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Enantioselective Intramolecular Carbene C−H Insertion Catalyzed by a Chiral Iridium(III) Complex of D_4-Symmetric Porphyrin Ligand

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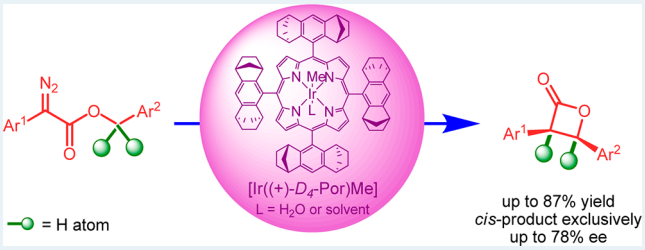
Supporting Information

ABSTRACT: The synthesis of iridium(III) complexes containing bulky porphyrin ligands is described. The chiral iridium(III) complex of the D_4-symmetric Halterman porphyrin ligand [Ir((+)-D_4-Por)Me(L)] (L = solvent) is an effective catalyst for enantioselective intramolecular carbene insertion into saturated C−H bonds of α-diazoesters, giving the corresponding *cis*-β-lactones in good isolated yields (up to 87%), excellent stereoselectivities (cis products exclusively), and good enantioselectivities (up to 78% ee).



KEYWORDS: *iridium porphyrin, C−H insertion, enantioselectivity, intramolecular, cis-β-lactone*

Direct C−H functionalization continues to be an area of interest in catalysis and organic synthesis.[1] Because of the huge abundance of C−H bonds in organic compounds, this strategy is appealing in streamlining the routes for the synthesis of organic molecules with complexity and diversity. However, the large bond energy of and selectivity among the saturated C−H bonds in organic compounds present major challenges in achieving selective C−H functionalization with practical interest. To achieve direct C−H functionalization, various transition metal catalysts, such as metalloporphyrin,[1i,j,2] metal-Schiff base,[3] metal-PyBOX,[1h,4] and dirhodium(II,II) complexes,[1b−d,g,h,k,l,5] have been developed over the past decades. We are interested in developing metalloporphyrin catalysts for oxidative C−H functionalization and for organic oxidation reactions for the following reasons: (1) Metalloporphyrins have been widely studied as mimics of biological oxidation reactions of cytochrome P450 enzymes.[2d,6] (2) The shape of metalloporphyrin catalysts can be fine-tuned by tailoring the functional group(s) or bulkiness of the substituent(s) on the periphery of the porphyrin ligand, thereby allowing control of the product selectivity of metalloporphyrin catalyzed organic transformations. (3) A high product turnover number can be achieved with metalloporphyrin catalysts, particularly the ones containing halogeno substituents on the porphyrin ligand.[1i,j,2a,d] (4) The isolation of reactive metal−ligand multiple bonded species of metalloporphyrins is instrumental to the study of the mechanisms of metalloporphrin-catalyzed atom/group transfer reactions.[1i,j,2a,d] (5) Chiral substituents can be incorporated onto the porphyrin ligand for catalytic enantioselective organic transformation reactions.

Since the report on intermolecular carbene insertion to C−H bonds of *n*-alkanes by Callot[7] in 1982 and the characterization of ruthenium porphyrin carbene intermediate by Collman[8] in 1985, a number of metalloporphyrin catalysts, such as that of iron,[9] ruthenium,[10] rhodium,[11] and osmium,[12] have been developed and were found to be catalytically active toward carbene C−H bond insertion. Recently, intermolecular cyclopropanation and carbene C−H insertion reactions have been reported by Katsuki,[13] Woo,[14] and Rodríguez-García[15] using iridium(III) salen, iridium(III) porphyrin, and iridium(I) porphyrin catalysts, respectively. Previously, we reported highly enantioselective intermolecular carbene C−H insertion reactions catalyzed by [Ir(D_4-Por)Me][16] supported on a D_4-Halterman porphyrin ligand.[17] Following this work, we would like to expand the scope of reactions of [Ir(D_4-Por)Me] catalyst to intramolecular carbene C−H insertion.

Transition-metal-catalyzed decomposition of diazoesters for intramolecular carbene C−H insertion has been studied by us[18] and by others.[1b,g−j] Herein, we report the synthesis of iridium(III) complexes supported on bulky porphyrin ligands. The methylated iridium(III) porphyrin complex [Ir(TTP)Me(L)] (H_2TTP = *meso*-tetrakis(*p*-tolyl)porphyrin; L = H_2O or solvent; Figure 1) was found to be catalytically active toward stereoselective intramolecular carbene C−H insertion of α-diazoesters, giving lactones exclusively in yields up to 87%. With chiral [Ir((+)-D_4-Por)Me] catalyst (Figure 1), *cis*-β-

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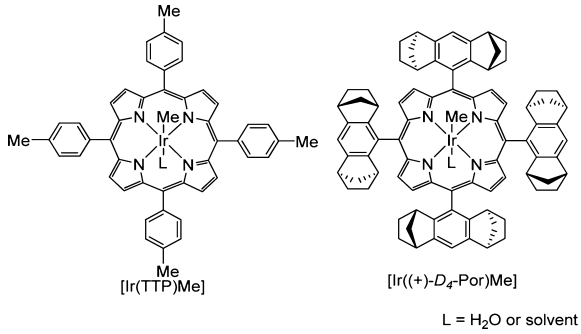
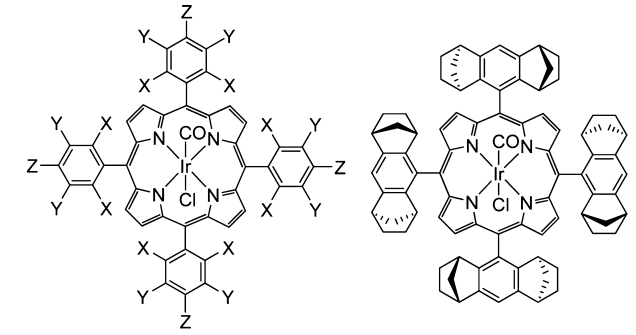


Figure 1. Structures of iridium(III) porphyrin catalysts used in this work.

lactones have been obtained with good stereoselectivity (cis product exclusively) and enantioselectivities (up to 78% ee).

A series of bulky porphyrin ligands with structures depicted in Scheme 1, including the bis-pocket porphyrin H_2TTPPP,[19]

Scheme 1. Synthesis of Iridium(Iii) Complexes Supported on Bulky Porphyrin Ligands

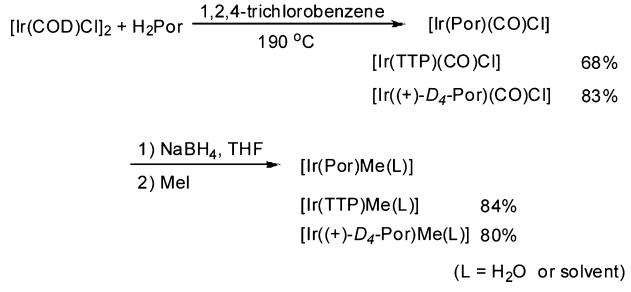


were synthesized according to literature procedures[19,20] and the D_4-symmetric Halterman ligand was synthesized according to the procedure reported by Halterman.[17] We found that iridium(III) ion could be efficiently incorporated to these bulky porphyrin ligands by reacting $[Ir(COD)Cl]_2$ (COD = 1,5-cyclooctadiene) with the corresponding free porphyrin ligand in 1,2,4-trichlorobenzene at 190 °C. The iridium(III) porphyrin complexes [Ir(Por)(CO)Cl] were obtained in 65−85% yields (Scheme 1). Oxygen from air is necessary to oxidize iridium(I) to iridium(III),[21] and a high reaction temperature of 190 °C and the use of high-boiling solvent 1,2,4-trichlorobenzene (bp = 214 °C) are essential. When xylene (bp = 137−140 °C) was used as the solvent, no iridium(III) porphyrin complex was observed.

The methylation of iridium(III) porphyrin complexes was performed by reductive alkylation of [Ir(Por)(CO)Cl] with $NaBH_4$/MeI (Scheme 2).[16] [Ir(TTP)Me(L)] and [Ir((+)-D_4-Por)Me(L)] (L = H_2O or solvent) were obtained in 84% and 80% yields, respectively. The solvent molecule L could be H_2O from the reaction mixture. In the case of [Ir((−)-D_4-Por)Me(EtOH)], the coordinated EtOH, that was incorporated into the Ir(III) center during recrystallization in THF/EtOH, has been revealed by X-ray crystallographic analysis.[16]

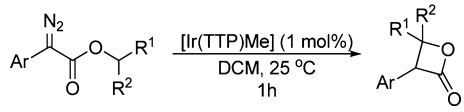
The catalytic activity of the achiral iridium porphyrin complex [Ir(TTP)Me] toward intramolecular carbene C−H

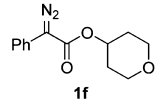
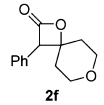
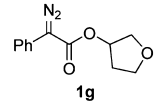
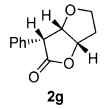
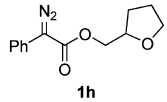
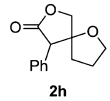
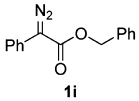
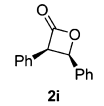
Scheme 2. Synthesis of Methylated Iridium(III) Porphyrin Catalysts



insertion was examined (Table 1). By referring to the reaction conditions employed in the analogous intermolecular carbene

Table 1. Intramolecular C−H Insertion of α-Diazoester Catalyzed by [Ir(TTP)Me][a]



entry	substrate		product		isolated yield %
1	R = H	**1a**	**2a**		82
2	R = *p*-Br	**1b**	**2b**		86
3	R = *p*-F	**1c**	**2c**		60
4	R = *p*-Me	**1d**	**2d**		53
5	R = *m*-Cl	**1e**	**2e**		76
6		**1f**		**2f**	53
7		**1g**		**2g**	81
8		**1h**		**2h**	74
9		**1i**		**2i**	68

[a]Reaction conditions: A mixture of α-diazoester **1** (0.2 mmol) and [Ir(TTP)Me] (1 mol %) in 2 mL of DCM was stirred at 25 °C for 1 h under Ar atmosphere.

C−H insertion,[16] α-diazoester **1a** (0.2 mmol) was treated with 1 mol % of [Ir(TTP)Me] in 2 mL of DCM at 25 °C for 1 h under Ar atmosphere. On the basis of ^{1}H NMR analysis of the crude reaction mixture, a complete substrate conversion was observed, and β-lactone **2a** (carbene insertion to 3° C−H bond) was isolated in 82% yield (Table 1, entry 1). This reaction worked well for a variety of *p*-substitued α-diazoesters (*p*-Br, **1b**; *p*-F, **1c**; and *p*-Me, **1d**), giving the corresponding β-lactones **2b−d** in moderate to good isolated yields (53−86%;

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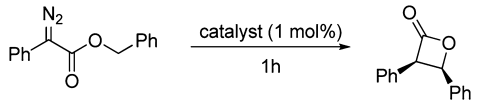
entries 2−4, Table 1). α-Diazoester **1e** with a *m*-Cl substituent also underwent cyclization to form β-lactone **2e** in 76% isolated yield (entry 5, Table 1). From these results, there is a high tendency for carbene insertion into the 3° C−H bond geminal to the ester oxygen atom[22] when [Ir(TTP)Me] is used as the catalyst, and in this work, β-lactones with 4-membered ring structure were formed as the only products.

Decomposition of α-diazoester **1f** bearing a tetrahydro-2*H*-pyran moiety led to carbene insertion into the 3° C−H bond geminal to the ester oxygen atom, giving β-lactone **2f** containing a spiro structure in 53% isolated yield (entry 6, Table 1); however, changing the tetrahydro-2*H*-pyran group to a tetrahydrofuran moiety favored carbene insertion to 2 °C−H geminal to the tetrahydrofuran oxygen atom rather than that of the ester oxygen atom, giving *cis*-γ-lactone **2g**, bearing a fused tetrahydrofuro[3,2-*b*]furan-2(5*H*)-one system in 81% isolated yield (entry 7, Table 1). The stereochemistry of **2g** was confirmed by X-ray crystallography (see Figure S1, Supporting Information). The same directed regioselectivity by the geminal tetrahydrofuran oxygen atom was also observed for carbene C−H insertion of **1h** bearing a (tetrahydrofuran-2-yl)methyl group, giving γ-lactone **2h** containing a spiro structure in 74% isolated yield (entry 8, Table 1). Cyclization of the α-diazoester **1i** gave *cis*-β-lactone **2i** in 68% isolated yield, without detection of a trans isomer (entry 9, Table 1).

With the success of intramolecular carbene C−H insertion of α-diazoesters catalyzed by [Ir(TTP)Me], we further expanded our study to asymmetric catalytic reactions. The intramolecular carbene C−H insertion of the α-diazoester **1i** was selected as a model reaction for the optimization of reaction conditions using [Ir((+)-D_4-Por)Me(L)] (L = H_2O or solvent) as catalyst (Table 2). By treating 0.2 mmol of α-diazoester **1i** with 1 mol % of [Ir((+)-D_4-Por)Me] in 2 mL of DCM at 25 °C for 1 h, a 90% yield of *cis*-β-lactone **2i** was found, on the basis of ^{1}H NMR analysis of the crude reaction mixture using phenyltrimethylsilane as the internal standard, and **2i** was isolated in 87% yield with 76% ee (entry 1, Table 2). Lowering the reaction temperature to 0 °C or −40 °C significantly reduced the yield of **2i** to <5% (entries 2−3, Table 2). Increasing the reaction temperature to 40 °C did not impose any significant effect on the yield and enantioselectivity of **2i** (entry 4, Table 2).

Table 2. Condition Optimization and Catalyst Screening for Enantioselective C−H Insertion of α-Diazoester 1i[a]



1i **2i**

entry	catalyst	temp °C	solvent	yield,[b] %	ee,[c] %
1	[Ir((+)-D_4-por)Me]	25	DCM	90 (87)[d]	76
2	[Ir((+)-D_4-por)Me]	0	DCM	5	
3	[Ir((+)-D_4-por)Me]	−40	DCM	<5	
4	[Ir((+)-D_4-por)Me]	40	DCM	85	72
5	[Ir((+)-D_4-por)Me]	25	DCE	85	72
6	[Ir((+)-D_4-por)Me]	25	cyclohexane	22	69
7	[Ir((+)-D_4-por)Me]	25	*n*-hexane	27	61
8	[Ir((+)-D_4-por)Me]	25	toluene	61	73
9	[Ir((+)-D_4-por)Me]	25	benzene	19	80
10[e]	[Rh_2(*S*-PTAD)$_4$]	25	DCM	25	30
11[e]	[Rh_2(*S*-MEPY)$_4$]	25	DCM	<5	

[a]Reaction conditions: A mixture of **1i** (0.2 mmol) and catalyst (1 mol %) in 2 mL of solvent was stirred for 1 h under Ar atmosphere. [b]Determined by ^{1}H NMR using PhTMS as internal standard. [c]Determined by HPLC with Chiralpak AD-H column. [d]Datum in parentheses was isolated yield. [e]**1i** was added via syringe pump over 80 min.

The effect of solvent was examined. The intramolecular carbene C−H insertion of α-diazoester **1i** catalyzed by [Ir((+)-D_4-Por)Me] was favored in a chlorinated solvent, such as DCM or DCE, giving *cis*-β-lactone **2i** in 85−90% NMR yields with 72−76% ee (entries 1 and 5, Table 2). The yield of **2i** was significantly reduced when a nonpolar solvent was used (19−27% NMR yields; entries 6−7 and 9, Table 2). When toluene was used as the solvent, **2i** was obtained in 61% NMR yield with 73% ee (entry 8, Table 2).

We also compared the catalytic activities of chiral dirhodium(II,II) carboxylate complexes, which are well-known catalysts for carbene transfer reactions,[1b−d,g,h,l,5] toward this intramolecular carbene C−H insertion as depicted in Table 2. When [Rh_2(*S*-PTAD)$_4$] (tetrakis[(*S*)-(1-adamantyl)-(*N*-phthalimido)acetate]dirhodium(II)) or [Rh_2(*S*-MEPY)$_4$] (tetrakis[methyl 2-pyrrolidone-5(*S*)-carboxylate]dirhodium(II)) was used as the catalyst for intramolecular carbene C−H insertion of α-diazoester **1i**, both the yields (<5−25% NMR yields) and enantioselectivity (30% ee) of *cis*-β-lactone **2i** were unsatisfactory, even when **1i** was slowly added to the reaction mixture via syringe pump over 80 min (entries 10−11, Table 2).

Because 1 mol % of [Ir((+)-D_4-Por)Me] gave the best result in terms of product yield and enantioselectivity in DCM at 25 °C, these reaction conditions were adopted for subsequent studies.

With the optimized reaction conditions, we examined the substrate scope of the [Ir((+)-D_4-Por)Me]-catalyzed enanatioselective intramolecular C−H insertion of α-diazoesters (Table 3). α-Diazoester **1j** bearing *p*-Br substitution on Ar^2 gave *cis*-β-lactone **2j** in 81% yield and with 78% ee for a reaction time of 20 min (entry 2, Table 3). Substitution on the o position significantly lengthened the reaction time to 10 h, but the product yield was reduced (54%; entry 3, Table 3). This could be explained by the steric hindrance exerted by the o substitution to the benzylic C−H where the carbene insertion takes place. α-Diazoester **1l** with electron-withdrawing *m*-Cl substitution on Ar^2 required a further extension of the reaction time to 24 h to give *cis*-β-lactone **2l** in 58% yield and with 77% ee (entry 4, Table 3). From these results, the substitution on the Ar^2 group of α-diazoester did not have a significant effect on the enantioselectivity of the intramolecular carbene C−H insertion reaction.

We then proceeded to examine the effect of substitution onto the Ar^1 of α-diazoesters (Table 3). The intramolecular carbene C−H insertion of α-diazoester **1m** bearing an electron-donating *p*-Me group onto the Ar^1 required a reaction time of 24 h to give *cis*-β-lactone **2m** in 63% yield and 78% ee (entry 5, Table 3). Changing the substituent(s) of Ar^1 to electron-withdrawing halogen group(s) (*p*-F, **1n**; *m*-Cl; **1o**; *m*-Br, **1p**) significantly shortened the reaction time to 10 min with the desired *cis*-β-lactones obtained in 80−88% yields (entries 6−8, Table 3); however, the enantioselectivities were all reduced (39−76% ee) (entries 6−8, Table 3). From these results, the substitution on the Ar^1 of α-diazoester significantly affects both the rate and enantioselectivity of the intramolecular carbene

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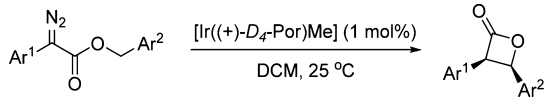
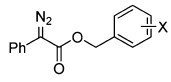
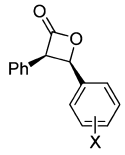
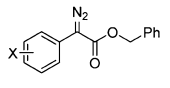
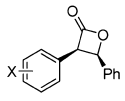
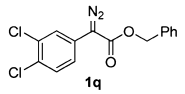
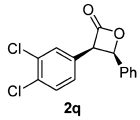
Table 3. Substrate Scope for Enantioselective Intramolecular C−H Bond Insertion of α-Diazoesters Catalyzed by [Ir((+)-D_4-Por)Me][a]



entry	substrate		product	reaction time	yield[b] %	ee[c] %
						
1	X = *p*-H	**1i**	**2i**	20 min	90 (87)	76
2	X = *p*-Br	**1j**	**2j**	20 min	81 (53)	78
3	X = *o*-Br	**1k**	**2k**	10h	54 (50)	67
4	X = *m*-Cl	**1l**	**2l**	24h	58 (53)	77
						
5	X = *p*-Me	**1m**	**2m**	24h	63 (54)	78
6	X = *p*-F	**1n**	**2n**	10 min	85 (80)	76
7	X = *m*-Cl	**1o**	**2o**	10 min	80 (75)	50
8	X = *m*-Br	**1p**	**2p**	10 min	88 (72)	39
9	 **1q**		 **2q**	4h	60 (60)	64

[a]Reaction conditions: A mixture of α-diazoester **1** (0.2 mmol) and [Ir((+)-D_4-Por))Me] (1 mol %) in 2 mL of DCM was stirred at 25 °C under Ar atmosphere. Completion of the reaction was monitored by TLC analysis for complete consumption of the α-diazoester **1**. [b]Determined by ^{1}H NMR using PhTMS as internal standard. Data in parentheses were the isolated yields. [c]Determined by HPLC with chiral columns.

C−H insertion. The intramolecular carbene C−H insertion reaction also proceeded smoothly in the case of α-diazoester **1q** having 3,4-dichloro-substitution on the Ar^1, with the *cis*-β-lactone **2q** in 60% yield with 64% ee in 4h.

In summary, a general method for the synthesis of iridium(III) complexes bearing bulky porphyrin ligand has been developed. The methylated chiral iridium(III) porphyrin complex [Ir((+)-D_4-Por)Me(L)] (L = solvent) is an effective catalyst for enantioselective intramolecular carbene insertion into saturated C−H bonds of α-diazoesters, and in this work, giving the corresponding *cis*-β-lactones in moderate to good isolated yields (up to 87%), excellent stereoselectivity (*cis*-products exclusively), and good enantioselectivities (up to 78% ee).

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, characterization of compounds, and Figure S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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