Supporting Information

A layered Mn-based coordination polymer as an efficient heterogeneous catalyst for CO_2 cycloaddition under mild condition

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1. Experimental

1.1 Materials and Physical Measurements

Powder X-ray diffraction (PXRD) measurement was performed by employing a Rigaku Dmax 2000 diffractometer using Cu Kα radiation. The mass ratio of C, H, N was determined by using VarioEL III Elemental Analyzer. The infrared (IR) spectrum was collected on a Nicolet iS50 FT-IR spectrometer. Thermogravimetric analysis (TGA) measurement was determined on a STA 449 F3 Jupiter Synchronous thermalanalyzer under nitrogen gas. ^{1}H NMR spectra were determined on a Bruker Avance III HD 400 MHz. The nitrogen adsorption Brunauer-Emmett-Teller (BET) analyses (Micromeritics, ASAP 2460) was utilized to evaluate the specific surface area.

1.2 X-ray Crystallography

Crystallographic data of **JLNU-104** was collected on an Oxford diffraction Gemini R CCD diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å). Absorption correction was performed by a multi-scan technique. The structure was solved by direct methods with SHELXS-2014 and then refined on F2 by full-matrix least-squares using the SHELXTL-2018 program within WINGX [1,2]. The positions of non-hydrogen atoms were refined with anisotropic displacement factors, and hydrogen atoms were positioned geometrically. The crystallographic data for **JLNU-104** is listed in Table 1, and the selected bond lengths (Å) and bond angle (°) are summarised in Table 2. CCDC 2167660 contains the supplementary crystallographic data.

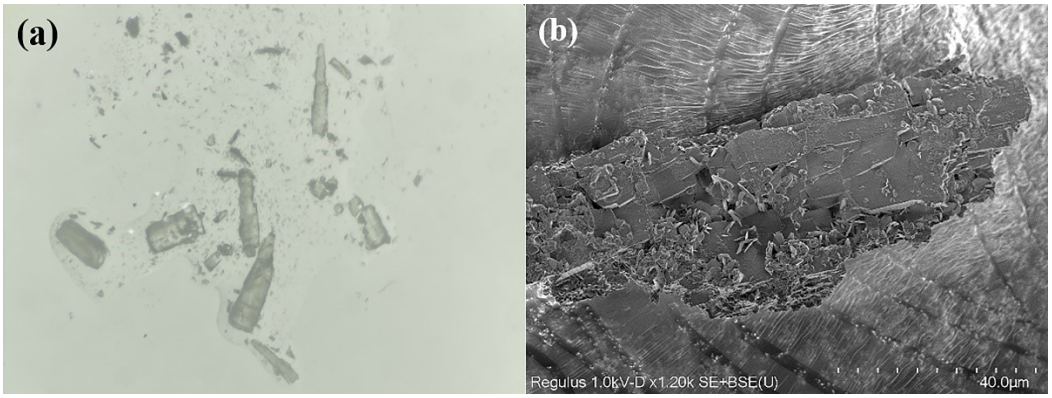

Fig. S1 The photograph (a) and SEM image (b) of **JLNU-104**

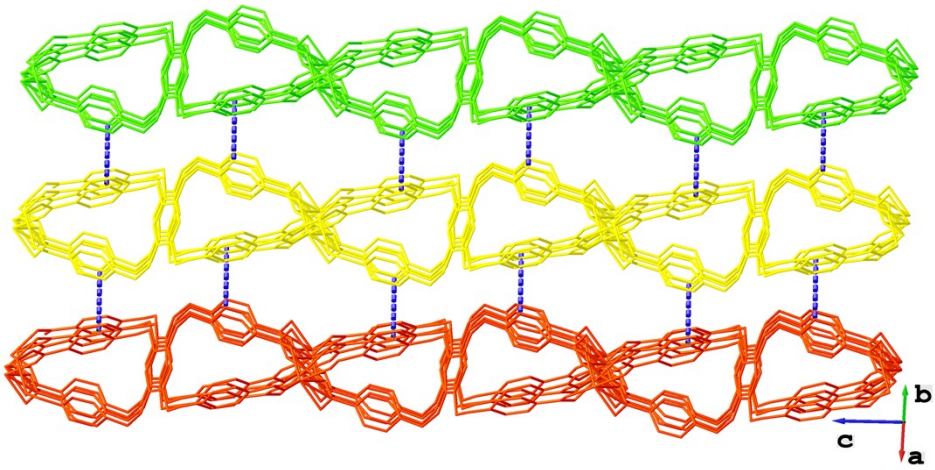

Fig. S2 The 3D architecture of **JLNU-104**.

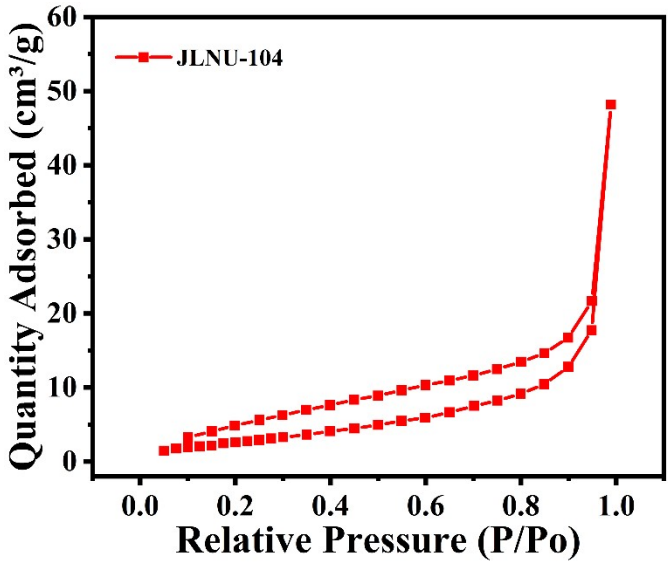

Fig. S3 The N_2 adsorption-desorption isotherm of **JLNU-104**.

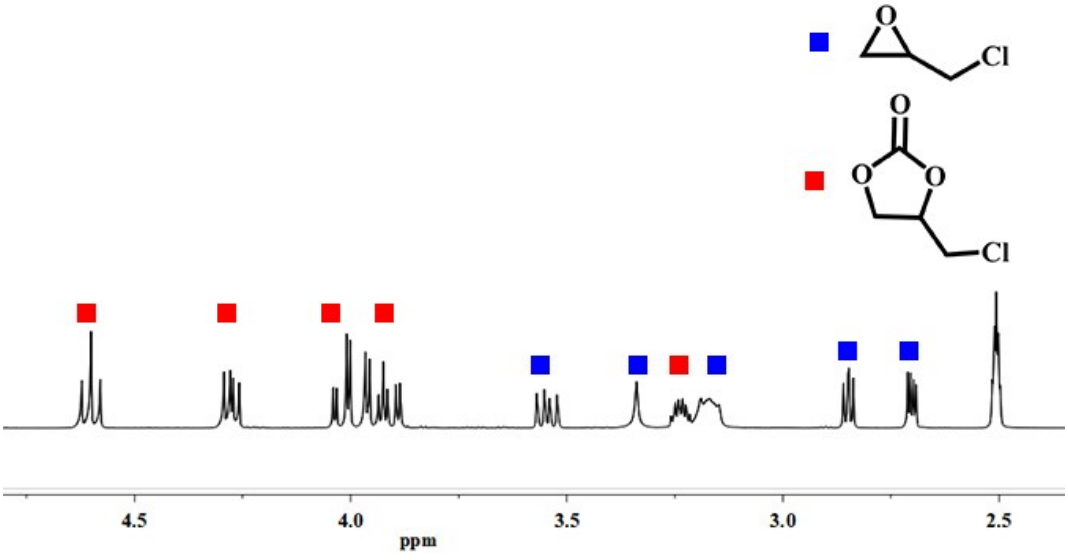

Fig. S4 ^{1}H NMR spectrum of cycloaddition reaction of epichlorohydrin with **JLNU-104**/TBAB

after 2 h.

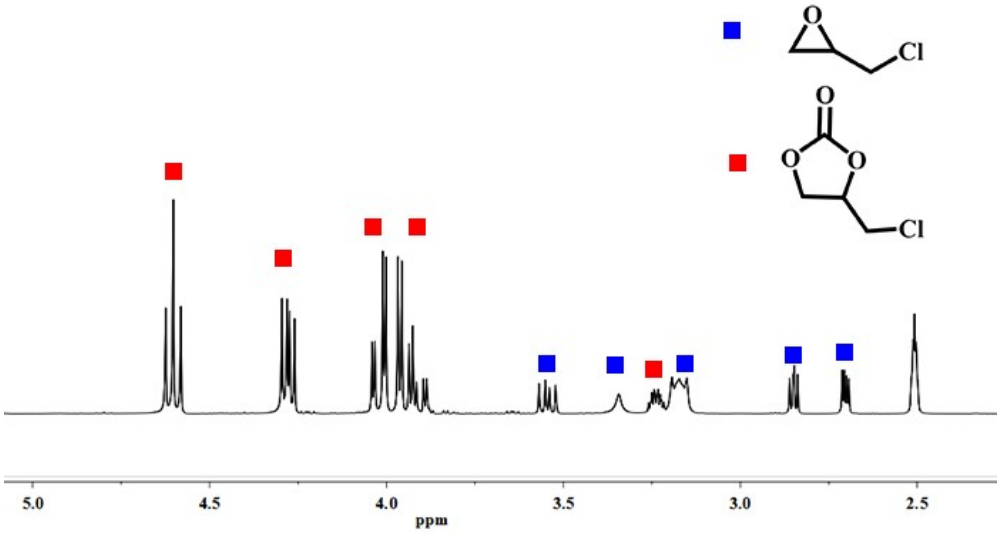

Fig. S5 ^{1}H NMR spectrum of cycloaddition reaction of epichlorohydrin with **JLNU-104**/TBAB after 4 h.

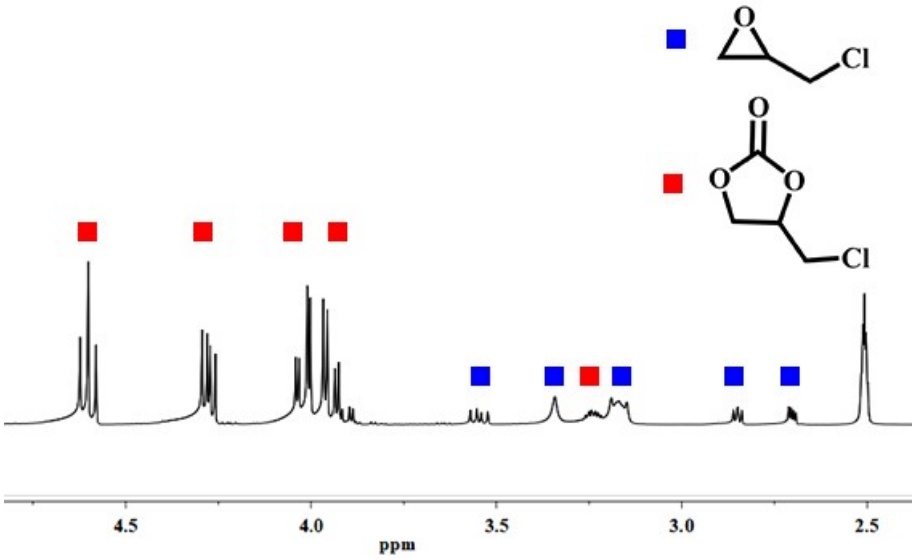

Fig. S6 ^{1}H NMR spectrum of cycloaddition reaction of epichlorohydrin with **JLNU-104**/TBAB after 6 h.

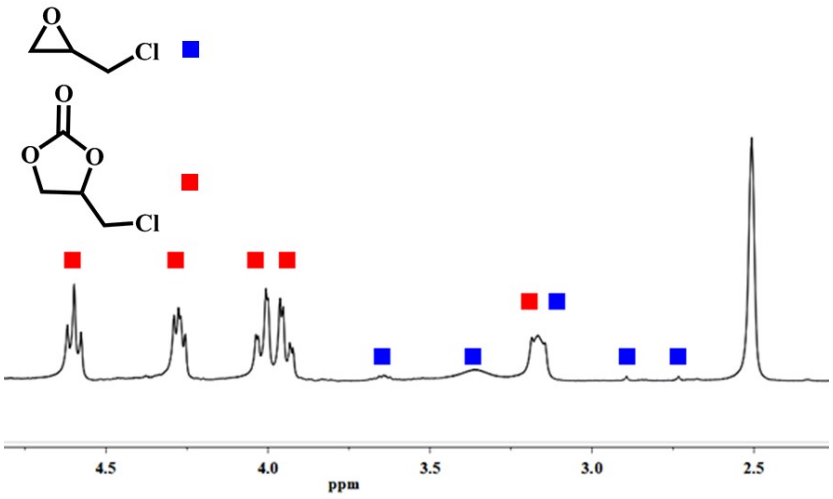

Fig. S7 ^{1}H NMR spectrum of cycloaddition reaction of epichlorohydrin with **JLNU-104**/TBAB after 8 h.

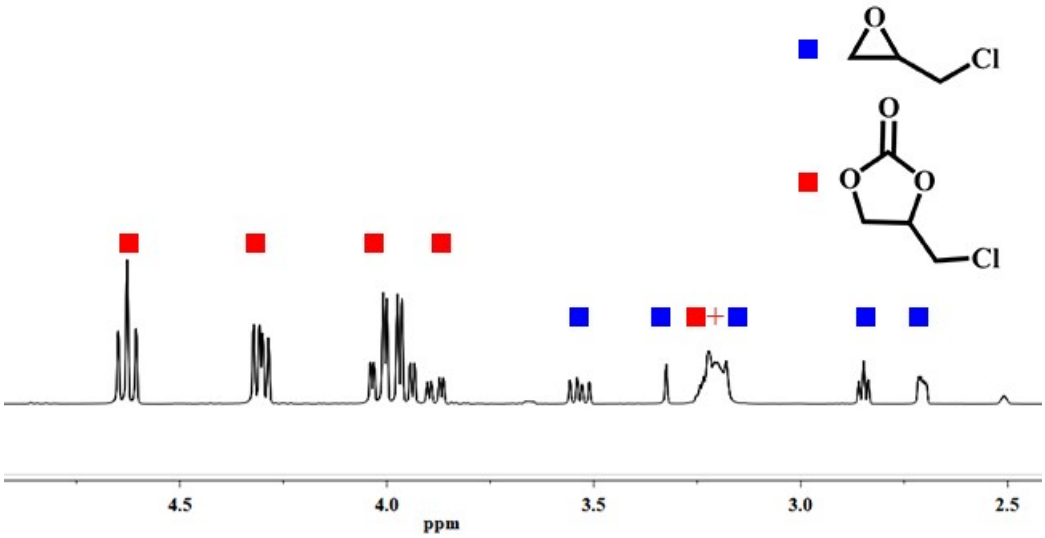

Fig. S8 ^{1}H NMR spectrum of cycloaddition reaction of epichlorohydrin with TBAB after 8 h.

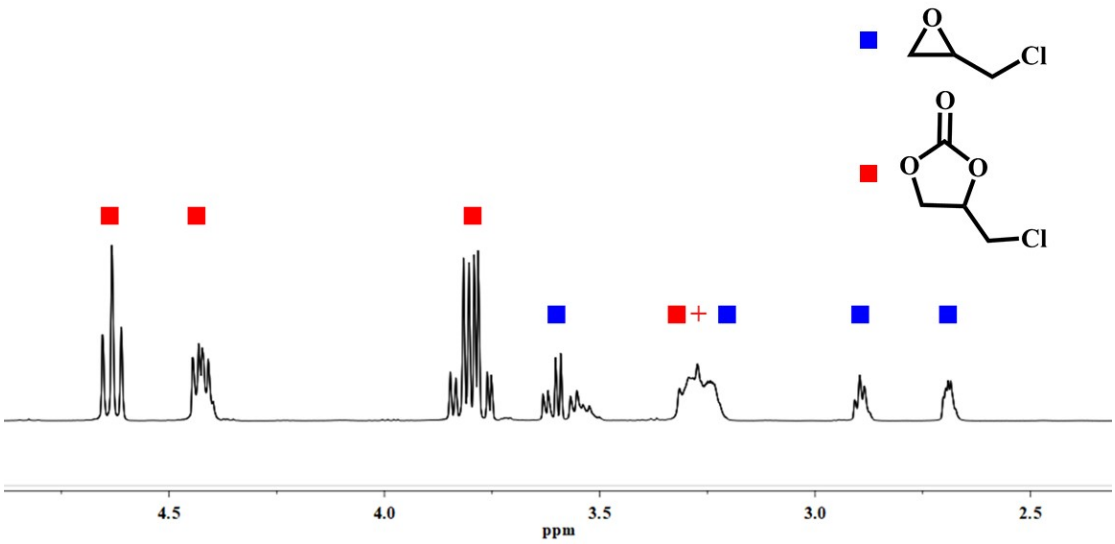

Fig. S9 ^{1}H NMR spectrum of cycloaddition reaction of epichlorohydrin with **JLNU-104** after 8 h.

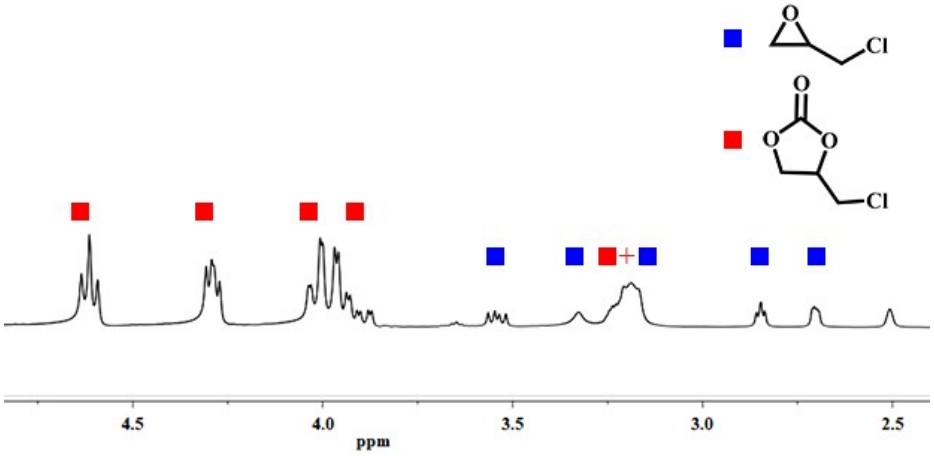

Fig. S10 ^{1}H NMR spectrum of cycloaddition reaction of epichlorohydrin with $MnCl_2$ after 8 h.

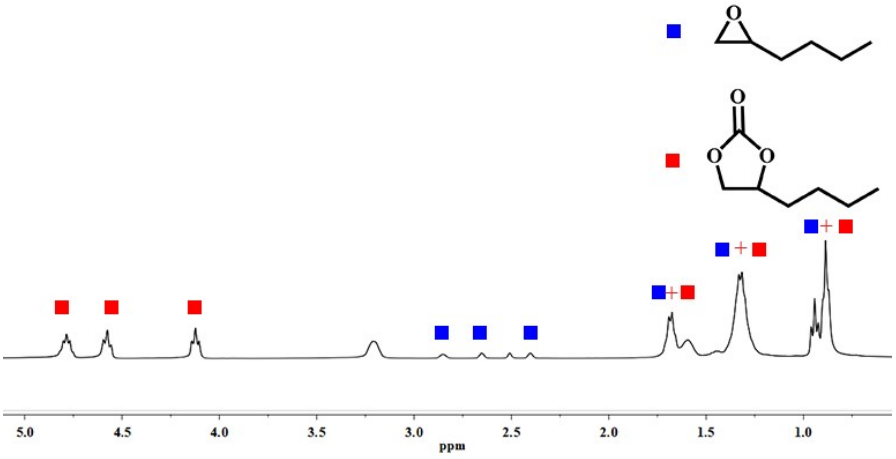

Fig. S11 ^{1}H NMR spectrum of cycloaddition reaction of 1,2-epoxyhexane with **JLNU-104**/TBAB.

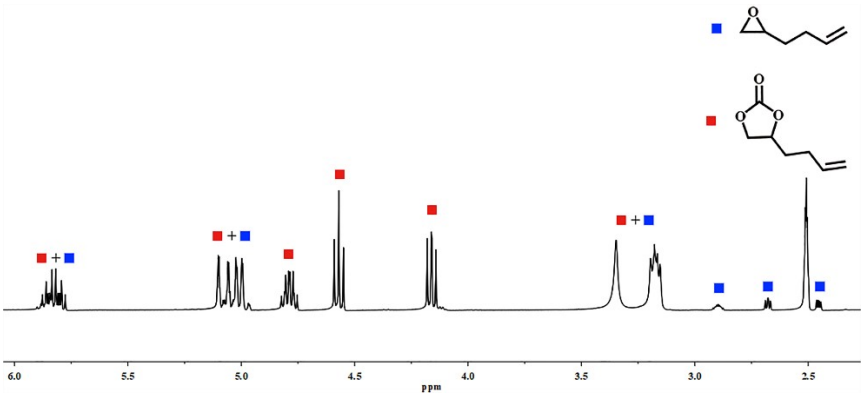

Fig. S12 ^{1}H NMR spectrum of cycloaddition reaction of 1,2-epoxy-5-hexene with **JLNU-104**/TBAB.

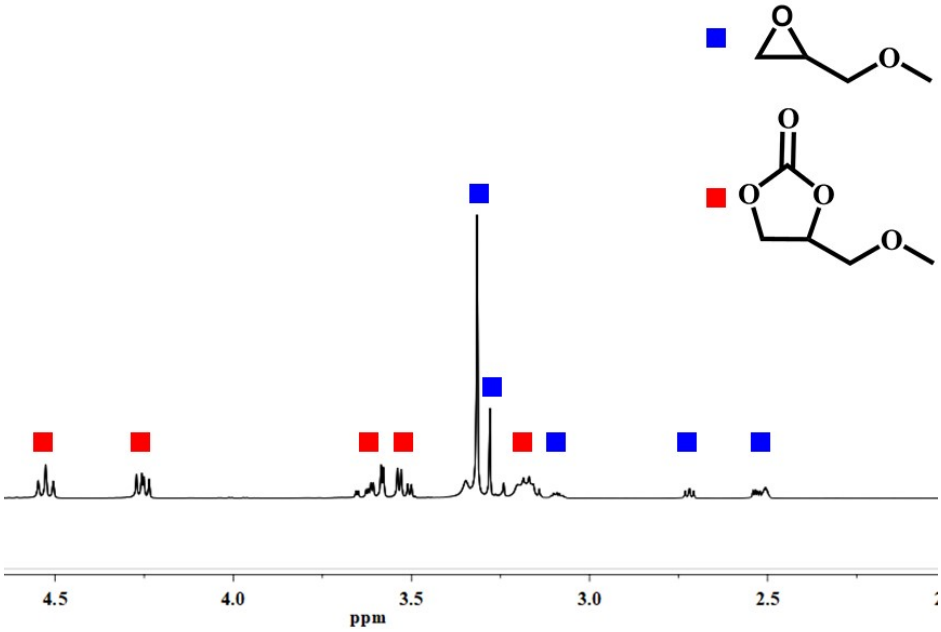

Fig. S13 ^{1}H NMR spectrum of cycloaddition reaction of glycidyl methyl ether with **JLNU-104**/TBAB.

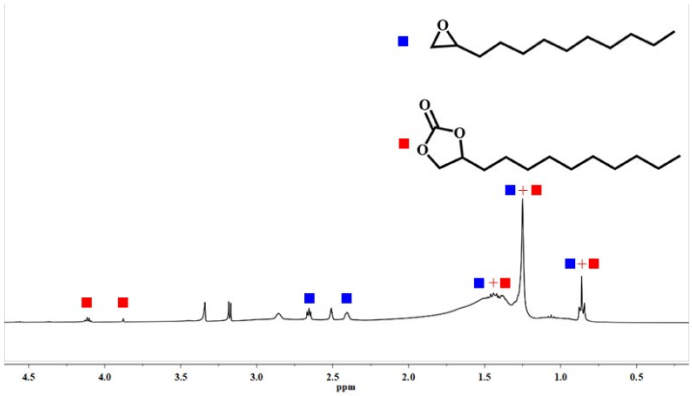

Fig. S14 ^{1}H NMR spectrum of cycloaddition reaction of 1,2-epoxydodecane ether with **JLNU-104**/TBAB.

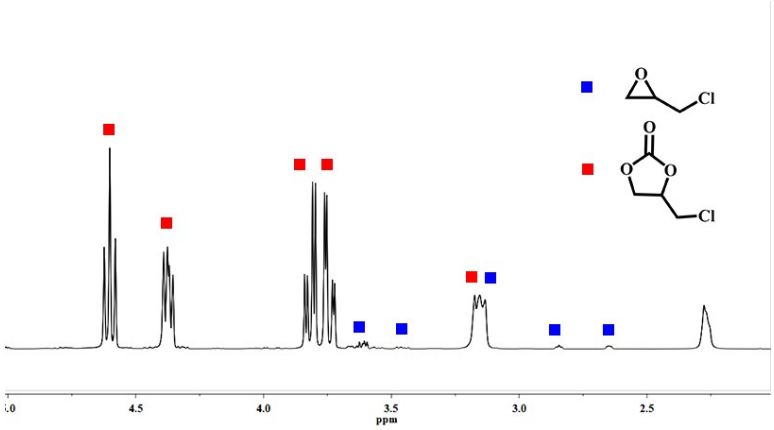

Fig. S15 ^{1}H NMR spectrum of cycloaddition reaction of epichlorohydrin ether with **JLNU-104**/TBAB after second cycle.

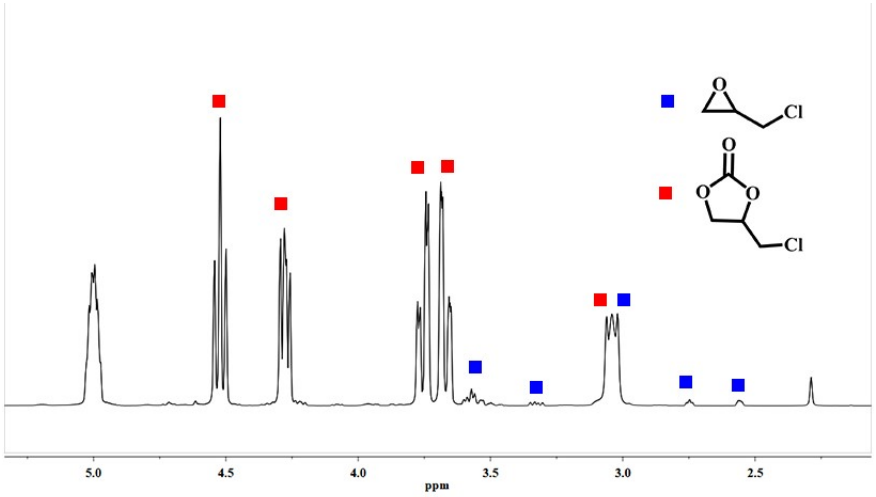

Fig. S16 ^{1}H NMR spectrum of cycloaddition reaction of epichlorohydrin ether with **JLNU-104**/TBAB after third cycle.

Table S1. Crystal data and structure refinements for **JLNU-104**.

Compound	**JLNU-104**
Formula	$C_{83}H_{76}Mn_3N_3O_{25.50}$
Mr	1688.28
Crystal system	Triclinic
Space group	*P*-1
a (Å)	10.269(7)
b (Å)	10.620(6)

c (Å)	18.045(12)
α (°)	100.310(12)
β (°)	95.681(12)
γ (°)	108.820(11)
V (Å^3)	1806(2)
Z	1
D_{calc} (g cm^{-3})	1.552
F(000)	775
R_{int}	0.1877
GOF on F^2	1.237
$R_1{}^a$ [I>2σ(I)]	0.1264
$wR_2{}^b$ (all data)	0.3393

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^bwR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma w(F_o^2)^2]\}^{1/2}$.

Table S2 Selected bond distances (Å) and angles (°) for **JLNU-104**.

Bond	Distance	Bond	Distance
Mn1-O5	2.307(7)	Mn1-O1$^{\#1}$	2.161(6)
Mn1-O1$^{\#4}$	2.161(7)	Mn1-O3$^{\#5}$	2.190(6)
Mn1-O3	2.190(6)	Mn1-O5$^{\#5}$	2.307(7)
Mn2-O3	2.438(7)	Mn2-O4	2.164(8)
Mn2-O6	2.096(8)	Mn2-O8$^{\#2}$	2.075(7)
Mn2-O7$^{\#3}$	2.142(8)	Mn2-O2$^{\#4}$	2.145(7)
Angle	(°)	Angle	(°)
O1$^{\#1}$-Mn1-O3	87.4(3)	O1$^{\#4}$-Mn1-O3	92.6(3)
O1$^{\#1}$-Mn1-O3$^{\#5}$	87.4(3)	O1$^{\#4}$-Mn1-O3$^{\#5}$	92.6(3)
O1$^{\#1}$-Mn1-O5	92.8(3)	O1$^{\#4}$-Mn1-O5	87.2(3)
O3-Mn1-O5	96.2(3)	O3$^{\#5}$-Mn1-O5	83.8(3)
O1$^{\#1}$-Mn1-O5	87.2(3)	O1$^{\#4}$-Mn1-O5$^{\#5}$	92.8(3)
O3-Mn1-O5$^{\#5}$	83.8(3)	O3$^{\#5}$-Mn1-O5$^{\#5}$	96.2(3)

O1$^{\#1}$-Mn1-O5$^{\#5}$	87.2(3)	O4-Mn2-O3	57.1(3)
O8$^{\#2}$-Mn2-O6	107.1(3)	O8$^{\#2}$-Mn2-O7$^{\#3}$	96.8(3)
O6-Mn2-O7$^{\#3}$	89.0(4)	O8$^{\#2}$-Mn2-O2$^{\#4}$	92.5(3)
O6-Mn2-O2$^{\#4}$	87.6(3)	O7$^{\#3}$-Mn2-O2$^{\#4}$	170.7(3)
O8$^{\#2}$-Mn2-O4	104.9(3)	O6-Mn2-O4	147.8(3)
O7$^{\#3}$-Mn2-O4	83.8(4)	O2$^{\#4}$-Mn2-O4	94.6(3)
O8$^{\#2}$-Mn2-O3	161.9(3)	O6-Mn2-O3	90.8(3)
O7$^{\#3}$-Mn2-O3	80.4(3)	O2$^{\#4}$-Mn2-O3	91.1(3)

#1 -x+1,-y,-z-1; #2 -x+2,-y+1,-z+1; #3 x,y,z-1; #4 x,y,z+1; #5 -x+1,-y,-z

Reference

[1] G. M. Sheldrick *SHELXS-2014*, *Program for the Solution of Crystal Structures* (University of Göttingen, Germany, 2014).

[2] G. M. Sheldrick *SHELXL-2014*, *Program for the Refinement of Crystal Structure* (University of Göttingen, Germany, 2014).