

Asymmetric Diels–Alder Reaction of α,β -Unsaturated Oxazolidin-2one Derivatives Catalyzed by a Chiral Fe(III)-Bipyridine Diol Complex

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(5) Supporting Information

ABSTRACT: An asymmetric Fe^{III} -bipyridine diol catalyzed Diels–Alder reaction of α,β -unsaturated oxazolidin-2-ones has been developed. Among various $Fe^{II}/$ Fe^{III} salts, $Fe(ClO_4)_3$ · $6H_2O$ was selected as the Lewis acid of choice. The use of a low catalyst loading (2 mol % of $Fe(ClO_4)_3$ · $6H_2O$ and 2.4 mol % of Bolm's ligand) afforded high yields (up to 99%) and high enantiomeric excesses (up to 98%) of *endo*-cycloadducts for the Diels–Alder reaction between cyclopentadiene and substituted acryloyloxazolidin-2-ones. Other noncyclic dienes led to decreased enantioselectivities. A proposed model supports the observed stereoinduction.

The Diels–Alder reaction is one of the most straightforward and atom economical methods to construct chiral six-membered rings in organic chemistry¹ and represents a great interest in total synthesis and for the preparation of biologically active compounds.^{1b,2} This reaction is an attractive synthetic transformation providing regio- and stereoselective compounds. Much effort has been invested for better stereocontrol of the process with the use of chiral Lewis acids. The Diels–Alder reaction between oxazolidinones and cyclopentadiene is one of the most successful reactions to evaluate the catalytic activity of a metal Lewis acid catalyst.^{1c,d} Asymmetric Diels–Alder reactions are well-known involving Cu,³ Mg,⁴ Zn,⁵ Al,⁶ Pd,⁷ B,⁸ Ti,⁹ Sc,¹⁰ Ni,¹¹ and lanthanides.¹² Pioneering work by Narasaka,^{9b} Corey,¹³ Evans,¹⁴ Bolm,¹⁵ and others¹⁶ involved oxazolidinone derivatives chosen as substrates.

Iron complexes show major advantages due to their low toxicity, environmental benignity, commercial availability, and low cost.¹⁷ From a green chemistry point of view, the development of novel iron-catalyzed reactions represents a challenge.¹⁸ A few iron catalysts were used in the asymmetric Diels-Alder reaction since the 1990s, the reaction of 3acryloyloxazolidin-2-one being usually chosen as benchmark reaction.¹⁹ An efficient C₂-symmetrical chiral bis-oxazoline-FeI₃ catalyst, ^{19a} and *pybox*-FeBr₃ catalyst with AgSbF₆^{19b} have been disclosed by Corey and Shibasaki, respectively, providing high enantioselectivities. Good ee's have also been reported using chiral bidentate C_2 -symmetrical bis(sulfoxide) ligands with FeI_{3} ,^{19c} *diphosphine* with Fe^{II} and Fe^{III} ,^{19d,e} and a 2,2'-*binaphthyl-diimine* ligand with $FeCl_{2}$.^{11b} However, some of the methods suffer from a number of drawbacks, such as limited scope and lack of generality. Chiral 2,2'-bipyridyl ligands have been often used in asymmetric reactions due to their stability and excellent coordinating ability to a wide range of metal ions. As part of an ongoing interest in iron catalysis, our laboratory studied the use of a chiral 2,2'-bipyridyl diol ligand developed by Bolm,²⁰ coordinated with Fe^{II}, capable of catalyzing asymmetric Mukaiyama aldol,²¹ epoxide-opening with anilines



and indoles,²² and thia-Michael addition reactions.²³ The present investigation provides attractive new conditions for the asymmetric Diels–Alder reaction between various dienes and oxazolidinone dienophiles, catalyzed by Bolm's ligand (L*) combined with various iron salts.

Initial studies were focused on screening the efficiency of various solvents on the Diels–Alder reaction (Table 1).

 Table 1. Fe^{III}-Catalyzed Reaction of Cyclopentadiene with 3

 Acryloyloxazolidin-2-one 2a: Solvent Study^a

entry	solvent	yield (%) ^b	endo/exo ^c	ee (%) ^d
1	CH_2Cl_2	83	82:18	90
2	$(CH_2Cl)_2$	83	87:13	90
3	MeCN	85	90:10	96
4	THF	52	85:15	76
5	CHCl ₃	62	87:13	12
6	DMC ^e	76	91:9	92
7	H_2O	92	90:10	0

^{*a*}Conditions: $Fe(ClO_4)_3 \cdot 6H_2O$ (5 mol %), L* (6 mol %), 1 (3.5 mmol), 2a (0.5 mmol), and solvent. ^{*b*}Yield of isolated products (diastereomeric mixture). ^{*c*}Determined by ¹H NMR. ^{*d*}Determined for the *endo* isomer by chiral HPLC. ^{*e*}Carried out at 2 °C.

Cyclopentadiene (1) and 3-acryloyloxazolidin-2-one (2a) were selected as model substrates to optimize the reaction conditions. It was noted that the conversion and enantio-selectivity are strongly influenced by the solvents used. High ee's (90%) were first obtained by using polar, aprotic, and noncoordinating solvents, such as CH₂Cl₂ and (CH₂Cl)₂ (entries 1 and 2), but long reaction times (48 h) were needed to obtain complete conversions. By using a coordinating solvent, such as MeCN, the reaction time was decreased to 1.5 h with a higher ee (96%) and a good isolated yield (85%) (entry 3). When the reaction was run in another polar, aprotic,

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and coordinating solvent, such as THF, a longer reaction time was needed (15 h), and a low yield and *ee* were obtained (entry 4). Chloroform was also tested but afforded a low yield and enantioselectivity (entry 5). Then, a greener solvent, dimethyl carbonate (DMC), was tested (entry 6), and an *ee* of 92% was obtained after 5 h.²⁴ Water, known as often being beneficial in the Diels–Alder reaction,²⁵ was then tested as a solvent, and the reaction was needed, and no enantioselectivity was observed. However, none of these solvents gave results superior to MeCN (entry 3), which was consequently chosen in further studies.

To improve the efficiency of the reaction, various catalyst loadings and temperatures were screened. A temperature decrease led to an increase in *ee* (Table 2, entries 1-3).

Table 2. Fe^{III}-Catalyzed Reaction of Cyclopentadiene with 3-Acryloyloxazolidin-2-one 2a: Screening of the Catalyst Loading^a

entry	x	у	temp (°C)	yield (%) ^b	endo/exo ^c	ee (%) ^d
1	5	6	rt	85	92:8	96
2	5	6	0	84	91:9	98
3	5	6	-30	96	93:7	98
4	5	10	-30	91	88:12	96
5	2.5	5	-30	93	90:10	98
6	2	2.4	-30	99	92:8	98
7	1	1.2	-30	82	92:8	92
8	2	2.4	-40	89	92:8	70

^{*a*}Conditions: $Fe(ClO_4)_3$ ·6H₂O (*x* mol %), L* (*y* mol %), **1** (3.5 mmol), **2a** (0.5 mmol), and MeCN. ^{*b*}Yield of isolated products (diastereomeric mixture). ^{*c*}Determined by ¹H NMR. ^{*d*}Determined for the *endo* isomer by chiral HPLC.

Indeed, by lowering the temperature, the reaction proceeded smoothly to afford the desired product. Using -30 °C as the optimized reaction temperature, various catalyst loadings and ratios of Fe(ClO₄)₃·6H₂O to L* were tested (entries 4–7). A low catalyst loading, i.e. 2 mol % of Fe(ClO₄)₃·6H₂O, together with 2.4 mol % of L*, turned out to be efficient enough to afford an excellent yield (99%), good diastereoselectivity (*endo/exo* = 92:8), and a high *ee* of 98% (entry 6). A lower catalyst loading of 1 mol % of Fe(ClO₄)₃·6H₂O, together with 1.2 mol % of L*, led to a decrease of the catalytic efficiency and the *ee* (entry 7). A control experiment was performed at a lower temperature (-40 °C, entry 8). Surprisingly, the level of enantioselectivity was neither increased nor maintained.

Other Fe^{II}/Fe^{III} salts, i.e. Fe(ClO₄)₂·6H₂O, Fe(OTf)₂, and Fe(OTf)₃, provided excellent yields (Table 3, entries 1–3, 95– 97%), although the highest *ee* was obtained with the Fe^{III} salt. No enantioselectivity was observed by using FeCl₂ and FeCl₃ (entries 4–5). FeI₃, previously used by Corey with a *bisoxazoline* ligand,^{19a} appeared to be inefficient in terms of conversion and enantioselectivity were obtained (entry 7). As previously disclosed by Shibasaki,^{19b} the use of AgSbF₆ as an additive with FeBr₃ had a positive impact on both yield and enantioselectivity of the Diels–Alder reaction (entry 8). However, Fe(ClO₄)₃·6H₂O and Fe(OTf)₃ were still far more superior. The optimized reaction conditions (2 mol % of Fe(ClO₄)₃·6H₂O and 2.4 mol % of L* in MeCN) were selected for further studies.²⁶

Table 3. Optimization of the Iron Salt Used in the Model Reaction a^{a}

entry	FeX _n	yield (%)	endo/exo ^b	ee (%) ^c
1	Fe(ClO ₄) ₂ ·6H ₂ O	97 ^d	90:10	78
2	Fe(OTf) ₂	95 ^d	94:6	40
3	Fe(OTf) ₃	96 ^d	96:4	96
4	FeCl ₂	22^e	88:12	0
5	FeCl ₃	7^e	90:10	2
6	FeI ₃	14^e	76:24	2
7	FeBr ₃	11^e	83:17	2
8	FeBr ₃ + AgSbF ₆	50 ^e	87:13	36

^{*a*}Conditions: FeX_n (2 mol %), L* (2.4 mol %), 1 (3.5 mmol), 2a (0.5 mmol), and MeCN. ^{*b*}Determined by ¹H NMR. ^{*c*}Determined for the *endo* isomer by chiral HPLC. ^{*d*}Yield of isolated product (diastereomeric mixture). ^{*e*}Yield determined by ¹H NMR.

Having identified optimal conditions, we next sought to demonstrate the scope of this procedure. Under the optimized reaction conditions,²⁷ the range of dienophiles was broadened, and the results are listed in Scheme 1. First, dienophile

Schen	ne 1. Influ	ence of th	ne Dienoj	phile on	the Reaction	on of
Cyclo	pentadiene	e and Var	ious Acry	loyloxaz	olidin-2-on	es ^a



^{*a*}Conditions: $Fe(ClO_4)_3 \cdot 6H_2O$ (2 mol %), L* (2.4 mol %), 1 (3.5 mmol), 2a (0.5 mmol), and MeCN. ^{*b*}Yield of isolated products (diastereomeric mixture). ^{*c*}Determined by ¹H NMR. ^{*d*}Determined for the *endo* isomer by chiral HPLC. ^{*e*}Fe(ClO₄)₃ \cdot 6H₂O (4 mol %), L* (4.8 mol %), CH₂Cl₂.

(*E*)-3-(but-2-enoyl)oxazolidin-2-one **2b** was employed. After 1 day, this dienophile efficiently reacted with the cyclopentadiene and afforded compound **3b** with an excellent yield (95%) and a high *ee* (98%). Cycloadduct **3c** was obtained with a moderate yield (70%) and 80% *ee* even when using a catalyst loading of 4 mol % of Fe(ClO₄)₃·6H₂O and 4.8 mol % of L* in CH₂Cl₂.²⁸ This decrease could be attributed to the steric effect of the Ph ring on dienophile **2c**. Using dienophile (*E*)-3-(4,4,4-trifluor-obut-2-enoyl)oxazolidin-2-one **2d**, the reaction proceeded

smoothly at -10 °C and was complete after 8 h. However, a dramatic decrease of ee (14%) was observed. Analogous dienophiles 2e and 2f were also tested to get further insight on the role of the structure of the dienophile. A high ee (96%) was achieved by employing dienophile 2e after a short reaction time (8 h). This means that the absence of an oxygen atom in the oxazolidinone ring has no impact on the selectivity. Using dienophile 2f, no enantiomeric excess was observed. This result suggests that the coordination of the two carbonyl oxygens of the dienophile to the complex is essential to afford enantioselectivity. To extend the scope of the Diels-Alder reaction, other electron-poor dienophiles incorporating 2alkenovlpyridine and N-oxide substitution were also tested (2g-i). These similar substrates have been used previously by others in a Cu^{II} catalyzed Diels-Alder reaction^{3d} and are known to coordinate to the metal center by the pyridine and the carbonyl group lone pairs. Unfortunately, no ee was observed by using 2-alkenoylpyridine N-oxide 2g, suggesting that the chelation of 2g to the Fe^{III} complex by the carbonyl group and the negatively charged oxygen coming from the oxide does not occur. Using 2-alkenoylpyridine dienophiles 2h and 2i, possessing a Ph or an electron-withdrawing group, such as p-ClC₆H₄, 84% ee and 70% ee were respectively obtained. Otherwise, an electron-donating group such as p-MeOC₆H₄ (2j) was not beneficial to the enantioselectivity (12%).

Various dienes were then tested in the Diels–Alder reaction using the same model dienophile, i.e. 3-acryloyloxazolidinone 2a. All dienes afforded good yields and moderate to high *ee's* of products (Scheme 2). However, a higher catalyst loading and

Scheme 2. Influence of the Diene on the Enantioselectivity of the Reaction with 3-Acryloyloxazolidinone^{α}



^{*a*}Conditions: Fe(ClO₄)₃·6H₂O (4 mol %), L* (4.8 mol %), 1k-n (3.5 mmol), 2a (0.5 mmol), and MeCN. ^{*b*}Carried out at -10 °C for 72 h. ^{*c*}Yield of isolated products (diastereomeric mixture). ^{*d*}Determined by chiral HPLC. ^{*e*}*ee* of the major isomer. ^{*f*}Determined by ¹H NMR. ^{*g*}Fe(ClO₄)₃·6H₂O (8 mol %) and L* (9.6 mol %) were used.

longer reaction time were needed to complete the reactions. The Diels-Alder reaction between less reactive 1,3-cyclohexadiene 1k and 3-acryloyloxazolidinone 2a afforded a moderate yield of product 3k (70%), a high diastereoselectivity (*endo/exo* = 94:6), and a 92% *ee* for the *endo* adduct. By employing unsubstituted butadiene 1l, an 88% *ee* with a 73% yield of 3l was obtained. With methyl-substituted dienes (1m and 1n), the enantioselectivities were decreased (50% *ee* and 60% *ee*, respectively).

Based on the above results, transition states are proposed (Figure 1). Previous X-ray studies obtained with L^* coordinated to iron have demonstrated the coordination of the bipyridine diol ligand to the metal center in a tetradentate fashion by the chelation of four donating atoms in the equatorial sites of a pentagonal bipyramidal geometry.^{21a,22} A



Figure 1. Proposed transition states involving the Fe^{III} chiral catalyst.

solvent molecule (noted as S) is coordinated to the axial site and a fifth labile equatorial position is occupied by the reversible chelation of an oxygen of the *cis*-oxazolidinone,^{3h} as supported by DFT.²³ Consequently, the favored transition state (A) shows the *endo* approach of the diene from the back side, with the oxazolidin-2-one carbonyl occupying the equatorial position. The *endo* approach arises from the steric hindrance of the *tert*-butyl group of L*, which shields the diene approach from the front side.

In summary, we have successfully demonstrated an efficient catalytic system capable of catalyzing the Diels–Alder reaction between various dienophiles and dienes to give high isolated yields (up to 99%) with high *ee's* (up to 98%) of the desired products. This method includes using 2.4 mol % of L* and 2 mol % of Fe(ClO₄)₃·6H₂O to generate the Fe^{III} complex *in situ*. To the best of our knowledge, this is the first example of an iron-catalyzed Diels–Alder reaction using a chiral bipyridine diol ligand. Work is currently focused on further applications of the method toward the synthesis of biologically active targets and will be reported in due course.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.7b03939.

Experimental details, characterization date, NMR spectra, and chromatograms (PDF)

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Notes

The authors declare no competing financial interest.

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(24) 2-MeTHF and CPME were also tested and afforded 74% and 78% of yields, for 88:12 and 86:14 *endo/exo* ratios and *ee's* of 76% and 52%, respectively, after 5 h.

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(26) Interestingly, when 20 mol % of hexafluoroisopropanol (HFIP) was used as an additive, the same yield and stereoselectivities were obtained.

(27) A fine-tuning of the temperature was done to avoid longer reaction times.

(28) No conversion was observed using 2 mol % of Fe(ClO₄)₃·6H₂O and 2.4 mol % of L* in MeCN because the substrate was not soluble. CH₂Cl₂ and a double catalyst loading to ensure higher conversion were used.