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N-杂环卡宾-吡啶锰配合物/四丁基碘化铵催化 CO_2 和环氧化物合成环状碳酸酯

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摘要 该工作发展了一类二齿 *N*-杂环卡宾(NHC)-吡啶锰配合物催化 CO_2 和环氧化物偶联反应的方法. 锰配合物和四丁基碘化铵(TBAI)构成的二元催化体系对环氧化物和 CO_2 合成环状碳酸酯的反应表现出了较高的活性. 该二元催化体系适用于广泛的底物范围, 例如端环氧化物和高位阻的内环氧化物. 通过紫外-可见光谱、红外光谱和高分辨质谱的研究对反应机理进行了阐述.

关键词 锰催化; 二氧化碳; 环状碳酸脂; CO_2 利用; *N*-杂环卡宾

N-Heterocyclic Carbene-Pyridine Manganese Complex/ Tetrabutylammonium Iodide Catalyzed Synthesis of Cyclic Carbonate from CO_2 and Epoxide

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Abstract The bidentate *N*-heterocyclic carbene (NHC)-pyridine nitrogen manganese complex catalyzed coupling reaction of epoxides with CO_2 was developed. The binary system resulting from the manganese complex **Mn-2** in combination with tetrabutylammonium iodide (TBAI) exhibits the high activity for the synthesis of cyclic carbonate from epoxides and CO_2. The binary catalytic system is suitable for a broad range of substrates scope, such as terminal epoxides and sterically hindered internal epoxides. A possible catalytic pathway was elaborated by UV-vis, FT-IR and HRMS method.

Keywords manganese catalysis; carbon dioxide; cyclic carbonate; CO_2 utilization; *N*-heterocyclic carbene

1 Introduction

Carbon dioxide (CO_2) is an important C1 building block in the field of organic synthesis.[1] As a non-toxic, abundant, and widely available raw material, CO_2 has wide applications in various organic conversion reactions.[2] The cyclic carbonate from CO_2 and epoxide is an effective strategy for CO_2 utilization that has become the most widely studied reaction.[3] Based on the high catalytic activity and relatively mild reaction conditions of homogeneous metal catalysts, a wide range of metal catalysts, including Fe,[4] Al,[5] Zn,[6] Co,[7] Ni,[8] Cr,[9] Ca,[10] In,[11] Zr,[12] rare-earth metal,[13] have been developed for the synthesis of cyclic carbonate from CO_2 and epoxide. Among them, Mn catalysts bearing different ligands, such as porphyrin ligand,[14] salen ligand,[15] cyclen ligand,[16] corrole ligand,[17] have been widely investigated. In addition, polyoxometalate-supported Mn carbonyl derivatives[18] and heterobimetallic Ru-Mn complexes,[19] respectively, were used as catalysts for the synthesis of cyclic carbonate. It is well known that the structure of ligand, such as their steric and electronic properties, is important for their catalytic activity. Therefore, the study of other coordination types of Mn complexes provides some new insight to the rational design of metal complexes for cycloaddition reaction of epoxides with CO_2. Recently, we[20] reported Mn(I) *N*-heterocyclic carbene (NHC)-pyridine complexes catalyzed method for amide bond formation of

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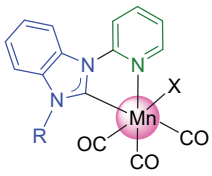
esters with amines. In this work, the Mn(I) NHC-pyridine complexes (as shown in Figure 1)[20] were used as catalysts and tested their catalytic performance in cycloaddition reaction of epoxides with CO_2.



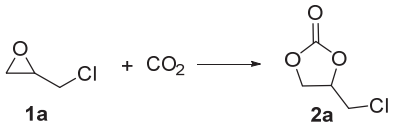
Mn-1, R = Me, X = I
Mn-2, R = *n*-Pr, X = I
Mn-3, R = *n*-Pr, X = Br
Mn-4, R = *n*-Bu, X = I
Mn-5, R = Et, X = I

Figure 1 Mn complexes tested in cycloaddition reaction

2 Results and discussion

The Mn complexes **Mn-1**, **Mn-2**, **Mn-3**, **Mn-4** and **Mn-5** were prepared by previously reported method (Figure 1).[20] The structure activity relationship of five Mn complexes for the synthesis of cyclic carbonate was evaluated using the cycloaddition of ECH (epichlorohydrin) with CO_2 as benchmark reaction (Table 1). The effect of *N*-substituted groups bearing benzimidazolium salts was first investigated (Table 1, Entries 1, 2 and 4, 5). The product yields have slightly increased when *N*-methyl **Mn-1** complex or *N*-ethyl **Mn-5** complex was replaced by *N*-propyl **Mn-2** complex (Table 1, Entries 1 vs 2 and 5). The stability of the imidazolium salts was improved with increasing the chain length of *N*-alkyl groups,[21] so the **Mn-2** complex with the relative long *N*-propyl group would be beneficial in the stabilize of Mn active species in reaction. However, an obvious yield decreased from 37% to 18% was observed when *N*-propyl **Mn-2** complex was changed to *N*-butyl **Mn-4** complex (Table 1, Entries 2 vs 4). This may be related to the catalytic process of the Mn complexes. Epoxide generally was activated by the interaction between the Mn center of complexes and carbon atom of epoxide. The long *N*-alkyl chain may hinder the exposure opportunity of Mn metal center to epoxide carbon atom, resulting in the reduction of catalytic activity. The effect of counter anion bearing Mn complexes was next explored. The results indicated that counter anion between bromine and iodine has not obviously influence on the catalytic activity of Mn complexes (Table 1, Entries

Table 1 Conditions optimization for Mn-catalyzed synthesis of cyclic carbonate[a]



1a **2a**

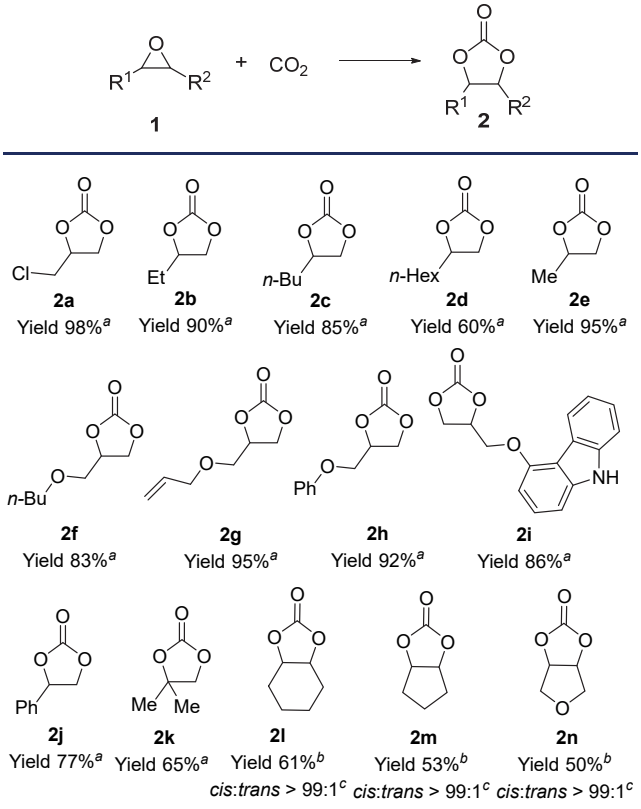
Entry	Catalyst (mol%)	Co-catalyst (mol%)	CO_2	*T*/℃	Time/h	Yield/%
1	**Mn-1** (0.15)	TBAB (1.5)	balloon	30	24	31
2	**Mn-2** (0.15)	TBAB (1.5)	balloon	30	24	37
3	**Mn-3** (0.15)	TBAB (1.5)	balloon	30	24	30
4	**Mn-4** (0.15)	TBAB (1.5)	balloon	30	24	18
5	**Mn-5** (0.15)	TBAB (1.5)	balloon	30	24	33
6	**Mn-2** (0.15)	TBAI (1.5)	balloon	30	24	43
7	**Mn-2** (0.15)	TBAC (1.5)	balloon	30	24	34
8	**Mn-2** (0.15)	TOAB (1.5)	balloon	30	24	30
9	**Mn-2** (0.15)	PPNCl (1.5)	balloon	30	24	38
10	**Mn-2** (0.15)	TBAA (1.5)	balloon	30	24	36
11	**Mn-2** (0.15)	TOPB (1.5)	balloon	30	24	38
12	**Mn-2** (0.3)	TBAI (1.5)	balloon	30	24	60
13	**Mn-2** (0.45)	TBAI (1.5)	balloon	30	24	76
14	**Mn-2** (0.3)	TBAI (1.5)	0.5 MPa	30	24	64
15	**Mn-2** (0.3)	TBAI (1.5)	1.0 MPa	30	24	67
16	**Mn-2** (0.3)	TBAI (1.5)	1.0 MPa	40	24	72
17	**Mn-2** (0.3)	TBAI (1.5)	1.0 MPa	60	24	79
18	**Mn-2** (0.3)	TBAI (1.5)	1.0 MPa	80	12	98
19	**Mn-2** (0.3)	TBAI (1.5)	1.0 MPa	80	6	90
20	**Mn-2** (0.3)	TBAI (3.0)	1.0 MPa	80	6	92
21	**Mn-2** (0)	TBAI (1.5)	1.0 MPa	80	12	40
22	**Mn-2** (0.3)	TBAI (0)	1.0 MPa	80	12	0

[a] Reaction conditions unless specified otherwise: epichlorohydrin (10.0 mmol), catalyst (as indicated in Table 1), co-catalyst (as indicated in Table 1), reaction temperature and time are shown in Table 1, neat, isolated yield. TBAB: tetrabutylammonium bromide; TBAC: tetrabutylammonium chloride; TBAI: tetrabutylammonium iodide; TOAB: tetraoctylammonium bromide; PPNCl: bis(triphenylphosphine)iminium chloride; TBAA: tetrabutylammonium acetate; TOPB: tetraoctylphosphonium bromide.

2 vs 3). The influence of co-catalysts in this reaction was investigated when **Mn-2** was employing as catalyst, and TBAI provides the best promoted performance (Table 1, Entries 6 vs 2 and 7～11). A range of reaction conditions, such as loading amount of **Mn-2** (Table 1, Entries 6, 12 and 13), CO_2 pressure (Table 1, Entries 12, 14 and 15), reaction temperature (Table 1, Entries 15～18), reaction time (Table 1, Entries 18 and 19), and loading amount of TBAI (Table 1, Entries 19 and 20), were evaluated. The results showed that 0.3 mol% of **Mn-2**, 1.5 mol% of TBAI, and 1.0 MPa of CO_2 at 80 ℃ for 12 h are the optimized reaction conditions (Table 1, Entry 18). The control experiments without catalyst or co-catalyst showed that the synergy of catalyst and co-catalyst is essential in the cycloaddition of epoxide with CO_2 (Table 1, Entries 21 and 22).

The scope and limitation of epoxides were investigated in Table 2. The terminal epoxides first evaluated using our developed Mn-catalyzed system. A broad range of terminal epoxides bearing different substituents reacted with CO_2, providing moderate to excellent the desired cyclic carbonates **2a**～**2j**. Di-substituted 4,4-dimethyl-1,3-dioxolan-2-one was suitable for the catalyzed system to give 65% yield of **2k**. In addition, more challenging steric substrates, such as six-membered bicyclic epoxides and five-membered bicyclic epoxides, were also tested in this system. The moderate product yields of **2l**～**2n** were obtained when co-catalyst was changed from TBAI to PPNCl and reaction time was prolonged to 24 h. **2l**～**2n** were formed in *cis*-isomer, which were detected by NMR and FT-IR spectroscopy.[22]

Table 2 Substrates scope for Mn-catalyzed synthesis of cyclic carbonate



[a] Conditions: epoxide (10.0 mmol), 1 MPa of CO_2, **Mn-2** (0.3 mol%), TBAI (1.5 mol%), 80 ℃, 12 h, neat, isolated yield. [b] Conditions: epoxide (10.0 mmol), 1 MPa of CO_2, **Mn-2** (0.3 mol%), PPNCl (1.5 mol%), 80 ℃, 24 h, neat, isolated yield. [c] *Cis* ∶ *trans* ratio was detected by NMR and FT-IR spectroscopy.

To investigate the cooperative effect between **Mn-2** and TBAI, a FT-IR spectroscopy method was used to explore the interaction mechanism. As shown in Figure 2, the shifts in infrared peaks position of **Mn-2** for the stretching vibration peaks of aromatic ring double bond and carbonyl groups were observed. FT-IR studies indicated that the structure of **Mn-2** has changed during the addition of TBAI.

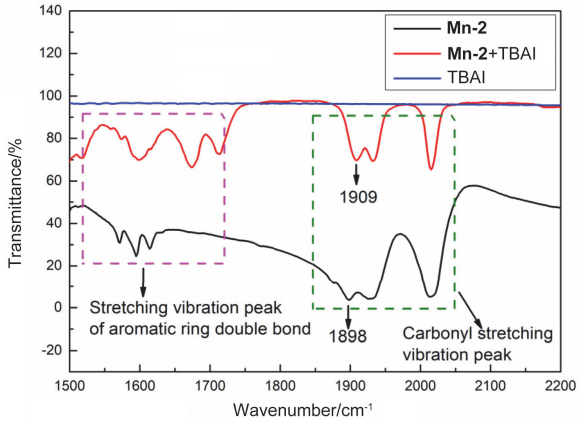


Figure 2 FT-IR spectra for reaction mechanism

To prove further the reaction mechanism, UV-vis titration experiments was performed in Figure 3. As shown in Figure 3, the isosbestic point (λ=273 nm) was observed in the UV-vis titration experiments. Kleij and co-workers[23] reported that the coordination environment of the metal complex was determined by UV-vis titration experiment. We inferred that a carbonyl group may undergo dissociating from **Mn-2** to form a new Mn complex during the addition of TBAI to **Mn-2**.

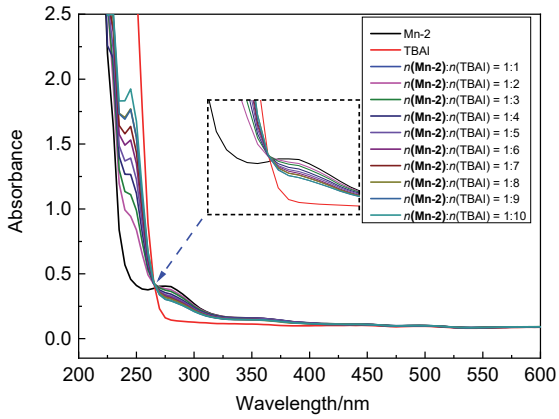
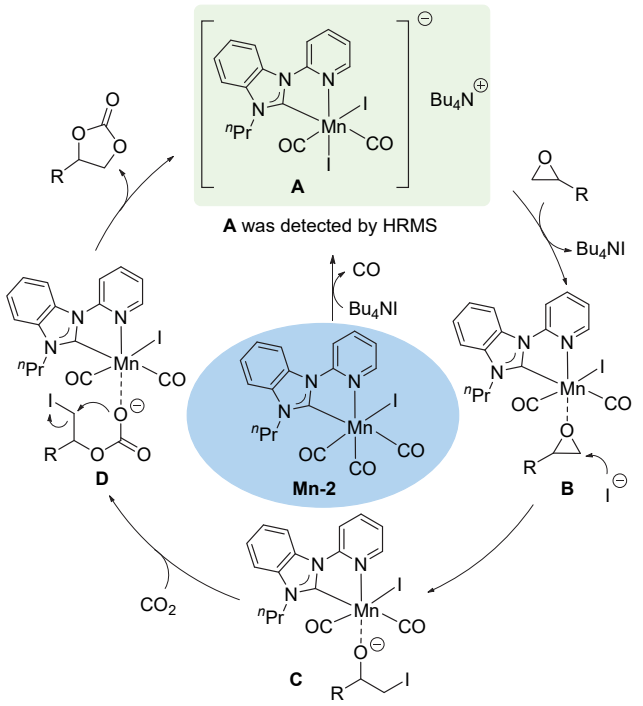


Figure 3 UV-vis titration experiments for reaction mechanism

North and co-workers[9a] reported that the Cr complex reacted with TBAB to form a new six-coordinate complex, which was considered to be an active species in the reaction. In order to further reveal the active intermediate, high resolution mass spectrometry (HRMS, ESI, negative ion mode) war performed. A new peak at *m*/*z* 601.8625 was detected attributed to intermediate **A** when 5 equiv. of TBAI was added to the dichloromethane solution of **Mn-2**. The combined FT-IR, UV-vis and HRMS experimental results and literature[9a,23] support the hypothesis that **Mn-2** undergoes a ligand exchange between carbonyl group and iodine anion by the reaction **Mn-2** with TBAI to generate intermediate **A** in Scheme 1. The intermediate **A** activates the epoxide by releasing iodine anion, which acts a nucleophile to attack carbon atom of epoxide. Their cooperative effect promotes the ring opening of epoxide to form the intermediate **C**. The intermediate **D** is present via the insertion reaction between CO_2 and **C**. The desired product is formed by the intramolecular nucleophilic attack of **D**, and regenerates catalytic species **A**.



Scheme 1 Mn-catalyzed mechanism for cycloaddition reaction of epoxides with CO_2

3 Conclusions

The combination use of bidentate *N*-heterocyclic carbene (NHC)-pyridine nitrogen manganese complex **Mn-2** with tetrabutylammonium iodide (TBAI) was developed. The binary catalytic system exhibits the high activity for the synthesis of cyclic carbonate from epoxides and CO_2 and is capable of tolerating a broad range of substrates, including terminal epoxides and challenging internal epoxides. UV-vis and FT-IR spectroscopic analysis suggested that a new Mn active species was formed by the reaction **Mn-2** with TBAI.

4 Experimental section

4.1 General information

Unless otherwise stated, all experimental procedures were performed under air using Schlenk techniques and stainless steel reactor. All solvents, potassium carbonate, 2-bromopyridine, benzimidazole, cuprous iodide, epoxide, CO_2 and other starting materials were purchased from commercial suppliers and used without further purification.

4.2 Analytical methods

The NMR spectra were recorded on a Bruker Avance III HD 400 spectrometer using TMS as the internal standard (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR). FT-IR spectra were recorded on a Tianjin Gangdong FTIR-650. UV-vis spectra were recorded on an Agilent Cary 60. High-resolution mass spectroscopy data were collected by using a Waters UPLC G2-XS Qtof mass spectrometer. The melting point data were measured with a melting point meter SGW X-4.

4.3 Preparation procedure for catalysts **Mn-1**～**Mn-5**

The synthesis of manganese complexes were prepared by the previous method.[20] A mixture of $MnBr(CO)_5$ (0.5 mmol, 1.0 equiv.), ligand (0.6 mmol, 1.2 equiv.), and *t*-BuOK (0.8 mmol, 1.6 equiv.) was stirred in a 25 mL of Schlenk tube, and the reaction tube was vacuumed and then filled with nitrogen three times under the Schlenk system. Subsequently, tetrahydrofuran (THF) (2 mL) was added to the reaction tube, and then the mixture was stirred in a heating mantle at 65 ℃ for 24 h. After cooling to room temperature, THF was removed under reduced pressure using a rotary evaporator. The reaction mixture was then further washed with acetonitrile (10 mL×3) to remove unreacted ligand and $MnBr(CO)_5$, and the crude products were filtered and dried to give the desired product.

4.4 General procedure for the synthesis of cyclic carbonates

Epoxides (10.0 mmol), catalyst **Mn-2** (0.3 mol%, 0.03 mmol), and TBAI (1.5 mol%, 0.15 mmol) were successively placed into a 25 mL stainless steel reactor that was equipped with a magnetic stirrer, and the reactor was pressurized with CO_2 to 1 MPa, then reacted under 80 ℃ for 12 h. After cooling to room temperature, the remaining CO_2 was removed slowly, the reaction liquid was removed under reduced pressure and the products were isolated by flash chromatography.

4.5 Characterization data of Mn complexes **Mn-1**～**Mn-5**

Manganese complexes **Mn-1**: **Mn-1** was prepared according to the previous method.[20] Yellow-orange solid (165.9 mg, 70%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.04 (brs, 1H), 8.48 (d, J=29.6 Hz, 2H), 8.26 (brs, 1H), 7.94 (brs, 1H), 7.58 (brs, 3H), 4.32 (s, 3H); Mn complex **Mn-1** is paramagnetic, and ^{13}C NMR spectra were not obtained; IR (KBr) ν: 2007, 1926, 1893, 1479, 1405, 1093, 1023,

802, 664, 615 cm^{-1}.

Manganese complexes **Mn-2**: **Mn-2** was prepared according to the previous method.[20] Yellow-orange solid (150.7 mg, 60%). ^1H NMR (400 MHz, DMSO-d_6) δ: 9.06 (brs, 1H), 8.48 (d, J=34.4 Hz, 2H), 8.25 (brs, 1H), 8.01 (brs, 1H), 7.56 (brs, 3H), 4.70 (s, 2H), 2.06 (brs, 2H), 1.07 (s, 3H); Mn complex **Mn-2** is paramagnetic, and ^{13}C NMR spectra were not obtained; IR (KBr) v: 2015, 1930, 1898, 1480, 1423, 1209, 1023, 776, 743, 671 cm^{-1}.

Manganese complexes **Mn-3**: **Mn-3** was prepared according to the previous method.[20] Yellow-orange solid (196.6 mg, 72%). ^1H NMR (400 MHz, DMSO-d_6) δ: 9.05 (brs, 1H), 8.48 (dd, J=7.6, 36.0 Hz, 2H), 8.25 (brs, 1H), 8.02 (d, J=6.4 Hz, 1H), 7.57 (brs, 3H), 4.71(s, 2H), 2.10～2.03 (m, 2H), 1.07 (s, 3H); Mn complex **Mn-3** is paramagnetic, and ^{13}C NMR spectra were not obtained; IR (KBr) v: 2018, 1943, 1901, 1473, 1427, 1210, 1088, 1024, 746, 668 cm^{-1}.

Manganese complexes **Mn-4**: **Mn-4** was prepared according to the previous method.[20] Yellow-orange solid (154.9 mg, 60%). ^1H NMR (400 MHz, DMSO-d_6) δ: 9.05 (brs, 1H), 8.48 (dd, J=7.6, 35.6 Hz, 2H), 8.25 (brs, 1H), 7.98 (brs, 1H), 7.57 (brs, 3H), 4.74 (s, 2H), 2.03 (brs, 2H), 1.50 (d, J=7.2 Hz, 2H), 0.96 (s, 3H); Mn complex **Mn-4** is paramagnetic, and ^{13}C NMR spectra were not obtained; IR (KBr) v: 2015, 1926, 1897, 1423, 1210, 768, 664 cm^{-1}.

Manganese complexes **Mn-5**: **Mn-5** was prepared according to the general procedure.[20] Yellow-orange solid (138.4 mg, 24%). ^1H NMR (400 MHz, DMSO-d_6) δ: 9.08 (brs, 1H), 8.48 (d, J=32.2 Hz, 2H), 8.23 (brs, 1H), 7.97 (brs, 1H), 7.57 (brs, 3H), 4.82 (s, 2H), 1.62 (s, 3H). Mn complex **Mn-5** is paramagnetic, and ^{13}C NMR spectra were not obtained; HRMS (ESI-TOF) calcd for $C_{17}H_{13}MnN_3O_3$ $[M-I]^+$ 362.0337, found 362.0334; IR (KBr) v: 2011, 1918, 1905, 1484, 1425, 1206, 1097, 765, 749, 672, 613 cm^{-1}.

4.6 Characterization data of cyclic carbonates 2a～2n

4-(Chloromethyl)-1,3-dioxolan-2-one (**2a**):[24] Purification by flash chromatography [V(petroleum ether)∶V(ethyl acetate)=2∶1]: Yellow oil (1.338 g, 98%). ^1H NMR (400 MHz, $CDCl_3$) δ: 5.01～4.95 (m, 1H), 4.57 (t, J=8.4 Hz, 1H), 4.38 (dd, J=5.6, 8.8 Hz, 1H), 3.81～3.69 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.4, 74.5, 67.0, 44.0.

4-Ethyl-1,3-dioxolan-2-one (**2b**):[25] Purification by flash chromatography [V(petroleum ether)∶V(ethyl acetate)=2∶1]: Yellow oil (1.0448 g, 90%). ^1H NMR (400 MHz, $CDCl_3$) δ: 4.69～4.62 (m, 1H), 4.51 (t, J=8.0 Hz, 1H), 4.07 (dd, J=7.2, 8.4 Hz, 1H), 1.85～1.70 (m, 2H), 1.02 (t, J=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.1, 78.0, 69.0, 27.0, 8.5.

4-Butyl-1,3-dioxolan-2-one (**2c**):[26] Purification by flash chromatography [V(petroleum ether)∶V(ethyl acetate)=5∶1]: Colorless oil (1.227g, 85%). ^1H NMR (400 MHz, $CDCl_3$) δ: 4.69～4.62 (m, 1H), 4.47 (t, J=8.0 Hz, 1H), 4.01 (t, J=7.2 Hz, 1H), 1.77～1.58 (m, 2H), 1.42～1.26 (m, 4H), 0.85 (t, J=6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.2, 77.2, 69.4, 33.5, 26.4, 22.2, 13.8.

4-Hexyl-1,3-dioxolan-2-one (**2d**):[27] Purification by flash chromatography [V(petroleum ether)∶V(ethyl acetate)=5∶1]: Colorless oil (0.643g, 60%). ^1H NMR (400 MHz, $CDCl_3$) δ: 4.71～4.64 (m, 1H), 4.50 (t, J=8.0 Hz, 1H), 4.03 (t, J=8.0 Hz, 1H), 1.81～1.60 (m, 2H), 1.48～1.26 (m, 8H), 0.85 (t, J=6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.2, 77.1, 69.4, 33.8, 31.5, 28.8, 24.3, 22.4, 14.0.

4-Methyl-1,3-dioxolan-2-one (**2e**):[5d] Purification by flash chromatography [V(petroleum ether)∶V(ethyl acetate)=2∶1]: Colorless oil (0.970 g, 95%). ^1H NMR (400 MHz, $CDCl_3$) δ: 4.81～4.73 (m, 1H), 4.46 (t, J=8.0 Hz, 1H), 3.93 (dd, J=7.2, 8.0 Hz, 1H), 1.36 (d, J=6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.2, 73.7, 70.7, 19.2.

4-(Butoxymethyl)-1,3-dioxolan-2-one (**2f**):[28] Purification by flash chromatography [V(petroleum ether)∶V(ethyl acetate)=5∶1]: Colorless oil (1.446 g, 83%). ^1H NMR (400 MHz, $CDCl_3$) δ: 4.81～4.75 (m, 1H), 4.46 (t, J=8.4 Hz, 1H), 4.35 (dd, J=6.4, 8.4 Hz, 1H), 3.64 (dd, J=3.6, 11.2 Hz, 1H), 3.56 (dd, J=3.6, 10.8 Hz, 1H), 3.48 (dd, J=0.4, 6.4 Hz, 2H), 1.55～1.48 (m, 2H), 1.37～1.28 (m, 2H), 0.88 (t, J=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.1, 75.2, 71.8, 69.6, 66.3, 31.5, 19.1, 13.8.

4-((Allyloxy)methyl)-1,3-dioxolan-2-one (**2g**):[29] Purification by flash chromatography [V(petroleum ether)∶V(ethyl acetate)=5∶1]: Colorless oil (1.502 g, 95%). ^1H NMR (400 MHz, $CDCl_3$) δ: 5.85～5.76 (m,1H), 5.24～5.13 (m, 2H), 4.81～4.76 (m, 1H), 4.45 (t, J=8.4 Hz, 1H), 4.32 (dd, J=6.0, 8.4 Hz, 1H), 4.00～3.97 (m, 2H), 3.64 (dd, J=3.6, 11.2 Hz, 1H), 3.54 (dd, J=3.6, 11.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.2, 133.8, 117.7, 117.6, 117.6, 75.3, 75.3, 75.3, 72.4, 72.4, 68.9, 66.2.

4-(Phenoxymethyl)-1,3-dioxolan-2-one (**2h**):[22d] Purification by flash chromatography [V(petroleum ether)∶V(ethyl acetate)=2∶1]: White solid (1.786 g, 92%), m.p. 101.1～102.8 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.30～7.23 (m, 2H), 6.99 (t, J=7.2 Hz, 1H), 6.88 (d, J=7.6 Hz, 2H), 5.02～4.97 (m, 1H), 4.60～4.54 (m, 1H), 4.50 (dd, J=6.0, 8.8 Hz, 1H), 4.21 (dd, J=4.0, 10.4 Hz, 1H), 4.11(dd, J=3.6, 10.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.8, 154.8, 129.7, 122.0, 114.7, 74.2, 66.9, 66.3.

4-(((9*H*-Carbazol-4-yl)oxy)methyl)-1,3-dioxolan-2-one (**2i**):[30] Purification by flash chromatography (dichloromethane): White solid (2.424 g, 86%), m.p. 208.1～209.8 ℃; ^1H NMR (400 MHz, DMSO-d_6) δ: 11.31 (s, 1H), 8.11 (d, J=7.6 Hz, 1H), 7.47 (d, J=8.0 Hz, 1H), 7.37～7.30 (m, 2H), 7.14～7.11 (m, 2H), 6.72 (d, J=8.0 Hz, 1H), 5.35 (dd, J=3.2, 5.6 Hz, 1H), 4.77 (t, J=8.8 Hz, 1H), 4.64～4.40 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 155.5, 154.6, 141.7, 139.5, 126.9, 125.2, 122.6, 121.9, 119.2, 111.9, 111.0, 105.0, 101.0, 75.4, 67.8, 66.7.

4-Phenyl-1,3-dioxolan-2-one (**2j**):[31] Purification by

flash chromatography [*V*(petroleum ether)∶*V*(ethyl acetate)=5∶1]: White solid (1.264 g, 77%), m.p. 48.6～49.0 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45～7.34 (m, 5H), 5.67 (t, J=8.0 Hz, 1H), 4.80 (t, J=8.4 Hz, 1H), 4.33 (dd, J=8.0, 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.9, 135.9, 129.8, 129.3, 125.9, 78.0, 71.2.

4,4-Dimethyl-1,3-dioxolan-2-one (**2k**):[32] Purification by flash chromatography [*V*(petroleum ether)∶*V*(ethyl acetate)=10∶1]: Yellow colorless oil (0.755 g, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.12 (s, 2H), 1.48 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.7, 81.8, 75.4, 26.0.

Cis-hexahydrobenzo[d] [1.3]dioxol-2-one (**2l**):[33] Purification by flash chromatography [*V*(petroleum ether)∶*V*(ethyl acetate)=5∶1]: Colorless oil (0. 867 g, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.66～4.64 (m, 2H), 1.86～1.84 (m, 4H), 1.61～1.52 (m, 2H), 1.42～1.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.4, 75.8, 26.7, 19.1.

Cis-tetrahydro-4*H*-cyclopenta[*d*][1,3]dioxol-2-one (**2m**):[22e] Purification by flash chromatography [*V*(petroleum ether)∶*V*(ethyl acetate)=5∶1]: White solid (0.679 g, 53%), m.p. 32.3～32.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.02 (s, 2H), 2.00 (d, J=8.8 Hz, 2H), 1.71～1.60 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.5, 82.0, 33.0, 33.0, 21.5.

Cis-tetrahydrofuro[3,4-*d*][1,3]dioxol-2-one (**2n**):[22e] Purification by flash chromatography [*V*(petroleum ether)∶*V*(ethyl acetate)=5∶1]: White solid (0.651 g, 50%), m.p. 72.9～73.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.20～5.19 (m, 2H), 4.24～4.21 (m, 2H), 3.57～3.53 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.5, 80.1, 73.0.

Supporting Information ^{1}H NMR, ^{13}C NMR and IR spectra of Mn complexes **Mn-1**～**Mn-5**. ^{1}H NMR and ^{13}C NMR spectra of cyclic carbonates **2a**～**2n**. IR, UV-vis, and HRMS spectra for catalytic mechanism of **Mn-2** with TBAI. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn/.

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