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HIGHLY REGIOSELECTIVE REARRANGEMENT OF 2,3-DIARYL-OXIRANES INTO 2,2-DIARYLACETALDEHYDES CATALYZED BY YTTERBIUM PORPHYRIN COMPLEX, Yb(TPP)OTf

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Abstract – [5,10,15,20-Tetraphenylporphynato]ytterbium(III) triflate, Yb(TPP)-OTf, is an efficient Lewis acid catalyst for the highly regioselective rearrangement of 2,3-diaryloxiranes into 2,2-diarylacetaldehydes. The catalytic process can be easily performed not only in dichloroethane but also in a more environmentally friendly solvent, benzotrifluoride.

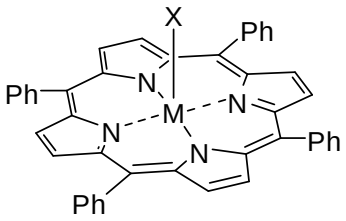
INTRODUCTION

2,2-Diarylacetaldehydes are useful synthetic precursors of many biologically active natural and synthetic products that contain diarylmethane structural motifs.[1] Among numerous methods for the preparation of 2,2-diarylacetaldehydes,[1,2] acid-promoted rearrangement of 2,3-diaryloxiranes constitutes one of the most straightforward strategies, and hence a number of different Lewis acid-catalyzed methods have been developed for this purpose.[3,4] However, most of these developed methods appear to suffer from lack of regioselectivity, usually affording a mixture of 2,2-diarylacetaldehydes and their regioisomeric products, 1,2-diarylethanones, and reduced yields of the desired aldehydes are therefore often obtained. Thus, there is a need to develop an alternative catalyst to promote such rearrangement with higher efficiency and regioselectivity.

Our laboratory has recently developed iron(III) and chromium(III) porphyrin complexes (Figure 1) as a new family of highly regio- and stereoselective Lewis acid catalysts for the ring-opening rearrangement of various epoxides, including α,β-epoxy silyl ethers, α,β-epoxy enones, and monoalkyl-substituted epoxides, to the corresponding carbonyl compounds.[5,6] This paper describes the efficient rearrangement of 2,3-diaryloxiranes **1** to 2,2-diarylacetaldehydes **2** that proceeds with high levels of yields and regio-

This paper is dedicated to Professor Emeritus Keiichiro Fukumoto on the occasion of his 75th birthday.

selectivity using a new porphyrin-based Lewis acid catalyst, [5,10,15,20-tetraphenylporphynato]-ytterbium(III) triflate, Yb(TPP)OTf. Another advantage of the method is that the reported rearrangements using the Yb(TPP)OTf catalyst system can be easily performed in benzotrifluoride (BTF),[7] which has recently emerged as a useful alternative solvent for organic reactions currently conducted in dichloromethane (DCM) and related solvents, without deterioration in yields and regioselectivity. This is considered of increasing importance as greener processes are sought because of environmental concerns.



Fe(TPP)OTf: M = Fe, X = OTf
Cr(TPP)OTf: M = Cr, X = OTf
Yb(TPP)Cl: M = Yb, X = Cl
Yb(TPP)OTf: M = Yb, X = OTf

Figure 1. Structures of porphyrin-based Lewis acid catalysts

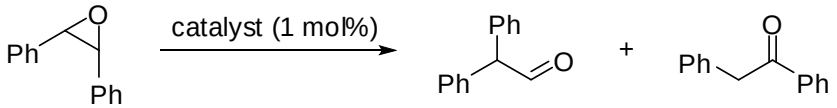
RESULTS AND DISCUSSION

cis-Stilbene oxide *cis*-**1a** was chosen as a test substrate in the initial experiments to optimize the reaction conditions, because *cis*-2,3-diaryloxiranes often provide lower regioselectivity than the *trans* isomers in Lewis acid-promoted rearrangements.[3a,3c] Thus, we evaluated various Lewis acid catalysts in the rearrangement of model substrate *cis*-**1a**, and the results are illustrated in Table 1. When we attempted the rearrangement of *cis*-**1a** with 1 mol% of porphyrin-based Lewis acid catalysts, Fe(TPP)OTf and Cr(TPP)OTf, in dichloroethane (DCE) at 83 °C, we obtained the corresponding aldehyde **2a** in only moderate yields along with substantial amounts of undesired isomeric ketone **3a** (entries 1 and 2). Other Lewis acids, such as $Er(OTf)_3$,[3a] $Yb(OTf)_3$, $Bi(O)ClO_4$,[3b] $Bi(OTf)_3$,[3c] and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(THF)]BF_4$,[3d] most of which are known as effective Lewis acid catalysts for the rearrangement of epoxides to carbonyl compounds, also gave unsatisfactory results to obtain moderate yields of the desired aldehyde **2a** (entries 7–11). In the case with $InCl_3$,[3e] no reaction occurred to recover the starting epoxide *cis*-**1a** (entries 12 and 13).[8] Despite these discouraging results, we recognized that lanthanide- and bismuth-based Lewis acids can afford slightly higher regioselectivity compared to the porphyrin-based Lewis acid catalysts (cf. entries 1, 2, and 7–10), and hence we assumed that the use of metalloporphyrin complexes possessing such central metal ions as Er(III), Yb(III), and Bi(III) as catalysts might improve the regioselectivity of the reaction. Among these porphyrin complexes, Yb(III)-containing complexes have been well-characterized with regard to their structures and physical properties, and several efficient methods for their preparation are available in the literature.[9] Therefore, we chose Yb(TPP)Cl and Yb(TPP)OTf as porphyrin-based Lewis acid catalysts, and assessed their catalytic ability toward the rearrangement of

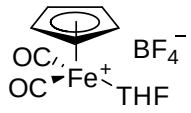
cis-**1a**. Indeed, while Yb(TPP)Cl could not promote the rearrangement (entry 3), treatment of epoxide *cis*-**1a** with 1 mol% of Yb(TPP)OTf in DCE at 83 °C resulted in a highly regioselective rearrangement to afford 89% yield of the desired aldehyde **2a** along with only a trace amount (<5%) of ketone **3a** (entry 4). Further optimization revealed that DCE was the optimal solvent (entries 4–6).

Using the optimal conditions, we next explored the scope and generality of the procedure (Table 2). As a whole, the Yb(TPP)OTf catalyst system could easily be applied to various 2,3-diaryloxiranes such as those having phenyl, naphthyl, and biphenyl moieties. Regardless of whether the stereochemistry of a substrate is *cis* or *trans*, excellent yields and high regioselectivity are typically obtained (entries 1 and 2). Thus, this catalytic protocol can obviate the need for careful separation of the *cis* and *trans* isomers of

Table 1. Lewis acid-catalyzed rearrangement of *cis*-stilbene oxide *cis*-**1a**



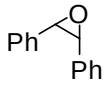
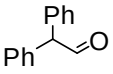
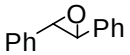
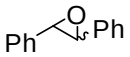
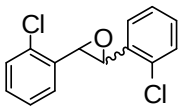
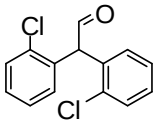
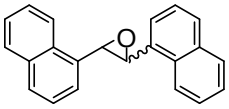
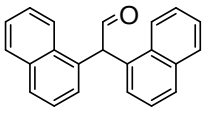
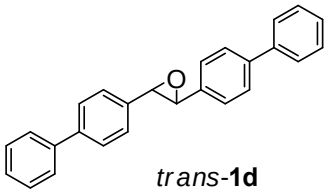
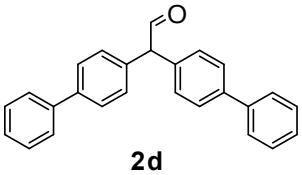
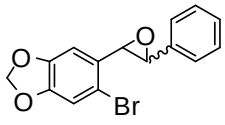
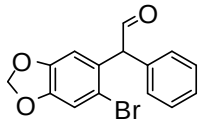
cis-**1a** **2a** **3a**

entry	catalyst	conditions solvent/temp/time	yield (%)[a] of **2a**	yield (%)[a] of **3a**
1	Fe(TPP)OTf	DCE/83 ºC/1 h	73	23
2	Cr(TPP)OTf	DCE/83 ºC/3 h	66	32
3	Yb(TPP)Cl	DCE/83 ºC/12 h	no reaction	
4	Yb(TPP)OTf	DCE/83 ºC/4 h	89	<5
5	Yb(TPP)OTf	dioxane/100 ºC/2 h	55	21
6	Yb(TPP)OTf	toluene/110 ºC/6 h	44	21
7	$Er(OTf)_3$	DCM/rt/2 h	73	15
8	$Yb(OTf)_3$	DCM/rt/1 h	62	16
9	$Bi(O)ClO_4$	DCM/rt/10 h	69	13
10	$Bi(OTf)_3$	DCM/rt/1 h	74	13
11		DCM/rt/15 h	75	15
12	$InCl_3$	THF/50 °C/24h	no reaction	
13	$InCl_3$	DCM/40 °C/24h	no reaction	

a) Isolated yield.

2,3-diaryloxiranes prior to using these epoxides as the substrates in the rearrangement. For example, subjecting 1 mol% of Yb(TPP)OTf to a 1:1 mixture of *cis*- and *trans*-**1a** led to the formation of aldehyde **2a** as the major product, the yield of which (87%) was comparable to that obtained from the corresponding single isomers (entry 3). Similar results were obtained for epoxides **1b** and **1c** that consist of their *cis* and *trans* isomers (entries 4 and 5). As expected, biphenyl-substituted derivative *trans*-**1d** could easily be converted to the corresponding aldehyde **2d**, a useful synthetic intermediate for a clay mimic organic host,[10] in a high yield (entry 6). The asymmetrical epoxide **1e** that possesses different aryl substituents on the oxirane ring also proved to be a suitable substrate for this catalytic rearrangement, fur-

Table 2. Yb(TPP)OTf-catalyzed rearrangement of 2,3-diaryloxirane to 2,2-diaryl-acetaldehyde[a]

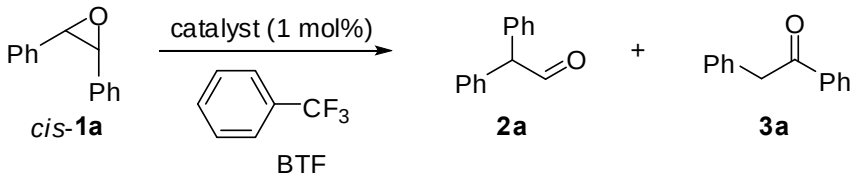
entry	substrate	time (h)	product	yield (%)[b]
1	 *cis*-**1a**	4	 **2a**	89
2	 *trans*-**1a**	4	**2a**	94
3	 **1a** (*cis*/*trans* = 1:1)	4	**2a**	87
4	 **1b** (*cis*/*trans* = 1:1)	12	 **2b**	90
5	 **1c** (*cis*/*trans* = 1:1)	4	 **2c**	87
6	 *trans*-**1d**	5	 **2d**	85
7	 **1e** (*cis*/*trans* = 1:1)	12	 **2e**	92

a) Conditions: Yb(TPP)OTf (1 mol%), DCE, 83 ºC. b) Isolated yield.

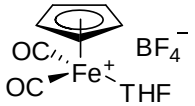
nishing the desired aldehyde **2e** in 92% yield (entry 7). In all cases, only trace amounts (<5%) of undesired isomeric ketones could be detected in the ^{1}H-NMR spectra of the crude reaction mixtures.

We next turned our attention to the use of BTF as a solvent in place of DCE. As briefly mentioned above, BTF is a potential substitute for DCM and related solvents mainly because of its higher boiling point and lower toxicity, and its use as reaction media in preparative organic chemistry and homogeneous catalysis is a topic of ongoing interest.[7] However, Lewis acid-mediated reactions in BTF are still limited since BTF is somewhat labile toward Lewis acidic conditions; for example, the CF_3 group of BTF is known to react with strong Lewis acids such as $AlCl_3$ even at ambient temperature.[7] Thus, development of a new, milder Lewis acid catalyst that can be used in BTF is highly desirable. As illustrated in Table 3, the Yb(TPP)OTf-catalyzed rearrangement of *cis*-**1a** occurred in refluxing BTF with yield and regioselectivity fully comparable to those obtained from the counterpart reaction in DCE (entry 1, cf. entry 4 in Table 1), whereas other catalysts, such as $Er(OTf)_3$, $Yb(OTf)_3$, $Bi(OTf)_3$, $Bi(O)ClO_4$, and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(THF)]BF_4$, all of which did not work well in BTF, produced significant erosion of yields and regioselectivity as well as prolonged reaction time (entries 2–6). The present conditions using the Yb(TPP)OTf catalyst and BTF as a solvent translated smoothly to other 2,3-diaryloxiranes (Table 4). As expected, all the substrates examined readily undergo the rearrangement to afford the corresponding 2,2-diarylacetaldehydes in high yields. More noteworthy was the observation that the yields of these reactions

Table 3. Lewis acid-catalyzed rearrangement of *cis*-stilbene oxide *cis*-**1a** in BTF



cis-**1a** **2a** **3a**

entry	catalyst	temp (°C)	time (h)	yield (%)[a] of **2a**	yield (%)[a] of **3a**
1	Yb(TPP)OTf	102	3	87	<5
2	$Er(OTf)_3$	rt	10	51	20
3	$Yb(OTf)_3$	rt	9	50	20
4	$Bi(O)ClO_4$	rt	24	40	12
5	$Bi(OTf)_3$	rt	5	51	17
6		rt	24	46	18

a) Isolated yield.

in BTF are generally higher than those of the parallel reactions performed in DCE (cf. Table 2). These results clearly show that BTF can be employed as an excellent replacement for DCE in Yb(TPP)OTf-catalyzed rearrangements.

Table 4. Yb(TPP)OTf-catalyzed rearrangement of 2,3-diaryloxirane to 2,2-diarylacetaldehyde in BTF[a]

entry	substrate	time (h)	product	yield (%)[b]
1	*cis*-**1a**	3	**2a**	87
2	**1a** (*cis*/*trans* = 1:1)	3	**2a**	91
3	**1b** (*cis*/*trans* = 1:1)	12	**2b**	93
4	**1c** (*cis*/*trans* = 1:1)	5	**2c**	90
5	*trans*-**1d**	6	**2d**	88
6	**1e** (*cis*/*trans* = 1:1)	12	**2e**	93

a) Conditions: Yb(TPP)OTf (1 mol%), BTF, 102 ºC. b) Isolated yield.

CONCLUSION

In summary, we have developed a new class of porphyrin-based Lewis acid catalyst, Yb(TPP)OTf, that can efficiently promote highly regioselective rearrangement of 2,3-diaryloxiranes to 2,2-diarylacetaldehydes. This rearrangement was successfully carried out in DCM but could also be performed in the more environmentally friendly solvent BTF. Mechanistic investigations and applications of this class of catalysts to new transformations are currently underway.

EXPERIMENTAL

General ^{1}H- and ^{13}C-NMR spectra were recorded on a JEOL JNM-AL300 spectrometer. The chemical shifts were reported in ppm relative to $CHCl_3$ (δ = 7.24) for ^{1}H-NMR and relative to the central resonance of $CDCl_3$ (δ = 77.0) for ^{13}C-NMR. IR spectra were recorded on a JASCO FT/IR-4100 spectrophotometer. The mass spectroscopic data were obtained on a JEOL JNM-DX302 spectrometer. UV-visible absorption spectra were measured with a Hitachi U-3210 spectrophotometer. Dichloroethane (DCE) and dichloromethane (DCM) were distilled under argon from CaH_2. Benzotrifluoride (BTF) was distilled under argon from P_2O_5. Tetrahydrofuran was distilled under argon from sodium benzophenone ketyl. Kanto Kagaku Silica Gel 60 (spherical) and Merck kiesel-gel 60 F254 were employed for silica gel column and thin layer chromatography, respectively. Both *cis*- and *trans*-stilbene oxides, *cis*-**1a** and *trans*-**1a**, were purchased from Aldrich. Other 2,3-diaryloxiranes **1b**–**e** were prepared as described in the

literature.[1d,4a,11] Porphyrin-based catalysts, Cr(TPP)OTf and Fe(TPP)OTf, were prepared by the literature methods.[5d] Unless otherwise stated, all commercially available chemicals were used without further purification.

Preparation of [5,10,15,20-tetraphenylporphynato]ytterbium(III) chloride [Yb(TPP)Cl][9]

A 300 mL three necked flask equipped with a magnetic stirring bar, a reflux condenser, and rubber septa was charged with 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine [H_2TPP] (1.0 g, 1.6 mmol) and 1-chloro-naphtalene (150 mL). The mixture was stirred at 150 °C for 30 min to dissolve the porphyrin. To the solution was added $YbCl_3 \cdot 6H_2O$ (1.0 g, 2.6 mmol), and the mixture was refluxed until the Soret band of the free base porphyrin was replaced by that of the ytterbium porphyrin complex at 416 nm. The reaction mixture was allowed to cool to rt and then concentrated under a reduced pressure. The resulting residue was dissolved in 10 mL of pyridine, and the solution was poured into ice-cooled water (300 mL). The resulting precipitate was collected by filtration and washed with copious amounts of water to give the pyridine-coordinated ytterbium porphyrin complex. The complex was recrystallized from CH_2Cl_2/hexane (twice times) and dried in a vacuum oven for 48 h at 150 °C under a reduced pressure (1 mmHg) to give the pyridine-free Yb(TPP)Cl complex (806 mg, 60%). UV/vis (CH_2Cl_2): λ_{max} (log ε): 416 (5.4), 552 (4.2) nm; Anal. Calcd for $C_{44}H_{28}ClN_4Yb \cdot H_2O$: C, 62.97; H, 3.60; N, 6.68. Found: C, 63.52; H, 3.49; N, 6.66.

Preparation of [5,10,15,20-tetraphenylporphynato]ytterbium(III) triflate [Yb(TPP)OTf]

A flame-dried 50 mL two necked flask equipped with a magnetic stirring bar, a reflux condenser, and rubber septa was charged with Yb(TPP)Cl (100 mg, 0.12 mmol) and AgOTf (30 mg, 0.15 mmol). The reaction vessel was evacuated and flushed with argon (three times), and absolute THF (25 mL) was added. The mixture was refluxed under argon for 10 h, allowed to reach rt, and concentrated under a reduced pressure. The residue was dissolved in CH_2Cl_2 (ca. 30 mL), and filtered through a pad of Celite. The filtrate was concentrated under a reduced pressure. The resulting solid was recrystallized from CH_2Cl_2/hexane (twice times) and dried in a vacuum oven for 24 h at 100 °C under a reduced pressure (1 mmHg) to give Yb(TPP)OTf (97 mg, 85%). UV/vis (CH_2Cl_2): λ_{max} (log ε): 418 (5.5), 549 (4.2) nm; Anal. Calcd for $C_{45}H_{28}F_3N_4O_3SYb \cdot H_2O$: C, 56.72; H, 3.17; N, 5.88. Found: C, 56.94; H, 3.25; N, 5.60.

General procedure for the Yb(TPP)OTf-catalyzed rearrangement of 2,3-diaryloxiranes to 2,2-diarylacetaldehydes

To a solution of 2,3-diaryloxirane **3** (0.5 mmol) in DCE or BTF (5 mL) was added Yb(TPP)OTf (4.8 mg, 0.005 mmol). The mixture was refluxed under argon. After completion of the reaction (monitored by TLC), the reaction mixture was concentrated under a reduced pressure. The residue was passed through a silica gel short column (1:3 AcOEt−hexane) to remove the catalyst. The eluate was concentrated in vacuo, and the residue was chromatographed on silica-gel (1:9 AcOEt−hexane) to give 2,2-diarylacetaldehyde **2**.

The aldehydes, **2a**,[12] **2c**,[4a] and **2e**,[1d] are known compounds and easily characterized by comparison with authentic samples.

2,2-Diphenylacetaldehyde (2a) ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 9.94 (1H, d, *J* = 2.5 Hz), 7.40-7.14 (10H, m), 4.88 (1H, d, *J* = 2.5 Hz).

2,2-Bis(2-chlorophenyl)acetaldehyde (2b) ^{1}H-NMR ($CDCl_3$, 300 MHz) 9.93 (1H, d, *J* = 0.5 Hz), 7.48-7.45 (2H, m), 7.31-7.22 (4H, m), 7.04-6.97 (2H, m), 5.84 (1H, brs); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 197.1, 135.1, 133.4, 130.5, 130.2, 129.2, 127.1, 58.3; IR (KBr): 3737, 1720, 1651, 1516, 1469, 1045, 748, 671 cm^{-1}; HRMS (EI) m/z: calcd for $C_{14}H_{10}Cl_2O$: 264.0109, found: 264.0107.

2,2-Di(naphthalen-1-yl)acetaldehyde (2c) ^{1}H-NMR ($CDCl_3$) δ: 10.22 (1H, d, *J* = 2.1 Hz), 7.92-7.7.89 (4H, m), 7.53-7.38 (6H, m), 7.24-7.19 (4H, m), 6.37 (1H, d, *J* = 2.1 Hz).

2,2-Di(biphenyl-4-yl)acetaldehyde (2d) ^{1}H-NMR ($CDCl_3$) δ: 10.01 (1H, d, J = 2.2 Hz), 7.73-7.31 (18H, m), 4.97 (1H, d, J = 2.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 198.3, 140.7, 140.5, 135.2, 130.7, 129.6, 128.8, 127.8, 127.1, 63.5; IR (KBr): 3737, 1701, 1647, 1516, 1115, 675, 671 cm^{-1}; HRMS (EI) m/z: calcd for $C_{26}H_{20}O$: 348.1514, found: 348.1516.

2-(6-Bromobenzo[d][1,3]dioxol-5-yl)-2-phenylacetaldehyde (2e) ^{1}H-NMR ($CDCl_3$) δ: 9.91 (1H, d, *J* = 0.9 Hz), 7.40-7.19 (5H, m), 7.06 (1H, s), 6.57 (1H, s), 5.95 (1H, d, *J* = 3.9 Hz), 5.94 (1H, d, *J* = 3.9 Hz), 5.39 (1H, brs).

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REFERENCES AND NOTES

1. See for example: (a) U. S. Sørensen, T. J. Bleisch, A. E. Kingston, R. A. Wright, B. G. Johnson, D. D. Schoepp, and P. L. Ornstein, *Bioorg. Med. Chem.*, 2003, **11**, 197. (b) G. R. Pettit, J. W. Lippert III, and D. L. Herald, *J. Org. Chem.*, 2000, **65**, 7438. (c) L. J. S. Knutsen, K. E. Andersen, J. Lau, B. F. Lundt, R. F. Henry, H. E. Morton, L. Nærum, H. Petersen, H. Stephensen, P. D. Suzdark, M. D. B. Swedberg, C. Thomsen, and P. O. Sørensen, *J. Med. Chem.*, 1999, **42**, 3447. (d) M. E. Jung, P. Y. -S. Lam. M. M. Mansuri, and L. M. Speltzs, *J. Org. Chem.* 1985, **50**, 1087. (e) J. A. Clark, M. S. G. Clark, D. V. Gardner, L. M. Gaster, M. S. Hadley, D. Miller, and A. Shah, *J. Med. Chem.*, 1979, **22**, 1373.

2. See for example: (a) O. Branytska, L. J. W. Shimon, and R. Neumann, *Chem. Commun.*, 2007, 3957. (b) P. Nilsson, M. Larhed, and A. Hallberg, *J. Am. Chem. Soc.*, 2001, **123**, 8217.

3. (a) A. Procopio, R. Dalpozzo, A. D. Nino, M. Nardi, G. Sindona, and A. Tagarelli, *Synlett*, 2004, 2633. (b) A. M. Anderson, J. M. Blazek, P. Garg, B. J. Payne, and R. S. Mohan, *Tetrahedron Lett.*,

2000, **41**, 1527. (c) K. A. Bhatia, K. J. Eash, N. M. Leonard, M. C. Oswald, and R. S. Mohan, *Tetrahedron Lett.*, 2001, **42**, 8129. (d) J. Picione, S. J. Mahmood, A. Gill, M. Hilliard, and M. M. Hossain, *Tetrahedron Lett.*, 1998, **39**, 2681. (e) I. Karamé, M. L. Tommasino, and M. Lemaire, *Tetrahedron Lett.*, 2003, **44**, 7687. (f) K. Smith, G. A. El-Hiti, and M. Al-Shamali, *Catal. Lett.*, 2006, **109**, 77. (g) M. W. C. Robinson, K. S. Pillinger, and A. E. Graham, *Tetrahedron Lett.*, 2006, **47**, 5919. (h) F. Martínez, C. Campo, and E. F. Llama, *J. Chem. Soc., Perkin Trans. 1*, 2000, 1749. (i) B. C. Ranu and U. Jana, *J. Org. Chem.*, 1998, **63**, 8212. (j) R. Sudha, K. M. Narasimhan, V. G. Saraswathy, and S. Sankararaman, *J. Org. Chem.*, 1996, **61**, 1877.

4. $BF_3 \cdot OEt_2$ and bulky organoaluminum complexes, such as methylaluminum bis(4-bromo-2,6-di-*tert*-butylphenoxide), are also known to be efficient Lewis acid reagents that can mediate the rearrangement of 2,3-diaryloxiranes to 2,2-diarylacetaldehydes. However, more than a stoichiometric amount of these reagents are necessary to promote the reaction, see: (a) H. E. Zimmerman, C. E. Caufield, and R. K. King, *J. Am. Chem. Soc.*, 1985, **107**, 7732. (b) K. Maruoka, T. Ooi, and H. Yamamoto, *J. Am. Chem. Soc.*, 1989, **111**, 6431. (c) K. Maruoka, S. Nagahara, T. Ooi, and H. Yamamoto, *Tetrahedron Lett.*, 1989, **30**, 5607. (d) Y. Ohba, K. Ito, T. Nagasawa, and S. Sakurai, *J. Heterocycl. Chem.*, 2000, **37**, 1071. (e) S. Roy, R. Banerjee, A. Nangia, and G. J. Kruger, *Chem. Eur. J.*, 2006, **12**, 3777.
5. (a) T. Takanami, R. Hirabe, M. Ueno, F. Hino, and K. Suda, *Chem. Lett.*, 1996, 1031. (b) K. Suda, K. Baba, S. Nakajima, and T. Takanami, *Tetrahedron Lett.*, 1999, **40**, 7243. (c) K. Suda, K. Baba, S. Nakajima, and T. Takanami, *Chem. Commun.*, 2002, 2570. (d) K. Suda, T. Kikkawa, S. Nakajima, and T. Takanami, *J. Am. Chem. Soc.*, 2004, **126**, 9554.
6. We have also reported metalloporphyrin-catalyzed Claisen rearrangement of allyl vinyl ethers, see: (a) T. Takanami, M. Hayashi, and K. Suda, *Tetrahedron Lett.*, 2005, **46**, 2893. (b) T. Takanami,; M. Hayashi, K. Iso, H. Nakamoto, and K. Suda, *Tetrahedron*, 2006, **62**, 9467.
7. (a) J. J. Maul, P. J. Ostrowski, G. A. Ublacker, B. Linclau, and D. P. Curran, 'Modern Solvents in Organic Synthesis: Topics in Current Chemistry,' Vol. 206, ed. by P. Knochel, Springer-Verlag, Berlin, 1999, pp. 79-105. (b) A. Ogawa and D. P. Curran, *J. Org. Chem.*, 1997, **62**, 450.
8. Lemaire, et al. reported that $IrCl_3$ can catalyze the rearrangement of *cis*- and *trans*-stilbene oxides into diphenylacetaldehyde **2a** in quantitative yields (see ref. 3e). However, we were unable to reproduce the results.
9. Preparation and characterization of [Yb(TPP)(Cl)(H_2O)(THF)] and related lanthanide porphyrin complexes are reported: (a) W. D. Horrocks, Jr. and C.-P. Wong, *J. Am. Chem. Soc.*, 1976, **98**, 7157. (b) W.-K, Wong, L. Zhang, W.-T. Wong, F. Xue, and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 1999, 615. (c) W.-K, Wong, L. Zhang, F. Xue, and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*,

1999, 3053. (d) T. J. Foley, K. A. Abboud, and J. M. Boncella, *Inorg. Chem.*, 2002, **41**, 1704.

10. V. S. S. Kumar and A. Nangia, *Chem. Commun.*, 2001, 2392.
11. (a) V. Mark, *Org. Synth. Coll. Vol. 5*, 1973, 358. (b) H. E. Zimmerman, C. E. Caufield, and R. K. King, *J. Am. Chem. Soc.*, 1985, **107**, 7732. (c) D. Yang, M.-K. Wong, Y.-C. Yip, X.-C. Wang, M.-W. Tang, J.-H. Zheng, and K.-K. Cheung, *J. Am. Chem. Soc.*, 1998, **120**, 5943.
12. Commercially available from Aldrich.