	
1	98	1.2:1	90	94	
2	96	1.2:1	90	94	
3	97	1.2:1	88	94	
4	93	1.2:1	86	90	
5	96	1.2:1	89	90	

 a Isolated yield. b *Exo/endo* selectivity was determined by $^1\rm H$ NMR analysis of crude reaction mixture.

As anticipated, the recycling of the imidazolidinone catalyst **I** in Diels-Alder reaction was successfully achieved as well. As shown in Table 5, no significant decrease in catalytic activity was observed when the ionic liquid-supported imidazolidinone catalyst **I** was recovered and reused in further reactions. Excellent enantioselectivities of 89% *exo ee* and 90% *endo ee* of the corresponding products were obtained even in the 5th cycle, making the catalyst **I** synthetically efficient and useful (entry 5).

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Understandably, in the absence of the ionic liquid unit, the recovery and recycling of the imidazolidinone catalyst will undoubtedly become very difficult.

Conclusions

- ⁵ In summary, we have described an efficient, economical, and practical method for enantioselective Diels-Alder reaction by using an ionic liquid-supported imidazolidinone catalyst I, leading to the desired products in moderate to good yields with good to excellent enantioselectivities. Especially noteworthy, the
- ¹⁰ ionic liquid-supported imidazolidinone catalyst **I** can be readily recovered and recycled in further transformations for at least five times while still retaining its high catalytic activity which is in accordance with the principle of Green Chemistry, rendering the catalyst potentially useful in organic synthesis.

15 Experimental

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General procedure for the enantioselective Diels-Alder reaction: To a solution of catalyst I (0.05 g, 0.1 mmol) in CH₃CN (or CH₃NO₂)/H₂O (1 mL, 95/5 v/v) was added trifluoroacetic acid (0.0114 g, 0.1 mmol) and α,β -unsaturated aldehyde (1 mmol). 20 The solution was stirred for 1-2 minutes before the addition of cyclopentadiene (0.331 g, 5 mmol). The reaction was stirred at room temperature for 21 h before the removal of CH₃CN (or CH₃NO₂) under vacuo. The residue was extracted by diethyl ether (5 mL x 5) with stirring on a magnetic stirrer, and the combined 25 organic layer was washed with brine, dried over Na₂SO₄ and filtered. The filtrate was concentrated under vacuo and purified by silica gel column chromatography using hexane and ethyl acetate as eluant to afford the desired product. The remaining oil compound in the flask (catalyst I) was dried under vacuo and 30 reused in further reactions by the addition of trifluoroacetic acid (0.0114 g, 0.1 mmol) and solvent.

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