

Supporting Information

A Covalent Triazine Framework-based Heterogenized Al–Co Bimetallic Catalyst for the Ring-expansion Carbonylation of Epoxide to β -lactone

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General consideration and physical measurements

All manipulations of air and water-sensitive compounds were carried out using glovebox under an argon atmosphere. Tetrahydrofuran (THF) and 1,2-Dimethoxyethane (DME) was refluxed over a sodium, benzoquinone and distilled under N₂ atmosphere. Pentane was purchased from Sigma-Aldrich, used as received. Propylene oxide was stirred over CaH₂ and distilled under N₂ atmosphere. Research-grade carbon monoxide was purchased from Sinyang Gas Company with 99.99% purity used as received. Co₂(CO)₈ was purchased from aldrich and anhydrous Al(OTf)₃ were purchased from Alfa-aesar. 3,5-Di-*tert*-butylsalicylaldehyde was purchased from TCI chemicals. KCo(CO)₄, [(salph)Al(THF)₂]⁺[Co(CO)₄]⁻ were synthesized as previously reported.^{S1} All new compounds were fully characterized by standard spectroscopic techniques. NMR spectra were recorded using a Bruker advance IV (¹H NMR, 400 MHz) at 298 K and chemical shifts were referenced to TMS Peak. IR spectra were collected on a Nicolet iS 50 (Thermo Fisher Scientific) spectrometer. All carbonylation reactions were performed in a 100-mL stainless steel reactor and fitted with a pressure gauge and pressure release valve. Scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) were measured on a JEOL LTD (JAPAN) JEM-7610F operated at an accelerating voltage of 15.0 kV. Complex both **1** and **2** dried under vacuum for 24 h, N₂ adsorption-desorption isotherms were measured at 77 K using an automated gas sorption system (Belsorp II mini, BEL japan, Inc.). Aluminum and cobalt content in complex **3** was determined by ICP-OES (iCAP-Q, Thermo Fisher Scientific) using microwave assisted acid system (MARS6, CEM/U.S.A). X-ray photoelectron Spectroscopy (XPS) analysis was performed on ESCA 2000 (VG microtech) at a pressure of $\sim 3 \times 10^{-9}$ mbar using Al Ka as the excitation source

($h\nu=1486.6$ eV) with concentric hemispherical analyzer. All carbonylation reactions were set up and run in a well-ventilated fume hood equipped with a carbon monoxide detector (see MSDS for proper handling of CO). PO conversion, β -lactone and acetone were quantified using naphthalene as an internal standard.

Synthesis of bpy-CTF^{S2}(1)

Compound 5,5'-dicyano-2,2'-bipyridine (0.10 g, 0.04 mmol) and zinc chloride (0.33 g, 2.4 mmol) were taken in a 1 mL ampoule (10 nos) under Ar atmosphere. The ampoule was sealed under vacuum and heated to 400 °C in a furnace with a heating rate of 60 °C h⁻¹. After 48 h, the furnace was cooled to room temperature. The crude product was ground well and stirred with 250 mL of water for 3 h. The black solid was filtered and washed with water and acetone. The resulting black solid was refluxed overnight in 1 M HCl (250 mL), filtered and washed with 1 M HCl (3x100 mL), H₂O (3x100 mL), THF (3x100 mL) and acetone (3x100 mL), respectively. The resulting solid was dried under vacuum at 200 °C for 16 h. Total yield=0.9 g, (90%) It was confirmed by FTIR spectroscopy (Figure S1).

Synthesis of [bpy-CTF-Al(OTf)₃] [Aluminum tris(trifluoromethanesulfonate)] (2)

The solution mixture of bpy-CTF (0.26 g) and Al(OTf)₃ (1.27 g, 2.67 mmol) in methanol (25 mL) was added to a hydrothermal reactor and was heated to 100 °C. After 24 h, the reactor was cooled to room temperature and the black precipitate was filtered and washed with methanol (3x15 mL). The obtained solid was dried under vacuum for 8 h. Yield= 0.28 g, (33%).

Synthesis of potassium cobalt tetracarbonyl KCo(CO)₄

To a solution of Co₂(CO)₈ (1.031 g, 3.015 mmol) in 15 mL THF excess KOH (0.506 g, 9.036 mmol) was added (two batch) and the resulting brown solution was stirred at room temperature for 4 h. The resulting pale yellow solution was filtered and the solvent was removed under vacuum to obtain a yellowish white precipitate. Total yield=1.25 g, (99%)

Synthesis of [bpy-CTF-Al(OTf)₂] [Co(CO)₄] [Aluminum tris(trifluoromethanesulfonate)](3)

A solution of [bpy-CTF-Al(OTf)₃] (0.28 g) and KCo(CO)₄ (1.34 g, 6.38 mmol) in methanol (5 mL) was stirred at room temperature. During reaction with methanol, the yellowish white color of the KCo(CO)₄ solution changed to red and then yellowish again, represent the exogenous

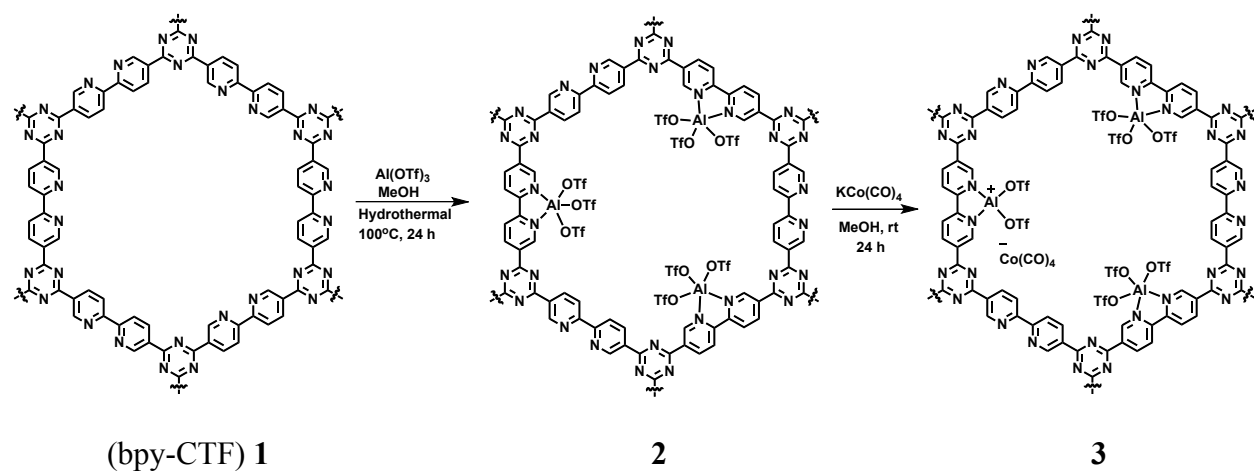
exchange of anion. After 24 h, the black precipitate was filtered and washed with methanol (3x10 mL) and dried completely. Yield= 0.29 g, (99%). IR=1870 cm⁻¹.

General procedure for epoxide-ring expansion carbonylation:

In a glove box, a stainless steel 100 mL tube reactor was equipped with a magnetic stir bar and charged with (0.033 g, 0.015 mmol of cobalt) [bpy-CTF-Al(OTf)₂][Co(CO)₄] (**3**) catalyst and PO (0.027g, 0.465 mmol) in 2.5 mL of dry DME. The reactor was sealed and purged with 0.5 MPa of CO (twice) and then pressurized to the desired CO pressure and performed carbonylation at the targeted temperature and time. After the allowed reaction time, the reactor was cooled to room temperature with CO gas carefully vent inside a fume hood. The crude samples were filtered through celite, weighed and analyzed using ¹H-NMR spectroscopy in CDCl₃ with naphthalene as an internal standard.

Procedure for regeneration of catalyst 3.

After the third run the catalyst **3** was filtered and washed with 5 mL of DME, dried for 6 h under vacuum. The catalyst **3** (0.029 g) was stirred with a freshly prepared yellowish KCo(CO)₄ (1.02 g, 4.86 mmol) in methanol (5 mL). After 24 h, black precipitates was washed with methanol (2x5 mL) and dried for 8 h. (Yield = 0.031 g)



Scheme S1: Systematic synthesis of complex **3** [structure was drawn based on the ICP-OES value]

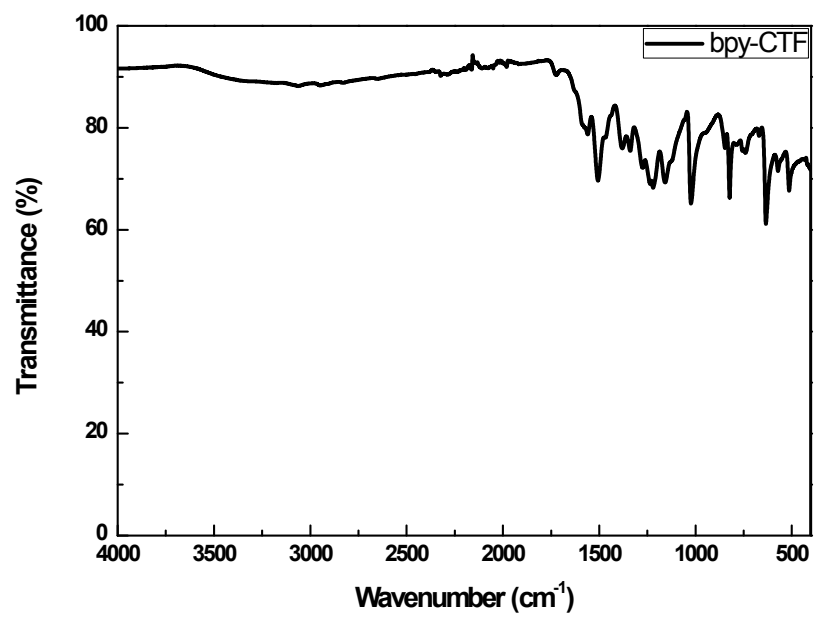


Figure S1: FT-IR spectra of bpy-CTF (**1**).

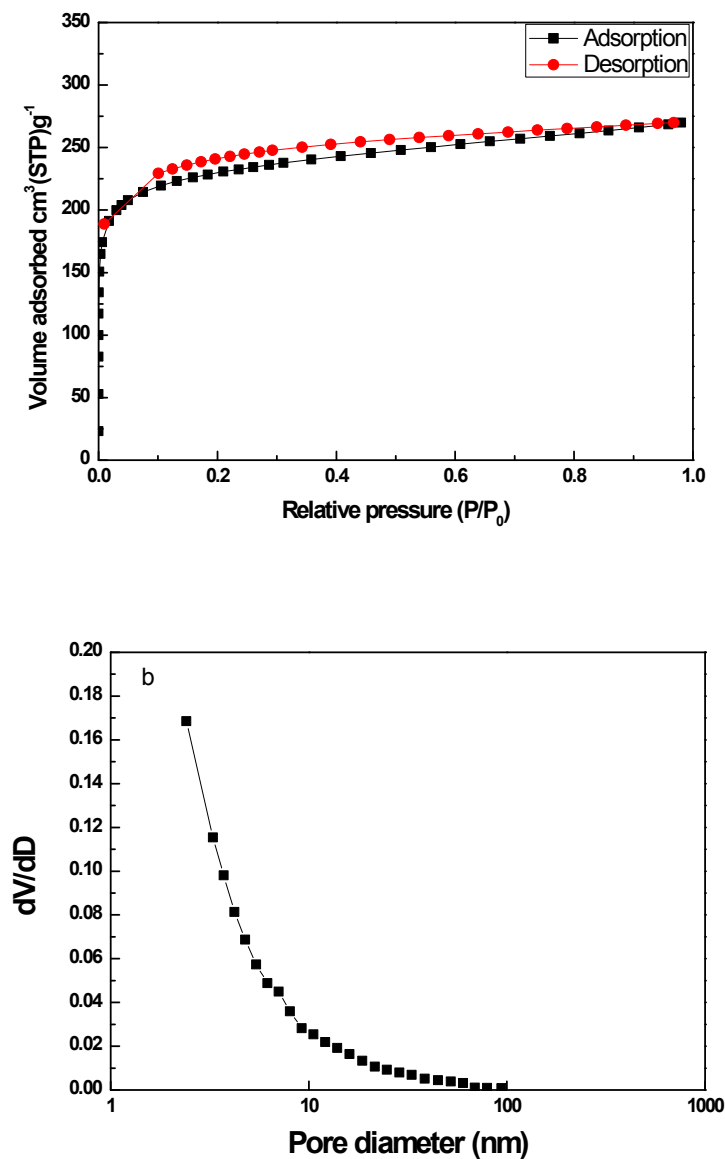


Figure S2. (a) Nitrogen adsorption and desorption isotherms of **bpy-CTF** and (b) pore size of the sample was *ca.* 2 nm, implying that sample **bpy-CTF** has microporous structure.

Table S1. BET physisorption data of **1** and **3**.

Entry	Catalyst	Pore surface (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore size (nm)
1	1	684	0.40	2.36
2	3	203	0.14	2.26

Element	Weight%	
C K	54.07	
N K	24.39	
O K	12.27	
F K	7.59	
Al K	0.54	
S K	1.14	
Totals	100.00	

Table S2. EDS analysis of [bpy-CTF-Al(OTf)₃]

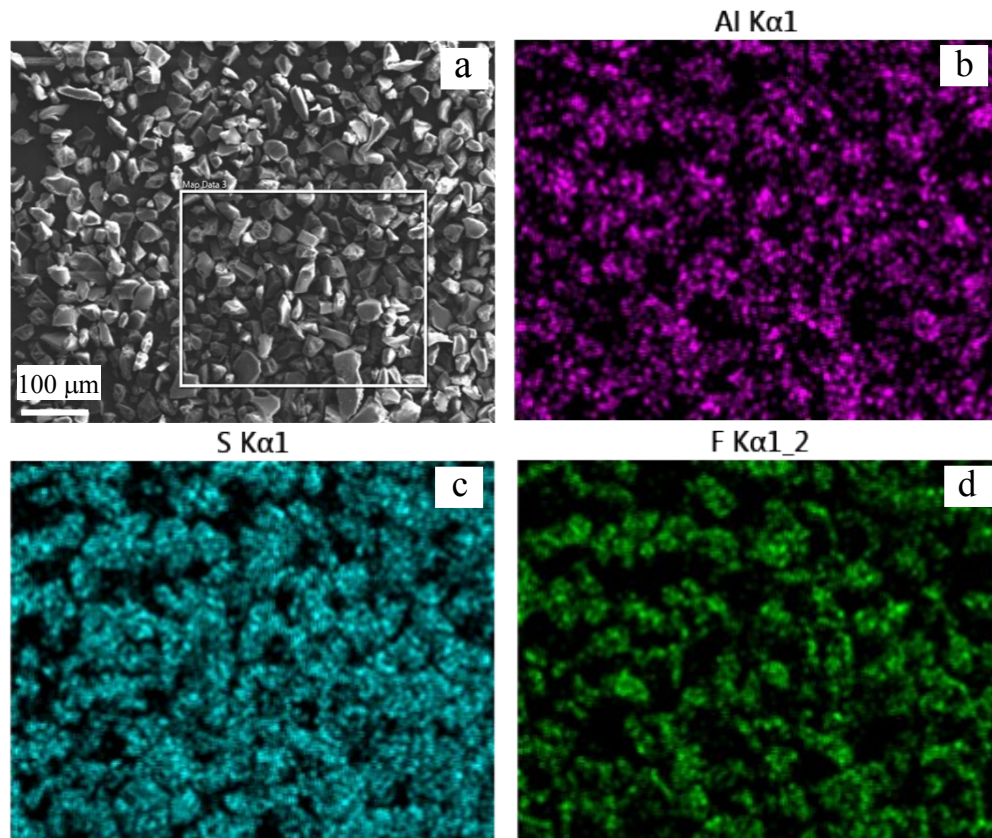


Figure S3. (a) SEM image and (b–d) EDS mapping of **2**.

Element	Wt%
C	49.84
N	14.73
O	15.02
F	11.53
Al	1.96
S	6.92
Total:	100.00

Table S3. EDS analysis of **2**



A



B

Figure S4. A = $[\text{CTF-bpy-Al}(\text{OTf})_3] + [\text{KCo}(\text{CO})_4]$ and B = $[\text{CTF-bpy-Al}(\text{OTf})_2]^+[\text{Co}(\text{CO})_4]$.

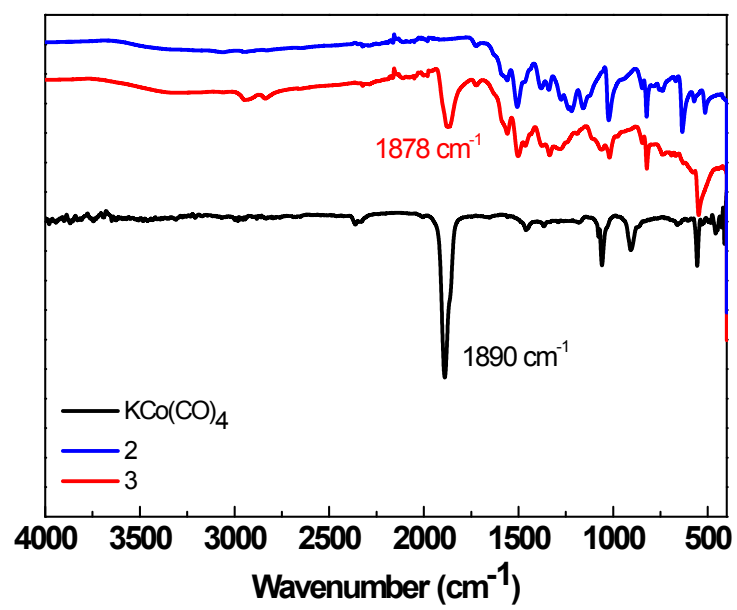


Figure S5: FTIR spectra of KCo(CO)₄, 2 and 3.

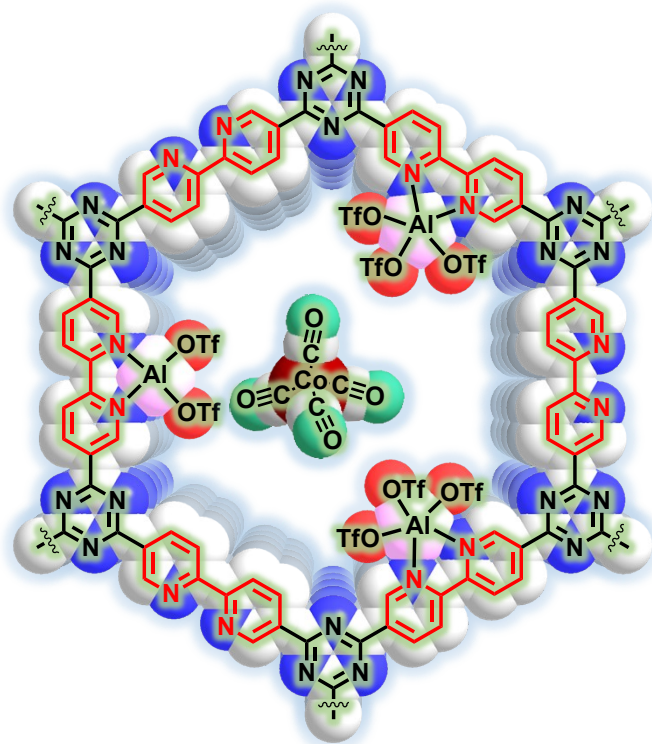


Figure S6: 3D-structure of complex **3** (structure drawn based on ICP-OES and XPS value)

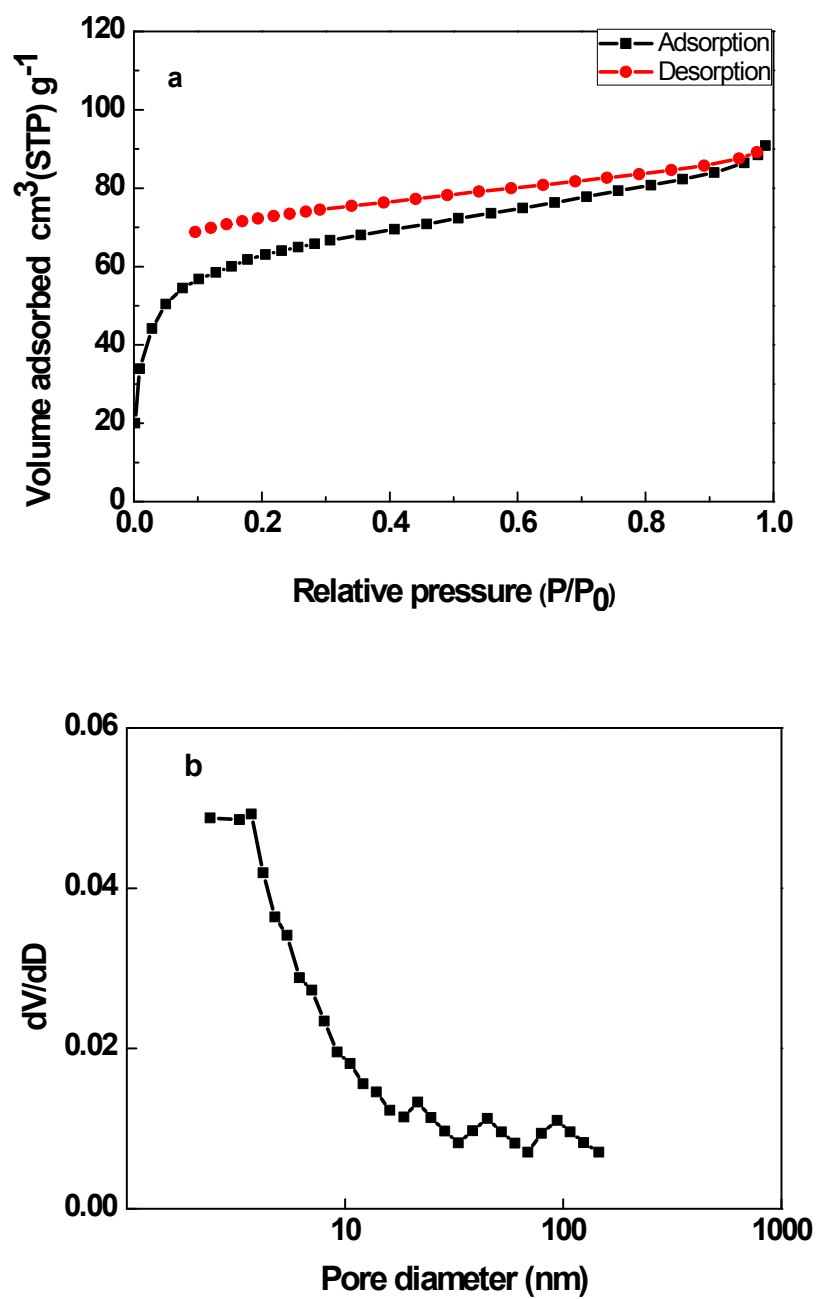


Figure S7. (a) Nitrogen adsorption and desorption isotherms of **3** and (b) pore size of the sample was *ca.* 2 nm, implying that sample **3** has a microporous structure.

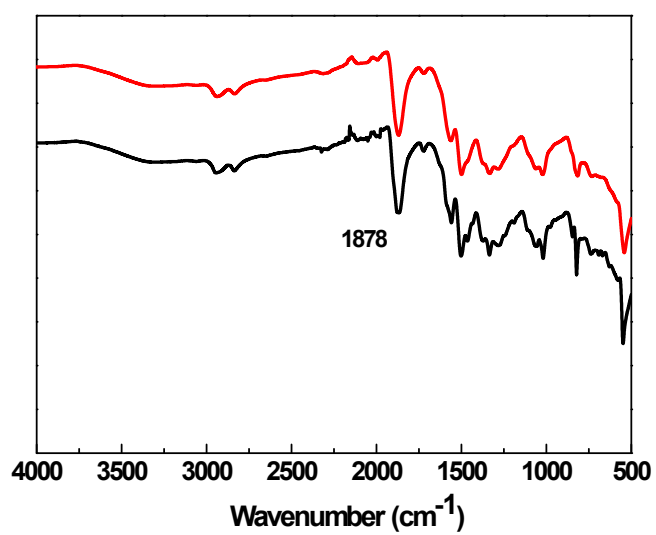


Figure S8. FT-IR spectra of **3** fresh (—) and recycled catalyst (—) (after first run).

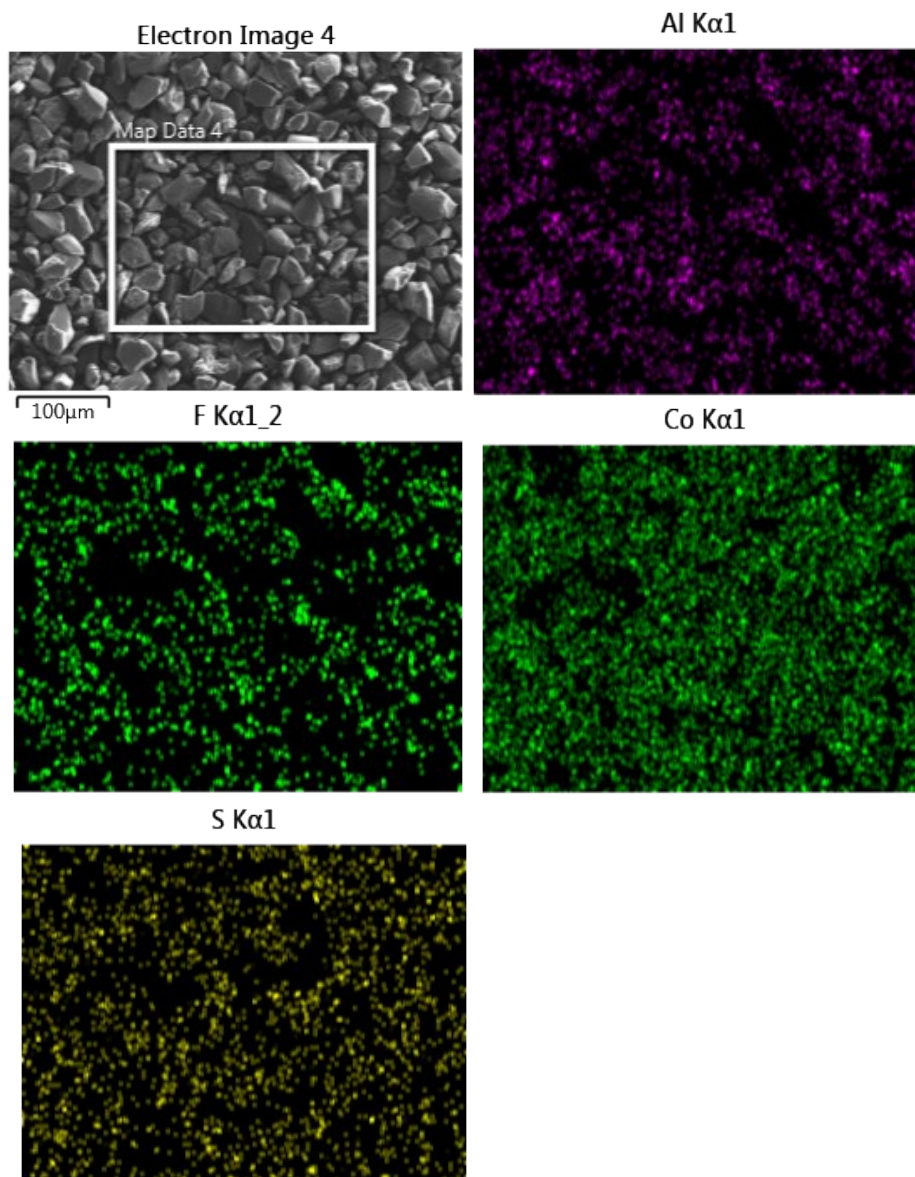


Figure S9. SEM image and EDS elemental mappings of recycled catalyst **3** (after first run).

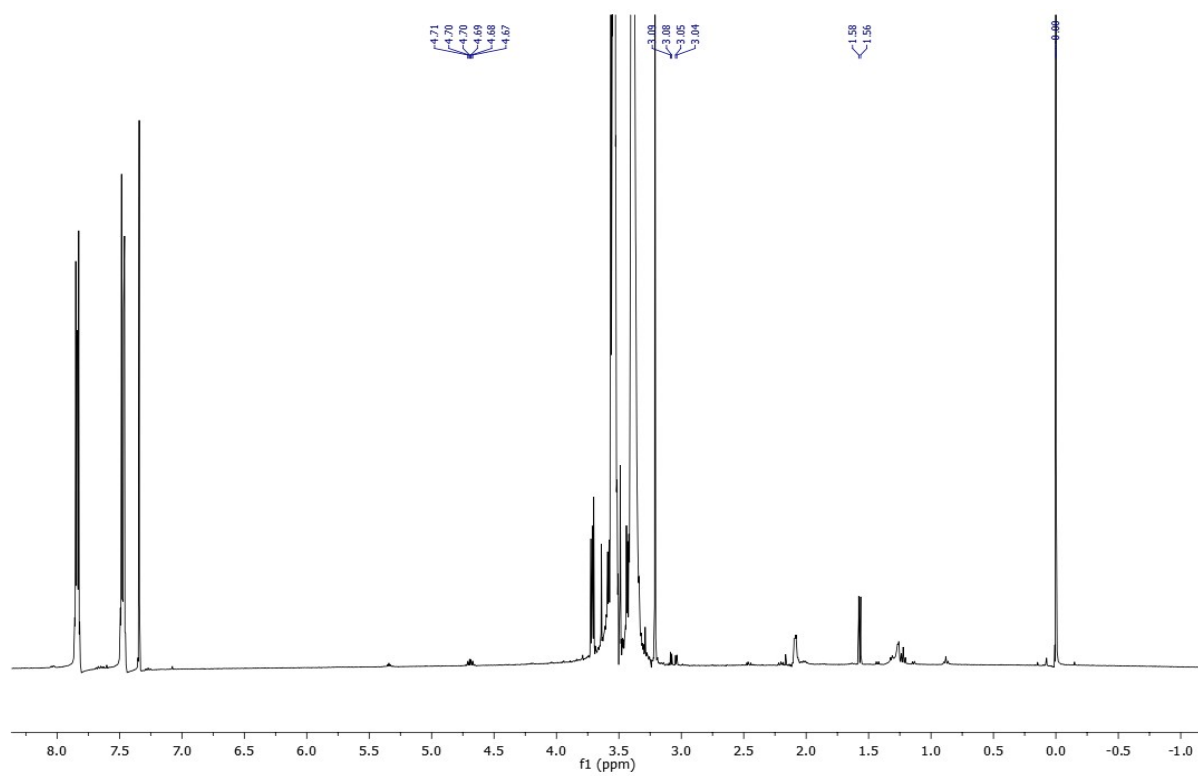


Figure S10: ^1H -NMR spectrum of entry **1** (unknown impurities are exist in ~ 0.7 , 1.25 and 2.2 ppm).

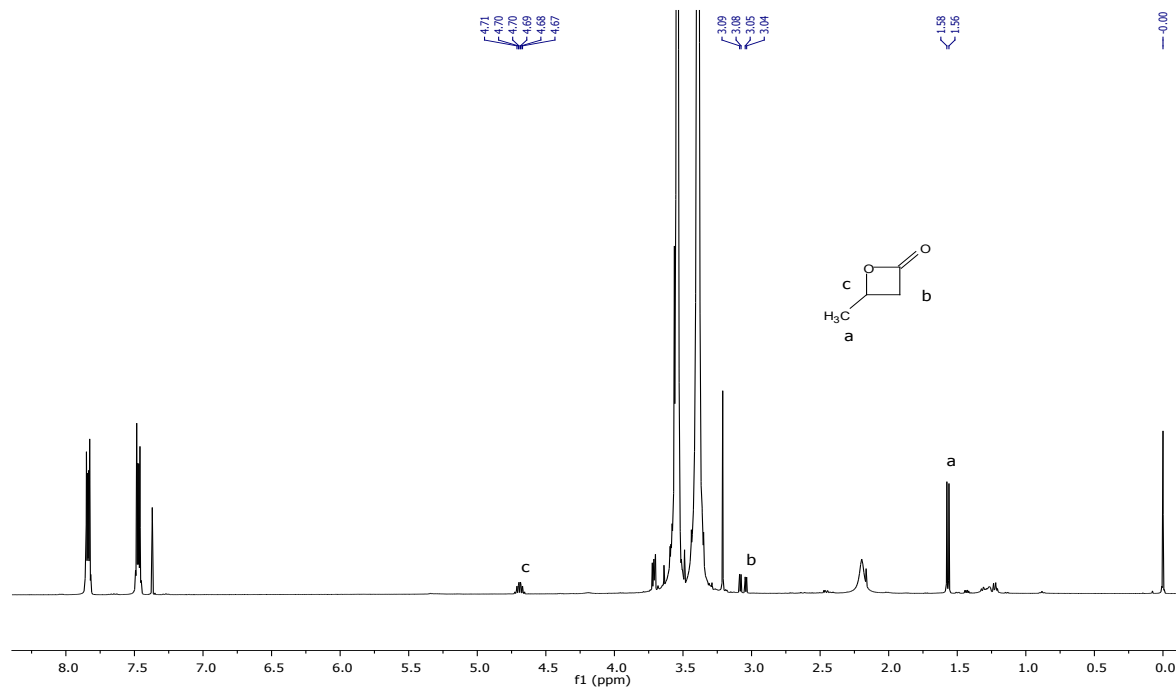


Figure S11: ^1H -NMR spectrum of entry 3 (unknown impurities are exist in the ~ 0.7 and 1.25 ppm).

References:

- S1. Getzler, Y. D. Y. L, Mahadevan, V, Lobkovsky, E. B, Coates G. W. *J. Am. Chem. Soc.*, **2002**, *124*, 1174.
- S2. (a) Park, K.; Gunasekar, G. H.; Prakash, N.; Jung, K. D.; Yoon, S. *ChemSusChem*. **2015**, *8*, 3410. (b) Hug, S.; Tauchert, M. E.; Li, S.; Pachmayr, U. E.; Lotsch, B. V. *J. Mater. Chem.* **2012**, *22*, 13956.