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

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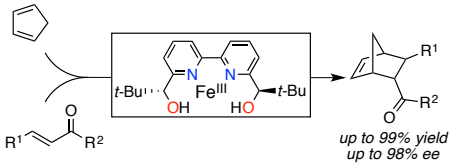
Supporting Information Placeholder



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, $Fe(ClO_4)_3{\cdot}6H_2O$ was selected as the Lewis acid of choice. The use of a low catalyst loading (2 mol % of $Fe(ClO_4)_3{\cdot}6H_2O$ 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 non-cyclic dienes led to decreased enantioselectivities. A proposed model supports the observed stereoinduction.

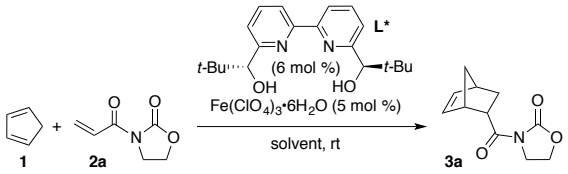
The Diels-Alder reaction is one of the most straightforward and atom economical methods to construct chiral six-membered rings in organic chemistry[1] and represents a great interest in total synthesis and for the preparation of biologically active compounds.[1b, 2] This reaction is an attractive synthetic 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, 1d] 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 others[16] 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 3-acryloyloxazolidin-2-one being usually chosen as benchmark reaction.[19] Efficient C_2-symmetrical chiral *bis-oxazoline*-FeI_3 catalyst,[19a] and *pybox*-$FeBr_3$ catalyst with $AgSbF_6$,[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, 19e] and *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). 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 the enantioselectivity are strongly influenced by the solvents used. High *ee's* (90%) were firstly obtained by using polar, aprotic, and non-coordinating solvents, such as CH_2Cl_2 and $(CH_2Cl)_2$ (entries 1 and 2), but long reaction times (48 h) were needed to get 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, and coordinating solvent, such as THF, a longer reaction time was needed (15 h), and 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 92% of *ee* was obtained after 5 h.[24] Water, known as being often beneficial in the Diels-Alder reaction,[25] was then tested

as a solvent, and the reaction was complete after 15 h (entry 7). A longer reaction time 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.

Table 1. Fe^{III}-catalyzed reaction of cyclopentadiene with 3-acryloyloxazolidin-2-one 2a–Solvent study[a]



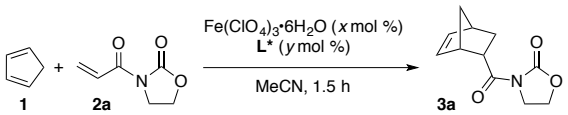
entry	solvent	yield (%)[b]	*endo*/*exo*[c]	*ee* (%)[d]
1	CH_2Cl_2	83	82:18	90
2	$(CH_2Cl)_2$	83	87:13	90
3	MeCN	85	90:10	96
4	THF	52	85:15	76
5	$CHCl_3$	62	87:13	12
6	DMC[e]	76	91:9	92
7	H_2O	92	90:10	0

[a]Conditions: $Fe(ClO_4)_3{\cdot}6H_2O$ (5 mol %), **L*** (6 mol %), **1** (3.5 mmol), and **2a** (0.5 mmol), 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.

To improve the efficiency of the reaction, various catalyst loadings and temperatures were screened. A temperature decrease led to an increase of the *ee* (Table 2, entries 1–3). 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 $Fe(ClO_4)_3{\cdot}6H_2O$ to **L*** were tested (entries 4–7). A low catalyst loading, i.e. 2 mol % of $Fe(ClO_4)_3{\cdot}6H_2O$, 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 high *ee* 98% (entry 6). A lower catalyst loading of 1 mol % of $Fe(ClO_4)_3{\cdot}6H_2O$, 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 the enantioselectivity was neither increased nor maintained.

Other Fe^{II}/Fe^{III} salts, ie. $Fe(ClO_4)_2{\cdot}6H_2O$, $Fe(OTf)_2$, 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 $FeCl_2$ and $FeCl_3$ (entries 4–5). FeI_3, previously used by Corey with a *bis-oxazoline* ligand,[19a] appeared to be inefficient in terms of conversion and enantioselectivity (entry 6). Using $FeBr_3$ low yield and no enantioselectivity were obtained (entry 7). As previously disclosed by Shibasaki,[19b] the use of $AgSbF_6$ as an additive with $FeBr_3$ had a positive impact on both yield and enantioselectivity of the Diels-Alder reaction (entry 8). However, $Fe(ClO_4)_3{\cdot}6H_2O$ and $Fe(OTf)_3$ were still far more superior. The optimized reaction conditions (2 mol % of $Fe(ClO_4)_3{\cdot}6H_2O$ and 2.4 mol % of **L*** in MeCN) were selected for further studies.[26]

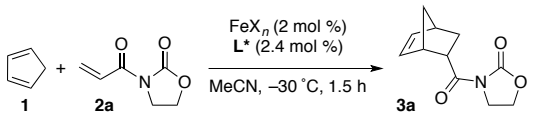
Table 2. Fe^{III}-catalyzed reaction of cyclopentadiene with 3-acryloyloxazolidin-2-one 2a–Screening of the catalyst loading[a]



entry	*x*	*y*	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: $Fe(ClO_4)_3{\cdot}6H_2O$ (*x* mol %), **L*** (*y* mol %), **1** (3.5 mmol), and **2a** (0.5 mmol), MeCN. [b]Yield of isolated products (diastereomeric mixture). [c]Determined by ^1H NMR. [d]Determined for the *endo* isomer by chiral HPLC.

Table 3. Optimization of the iron salt used in the model reaction[a]



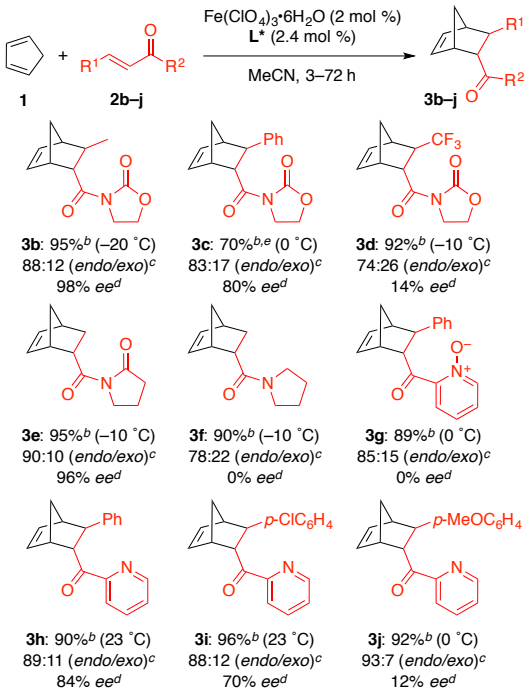
entry	FeX_n	yield (%)	*endo*/*exo*[b]	*ee* (%)[c]
1	$Fe(ClO_4)_2{\cdot}6H_2O$	97[d]	90:10	78
2	$Fe(OTf)_2$	95[d]	94:6	40
3	$Fe(OTf)_3$	96[d]	96:4	96
4	$FeCl_2$	22[e]	88:12	0
5	$FeCl_3$	7[e]	90:10	2
6	FeI_3	14[e]	76:24	2
7	$FeBr_3$	11[e]	83:17	2
8	$FeBr_3 + AgSbF_6$	50[e]	87:13	36

[a]Conditions: FeX_n (2 mol %), **L*** (2.4 mol %), **1** (3.5 mmol), and **2a** (0.5 mmol), 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 were listed in Scheme 1. First, dienophile (*E*)-3-(but-2-enoyl)oxazolidin-2-one **2b** was employed. After one 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

$Fe(ClO_4)_3{\cdot}6H_2O$ and 4.8 mol % of **L*** in CH_2Cl_2.[28] This decrease could be attributed to the steric effect of the Ph ring on dienophile **2c**. Using dienophile (*E*)-3-(4,4,4-trifluorobut-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 2-alkenoyl pyridine and *N*-oxide substituted were also tested (**2g–j**). 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-alkenoyl pyridine *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-alkenoyl pyridine dienophiles **2h** and **2i**, possessing a Ph or an electron withdrawing group, such as *p*-ClC_6H_4, 84% *ee* and 70% *ee* were respectively obtained. Otherwise, an electron donating group like *p*-$MeOC_6H_4$ (**2j**) was not beneficial to the enantioselectivity (12%).

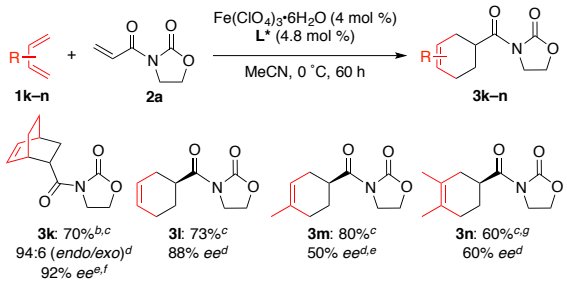
Scheme 1. Influence of the dienophile on the reaction of cyclopentadiene and various acryloyloxazolidin-2-ones[a]



[a]Conditions: $Fe(ClO_4)_3{\cdot}6H_2O$ (2 mol %), **L*** (2.4 mol %), **1** (3.5 mmol), and **2a** (0.5 mmol), MeCN. [b]Yield of isolated products (diastereomeric mixture). [c]Determined by ^1H NMR. [d]Determined for the *endo* isomer by chiral HPLC. [e]$Fe(ClO_4)_3{\cdot}6H_2O$ (4 mol %), **L*** (4.8 mol %), CH_2Cl_2.

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 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 92% *ee* of the *endo* adduct. Employing unsubstituted butadiene **1l**, 88% *ee* with 73 % yield of **3l** was obtained. With methyl-substituted dienes (**1m** and **1n**), the enantioselectivities were decreased (50 and 60% *ee*, respectively).

Scheme 2. Influence of the diene on the enantioselectivity of the reaction with 3-acryloyloxazolidinone[a]



[a]Conditions: $Fe(ClO_4)_3{\cdot}6H_2O$ (4 mol %), **L*** (4.8 mol %), **1k–n** (3.5 mmol), and **2a** (0.5 mmol), 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]$Fe(ClO_4)_3{\cdot}6H_2O$ (8 mol %) and **L*** (9.6 mol %) were used.

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 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. *Endo* approach arises from the steric hindrance of the *tert*-butyl group of **L***, which shields the diene approach from the front side.

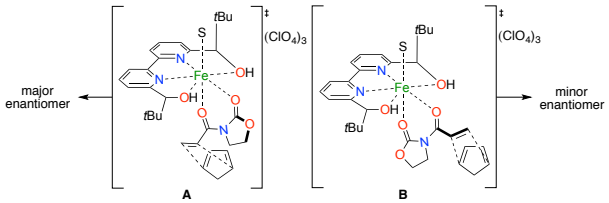


Figure 1. Proposed transition states involving the Fe^{III} chiral catalyst

To sum up, 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%) and high *ee's* (up to 98%) of the desired products. This method includes using 2.4 mol % of **L*** and 2 mol % of

$Fe(ClO_4)_3{\cdot}6H_2O$ 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 towards 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: xxx.

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

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(28) No conversion was observed using 2 mol % of $Fe(ClO_4)_3{\cdot}6H_2O$ and 2.4 mol % of L* in MeCN because the substrate was not soluble. CH_2Cl_2 and a double catalyst loading to ensure higher conversion were used.