Supporting Information:

Efficient carbonate synthesis under mild conditions through cycloaddition of carbon dioxide to oxiranes using a Zn(salphen) catalyst

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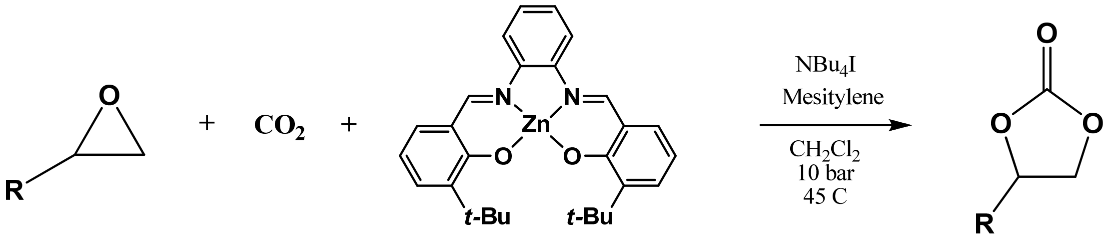
Content:

General catalytic procedure for the cycloaddition reaction of carbon dioxide to epoxides, and recycling experiment.

The Zn(salphen) catalyst **2** (0.025 g, 5.0×10^{-5} mol) and (co-catalyst) NBu_4I (0.018 g, 5×10^{-5} mol) were added in a two-necked round-bottomed flask under a gently flux of argon. Dry CH_2Cl_2 (5.0 mL) and mesitylene (0.27 mL, 2.0×10^{-3} mol) were then added and the solution stirred until complete dissolution occurred. To this mixture the epoxide (2.0×10^{-3} mol) was added and the solution transferred to a 25 mL stainless-steel reactor previously purged with argon. Three cycles of pressurisation and depressurisation of the reactor (with CO_2 at 5 bar) were carried out before finally stabilizing the pressure at 10 bar and the solution left stirring at 45°C for 18h. A sample of the solution was then analyzed by means of ^1H NMR spectroscopy (d_6-DMSO) and the yield determined using mesitylene as an internal standard.



(2)

Recycling experiment:

In a separate experiment the same reaction (see above) was carried out. After 18 h, the mixture was analyzed and the conversion of the cyclic carbonate determined at 84%. Then, the reaction mixture was carefully concentrated, and the residue extracted (6 × 2mL) with hexane (*the catalyst and co-catalyst are virtually insoluble in hexane as confirmed by NMR analysis of the combined hexane extracts*). To the residue of this extracted crude product was added a new batch of epoxyhexane dissolved in CH_2Cl_2 (5.0 mL), after which the mixture was pressurized with CO_2 to 10 bar. A second run of 18 h was then performed and analyzed by ^1H NMR (d_6-DMSO); the conversion of cyclic carbonate was determined at 82%.

Crystallographic comments and details

c-Hexene oxide structure based on complex **1**:

Comments: Two of the *tert*-butyl groups of the complex are showing rotational disorder (three different orientations). Also the six membered ring of the ligand attached to the Zn atom is showing some disorder. Since the structure was taken at room temperature it was not possible to separate the disordered positions of the six membered ring. Crystals of this compound measured at 100K cracked after few minutes making a structure determination at this temperature extremely difficult. The structure collected at room temperature has an R1 value of 5.4 %.

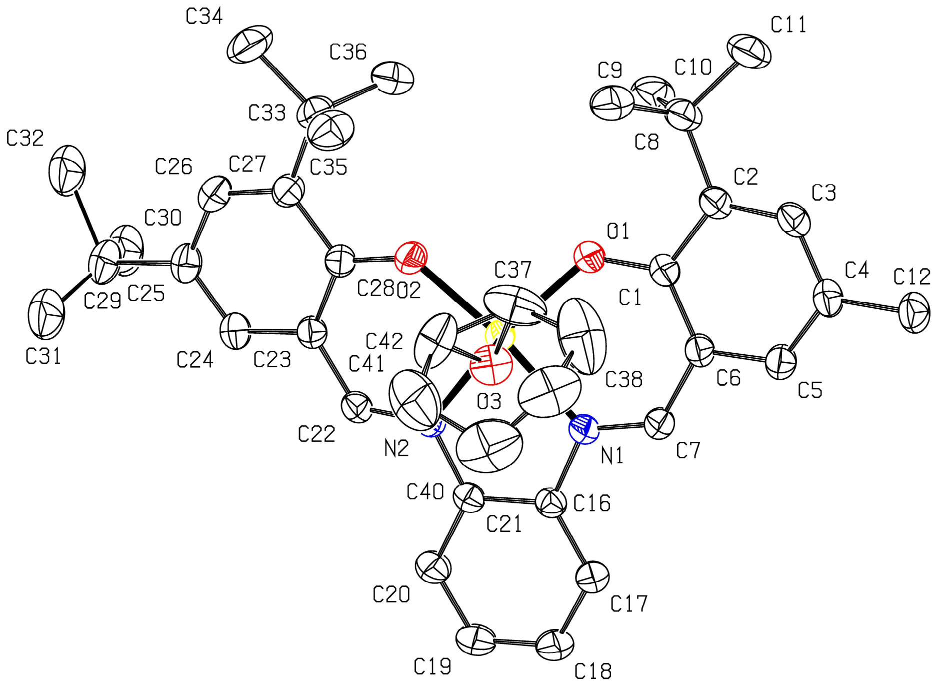


Figure S1. Other perspective view of the structure **1**·(*c*-hexene oxide). Disorder observed, co-crystallized solvent molecules and H-atoms are omitted for clarity.

Epoxyhexane oxide structure based on complex **1**:

<u>Comments</u>: The rest (i.e., ligand = epoxyhexane) attached to the Zn-atom is disordered in three orientations (50:25:25). Due to the disorder problems some of the atoms are showing large thermal ellipsoids. The structure has an R1 value of 5.3 %.

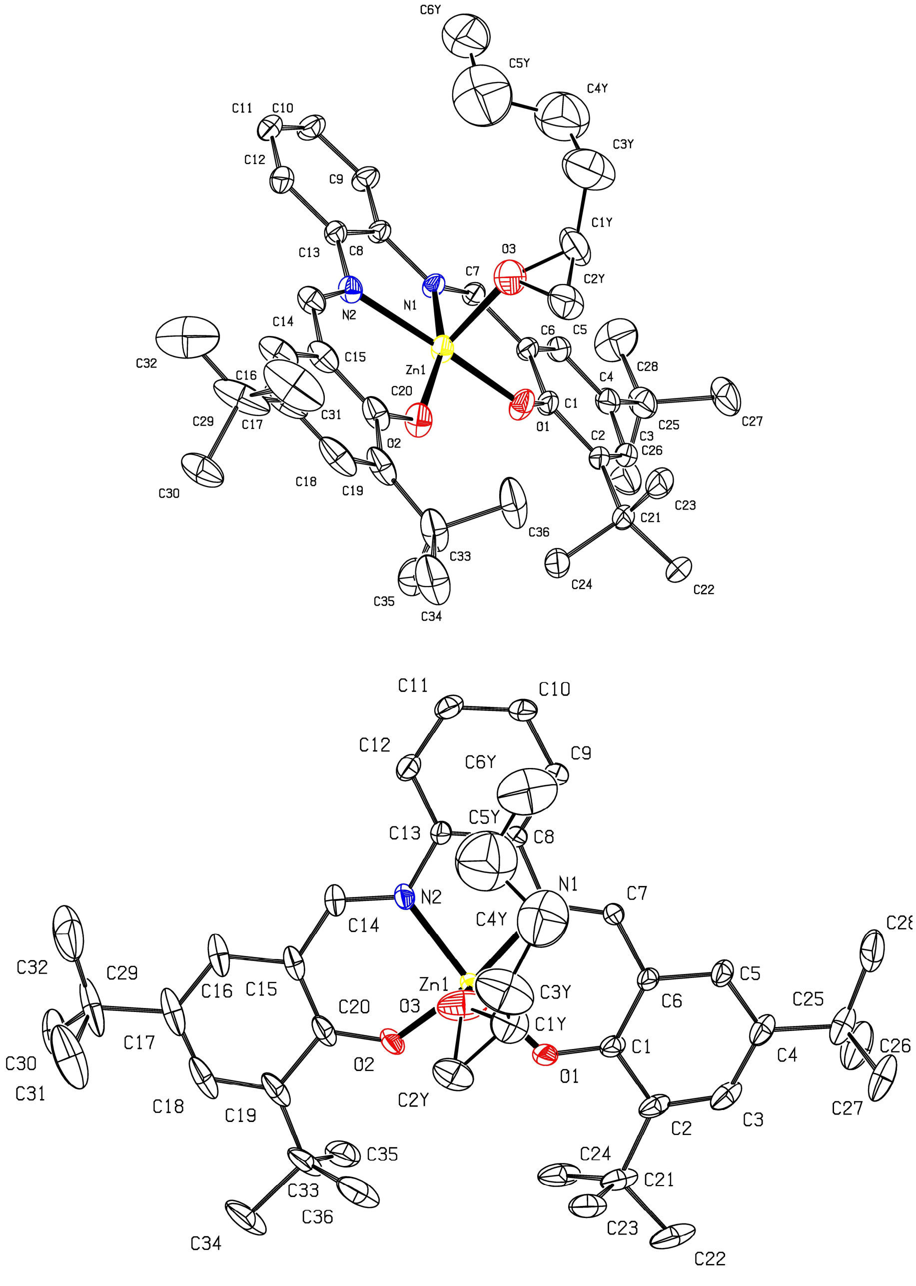


Figure S2. Some perspective views of the molecular structure of **1**·(epoxyhexane). Disorder, co-crystallized solvent molecules and H-atoms are omitted for clarity.

Crystallographic summaries of **1**·(epoxyhexane) and **1**·(*c*-hexene oxide).

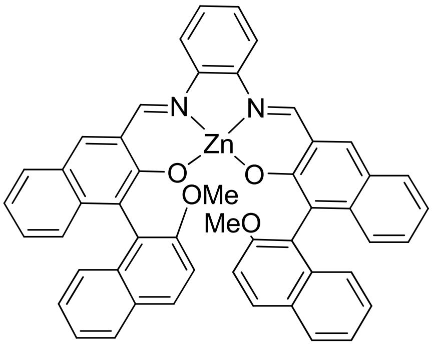
Table S1. Crystal data and structure refinement for **1**·(epoxyhexane).

Identification code	AD3p21c	
Empirical formula	C42 H58 N2 O3 Zn	
Formula weight	704.27	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 12.9860(5) Å	α= 90.00 °.
	b = 25.1822(9) Å	β = 94.087(2) °.
	c = 11.9067(5) Å	γ = 90.00 °.
Volume	3883.8(3) $Å^3$	
Z	4	
Density (calculated)	1.204 Mg/m^3	
Absorption coefficient	0.671 mm^{-1}	
F(000)	1512	
Crystal size	0.40 x 0.40 x 0.25 mm^3	
Theta range for data collection	1.57 to 35.02 °.	
Index ranges	-20 <=h<=20 ,-40 <=k<=40 ,-19 <=l<=18	
Reflections collected	17026	
Independent reflections	13521 [R(int) = 0.0421]	
Completeness to theta =35.02 °	0.995 %	
Absorption correction	Empirical	
Max. and min. transmission	0.8502 and 0.7751	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	17026 / 349 / 588	
Goodness-of-fit on F^2	1.074	
Final R indices [I>2sigma(I)]	R1 = 0.0527 , wR2 = 0.1400	
R indices (all data)	R1 = 0.0707 , wR2 = 0.1549	
Largest diff. peak and hole	1.635 and -1.123 e.$Å^{-3}$	

Table S2. Crystal data and structure refinement for **1**·(*c*-hexene oxide).

Identification code	AWK560RT_0m	
Empirical formula	C42 H56 N2 O3 Zn	
Formula weight	702.26	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.0200(12) Å	α= 91.604(6) °.
	b = 12.9735(13) Å	β = 98.646(6) °.
	c = 13.1293(14) Å	γ = 103.732(6) °.
Volume	1962.0(3) $Å^3$	
Z	2	
Density (calculated)	1.189 Mg/m^3	
Absorption coefficient	0.664 mm^{-1}	
F(000)	752	
Crystal size	0.40 x 0.40 x 0.30 mm^3	
Theta range for data collection	1.62 to 34.04 °.	
Index ranges	-18 <=h<=18 ,-20 <=k<=20 ,-20 <=l<=20	
Reflections collected	15605	
Independent reflections	10104 [R(int) = 0.0360]	
Completeness to theta =34.04 °	0.972 %	
Absorption correction	Empirical	
Max. and min. transmission	0.8256 and 0.7771	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15605 / 102 / 474	
Goodness-of-fit on F^2	1.056	
Final R indices [I>2sigma(I)]	R1 = 0.0601 , wR2 = 0.1801	
R indices (all data)	R1 = 0.0914 , wR2 = 0.2016	
Largest diff. peak and hole	0.716 and -0.664 e.$Å^{-3}$	

Synthesis and characterization of complex 5.



1,2-Phenylenediamine (20 mg, 0.18 mmol), (*S*)-2-hydroxy-2'-methoxy-1,1'-binaphthyl-3-carbaldehyde (63 mg, 0.39 mmol),[1] $Zn(OAc)_2 \cdot 2H_2O$ (45 mg, 0.20 mmol) were placed in a round bottom flask. MeOH (20 mL) was added and the resulting suspension was heated until it became a clear solution. Then, 3-4 drops of pyridine were added and the solution stirred overnight at room temperature. The solid that had precipitated was collected by filtration and recrystallized from $CHCl_3$/MeOH to give **5** as a bright orange solid (87.9 mg, 60%). ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta = 9.41$ (s, 2H, CH=N), 8.36 (d, 2H, $J = 4.6$ Hz, Pyr-H$_{ortho}$), 8.15 (s, 2H, ArH), 8.11 (d, 2H, $J = 8.74$ Hz, ArH), 8.05 (m, 2H, ArH), 8.02 (s, 1H, ArH), 7.99 (d, 2H, $J = 8.7$ Hz, ArH), 7.76 (t, 1H, $J = 7.8$ Hz, Pyr-H), 7.71 (d, 2H, $J = 7.8$ Hz, ArH), 7.50 (m, 2H, ArH), 7.29 (m, 4H, ArH+Pyr-H), 7.24 (m, 2H, ArH), 7.09 (m, 4H, ArH), 7.01 (m, 2H, ArH), 6.95 (m, 2H, ArH), 6.69 (d, 2H, $J = 8.7$ Hz, ArH), 2.92 (s, 6H, OMe); MS (MALDI+, pyrene): $m/z = 791.3$ $(M+H)^+$. Anal. calcd. for $C_{50}H_{34}N_2O_4Zn \cdot CHCl_3 \cdot$Pyr: C 68.83, H 3.89, N 4.38. Found: C 68.61, H 3.65, N 4.47. The presence of 1 equiv of pyridine was confirmed by ^{1}H NMR.

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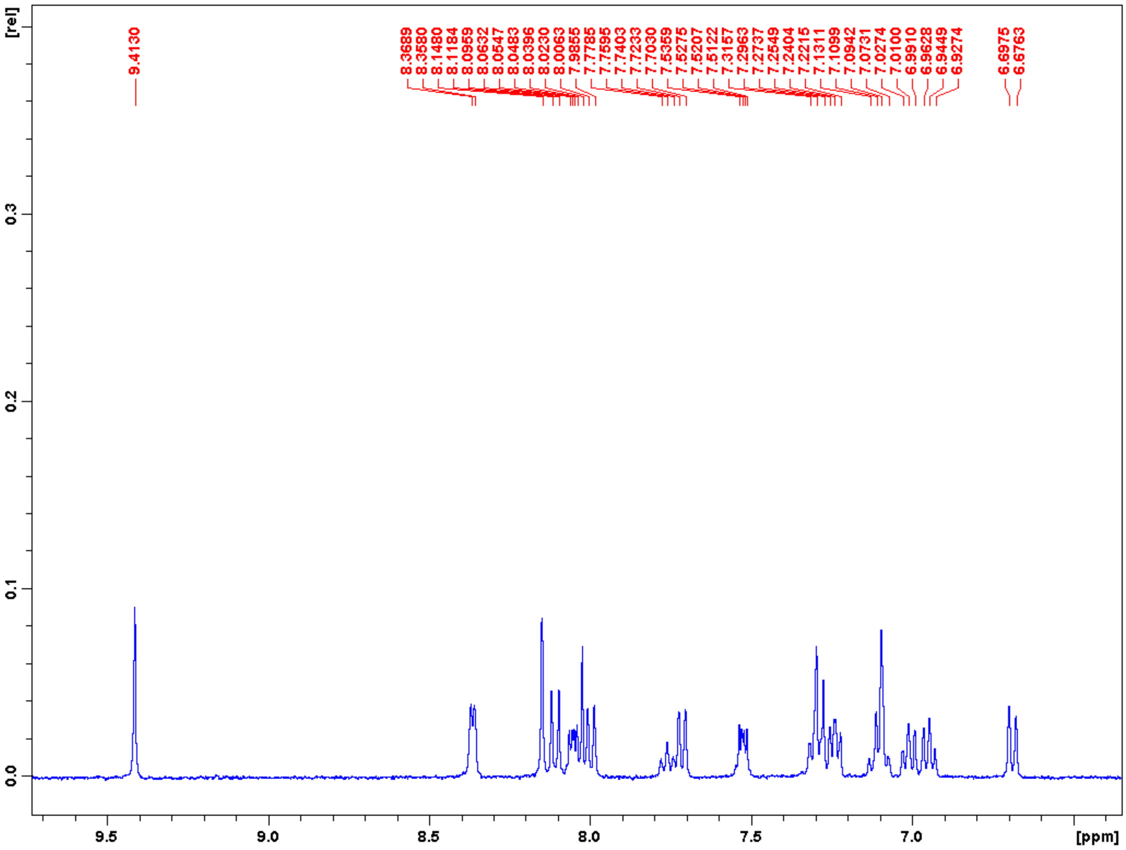
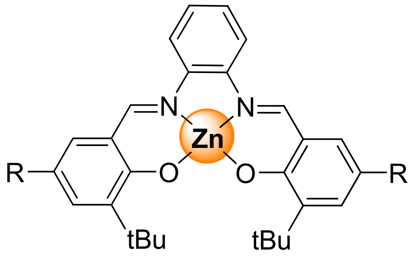
[1] The chiral binaphthaldehyde was prepared according to a previously reported procedures, see: a) A. R. van Doorn, D. J. Rushton, M. Bos, W. Verboom, D. N. Reinhoudt, *Recl. Trav. Chim. Pay-Bas*. **1992**, *111*, 415; b) L. Jin, Y. Huang, H. Jing, T. Chang, P. Yan, *Tetrahedron: Asymmetry* **2008**, *19*, 1947.

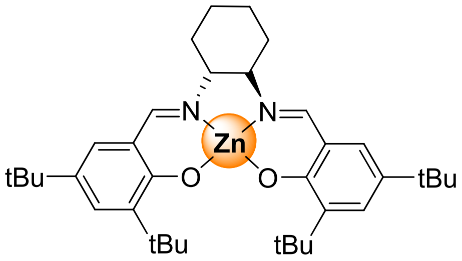
The aromatic region of the ^{1}H NMR (d_6-DMSO) of **5** is shown below:



General comments:



1. R = tBu
2. R = H



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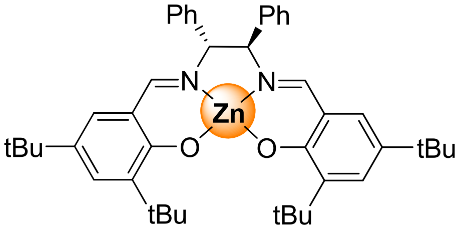

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Complexes **1-2**,[2] **3**,[3] and **4**[4] were prepared according to literature procedures.

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[2] A. W. Kleij, D. M. Tooke, M. Kuil, M. Lutz, A. L. Spek, J. N. H. Reek, *Chem.–Eur. J.* **2005**, *11*, 4743-4750.

[3] G. A. Morris, H. Zhou, C. L. Stern, S.T. Nguyen, *Inorg. Chem.* **2001**, *40*, 3222.

[4] Cozzi reported the *in situ* prepration of this Zn derivative using dialkyl-Zn reagents. See: P. G. Cozzi, *Angew. Chem. Int. Ed.* **2003**, *42*, 2895. We found that a simple salt such as $Zn(OAc)_2 \cdot 2H_2O$ is also effective for the synthesis of **4**.

Synthesis details of Zn(salphen) complexes

The Zn-salphen complexes are generally easily prepared by combination of the respective salicylaldehyde, o-phenylenediamine and $Zn(OAc)_2{\cdot}2H_2O$ *in a one-pot procedure: all components can be commercially purchased and are relatively cheap. A typical procedure for complex **1** is given below:*[5]

To a solution of *o*-phenylenediamine (1.26 g, 11.65 mmol) and 3,5-di-*tert*-butylsalicylaldehyde (5.79 g, 24.71 mmol) in MeOH (150 mL) was added solid $Zn(OAc)_2{\cdot}2H_2O$ (2.69 g, 12.26 mmol). The resultant orange solution was stirred for 2 h after which the obtained suspension was filtered to furnish a bright orange solid (7.06 g, 11.10 mmol, 95%). The isolated yield of **1** generally is in the range 90-98%. The product can be easily recrystallized from hot CH_3CN to afford analytically pure **1**. The synthesis of complex **2** can be carried out in a similar fashion with isolated yields exceeding 90%.

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[5] a) See reference 2 of this ESI. See also: b) A. W. Kleij, D. M. Tooke, M. Lutz, A. L. Spek, J. N. H. Reek, *Eur. J. Inorg. Chem.* **2005**, 4626. c) E. C. Escudero-Adán, J. Benet-Buchholz, A. W. Kleij, *Eur. J. Inorg. Chem.* **2009**, 3562.