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Chiral bis(2-oxazolinyl)xanthene (xabox)/transition-metal complexes catalyzed 1,3-dipolar cycloaddition reactions and Diels–Alder reactions

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Abstract

A series of chiral 4,5-bis(2-oxazolinyl)-(2,7-di-*tert*-butyl-9,9-dimethyl)-9*H*-xanthenes (xabox) and their transition-metal complexes were synthesized. The X-ray analysis of xabox–$RhCl_3$ complex shows a unique facial type structure. Xabox–Bn–Mn(II) and xabox–Bn–Mg(II) complexes were found to be efficient catalysts in nitrone 1,3-dipolar cycloaddition (1,3-D.C.) reaction resulting in good to excellent enantioselectivities ranging from 96:4 to >99:1of *endo*/*exo* ratio and 91–96% ee for the *endo* adduct. The correlation between enantiomeric excess of the ligand and the product in the nitrone 1,3-D.C. reaction shows a clear linear relationship, which suggests xabox–metal catalyst worked as a single molecular catalyst. In addition, xabox–*i*-Pr–Mn(II) complex was also found to be an active catalyst for Diels–Alder (D–A) reaction of acryloyloxazolidinone and cyclopentadiene affording the corresponding cycloadduct in quantitative yield along with 82% ee and 98:2 *endo*/*exo* ratio.

Keywords: 1,3-Dipolar cycloaddition; Chiral ligand; Diels–Alder reaction; Oxazoline; Xanthene

1. Introduction

Since chiral catalyst is one of the most efficient and promising protocols for providing optically pure organic molecules, asymmetric catalysts are represented as one of the most active areas in modern organic chemistry.[1] The development of chiral ligand for catalytic asymmetric transformation can create new strategies to access the target molecules. A number of asymmetric synthetic methods with a variety of chiral catalysts having new chiral ligands have been developed so far, and are being applied to both the total synthesis of natural products and biologically active artificial organic compounds with a high efficiency.[2] Among them, asymmetric cycloadditions are recognized as powerful methods for the synthesis of optically active complex molecules since multiple asymmetric centers can be constructed in one-step transformation.[3] Especially, 1,3-dipolar cycloaddition (1,3-D.C.) reaction of nitrones with alkenes is one of the most useful reactions in organic synthesis since the hetero-atoms such as nitrogen and oxygen are pharmacologically important.[4] It offers a straightforward and efficient synthesis of isoxazolidine derivatives with highly regio- and stereoselective construction of three new continuous chiral centers in the adduct. And the isoxazolidine formed can be transformed into many attractive biologically active compounds such as alkaloids, amino alcohols, amino sugars, and β-lactams.[5]

On the other hand, the Diels–Alder (D–A) reaction is one of the most powerful well known method for carbon–carbon bond formation, which afford cycloadducts having a double bond and two newly formed C–C single bonds.[6] It is also popular and useful synthetic tool in organic chemistry as well as 1,3-D.C. reaction, and has a long history compared to 1,3-D.C. reactions.

The progress in number of chiral Lewis acid catalysts employing chiral ligands based on bis- and tridentate oxazoline-derived C_2-symmetric chiral ligands has been reflected to the developing of these asymmetric 1,3-D.C.[7] and D–A[8] reactions. Chiral oxazoline ligands have played an important role

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in the field of asymmetric induction since these are easily accessible from amino alcohols and carboxylic acids.[9,10]

In this report, we present a new series of tridentate chiral ligands, which was derived from bis(2-oxazolinyl)xanthene (xabox). The transition-metal complexes prepared from this enantiopure ligand and various transition-metal(II) perchlorates were found to be an efficient catalyst for 1,3-D.C. reactions of nitrones with 3-alkenoyl-2-oxazolidinones and D–A reactions of cyclopentadiene with 3-acryloyl-2-oxazolidinone. With complexes of (*S*,*S*)-xabox–Bn and Mn(II), Mg(II), or Ni(II) perchlorate, respectively, the correlation between ligands' ee and product ee was also examined in 1,3-D.C. reactions to pursue the behavior of catalyst such as homo- and hetero-chiral complex formation.[11]

2. Results and discussion

2.1. Synthesis of bis(2-oxazolinyl)xanthene ligands

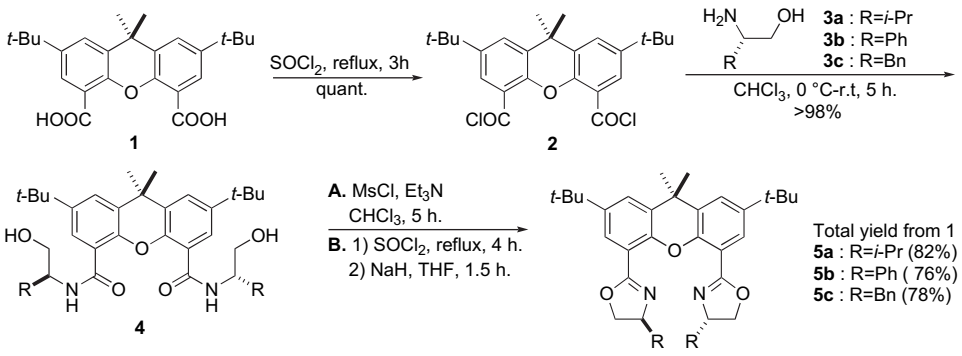
Chiral bis(2-oxazolinyl)xanthene (xabox) ligands having a xanthene backbone were synthesized from the corresponding commercially available xanthene carboxylic acid **1** and amino alcohols derived from the reduction of natural amino acids in three steps. Then excess thionyl chloride was removed under reduced pressure followed by the reaction with amino alcohols under basic conditions resulting in the corresponding amide alcohols in 80–90% yield. There are two different methods for oxazoline ring formation. One is mesylation of the amide alcohols with mesylchloride followed by oxazoline ring formation in one-pot procedure (method **A**) and the other is chlorination of the hydroxyl group with thionyl chloride to prepare the chloethyl moiety followed by oxazoline ring formation with sodium hydride (6 equiv) in tetrahydrofuran (method **B**). Both methods **A** and **B** gave (*S*,*S*)-xabox–R ligands as a new entry in tridentate oxazoline chiral ligands in 98% yields (Scheme 1).[12]

2.2. Xabox/transition-metal complex catalyzed 1,3-D.C. reactions of nitrones with oxazolidinone

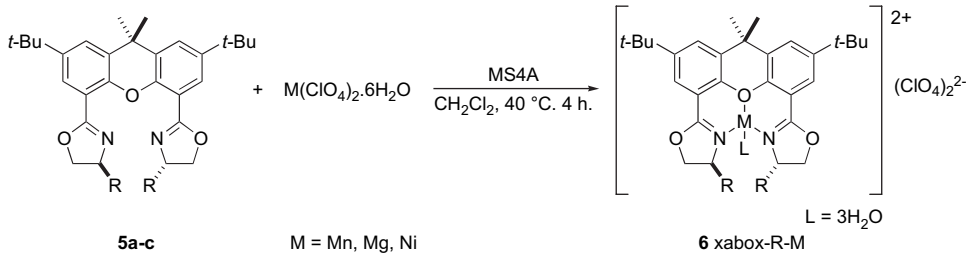
Recently, highly enantioselective 1,3-D.C. reactions of nitrones with alkenoyl oxazolidinone employing chiral bis(oxazolinyl)pyridine (pybox)–Ni(II) complexes have been reported from our research group.[13] Initially, we have selected $Ni(ClO_4)_2\cdot 6H_2O$ as a central metal and briefly examined the chiral shielding substituent effect on the oxazoline rings using a model reaction of nitrone **7a** with 3-crotonoyl-2-oxazolidinone **8a** in order to determine the efficiency of the new ligand system. The catalysts were prepared by heating a mixture of xabox ligands (**5a–c**) with $Ni(ClO_4)_2\cdot 6H_2O$ in the presence of activated 4 Å MS at 40 °C for 4 h in dichloromethane (Scheme 2). After complexation, the MS were filtered off to obtain a pale blue-green solution, which was again filtered via membrane filter. The resulting catalyst solution was then added to pre-activated 4 Å MS at room temperature. At this stage, 3-crotonoyl-2-oxazolidinone and nitrone were added to the catalyst. The resulting suspension was stirred at room temperature. The results of xabox–Ni(II) catalyzed 1,3-D.C. reactions are summarized in Table 1. xabox–*i*-Pr–Ni(II) and xabox–Bn–Ni(II) complexes catalyzed 1,3-D.C. reactions proceeded smoothly, affording the product **9a** in a high yield within 24 h with good *endo*/*exo* ratio and moderate to good enantioselectivities of *endo* product (61% ee and 85% ee), respectively (entries 1 and 3), whereas xabox–Ph shows only poor enantioselectivity (entry 2). As for these results, xabox–Bn **5c** was the best ligand for the nitrone 1,3-D.C. reaction.

The metal effect was screened for further optimization with xabox–Bn **5c** in the 1,3-D.C. reaction. Among the metal screened, the best results in both diastereo- and enantioselectivities were obtained in the case of Mn(II) and Mg(II) with 92:8 of *endo*/*exo* ratio with 93% ee for *endo* and 99:1 *endo*/*exo* ratio with 85% ee for *endo* (entries 7 and 10), respectively. The use of xabox–Bn–$Cu(OTf)_2$ complex gave **9a** in 86:14 *endo*/*exo* ratio with 77% ee for *endo* (entry4). However xabox–Bn–Sc complexes gave **9a** as a racemate, although higher than the use of $Cu(OTf)_2$ (entries 5 and 6).

Next, the temperature effects on the catalyst activity were investigated for both Mn(II) and Mg(II) (entries 7–12). The nitrone 1,3-D.C. reactions proceeded smoothly at 0 °C to room temperature in the presence of 10 mol % of **5c** and metals to afford the cycloadducts in high yields as well as high stereoselectivities though the reaction time was lengthened at low temperature. According to the marked results from both diastereo- and enantioselectivity, we examined the optimized catalytic conditions for catalytic asymmetric 1,3-



Scheme 1.



Scheme 2.

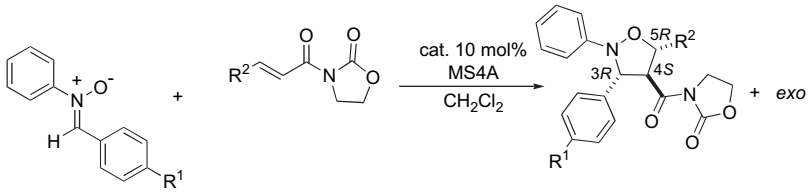
D.C. reaction of various nitrones **7b–d** with 3-crotonoyl-2-oxazolidinones **8a** (entries 13–15). Cycloadducts **9b–d** were obtained in a high yield with excellent stereoselectivities. Acryloyl dienophile **8b** also reacted with nitrone **7a** to afford cycloadduct **9e** in 97% yield with a high enantioselectivity (up to 96% ee) (entries 16 and 17). However, *endo* cycloadduct was observed in a 77:23 *endo*/*exo* ratio, when Mn(II) was used as a metal (entry 16).

N-Acryloyl-2-pyrrolidinones **10a**,**b** with nitrones **7a** and **12** can be similarly reacted in the presence of (*S*,*S*)-xabox–Bn–Mn(II) or Mg(II) complex to give the corresponding cycloadducts **11** and **13**, respectively, the former reaction provided a high chemical yield with an excellent diastereo- and enantioselectivity (Scheme 3). The benzyl group on the nitrogen atom of nitrone is exchanged to another functional group using Pd/C–H_2 reaction condition.

2.3. X-ray analysis of xabox–$RhCl_3$

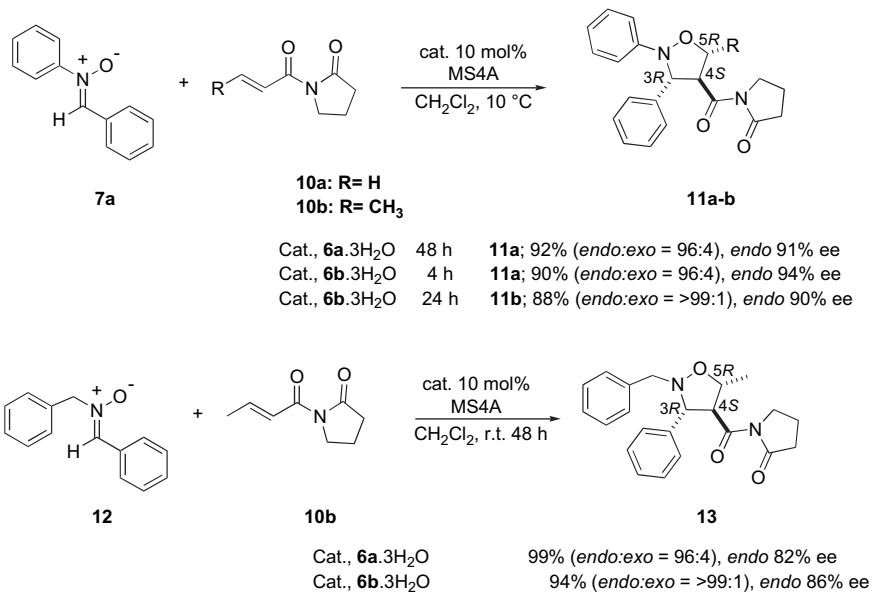
In order to pursue molecular structure of xabox–R–transition-metal complex, single X-ray analysis was carried out since NMR spectroscopic information as for xabox–Mn(II), Mg(II), and Ni(II) is not available because of their strong paramagnetic properties. Fortunately, xabox–*i*-Pr–$RhCl_3$ complex was isolated as a single crystal after equimolar amount of rhodium trichloride and xabox–*i*-Pr **5a** in ethanol at 60 °C for 1.5 h in 83% yield. The structure of rhodium complex **14** determined by X-ray analysis shows a unique facial coordination

Table 1
(*S*,*S*)-xabox–Bn and Mn(II) and Mg(II) catalyzed 1,3-D.C. reaction of nitrones **7a–d** and oxazolidinone **8a**,**b**



Entry	Ligand	Metal	7	8	Product	Temp (°C)	Time (h)	Yield (%)[a]	*endo*/*exo*[b]	*endo* ee[c]
1	**5a**	$Ni(ClO_4)_2 \cdot 6H_2O$	**7a**	**8a**	**9a**	rt	24	72	78:22	61
2	**5b**	$Ni(ClO_4)_2 \cdot 6H_2O$	**7a**	**8a**	**9a**	rt	24	80	88:12	3
3	**5c**	$Ni(ClO_4)_2 \cdot 6H_2O$	**7a**	**8a**	**9a**	rt	24	94	93:7	85
4	**5c**	$Cu(OTf)_2$	**7a**	**8a**	**9a**	rt	24	55	86:14	77
5	**5c**	$Sc(OTf)_3$	**7a**	**8a**	**9a**	rt	6	99	86:14	—
6	**5c**	$Sc(ClO_4)_3 \cdot nH_2O$	**7a**	**8a**	**9a**	rt	24	81	83:17	2
7	**5c**	$Mn(ClO_4)_2 \cdot 6H_2O$	**7a**	**8a**	**9a**	rt	21	85	92:8	93
8	**5c**	$Mn(ClO_4)_2 \cdot 6H_2O$	**7a**	**8a**	**9a**	10	48	85	96:4	95
9	**5c**	$Mn(ClO_4)_2 \cdot 6H_2O$	**7a**	**8a**	**9a**	0	72	78	96:4	93
10	**5c**	$Mg(ClO_4)_2 \cdot 6H_2O$	**7a**	**8a**	**9a**	rt	12	96	99:1	85
11	**5c**	$Mg(ClO_4)_2 \cdot 6H_2O$	**7a**	**8a**	**9a**	10	24	88	99:1	92
12	**5c**	$Mg(ClO_4)_2 \cdot 6H_2O$	**7a**	**8a**	**9a**	0	48	85	99:1	92
13	**5c**	$Mn(ClO_4)_2 \cdot 6H_2O$	**7b**	**8a**	**9b**	rt	12	90	96:4	94
14	**5c**	$Mn(ClO_4)_2 \cdot 6H_2O$	**7c**	**8a**	**9c**	rt	12	95	97:3	95
15	**5c**	$Mn(ClO_4)_2 \cdot 6H_2O$	**7d**	**8a**	**9d**	rt	24	81	98:2	91
16	**5c**	$Mn(ClO_4)_2 \cdot 6H_2O$	**7a**	**8b**	**9e**	rt	8	98	77:23	94
17	**5c**	$Mg(ClO_4)_2 \cdot 6H_2O$	**7a**	**8b**	**9e**	rt	6	97	96:4	96

[a] Isolated yield.
[b] The ratios were determined by ^1H NMR (300 MHz).
[c] The ees were determined by chiral HPLC analysis.



Scheme 3.

of the xabox ligand to rhodium, which was different from known tridentate-transition-metal complexes such as pybox–Rh(III)[14] and DBFOX–Ni(II)[8f] (Scheme 4 and Fig. 1). The selected bond lengths and angle are summarized in Table 2. Furthermore, on the basis of ^{1}H NMR analysis, the proton signal of dimethyl groups on the xanthene skeleton appears as two singlets at 1.67 (3H) and 1.90 (3H) ppm, respectively. In addition, the proton signals of the oxazoline rings appear as four sets of multiplet signals resulting from asymmetrical chemical environments for each protons. As for these results, xabox–transition metal behaves as facial structure in solution phase. And recently, we have clarified on the facial system of the xabox ligand in the oxidative addition reactions on (xabox)/rhodium(I) complex by using excess of chloroacetate in THF, which proved to be σ-symmetric on the basic of NMR study.[15] We now believe that the interaction between xabox–metal complex and the substrates might include a facial coordination intermediate in the 1,3-D.C. reactions of nitrone with dienophile, although different metals are used.

2.4. The correlation between enantiomeric excess of chiral ligand and product

We also investigated the relationship of xabox–Bn **5c** to the enantioselectivity of product **9a** *endo* and observed a non-linear effect from this point of view, but a completely linear relationship was observed for **5c** with all of the metal(II) perchlorate used (Fig. 2). There was no possibility that the mixture of doubly coordinated homo-chiral and hetero-chiral [metal(xabox-Bn)$_2$] or other complicated complexes could be formed. A mixture of xabox ligand and metal(II) can

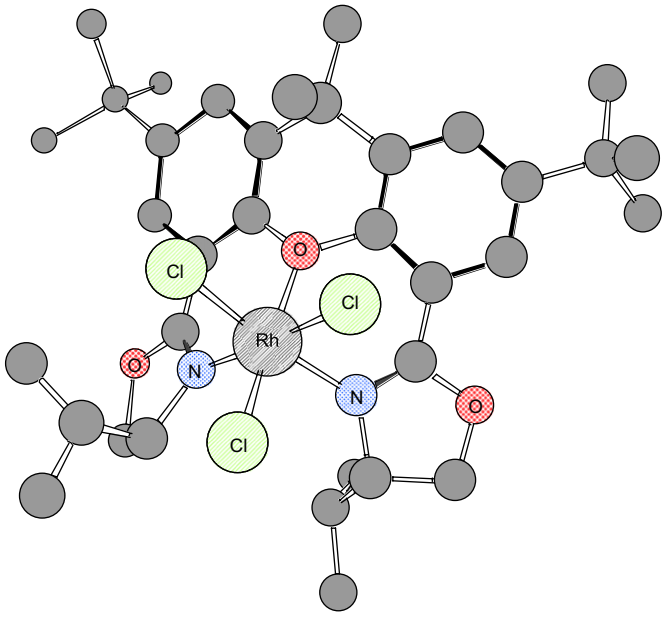
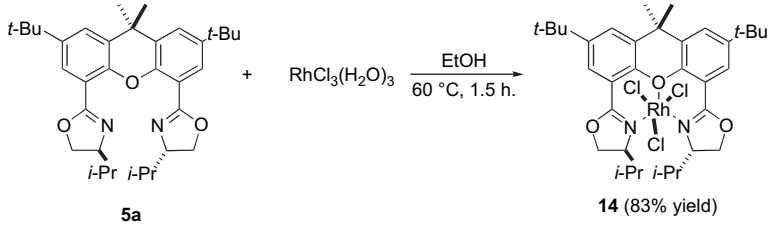


Figure 1. Crystal structure of xabox-*i*-Pr-RhCl$_3$ complex.



Scheme 4. Complexation of xabox–*i*-Pr **5a** and RhCl$_3$(H$_2$O)$_3$ and it crystal structure **14**.

Table 2
Selected bond length (Å) and angles (°) for [(*S*,*S*)-xabox–*i*-Pr]RhCl$_3$ **14**

O1–Rh1	2.129(7)	N1–Rh1	2.05(1)
N2–Rh1	2.07(1)	Cl1–Rh1	2.330(4)
Cl2–Rh1	2.331(4)	Cl3–Rh1	2.270(4)
N1–Rh1–O1	86.9(4)	O1–Rh1–N2	83.7(4)
N2–Rh1–Cl3	92.1(3)	N1–Rh1–Cl3	91.6(3)
N1–Rh1–Cl1	89.1(3)	Cl1–Rh1–Cl2	90.2(1)
N2–Rh1–Cl2	86.8(3)	N1–Rh1–N2	93.8(4)
O1–Rh1–Cl1	90.8(2)	Cl1–Rh1–Cl3	93.4(2)
O1–Rh1–Cl2	91.5(2)	Cl2–Rh1–Cl3	90.1(1)

produce only a singly coordinated complex in the preparation of the catalyst.

2.5. Asymmetric Diels–Alder reactions catalyzed xabox/transition-metal complexes

After we achieved the good results for 1,3-D.C. reaction, we did further studies on catalytic asymmetric Diels–Alder reactions using xabox–R with transition metal complexes. We attempted the typical Diels–Alder reaction between cyclopentadiene and 3-acryloyl-2-oxazolidinon **8b** with a combination of xabox ligands **5a–c** and $Mn(ClO_4)_2 \cdot 6H_2O$ as a catalyst, the results are summarized in Table 3.

The catalysts were prepared by reacting 10 mol % of the corresponding ligands (**5a–c**) with $Mn(ClO_4)_2 \cdot 6H_2O$ in the presence of activated 4 Å MS at 40 °C for 4 h in dichloromethane. After complexation, the MS were filtered off to give a pale yellow solution, which was again filtered via membrane filter. The catalyst solution was then added to pre-activated 4 Å MS at room temperature. To this was added a solution of 3-crotonoyl-2-oxazolidinone in dichloromethane followed by addition of cyclopentadiene (10 equiv) at −78 °C. xabox–transition-metal complexes catalyzed Diels–Alder reactions gave [4+2] cycloadduct in quantitative yields with preferentially *endo* selectivities along with good enantioselectivities. Among xabox-R ligands, the combination of xabox-*i*-Pr **5a** with Mn(II) complex was found to be the most effective catalyst that gave highest enantioselectivity (82% ee) for the *endo* of cycloadduct **15** (entry 1). In the case of **5c** with Mn(II) gave 70% ee of **15** (entry 3). The enantioselectivity was decreased when xabox–Ph **5b** was used (32% ee). Using 20 mol % catalysts does not improve the enantioselectivity (entries 4 and 8). According to the results obtained above, we have used xabox ligands **5a** and **5c** for further optimization (entries 4–14). The enantioselectivity was significantly affected by changing the solvent from dichloromethane to 1,2-dichloroethane and the enantioselectivity was decreased to 36% ee (entry 7). The reaction temperature also effected the enantioselectivity of the product, when the temperature was increased from 0 °C to room temperature. The reaction proceeded slowly and the enantioselectivity of the cycloadduct **15** was dramatically decreased. When the metal was changed, the enantioselectivity of the product was also

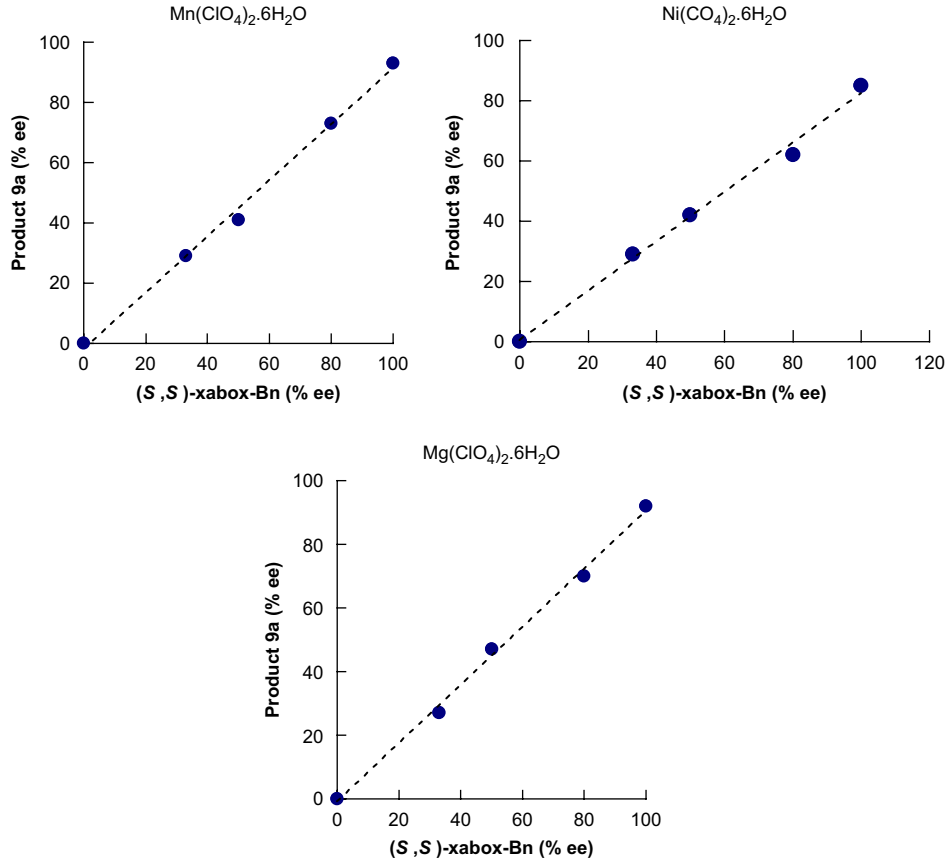
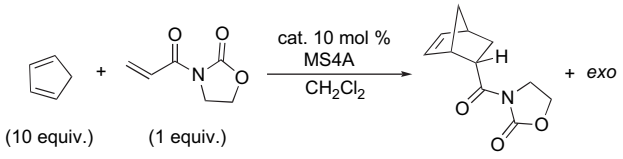


Figure 2.

Table 3
(*S*,*S*)-xabox–R and Mn(II) catalyzed Diels–Alder reaction of cyclopentadiene with acryloy-2-oxazolidinone **8b**



Entry	Ligand	Metal	Temp (°C)	Time (h)	Yield[a] (%)	*endo*/*exo*[b]	*endo* ee[c]
1	**5a**	$Mn(ClO_4)_2\cdot 6H_2O$	−78 to rt	24	98	98:2	82
2	**5b**	$Mn(ClO_4)_2\cdot 6H_2O$	−78 to rt	24	>99	98:2	32
3	**5c**	$Mn(ClO_4)_2\cdot 6H_2O$	−78 to rt	24	>99	97:3	74
4[d]	**5a**	$Mn(ClO_4)_2\cdot 6H_2O$	−78 to rt	24	>99	95:5	76
5	**5a**	$Mn(ClO_4)_2\cdot 6H_2O$	0 to rt	32	>99	89:11	55
6	**5a**	$Mn(ClO_4)_2\cdot 6H_2O$	rt	42	93	91:9	19
7[e]	**5a**	$Mn(ClO_4)_2\cdot 6H_2O$	−20 to rt	24	97	95:5	36
8[d]	**5c**	$Mn(ClO_4)_2\cdot 6H_2O$	−78 to rt	24	>99	97:3	70
9	**5c**	$Mn(ClO_4)_2\cdot 6H_2O$	0 to rt	36	94	97:3	56
10	**5c**	$Mn(ClO_4)_2\cdot 6H_2O$	rt	43	94	88:12	27
11	**5a**	$Ni(ClO_4)_2\cdot 6H_2O$	−78 to rt	24	>99	82:18	13
12	**5a**	$Cu(OTf)_2$	−78 to rt	24	66	82:18	48
13	**5a**	$Sc(OTf)_3$	−78 to rt	24	91	93:7	—
14	**5a**	$Mg(ClO_4)_2\cdot 6H_2O$	−78 to rt	24	95	93:7	9

[a] Isolated yield.
[b] The ratios were determined by ^{1}H NMR (300 MHz).
[c] The ees were determined by chiral HPLC analysis.
[d] Catalyst of 20 mol % was used.
[e] 1,2-Dichloroethane was used as a solvent.

decreased. Specifically changing to $Cu(OTf)_2$ gave lower yield of 66% with 48% ee (entry 12). Ni(II), Mg(II), and $Sc(OTf)_2$ gave very low enantiomeric excess of *endo* product in 13% ee, 9% ee and 1% ee, respectively (entries 11, 13, and 14).

Unfortunately, this xabox/Mn(II) complexes can work well only in asymmetric D–A reaction of cyclopentadiene and very active dienophile such as 3-acryloyl-2-oxazolidionone, but in the case of 3-crotonoyl-2-oxazolidionone and 3-methacryloyl-2-oxazolidinone, the reaction rate was very slow and gave only small amount of cycloadducts.

3. Conclusion

We found a novel catalytic system for asymmetric 1,3-D.C. reaction of nitrones with oxazolidinone and Diels–Alder reaction of cyclopentadiene with acryloyloxazolidinone by the use of a xabox–Mn(II) or Mg(II) complex resulted in good to excellent stereoselectivities. X-ray analysis of the complex revealed a facial coordination of xabox ligand to metal, which may give information on the mechanism of both 1,3-D.C. reactions and Diels–Alder reactions for the transition state. A series of tridentate chiral xanthene backbones, xabox, can be used for other catalytic asymmetric reactions as new chiral inducers.

4. Experimental section

4.1. General methods

All reactions were carried out under nitrogen atmosphere. Common solvents were purified before use. THF (anhydrous) and CH_2Cl_2 (anhydrous) are commercially available from Kanto Chemical Co. Ltd, and were used without further purification. All reagents were of reagent grade and purified when necessary. Reactions were monitored by TLC using 250 mm Merck (Art. 5715) precoated silica gel. Flash column chromatography was performed over Merck (Art. 7734) silica gel. Melting points were measured on a Yanaco MP-J3 melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on Varian Mercury-300 (300 MHz) spectrometer. ^{1}H NMR chemical shifts are reported as δ values (ppm) relative to internal tetramethylsilane and splitting patterns are designated as: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, br=broad. Coupling constants are given in hertz. IR spectra were recorded with JASCO FT/IR-230 spectrometer and are reported in reciprocal centimeter (cm^{-1}). Elemental analyzes were performed with Yanagimoto MT-3 CHN corder. Optical rotations were measured on JASCO DIP-140 polarimeter at the sodium D line (1 mL sample cell). High performance liquid chromatographic (HPLC) analysis was performed with a JASCO PU-980 HPLC pump, UV-975 and 980 UV/VIS detector using DAICEL CHIRALCEL OD, CHIRALCEL OD-H, CHIRALPAK AD and CHIRALPAK AS columns. Visualization was accomplished by UV light (254 nm), anisaldehyde, and phosphomolybdic acid.

4.2. Synthesis of ligand and xabox–$RhCl_3$ complex

4.2.1. 4,5-Bis[4′-(S)-iso-propyl-2′-oxazolin-2′-yl]-2,7-di-tert-butyl-9,9-dimethyl-xanthene (S,S)-xabox–i-Pr ***5a***

A mixture of xanthene dicarboxylic acid **1** (1.0 g, 2.44 mmol) and thionyl chloride (15 mL) was refluxed for

3 h. Thionyl chloride was removed under reduced pressure to give the acid chloride as a white solid. A $CHCl_3$ (20 mL) solution of the acid chloride was then added to the solution of 2-aminoethanol (L-valinon, 622 mg, 6.025 mmol) in $CHCl_3$ (15 mL). The mixture was stirred for 2.5 h at room temperature. After concentration of the solvent, the residue was purified by silica-gel column chromatography and eluted with hexane/ethyl acetate 10:1 to ethyl acetate only to give xanthene diamide alcohol **4a** of 1.21 g (2.08 mmol, 85.2%) as white solid; mp=117.4 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, J=2.5 Hz, 2H), 7.56 (d, J=2.5 Hz, 2H), 7.29–7.21 (m, 2H), 4.11–3.72 (m, 8H), 2.22–2.04 (m, 2H), 1.67 (s, 18H), 1.08 (d, J=6.6 Hz, 6H), 1.01 (d, J=6.6 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.44, 146.08, 145.79, 130.18, 126.11, 125.63, 121.98, 63.51, 57.77, 34.6, 34.55, 32.78, 31.40, 29.08, 19.90, 19.41 ppm; IR (KBr): ν=3280, 2963, 2873, 1718, 1629, 1534, 1440, 1364, 1268, 1128, 1080, 859 cm^{-1}.

To a solution of the xanthene diamide alcohol **4a** (1.21 g, 2.08 mmol) in dichloromethane (20 mL) were added triethylamine (2.9 mL) and then methanesulfonyl chloride (0.354 mL, 4.58 mmol). The mixture was stirred for 5 h at room temperature. The mixture was poured into aq K_2CO_3 solution (2 N) at 0 °C and was extracted with dichloromethane. After the organic layer was dried over Na_2SO_4 and concentrated, the residue was purified by recrystallization with dichloromethane and ether to give the xanthene bisoxazoline (xabox) **5a** (1107.0 mg, 2.03 mmol) in 97.8% yield (total yield, 83%) as white solid; $[\alpha]_D^{23.0}$ −3.7 (c 0.995, CH_3OH); mp=237.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, J=2.5 Hz, 2H), 7.48 (d, J=2.5 Hz, 2H), 4.47 (dd, J=9.6, 8.0 Hz, 2H), 4.20 (t, J=8.0 Hz, 2H), 4.10 (ddd, J=9.6, 8.0, 6.1 Hz, 2H), 1.94 (dsept, J=6.6, 6.1 Hz, 2H), 1.62 (s, 18H), 1.08 (d, J=6.6 Hz, 6H), 0.97 (d, J=6.6 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.73, 147.08, 145.33, 130.46, 126.29, 125.17, 116.70, 75.55, 70.53, 34.77, 34.53, 32.09, 32.00, 31.47, 19.33, 18.17 ppm; IR (KBr): ν=3382, 2962, 1659, 1450, 1364, 1275, 1242, 1133, 1094, 984, 891, 863 cm^{-1}. Anal. Calcd for $C_{43}H_{48}N_2O_3$: C, 77.17; H, 8.88; N, 5.14; C, 75.96; H, 8.78; N, 5.00 (1/2H_2O). Found: C, 75.91; H, 8.92; N, 5.06.

4.2.2. 4,5-Bis[4′-(S)-phenyl-2′-oxazolin-2′-yl]-2,7-di-tert-butyl-9,9-dimethylxanthene (S,S)-xabox–Ph ***5b***

A mixture of the xanthene dicarboxylic acid **1** (1.0 g, 2.44 mmol) and thionyl chloride (15 mL) was refluxed for 3 h. Thionyl chloride was removed under reduced pressure to give the acid chloride as a white solid. A $CHCl_3$ (20 mL) solution of the acid chloride was then added to solution of 2-aminoethanol ((*S*)-(+)-2-phenyl, 830 mg, 6.05 mmol) in $CHCl_3$ (15 mL). The mixture was stirred for 3.5 h at room temperature. After concentration of the solvent, the residue was purified by silica-gel column chromatography and eluted with hexane/ethyl acetate 10:1 to ethyl acetate only to give the xanthene diamide alcohol **4b** of 1.235 g (2.08 mmol, 78.7%) as white solid; mp=124.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, J=7.7 Hz, 2H), 7.78 (d, J=2.5 Hz, 2H), 7.57 (d, J=2.5 Hz, 2H), 7.40–7.22 (m, 10H), 5.31–5.25 (m, 2H), 4.05–3.92 (m, 4H), 3.61–3.57 (m, 2H), 1.67 (s, 6H), 1.34 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.12, 146.11, 146.02, 139.56, 130.22, 128.66, 127.44, 126.91, 126.23, 125.93, 121.65, 65.49, 56.75, 34.59, 34.54, 32.72 ppm; IR (KBr): ν=3299, 2962, 2871, 1640, 1525, 1441, 1267, 1130, 699 cm^{-1}.

To a solution of the xanthene diamide alcohol **4b** (1.235 g, 2.08 mmol) in dichloromethane (20 mL) was added triethylamine (2.7 mL) and then methanesulfonyl chloride (0.323 mL, 4.18 mmol). The mixture was stirred for 5 h at room temperature. The mixture was poured into aq K_2CO_3 solution (2 N) at 0 °C, and was extracted with dichloromethane. After the organic layer was dried over Na_2SO_4 and concentrated, the residue was purified by recrystallization with dichloromethane and ether to give the xanthene bisoxazoline (xabox) **5b** (1144 mg, 2.10 mmol) in 86.06% yield (total yield, 86.77%) as white solid; $[\alpha]_D^{18.5}$ −38.2 (c 1.06, CH_3OH); mp=176.9 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, J=2.5 Hz, 2H), 7.55 (d, J=2.5 Hz, 2H), 7.324–7.36 (m, 10H), 5.27 (dd, J=10.2, 8.2 Hz, 2H), 4.52 (dd, J=10.2, 8.2 Hz, 2H), 4.52 (dd, J=10.2, 8.2 Hz, 2H), 4.05 (d, J=8.2 Hz, 2H), 1.68 (s, 6H), 1.34 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.07, 147.30, 145.61, 142.77, 130.59, 128.80, 127.59, 126.94, 126.63, 125.60, 116.41, 75.24, 70.02, 34.89, 34.66, 32.17, 31.55 ppm; IR (KBr): ν=2963, 2884, 1650, 1446, 1362, 1267, 1093, 988, 757, 700 cm^{-1}. Anal. Calcd for $C_{41}H_{44}N_2O_3$: C, 80.31; H, 7.24; N, 4.57. Found: C, 80.31; H, 7.32; N, 4.49.

4.2.3. 4,5-Bis[4′-(S)-benzyl-2′-oxazolin-2′-yl]-2,7-di-tert-butyl-9,9-dimethylxanthene (S,S)-xabox–Bn ***5c***

A mixture of the xanthene dicarboxylic acid **1** (1.0 g, 2.44 mmol) and thionyl chloride (15 mL) was refluxed for 3 h. Thionyl chloride was removed under reduced pressure to give the acid chloride as a white solid. A $CHCl_3$ (20 mL) solution of the acid chloride was then added to solution of 2-aminoethanol (L-phenylalaninol, 834 mg, 5.52 mmol) in $CHCl_3$ (15 mL). The mixture was stirred for 3.5 h at room temperature. After concentration of the solvent, the residue was purified by silica-gel column chromatography and eluted with hexane/ethyl acetate 10:1 to ethyl acetate only to give the xanthene diamide alcohol **4c** of 1.172 g (1.73 mmol, 71.3%) as white solid; mp=107.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, J=2.4 Hz, 2H), 7.53 (d, J=2.4 Hz, 2H), 7.39–7.20 (m), 4.62–4.58 (m, 2H), 3.85 (dd, J=4.0, 11.6 Hz, 2H), 3.70 (dd, J=5.6, 11.6 Hz, 2H), 3.17 (dd, J=7.6, 13.6 Hz, 2H), 3.03 (dd, J=6.8, 13.6 Hz, 2H), 2.57–2.39 (m, 2H), 1.63 (s, 6H), 16.3 (s, 6H), 1.32 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.14, 146.13, 145.8, 138.09, 130.18, 129.49, 128.65, 126.62, 126.06, 125.60, 121.69, 63.98, 53.51, 37.14, 34.64, 34.54, 32.59, 31.41 ppm; IR (KBr): ν=3319, 2961, 2870, 1634, 1527, 1441, 1364, 1268, 1130, 1039, 891, 855, 749, 700 cm^{-1}. Anal. Calcd for $C_{41}H_{44}N_2O_3$: C, 76.30; H, 7.74; N, 4.14. Found: C, 76.32; H, 7.75; N, 4.15.

To a solution of the xanthene diamide alcohol **4c** (1.172 g, 1.73 mmol) in dichloromethane (20 mL) were added triethylamine (2.3 mL) and then methanesulfonyl chloride (0.323 mL, 4.18 mmol). The mixture was stirred for 5 h at room temperature. The mixture was poured into aq K_2CO_3 solution (2 N) at 0 °C and was extracted with

dichloromethane. After the organic layer was dried over Na_2SO_4 and concentrated, the residue was purified by recrystallization with dichloromethane and ether to give the xanthene bisoxazoline (xabox) **5c** (1043 mg, 1.63 mmol) in 98.4% yield (total yield, 66.80%) as white solid; $[\alpha]_D^{20.4}$ +24.8 (*c* 1.03, CH_3OH); mp=194.2 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, *J*=2.5 Hz, 2H), 7.50 (d, *J*=2.5 Hz, 2H), 7.33–7.19 (m, 10H), 4.60 (dddd, *J*=9.3, 9.1, 8.0, 4.4 Hz, 2H), 4.37 (dd, *J*=9.3, 8.4 Hz, 2H), 4.18 (dd, *J*=8.4, 8.0 Hz, 2H), 13.32 (dd, *J*=13.7, 4.4 Hz, 2H), 2.79 (dd, *J*=13.7, 9.1 Hz, 2H), 1.63 (s, 6H), 1.34 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.02, 147.29, 145.43, 138.14, 130.67, 129.30, 128.69, 126.58, 126.28, 125.18, 116.46, 72.19, 67.92, 41.82, 34.87, 34.59, 31.74, 31.49 ppm; IR(KBr): ν=3420, 2963, 2906, 1652, 1446, 1364, 1243, 1094, 986, 860, 702 cm^{-1}. Anal. Calcd for $C_{43}H_{48}N_2O_3$: C, 80.59; H, 7.55; N, 4.37. Found: C, 80.30; H, 7.49; N, 4.32.

*4.3. 4,5-Bis[4′-(R)-benzyl-2′-oxazolin-2′-yl]-2,7-di-tert-butyl-9,9-dimethylxanthene (R,R)-xabox–Bn **5c′***

The synthesis procedure was same as (*S*,*S*)-xabox–Bn **5c**; $[\alpha]_D^{23.5}$ −24.7 (*c* 1.04, CH_3OH); mp=192.8 °C; ^1H and ^{13}C NMR are the same as **3c**; IR (KBr): ν=3419, 3029, 2964, 1651, 1452, 1365, 1276, 1093, 984, 928, 891, 862, 729, 700 cm^{-1}. Anal. Calcd for $C_{43}H_{48}N_2O_3$: C, 80.59; H, 7.55; N, 4.37. Found: C, 80.41; H, 7.46; N, 4.27.

*4.3.1. [(S,S)-xabox–i-Pr]RhCl$_3$ **14***

A mixture of (*S*,*S*)-xabox–*i*-Pr **5a** (54.5 mg, 0.1 mmol) and $RhCl_3(H_2O)_3$ (26.3 mg, 0.1 mmol) in ethanol was stirred for 2 h at 60 °C to give light brown precipitate, which was filtered and washed with hexane and ether. The solid was dried under reduced pressure to give the complex **14** (62.9 mg, 0.0834 mmol) in 83.4% yield; light brown solid; mp=247.3 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, *J*=2.2 Hz, 1H), 7.80 (d, *J*=2.2 Hz, 1H), 4.62 (t, *J*=2.5 Hz, 2H), 5.26–5.20 (m, 1H), 4.82–4.77 (m, 2H), 4.66–4.55 (m, 2H), 4.38 (m, 1H), 3.09–2.99 (m, 1H), 2.41–2.31 (m, 1H), 1.90 (s, 3H), 1.67 (s, 3H), 1.35 (s, 9H), 1.33 (s, 9H), 1.03 (d, *J*=7.1 Hz, 3H), 0.96 (d, *J*=7.1 Hz, 3H), 0.88 (d, *J*=6.9 Hz, 3H), 0.81 (d, *J*=6.9 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.64, 161.10, 149.53, 149.43, 149.31, 148.83, 137.58, 137.01, 126.70, 125.60, 126.63, 125.99, 124.87, 115.10, 114.05, 73.69, 68.18, 68.02, 36.23, 35.06, 31.35, 30.72, 29.89, 29.15, 22.79, 18.87, 18.81, 15.12, 14.63 ppm; IR (KBr): ν=3473, 2964, 1621, 1454, 1376, 1236, 1188, 1097, 999, 956, 857, 729, 652 cm^{-1}. Anal. Calcd for $C_{35}H_{46}Cl_3N_2O_3$: C, 55.75; H, 6.42; N, 3.72. Found: C, 55.70; H, 6.42; N, 3.60.

4.4. Typical procedure for nitrone 1,3-dipolar cycloaddition reaction with acryloyl oxazolidinone catalyzed by (S,S)-xabox–Bn/Mg(II) complex

A mixture of $Mg(ClO_4)_2 \cdot 6H_2O$ (8.3 mg, 0.025 mmol) and (*S*,*S*)-xabox–Bn **5c** (16.0 mg, 0.025 mmol) in CH_2Cl_2 (1.5 mL) was refluxed for 4 h under nitrogen atmosphere in the presence of activated 4 Å MS (250 mg). After cooling the flask to room temperature, the pale light yellow suspension was filtered off via a membrane filter. The filtrate was added to activated 4 Å MS (250 mg). To this were added oxazolidinone **8b** (35.3 mg, 0.25 mmol) and nitrone **7a** (49.3 mg, 0.25 mmol) at room temperature. The resulting mixture was stirred for 6 h at room temperature. The reaction was monitored by TLC (eluted with CH_2Cl_2). At the end of this period, the reaction mixture was purified by flask column chromatography on silica gel (eluted with CH_2Cl_2) to afforded the resulting product **9e** (81.7 mg, 0.242 mmol) as a white solid with 96.8% yield (*endo*: 3*R*, 4*S*), *endo*/*exo*=94:6, 95.8% ee. The *endo*/*exo* ratio was determined by ^1H NMR spectrum and the enantiomeric purity was determined by HPLC analysis (DAICEL CHIRALPAK AD, 254 nm (UV), eluted with hexane/IPA=5:1, flow rate=1 mL/min).

The ^1H and ^{13}C NMR of compounds **9a–c**,[7e] **9d**,[13c] **9e**,[16] **11a**,**b**,[13c] **13**,[7e] and **15**[8f] are referred to the literature.

*4.4.1. (3R,4S)-3-Phenyl-4-(2-oxo-1,3-oxazolidine-1-carbonyl)-2-phenylisoxazolidine (**9e**)[16]*

Table 1, entry 17; 97% yield, 96:4 (*endo*/*exo* ratio), 96% ee determined by HPLC analysis (DAICEL CHIRALPAK AD, UV=254 nm, eluted with hexane/IPA=5:1, flow rate=1 mL/min); t_{minor}=55.30 min (3*S*,4*R*,5*S*), t_{major}=46.04 min (3*R*,4*S*).

4.5. Typical procedure for nitrone 1,3-dipolar cycloaddition reaction with crotonoyl oxazolidinone catalyzed by (S,S)-xabox–Bn/Mn(II) complex

A mixture of $Mn(ClO_4)_2 \cdot 6H_2O$ (9.0 mg, 0.025 mmol) and (*S*,*S*)-xabox–Bn **5c** (16.0 mg, 0.025 mmol) in CH_2Cl_2 (1.5 mL) was refluxed for 4 h under nitrogen atmosphere in the presence of activated 4 Å MS (250 mg). After cooling the flask to room temperature, the pale light yellow suspension was filtered off via a membrane filter. The filtrate was added to activate the 4 Å MS (250 mg). To this were added oxazolidinone **8a** (38.9 mg, 0.25 mmol) and nitrone **7a** (49.3 mg, 0.25 mmol) at 10 °C. The resulting mixture was stirred at 48 h at 10 °C. The reaction was monitored by TLC (eluted with CH_2Cl_2). At the end of this period, the reaction mixture was purified by flask column chromatography on silica gel (eluted with CH_2Cl_2) to afford the resulting product **9a** (68.7 mg, 0.195 mmol) as a white solid with 85% yield (*endo*: 3*R*,4*S*,5*R*), *endo*/*exo*=96:4, 95.0% ee. The *endo*/*exo* ratio was determined by ^1H NMR spectrum and the enantiomeric purity was determined by HPLC analysis (DAICEL CHIRALPAK AD, 254 nm (UV), eluted with hexane/IPA=5:1, flow rate=1 mL/min).

*4.5.1. (3R,4S,5R)-5-Methyl-3-phenyl-4-(2-oxo-1,3-oxazolidine-3-carbonyl)-2-phenylisoxazolidine (**9a**)[7e]*

Table 1, entry 11; 88% yield, 99:1 (*endo*/*exo* ratio), 92% ee determined by HPLC analysis (DAICEL CHIRALPAK OD, UV=254 nm, eluted with hexane/IPA=5:1, flow rate=1 mL/min); t_{minor}=13.20 min (3*S*,4*R*,5*S*), t_{major}=19.24 min (3*R*,4*S*,5*R*).

4.5.2. (3R,4S,5R)-5-Methyl-3-p-methylphenyl-4-(2-oxo-1,3-oxazolidine-3-carbonyl)-2-phenylisoxazolidine (**9b**)[7e]

Table 1, entry 13; 90% yield, 96:4 (*endo*/*exo* ratio), 94% ee determined by HPLC analysis (DAICEL CHIRALPAK OD-H, UV=254 nm, eluted with hexane/IPA=9:1, flow rate=1 mL/min); t_{minor}=29.9 min (3*S*,4*R*,5*S*), t_{major}=20.2 min (3*R*,4*S*,5*R*).

4.5.3. (3R,4S,5R)-5-Methyl-3-p-methoxylphenyl-4-(2-oxo-1,3-oxazolidine-3-carbonyl)-2-phenylisoxazolidine (**9c**)[7e]

Table 1, entry 16; 95% yield, 97:3 (*endo*/*exo* ratio), 95% ee determined by HPLC analysis (DAICEL CHIRALPAK AD, UV=254 nm, eluted with hexane/IPA=5:1, flow rate=1 mL/min); t_{minor}=36.5 min (3*S*,4*R*,5*S*), t_{major}=27.2 min (3*R*,4*S*,5*R*).

4.5.4. (3R,4S,5R)-5-Methyl-3-p-bromophenyl-4-(2-oxo-1,3-oxazolidine-3-carbonyl)-2-phenylisoxazolidine (**9d**)[13c]

Table 1, entry 15; 81% yield; 98:2 (*endo*/*exo* ratio); 91% ee determined by HPLC analysis (DAICEL CHIRALPAK AD, UV=254 nm, eluted with hexane/IPA=3:1, flow rate=1 mL/min); t_{minor}=12.4 min (3*S*,4*R*,5*S*), t_{major}=17.2 min (3*R*,4*S*,5*R*).

4.5.5. (3R,4S)-3-Phenyl-4-(2-oxo-pyrrolidine-1-carbonyl)-2-phenylisoxazolidine (**11a**)[13c]

Yield 90%, 96:4 (*endo*/*exo* ratio), 94% ee determined by HPLC analysis (DAICEL CHIRALPAK AD, UV=254 nm, eluted with hexane/IPA=5:1, flow rate=1 mL/min); t_{minor}=31.0 min (3*S*,4*R*,5*S*), t_{major}=35.3 min (3*R*,4*S*,5*R*).

4.5.6. (3R,4S,5R)-5-Methyl-3-phenyl-4-(2-oxo-pyrrolidine-1-carbonyl)-2-phenylisoxazolidine (**11b**)[13c]

Yield 88%, >99:1 (*endo*/*exo* ratio), 90% ee determined by HPLC analysis (DAICEL CHIRALPAK AD, UV=254 nm, eluted with hexane/IPA=5:1, flow rate=1 mL/min); t_{minor}=30.1 min (3*S*,4*R*,5*S*), t_{major}=22.7 min (3*R*,4*S*,5*R*).

4.5.7. (3R,4S,5R)-3-Phenyl-4-(2-oxo-pyrrolidine-1-carbonyl)-2-benzylisoxazolidine (**13**)[7e]

Yield 94%, >99:1 (*endo*/*exo* ratio), 86% ee determined by HPLC analysis (DAICEL CHIRALPAK AD, UV=254 nm, eluted with hexane/IPA=5:1, flow rate=1 mL/min); t_{minor}=31.7 min (3*S*,4*R*,5*S*), t_{major}=46.6 min (3*R*,4*S*,5*R*).

4.6. Typical procedure for Diels–Alder reaction of cyclopentadiene with acryloyl oxazolidinone catalyzed by (S,S)-xabox–i-Pr/Mn(II) complex

A mixture of $Mn(ClO_4)_2 \cdot 6H_2O$ (52 mg, 0.144 mmol) and (*S*,*S*)-xabox–*i*-Pr **5c** (20 mg, 0.036 mmol) in CH_2Cl_2 (1.5 mL) was refluxed for 4 h under nitrogen atmosphere in the presence of activated 4 Å MS (250 mg). After cooling the flask to room temperature, the pale light yellow suspension was filtered off via a membrane filter. The filtrate was added to activate 4 Å MS (250 mg). To this was added oxazolidinone **8b** (52 mg, 0.36 mmol), the resulting mixture was stirred at −78 °C and continuously added cyclopentadiene (298 μL, 3.6 mmol), and stirred until to room temperature for 24 h. The reaction was monitored by TLC (eluted with CH_2Cl_2). At the end of this period, the reaction mixture was purified by flask column chromatography on silica gel (eluted with CH_2Cl_2) to afford the resulting product **15** (73.38 mg, 0.354 mmol) as a white solid with 98.36% yield (*endo*: 1*S*,2*S*,4*S*), *endo*/*exo*=98:2, 82% ee. The *endo*/*exo* ratio was determined by ^{1}H NMR spectrum and the enantiomeric purity was determined by HPLC analysis (DAICEL CHIRALPAK OD, 240 nm (UV), eluted with hexane/IPA=90:1, flow rate=1 mL/min).

4.6.1. (1S,2S,4S)-3-Bicyclo[2.2.1]hept-5-en-2-oxazolidinone (**15**)[8f]

Table 2, entry 1; 98% yield, 98:2 (*endo*/*exo* ratio), 82% ee determined by HPLC analysis (DAICEL CHIRALPAK OD, UV=240 nm, eluted with hexane/IPA=90:1, flow rate=1 mL/min); t_{minor}=64.99 min (1*R*,2*R*,4*R*), t_{major}=72.96 min (1*S*,2*S*,4*S*).

4.7. X-ray analysis of [(S,S)-xabox–i-Pr]RhCl$_3$

A single crystal (0.15×0.2×0.6 mm) was obtained by recrystallization from $CHCl_3$/ether/hexane. Selected bond lengths and angle: 2.129 Å, Rh–O; 2.05 Å, Rh–N1; 2.07 Å, Rh–N2; 2.330 Å, Rh–Cl1; 2.331 Å, Rh–Cl2; 2.270 Å, Rh–Cl3; 93.8°, N1–Rh–N2; 86.9°, N1–Rh–O; 83.7°, N2–Rh–O; 89.1°, N1–Rh–Cl1; 178.2°, N1–Rh–Cl2; 91.6°, N1–Rh–Cl3; 173.7°, N2–Rh–Cl1; 86.8°, N2–Rh–Cl2; 92.1°, N2–Rh–Cl3; 90.8°, O–Rh–Cl1; 91.5°, O–Rh–Cl2; 175.5°, O–Rh–Cl3.

4.7.1. Crystal data

$C_{39}H_{48}N_2O_3Cl_6Rh$, orthorhombic, space group $P2_12_12_1$ (No. 19), a=16:735(2) Å, b=27:482(6) Å, c=9:067(2) Å, V=4169(1) Å^3, ρ_{calcd}=1:447 g cm^{-1}, Z=4, μ=8:31 cm^{-1}. The crystal contains a 1:1 mole ratio of **8** and $CHCl_3$: the solvent molecules in the crystal were omitted in Figure 1. The intensity data (28:99<#<29:88°) were collected on a Riigaku AFC-7R diffractometer with graphite-monochromated Mo Kα radiation (λ=0:71069 Å) and the structure was solved by Patterson methods (DIRDIF92, PATTY). The final cycle of refinement was based on 2686 observed reflections (I>3:00σ(I)) and 433 variable parameters and converged with R=5.6% and R_w=6.1%. Crystallographic data for **4** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC-199961. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK [fax: +44(0) 1223336033 or e-mail: deposit@ccdc.cam.ac.uk].

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