Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

An aluminum(III) picket fence phthalocyanine-based heterogeneous catalyst for ring-expansion carbonylation of epoxides

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Supporting Information

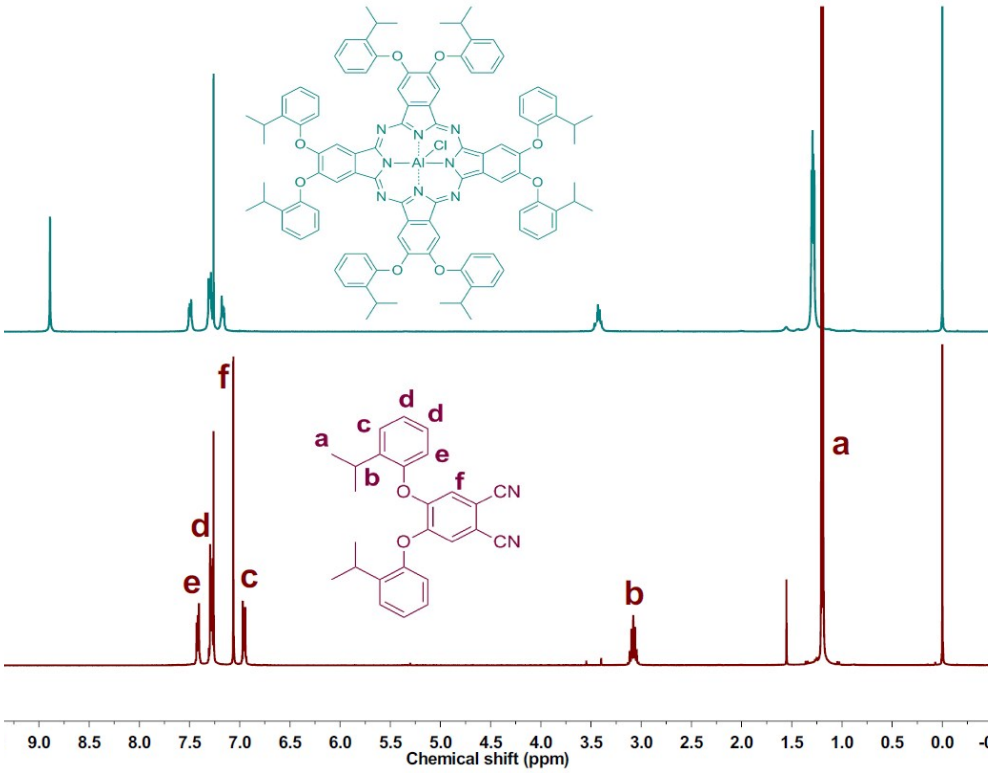
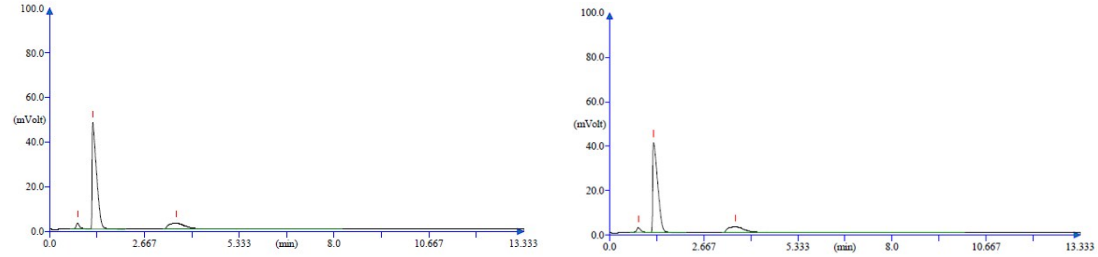


Fig. S1 ^{1}H NMR spectra of the ligand and AlPc'Cl monomer.



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Printed: 2018-05-09 09:13
Elemental Analyser method:
Sampler method:
Sample ID: JJ1 (# 50)
Analysis type: UnkNown
Chromatogram filename: Q049.dat
Calibration method: K Factors
Sample weight: 1.127
Protein factor: 6.25

Element Name		Ret.Time	Area	BC	Area ratio	K factor
Nitrogen	6.6211	47	167680	RS	24.536740	.202058E+07
Carbon	75.4500	73	4114309	RS	1.000000	.480874E+07
Hydrogen	5.9748	214	976235	RS	4.214465	.144163E+08
Totals	88.0459		5258223			

Operator ID: LEE HK
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Method name: NCHS
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Sampler method:
Sample ID: JJ2 (# 51)
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Chromatogram filename: Q050.dat
Calibration method: K Factors
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Protein factor: 6.25

Element Name		Ret.Time	Area	BC	Area ratio	K factor
Nitrogen	6.1183	49	163648	RS	24.267260	.202058E+07
Carbon	69.1305	75	3971288	RS	1.000000	.480874E+07
Hydrogen	5.6067	214	964932	RS	4.115616	.144163E+08
Totals	80.8556		5099868			

Fig. S2 Elemental analysis of the ligand (left) and AlPc'Cl monomer (right).

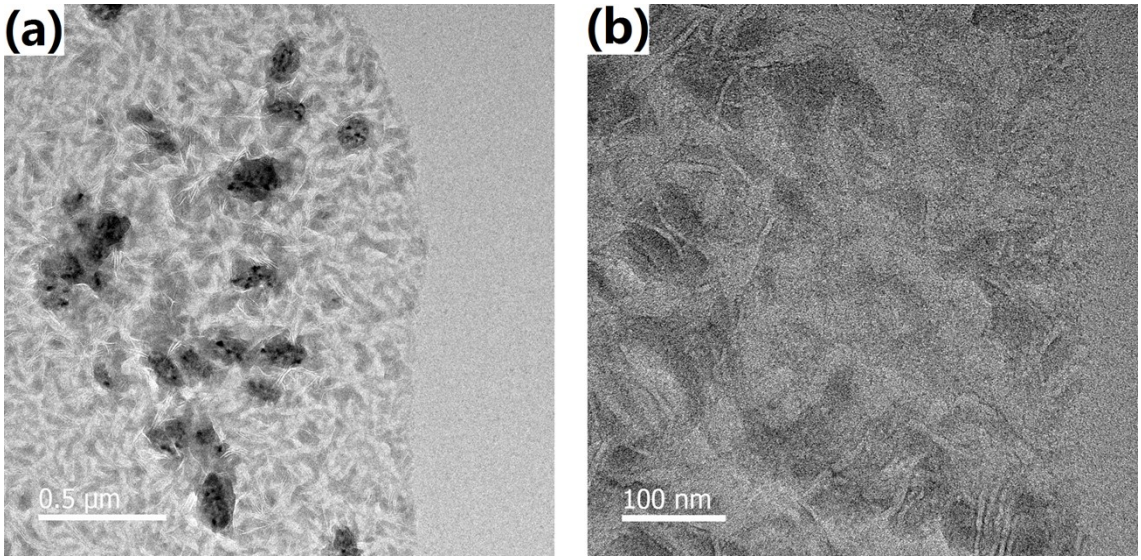
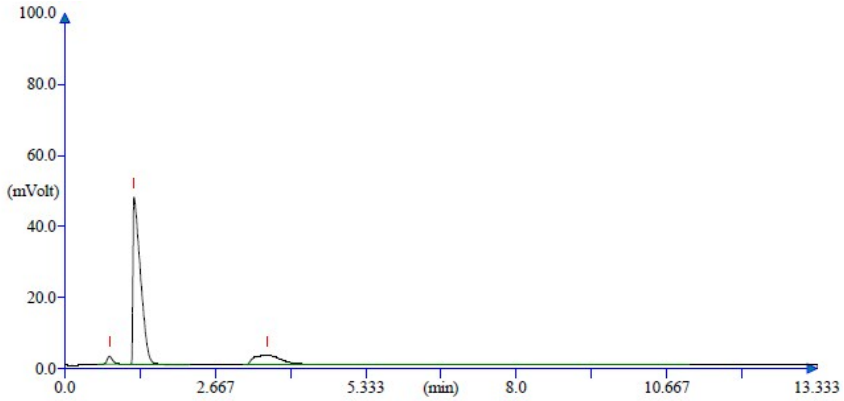


Fig. S3 TEM images of the network **2**.



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Sampler method:	
Sample ID:	JJ3 (# 52)
Analysis type:	UnkNown
Chromatogram filename:	Q051.dat
Calibration method:	K Factors
Sample weight:	1.343
Protein factor:	6.25

Element Name	Ret.Time	Area	BC	Area ratio	K factor
Nitrogen	5.3248	48	161400 RS	27.257450	.202058E+07
Carbon	67.7286	74	4399339 RS	1.000000	.480874E+07
Hydrogen	5.3120	215	1033964 RS	4.254828	.144163E+08
Totals	78.3654		5594703		

Fig. S4 Elemental analysis of the network **2**.

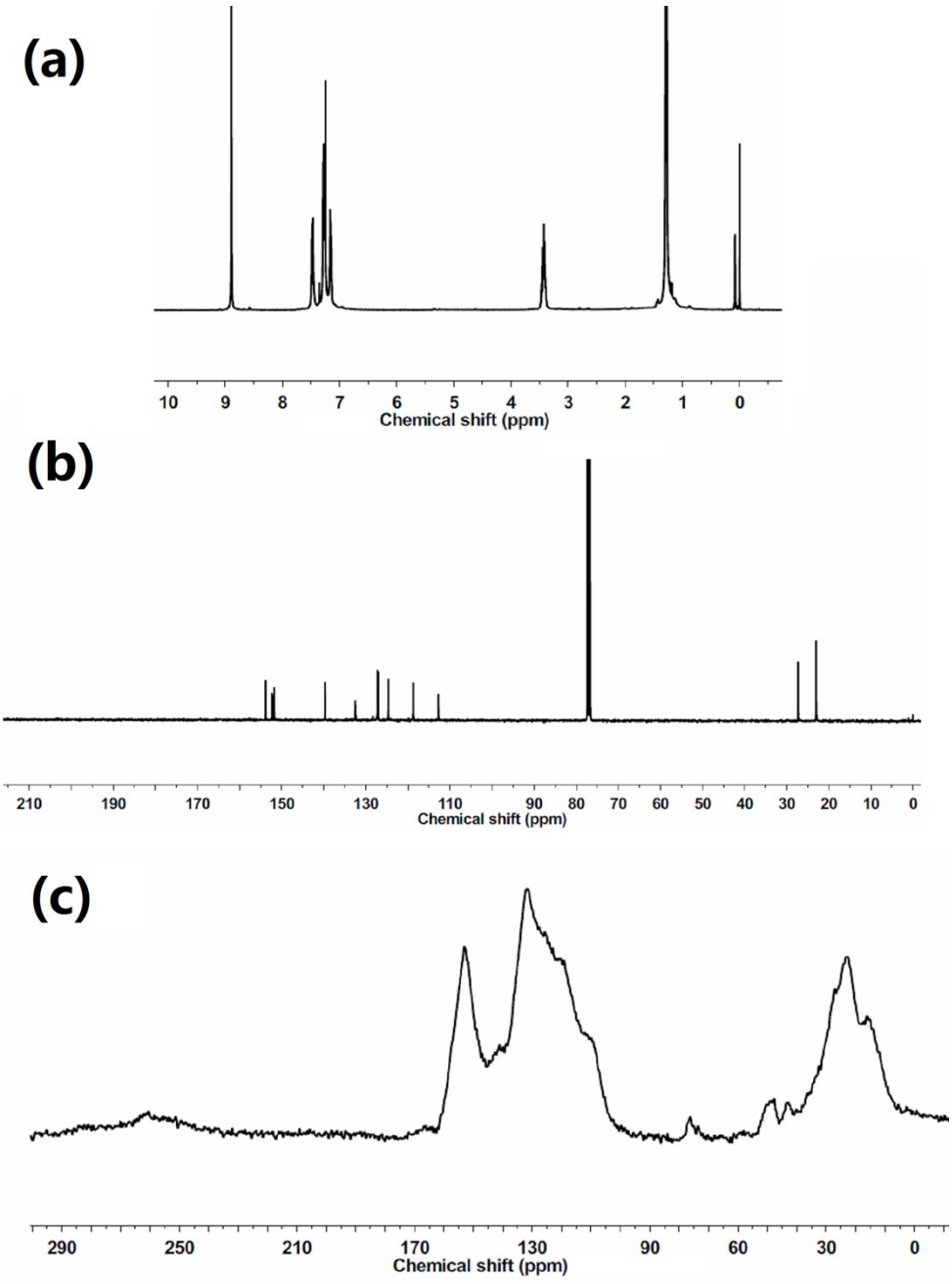


Fig. S5. ^{1}H NMR (a) and ^{13}C NMR (b) spectra of monomer **1**. The solid-state ^{13}C NMR of network **2** (c).

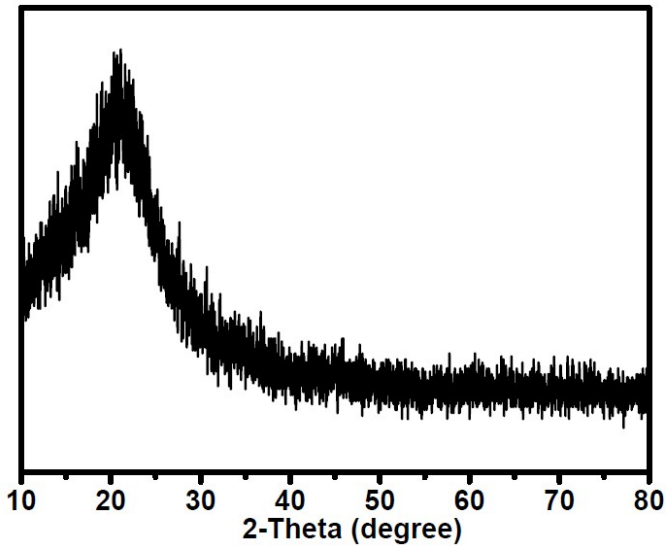
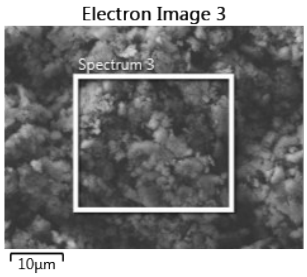
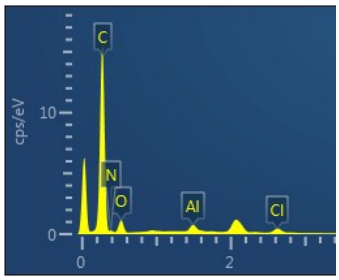


Fig. S6 XRD pattern of the network **2**.





Element	Wt%	Atom %
C	80.87	85.32
N	6.41	5.79
O	9.65	7.65
Al	1.29	0.61
Cl	1.78	0.64
Total	100.00	100.00

the atomic ratio of Al/N: $\frac{0.61}{5.79} = 0.1053$

Theoretically, the ratio of Al/N: 1/8 = 0.125

Therefore, the proportion of Al metalated Pc' ring in the networs:

$$\frac{0.1053}{0.125} \times 100\% = 84.2\%$$

Fig. S7 SEM and EDX of the network **2**.

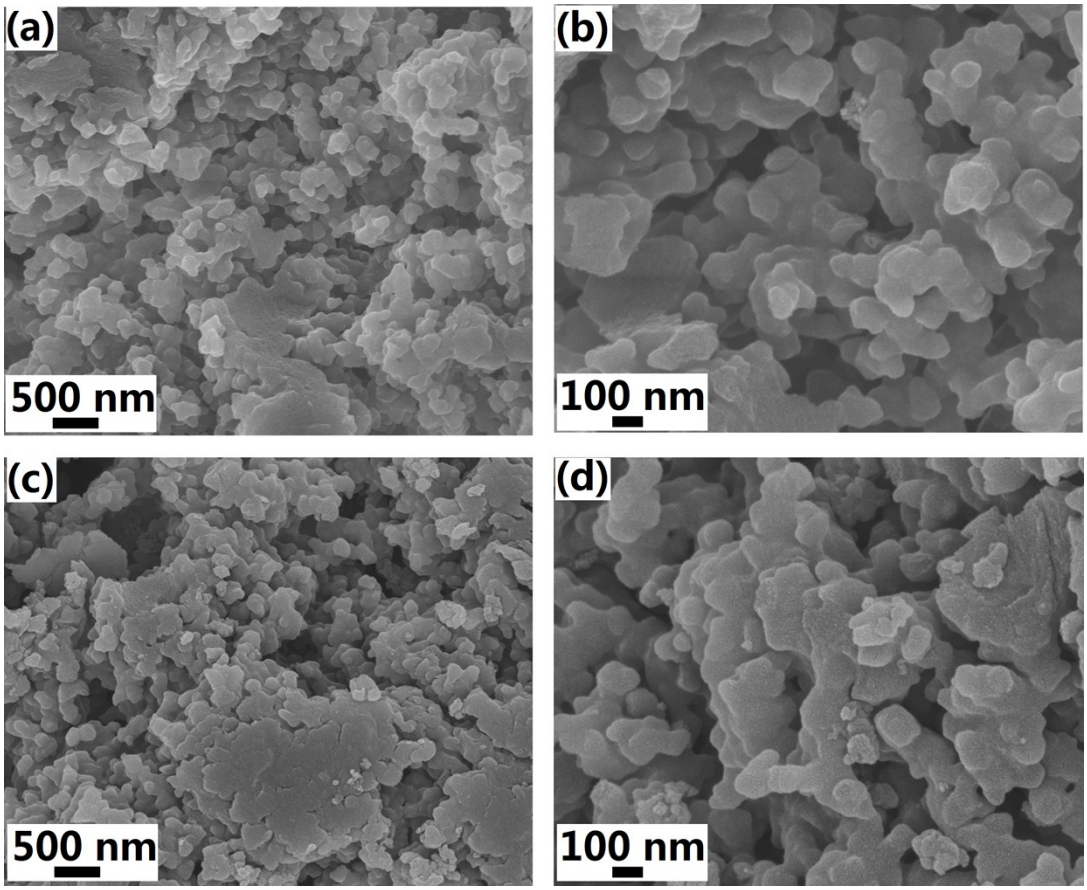


Fig. S8 SEM images of the network **2** (a, b) and catalyst **3** (c, d).

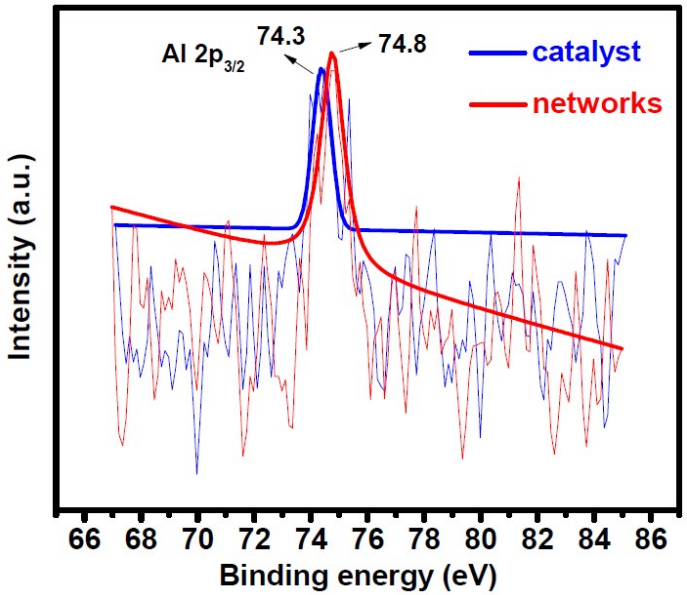
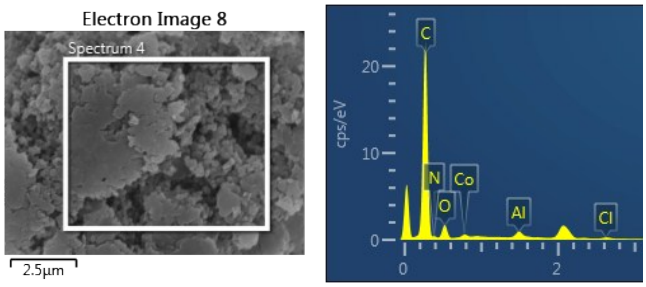


Fig. S9 Al ($2p_{3/2}$) electron binding energy of the network **2** and catalyst **3**.



Element	Wt%	Atom %
C	79.81	84.86
N	6.55	5.97
O	9.96	7.95
Al	1.18	0.56
Cl	0.55	0.20
K	0.40	0.13
Co	1.56	0.34
Total:	100.0	100.0

Fig. S10 SEM and EDX of catalyst **3**.

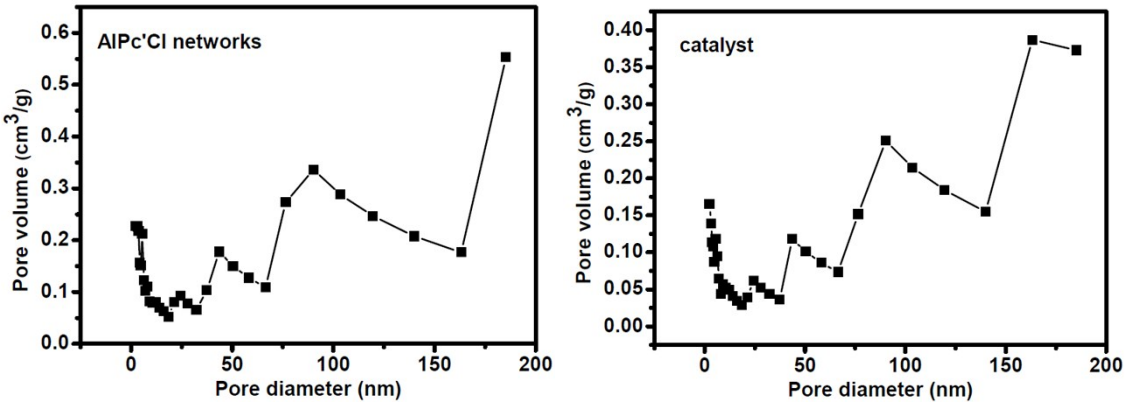


Fig. S11 BJH pore-size distribution for the network **2** and catalyst **3**.

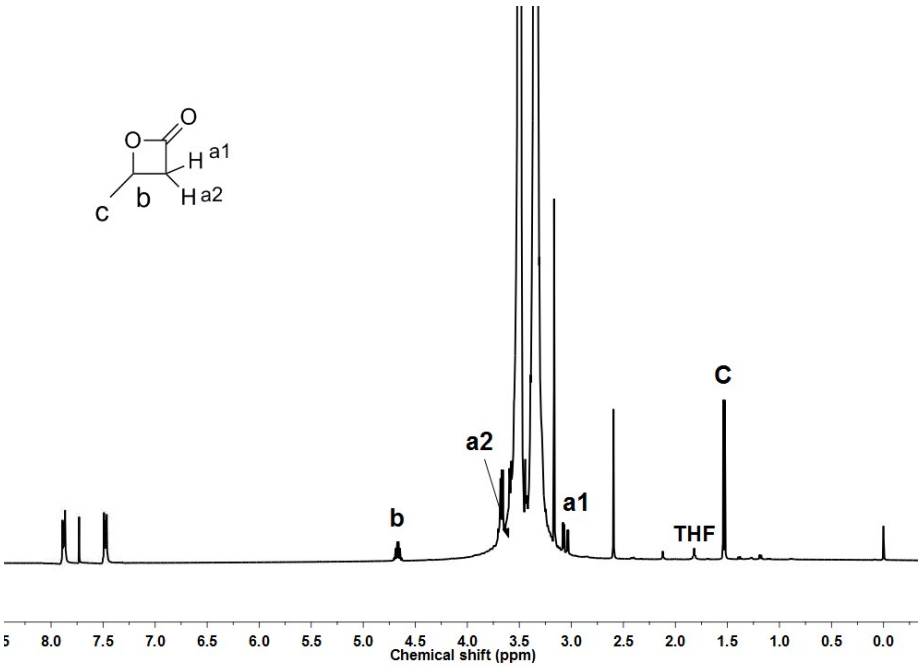


Fig. S12-1 ^{1}H NMR spectrum of the product from PO carbonylation in DME solvent using AlPc'-based heterogeneous catalyst **3**, 40 bar CO, 23 °C, 1 h (Table 1, entry 1).

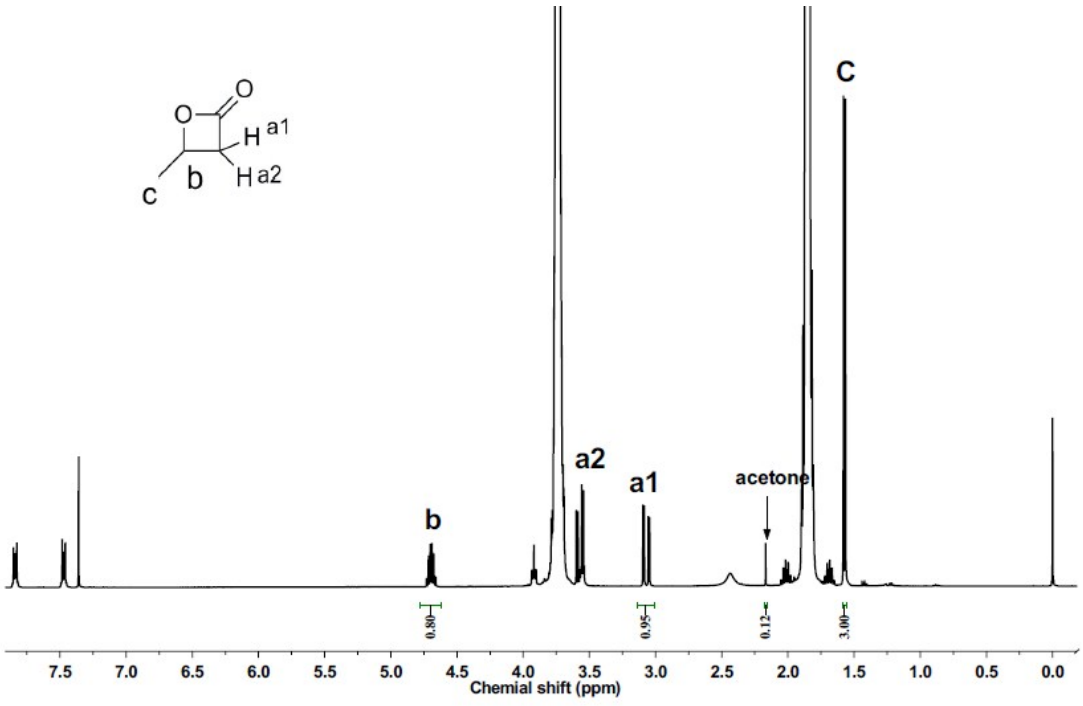


Fig. S12-2 ^{1}H NMR spectrum of the product from PO carbonylation using an *in situ* generated catalyst from AlPcCl and $Co_2(CO)_8$). (4 mol% AlPcCl, 6 mol% $Co_2(CO)_8$, 0.5 M PO in THF, 40 bar CO, 23 °C, 1 h).

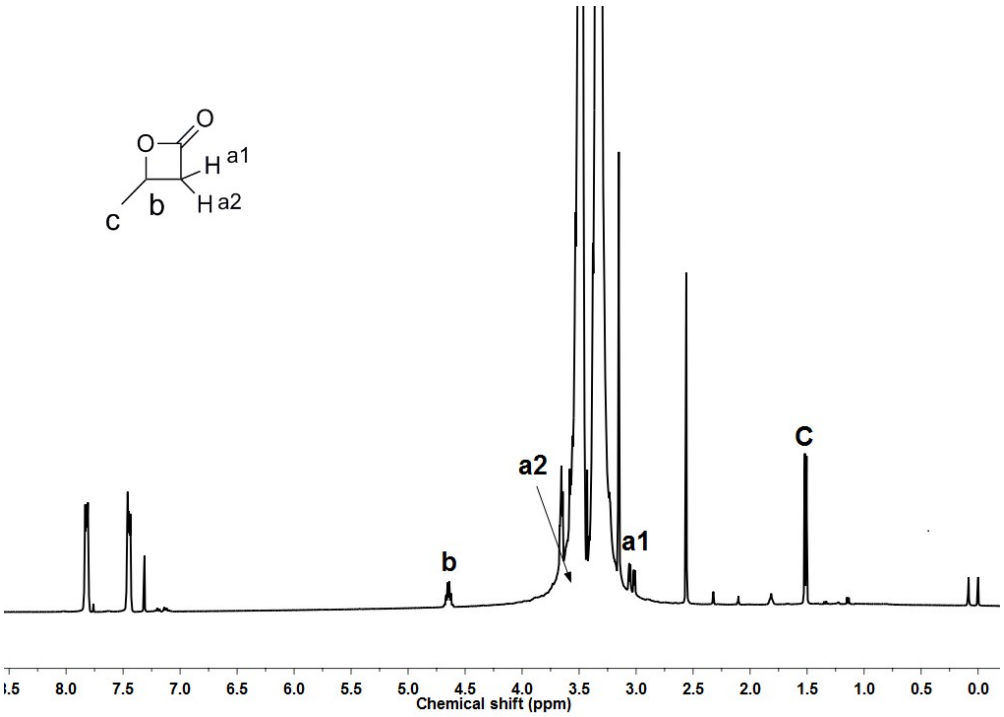


Fig. S13 ^{1}H NMR spectrum of the product from PO carbonylation in DME solvent using catalyst **3**, 10 bar CO, 23 °C, 1 h (Table 1, entry 2).

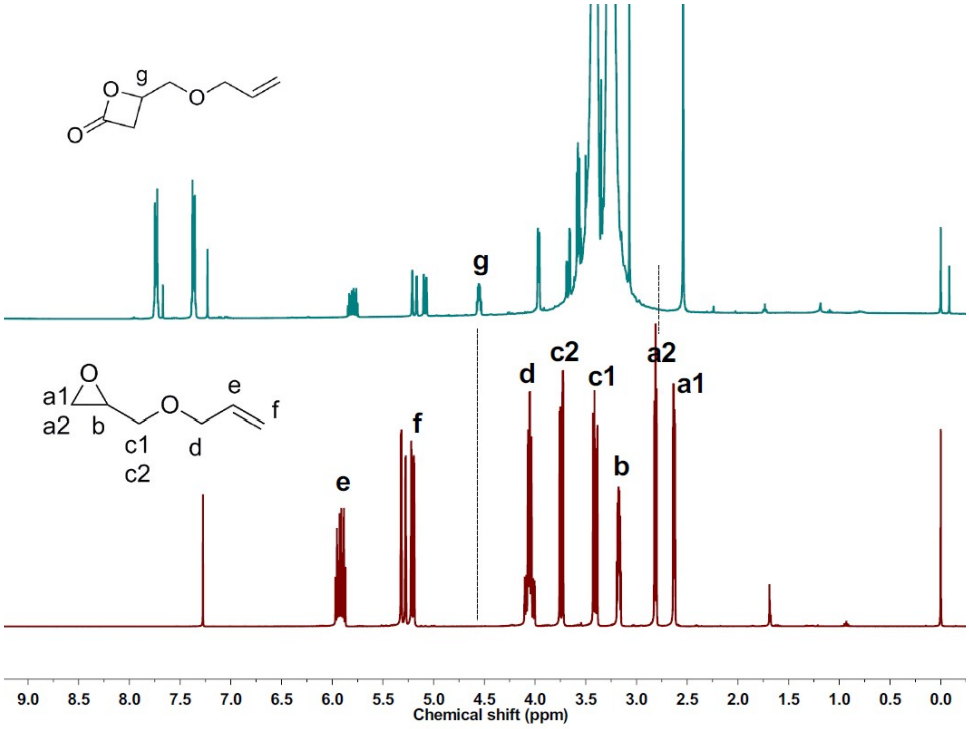


Fig. S14 ^{1}H NMR spectrum of the product from allyl glycidyl ether carbonylation (Table 1, entry 3).

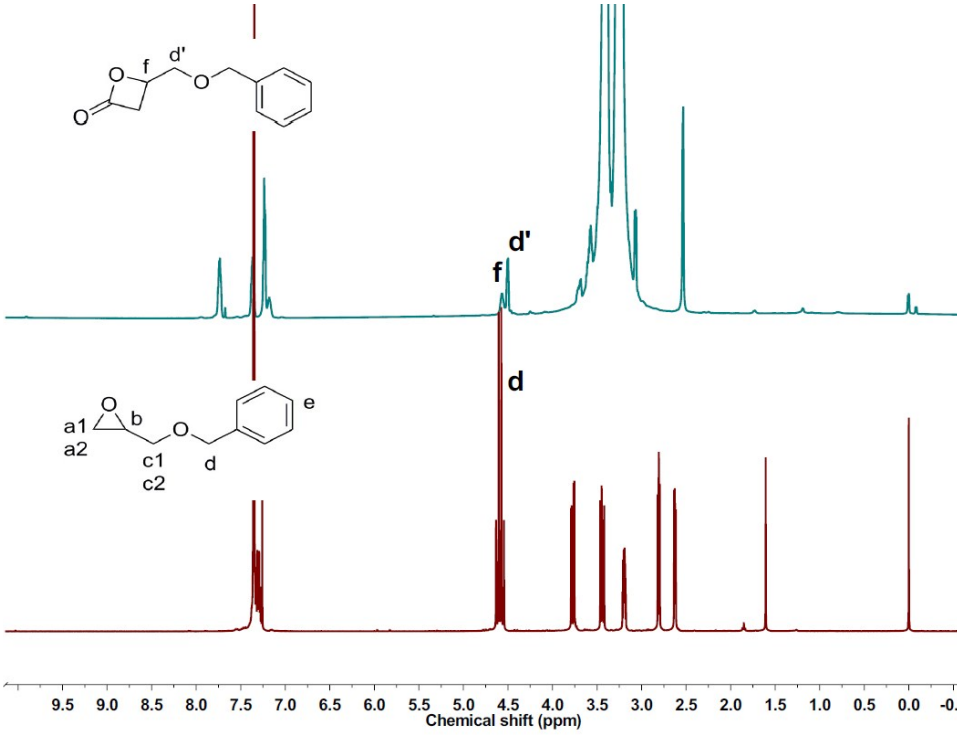


Fig. S15 ^{1}H NMR spectrum of the product from benzyl glycidyl ether carbonylation (Table 1, entry 4).

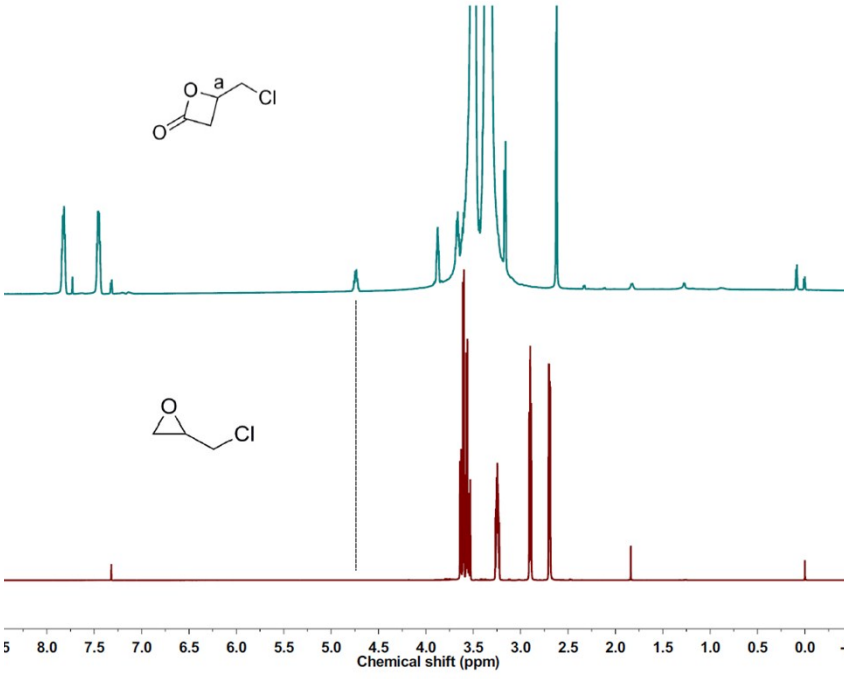


Fig. S16 ^{1}H NMR spectrum of the product from epichlorohydrin carbonylation (Table 1, entry 5).

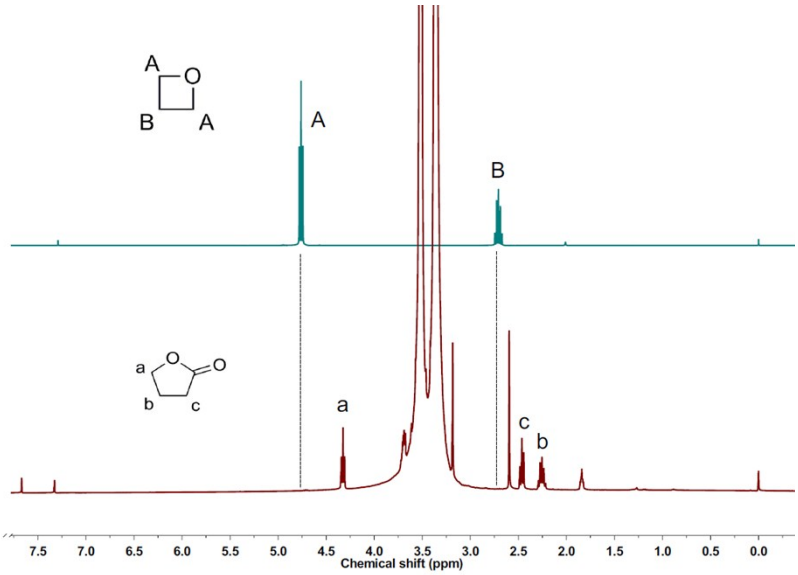


Fig. S17 [1]H NMR spectrum of the product from oxetane carbonylation in DME (Table 1, entry 6).

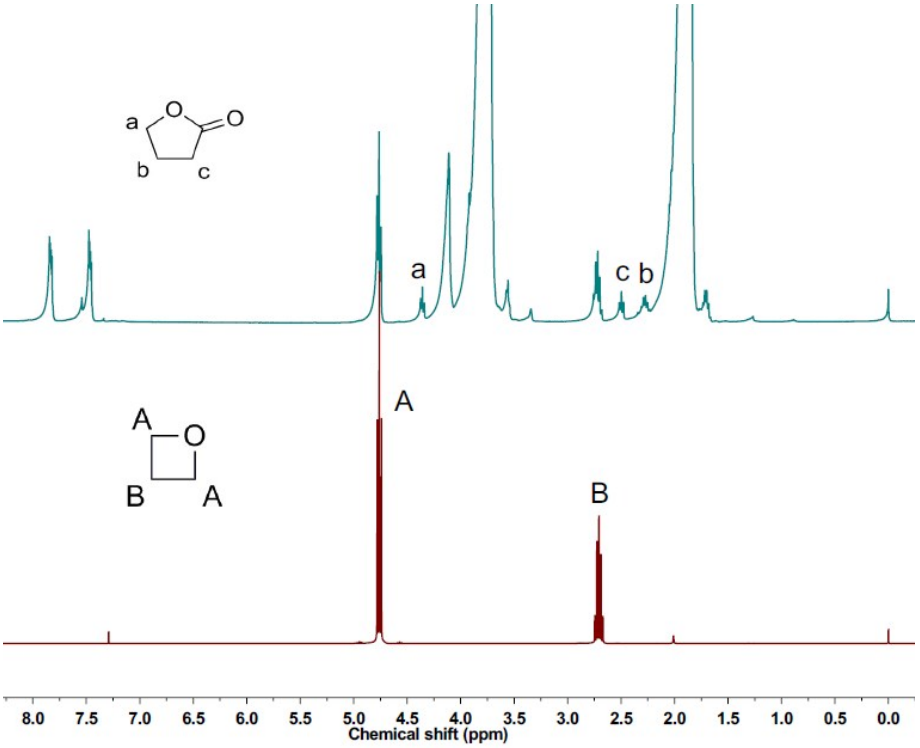


Fig. S18 [1]H NMR spectrum of the product from oxetane carbonylation in THF (Table 1-6).

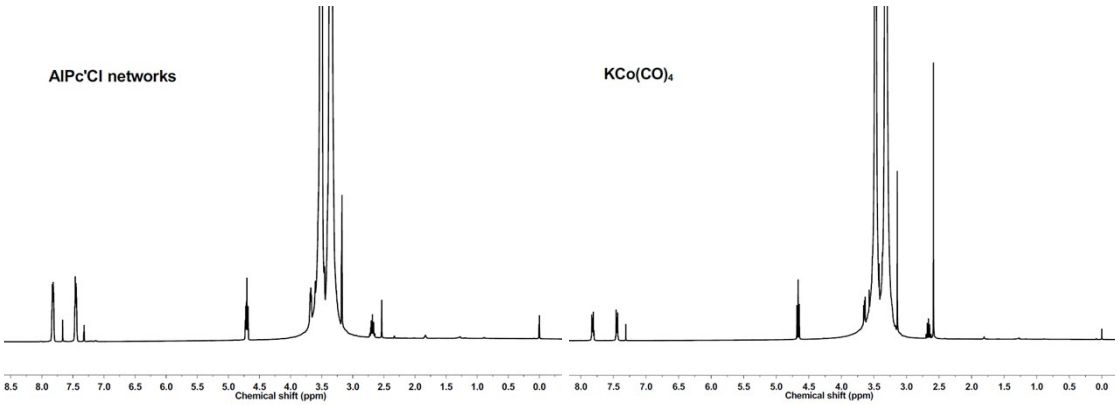


Fig. S19 ^{1}H NMR spectrum of the product from oxetane carbonylation using the network **2** or $KCo(CO)_4$ alone.

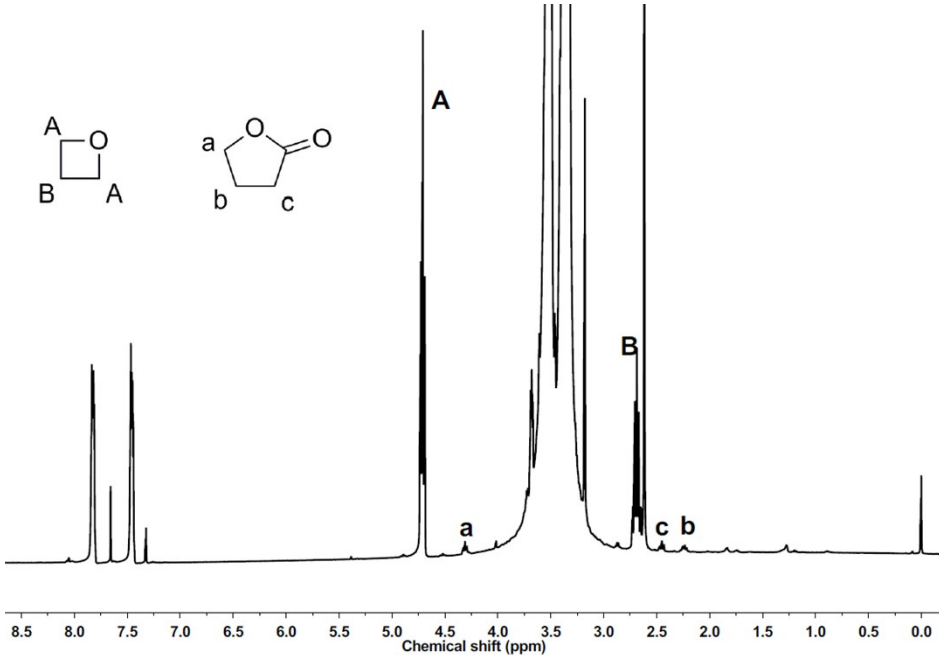


Fig. S20 ^{1}H NMR spectrum of the product from oxetane carbonylation using an equimolar mixture of the network **2** and $KCo(CO)_4$.

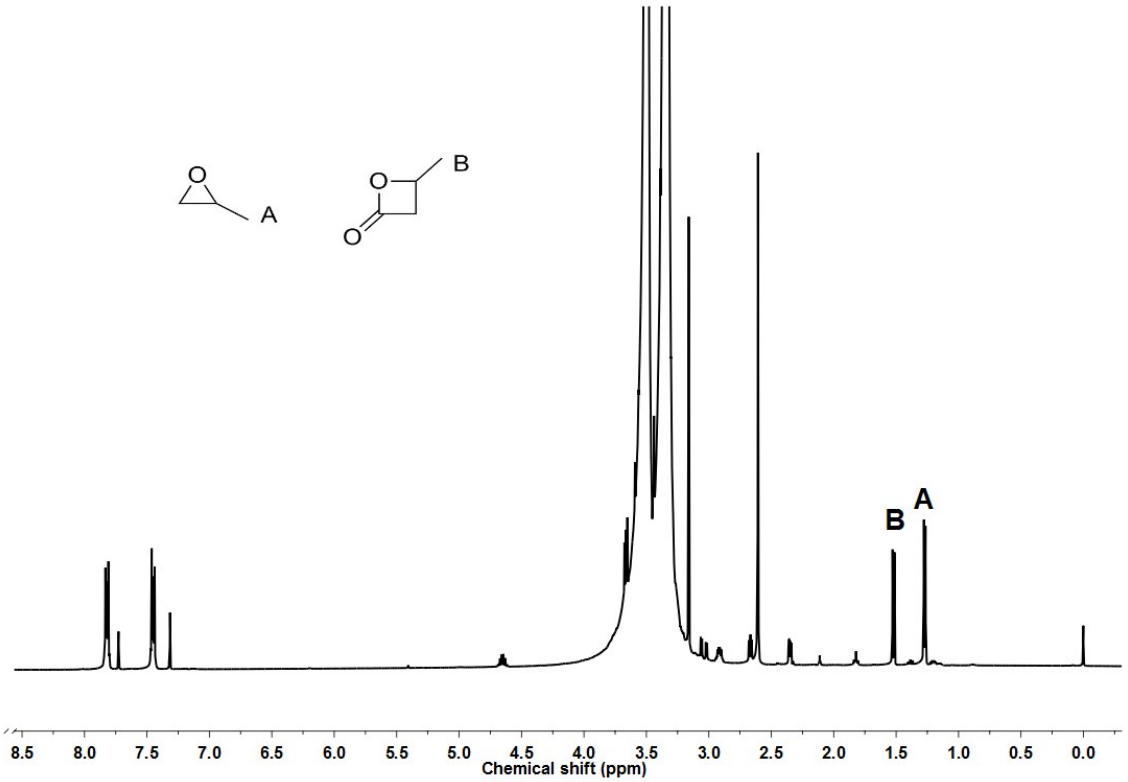


Fig. S21 ^{1}H NMR spectrum of the product from filteration test.

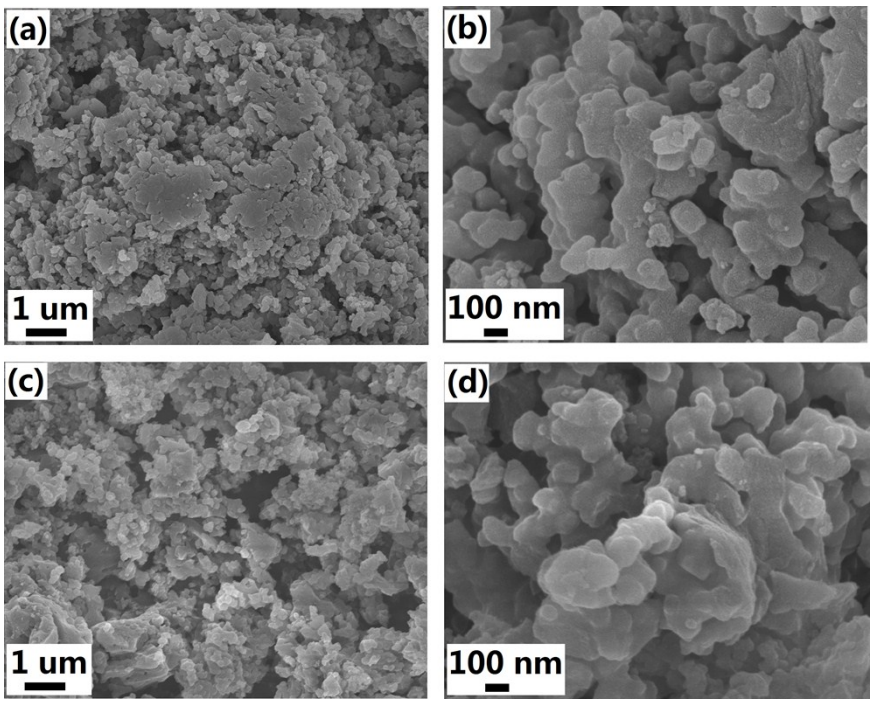


Fig. S22 SEM images of catalyst **3** before (a, b) and after (c, d) 3 catalytic cycles.

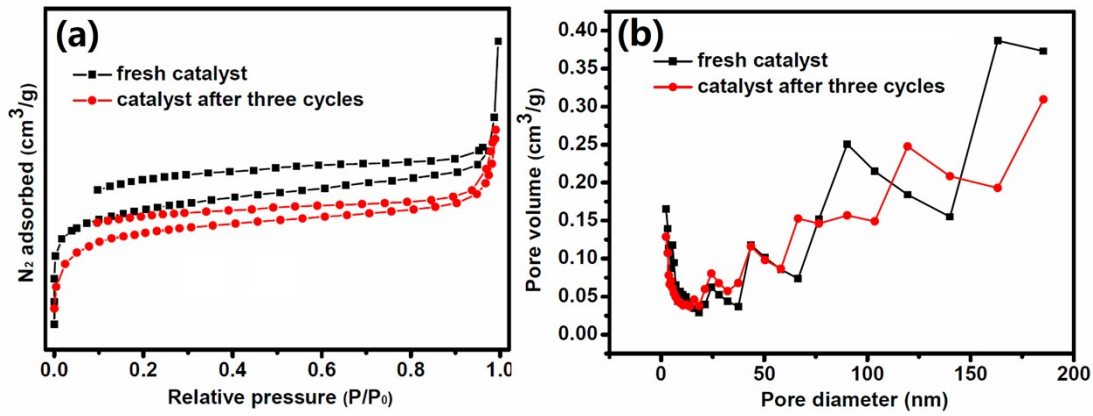


Fig. S23 The BET surface areas (a) of catalyst before and after three catalytic cycles, with corresponding BJH pore-size distributions (b).