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A heterogenized cobaltate catalyst on bis-imidazolium-based covalent triazine framework for hydroesterification of epoxides

Senkuttuvan Rajendiran, Gunniya Hariyanandam Gunasekar and Sungho Yoon*

Department of Applied Chemistry, Kookmin University, 861-1, Jeongneung-dong, Seongbuk-gu, Seoul 136-702, Republic of Korea.

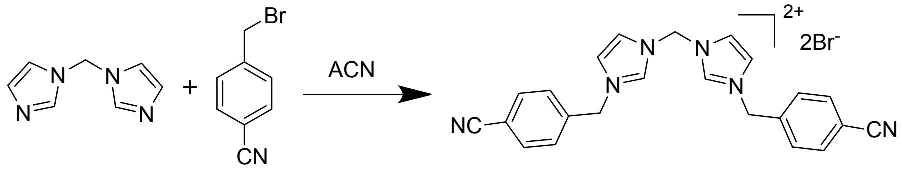
Experiment Section

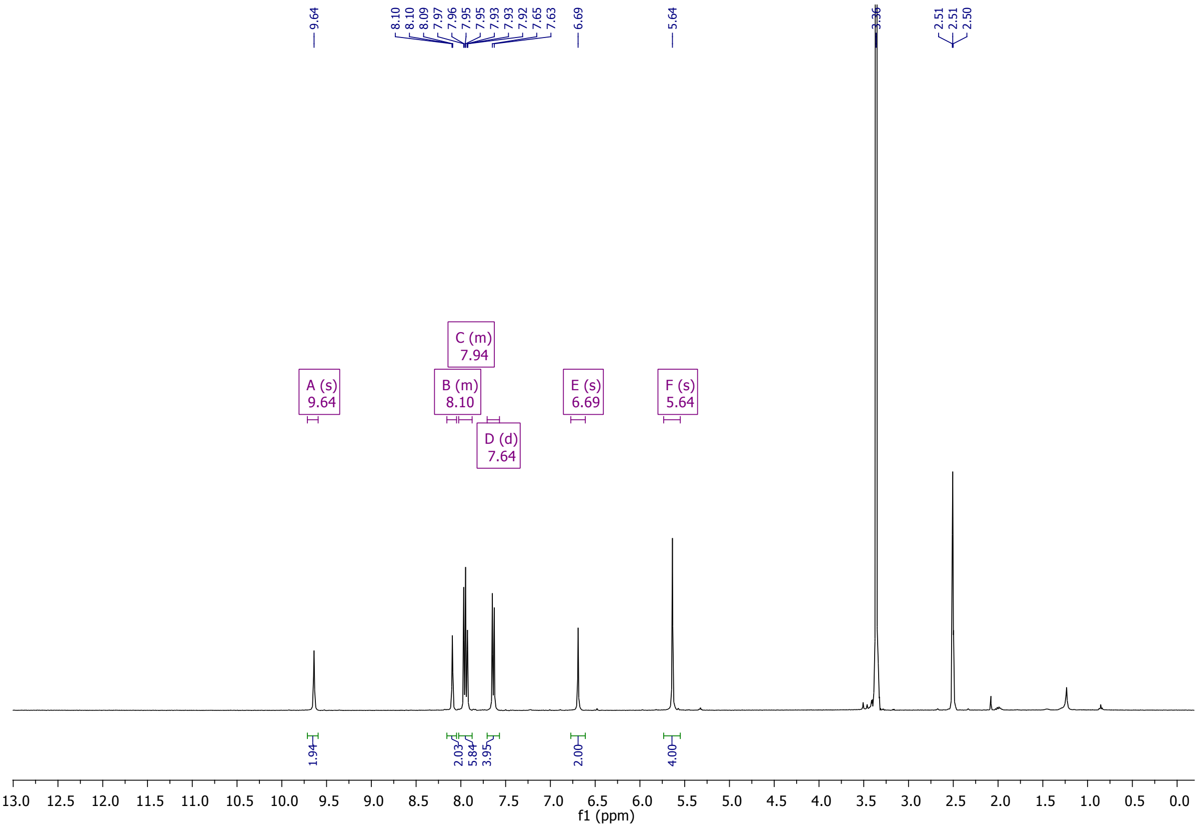
General Considerations and Physical Measurements

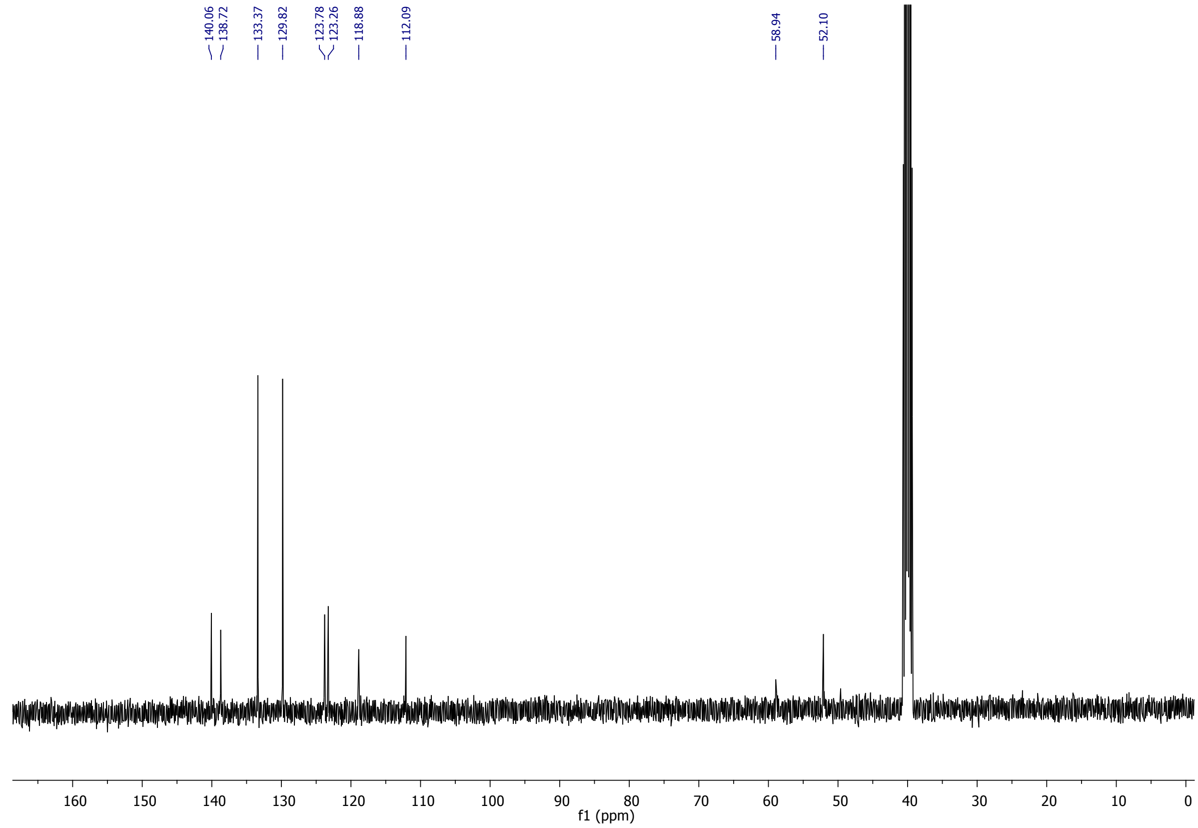
All manipulations of air and water-sensitive compounds were carried out using glovebox under an argon atmosphere. All the chemicals purchased were of analytical grade and were used as received unless otherwise indicated. Tetrahydrofuran was refluxed over sodium/benzoquinone and distilled under N_2 atmosphere. MeOH was refluxed over Mg/I and distilled under N_2 atm. PO was distilled over calcium hydride. Acetonitrile 99 % was purchased from Sigma Aldrich and used as received. Research-grade carbon monoxide was purchased from Sinyang Gas Company, Korea, with 99.995% purity used as received. $Co_2(CO)_8$ was purchased from aldrich used as received. $KCo(CO)_4$ were synthesized by following reported procedure.[1] All new compounds were fully characterized by standard spectroscopic techniques. NMR spectra were recorded using a Bruker advance IV (^{1}H 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. 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. N_2 adsorption/desorption was measured at 77 K using an automated gas sorption system (Belsorp II mini, BEL japan, Inc.,). Cobalt content in complex **3** was determined using Inductively Coupled Plasma Optical Emission Spectroscopy (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 ~3 x 10^{-9} mbar using Al Ka as the excitation source (hγ=1486.6 eV) with concentric hemispherical analyzer. Powder X-ray diffraction (PXRD) was measured on an RIGAKU D/Max 2500V using Cu (40 kV, 30 mA) radiation. The elemental analysis was performed with an elemental analyzer (Vario Micro cube, Germany).

^{13}C cross-polarization magic-angle spinning solid-state nuclear magnetic resonance spectroscopy (^{13}C CPMAS ssNMR) data were acquired at ambient temperature on 400 MHz Solid state NMR spectrometer (AVANCE III HD, Bruker, Germany) at KBSI Western Seoul center with an external magnetic field of 9.4 T. The operating frequency was 100.66 MHz for ^{13}C and the spectra were referenced to TMS. The samples were contained in HX CPMAS probe, with 4 mm o.d. Zirconia rotor. Thermogravimetric analysis (TGA) was performed on Q600 analyzer (TA Instrument, US) with a heating rate of 10 ˚C per minute up to 800 □C under nitrogen atmosphere. All carbonylation reactions were performed in a 100-mL stainless steel reactor and fitted with a pressure gauge and pressure release valve. 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, MHB, 1-Methoxypropanol (1-MP), 2-Methoxypropanol (2-MP), and acetone were quantified using naphthalene as an internal standard.

Synthesis of 1,1'-methylene bis(3-(4-cyanobenzyl)-1H-imidazol-3-ium) bromide (1)

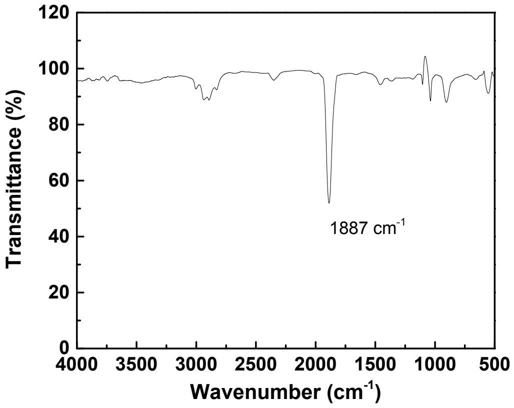




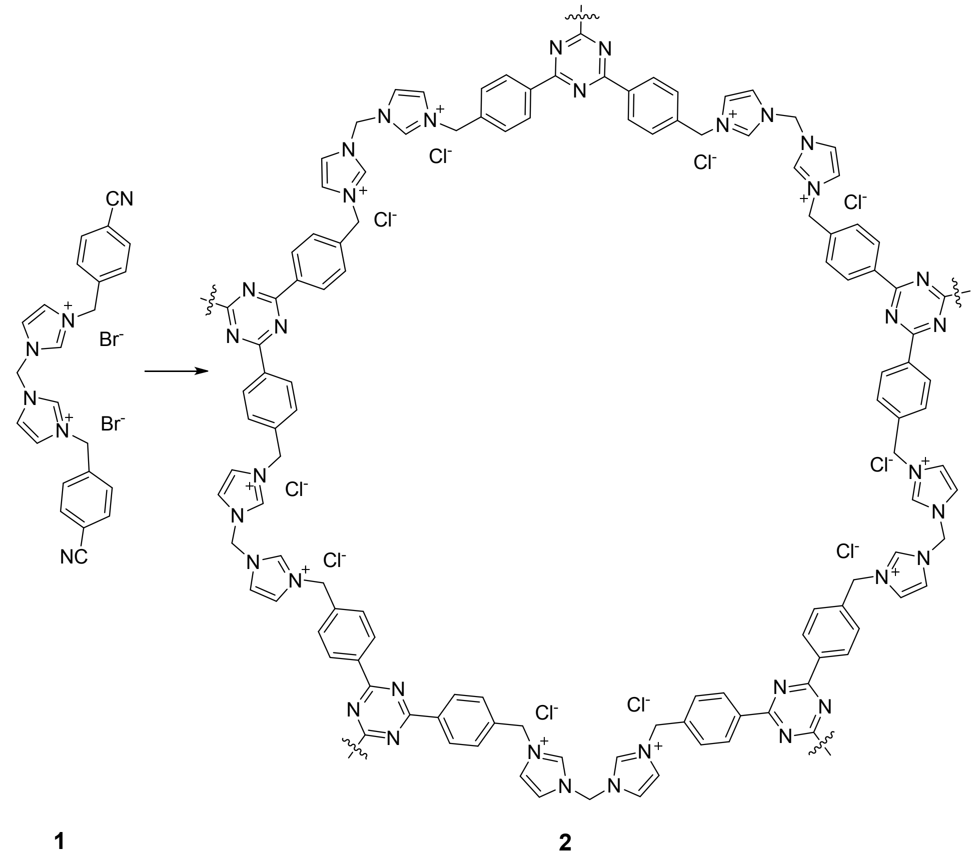


Synthesis of potassium cobalt tetracarbonyl [$KCo(CO)_4$]

To a solution of $Co_2(CO)_8$ (1.031 g, 3.015 mmol) in 15 mL THF excess KOH (0.506 g, 9.036 mmol) was added and the brown solution was stirred at RT for 4 h. The resulting pale yellow solution was filtered and the solvent was removed under vacuum to afford off-white precipitate. Yield=1.2g, 98%



Synthesis of [bis-imidazolium-CTF]Cl (2)



1

2

General procedure for epoxide-ring opening carbonylation

In a glovebox, a stainless steel 100 mL tube reactor was equipped with a magnetic stir bar and charged with (0.028 g of catalyst, 0.0075 mmol of cobalt content based on ICP-OES) [bis-imidazolium-CTF][$Co(CO)_4$] and PO (0.026 g, 0.45 mmol) in 2.5 mL of dry MeOH under Ar atmosphere. The reactor was cooled to 0 °C, 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 and CO gas was slowly released inside a fume hood. The crude sample was weighed and filtered through celite and analyzed using ^{1}H-NMR spectroscopy in $CDCl_3$ using naphthalene as an internal standard.

Procedure for regeneration of catalyst 3.

After the fifth run the catalyst **3** was filtered and washed with 5 mL of MeOH, dried for 10 h under vacuum. The catalyst **3** (0.038 g) was stirred with a freshly prepared yellowish $KCo(CO)_4$ (1.12 g, 5.33 mmol) in methanol (5 mL) under 5 bar CO. After 24 h, black precipitates was washed with methanol (10 mL) and dried for 12 h. (Yield = 0.037 g) (~0.96 g of $KCo(CO)_4$ was recovered from the filtrate).

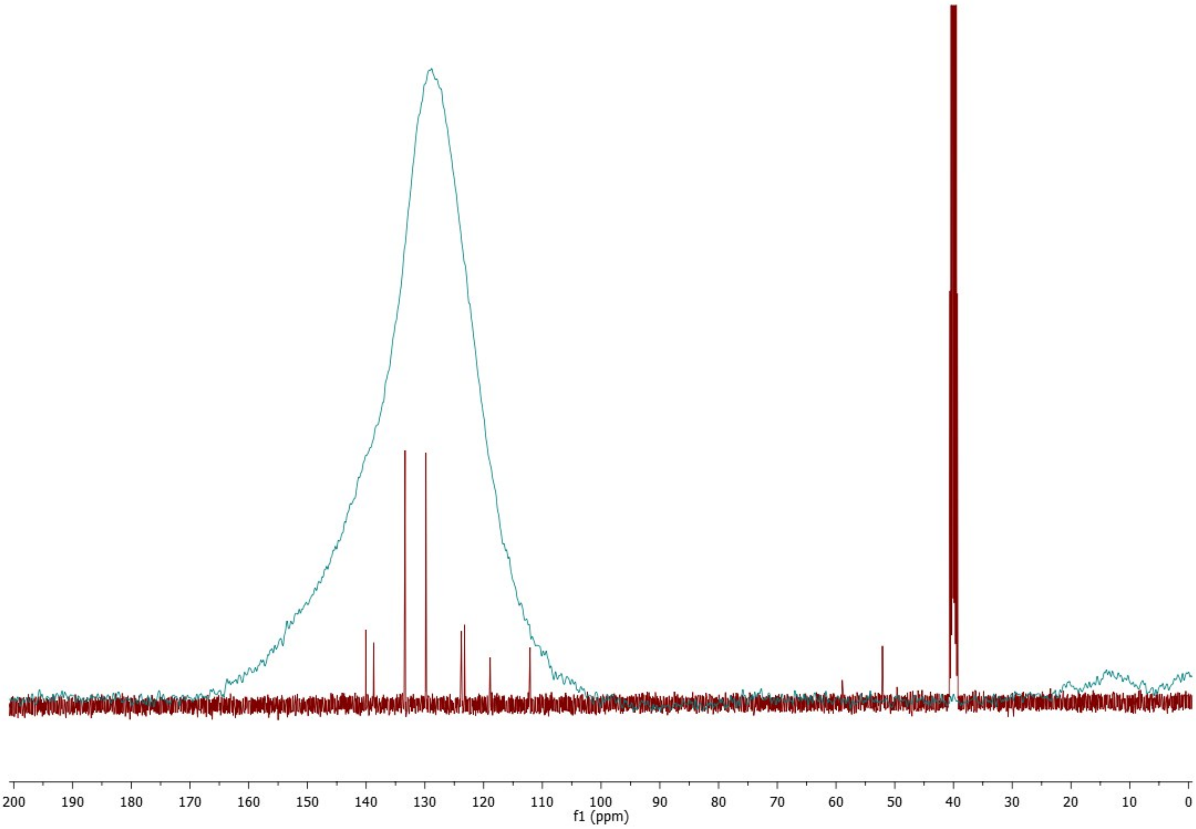


Figure S1. ^{13}C ssNMR spectrum of **2**.

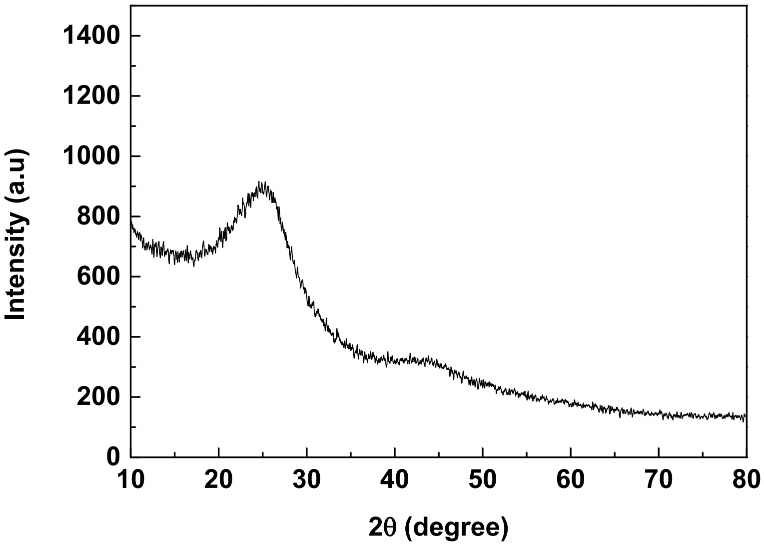


Figure S2. PXRD spectrum of **2**.

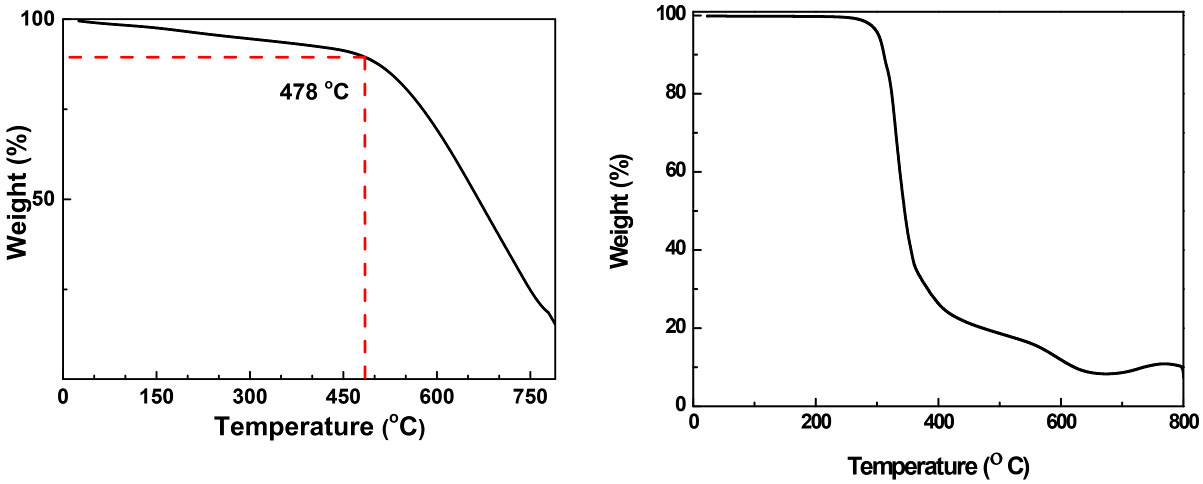


Figure S3. TGA thermograms of **2 (left)** and **1(right)**

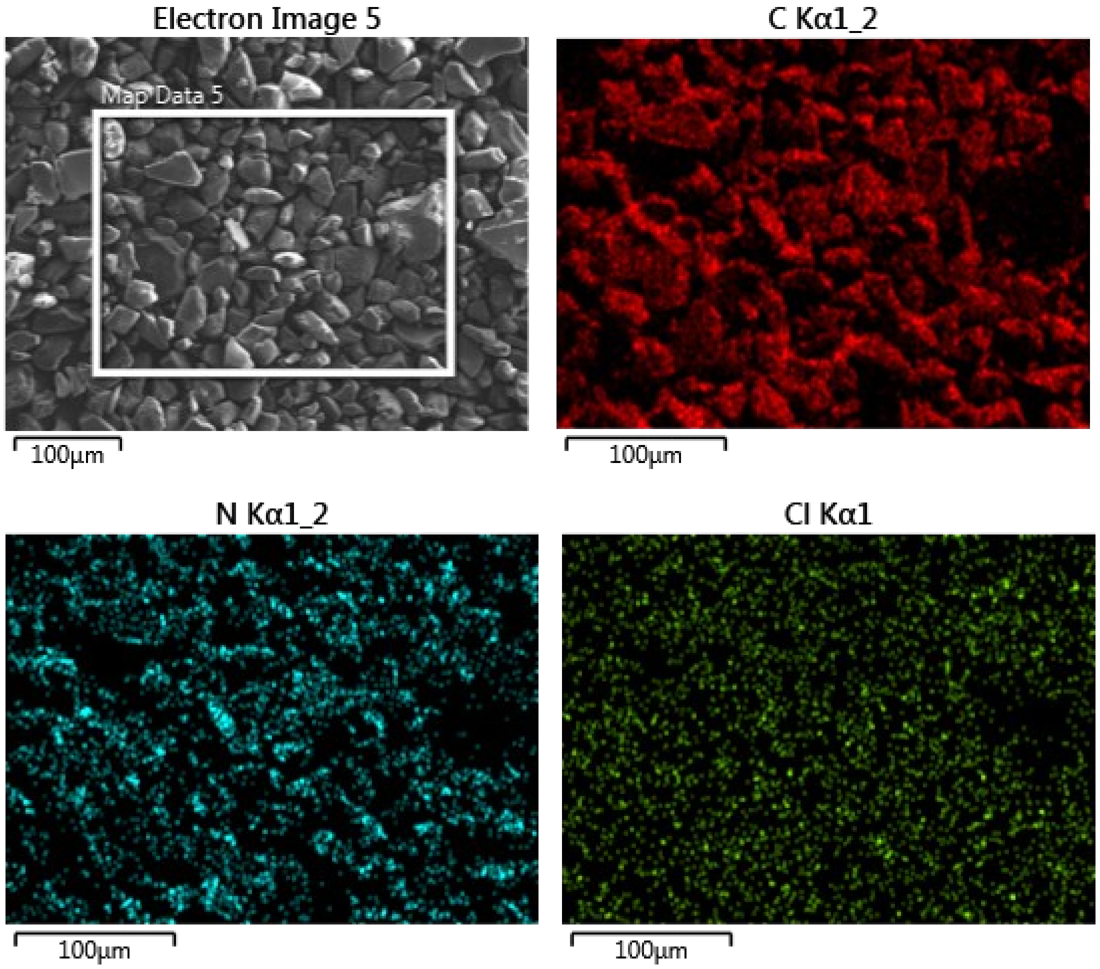


Figure S4. SEM image and EDS mapping of **2**.

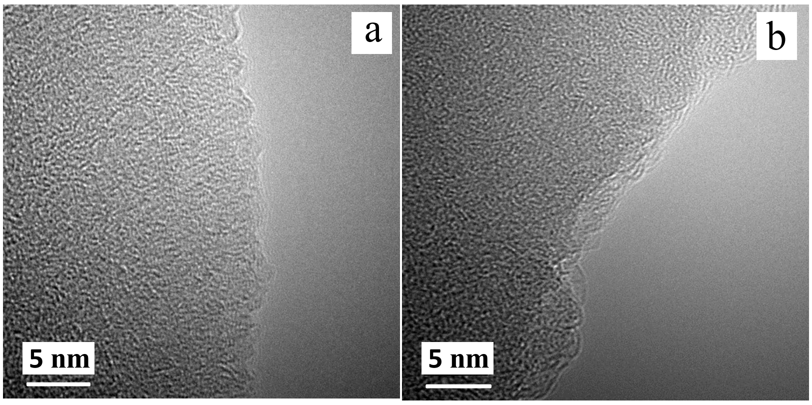


Figure S5. TEM image of (a) **2** and (b) **3**.

Table S1. BET physisorption data of **2** and **3.**

Entry	Catalyst	Pore surface ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Pore size (nm)	DFT (total pore area) nm
1	2	830	0.44	3.2	0.46
2	3	570	0.28	3.1	0.46

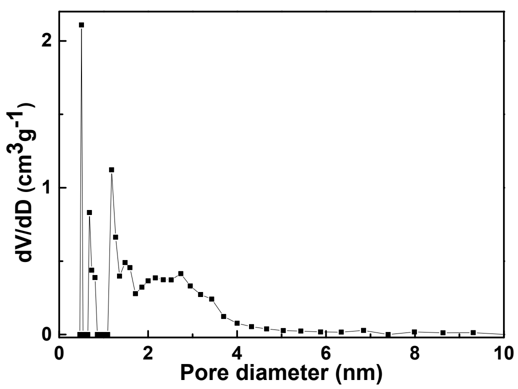
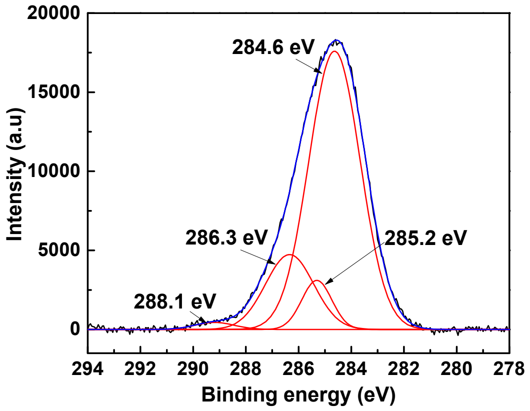


Figure S6. NL-DFT pore distribution of **2**.



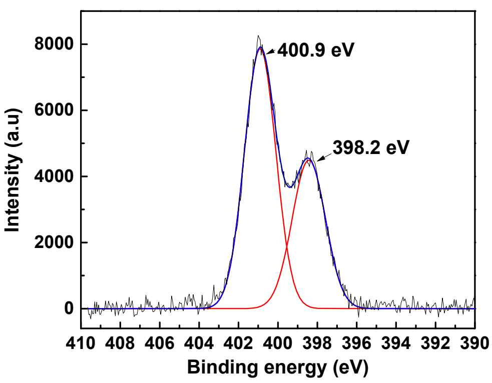


Figure S7: X-ray photoelectron C1s spectrum of **1 (left)** and N1s spectrum of **1 (right)**

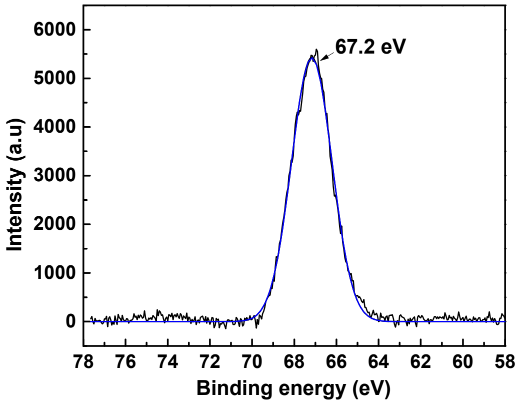


Figure S7-1: X-ray photoelectron Br spectrum of **1**

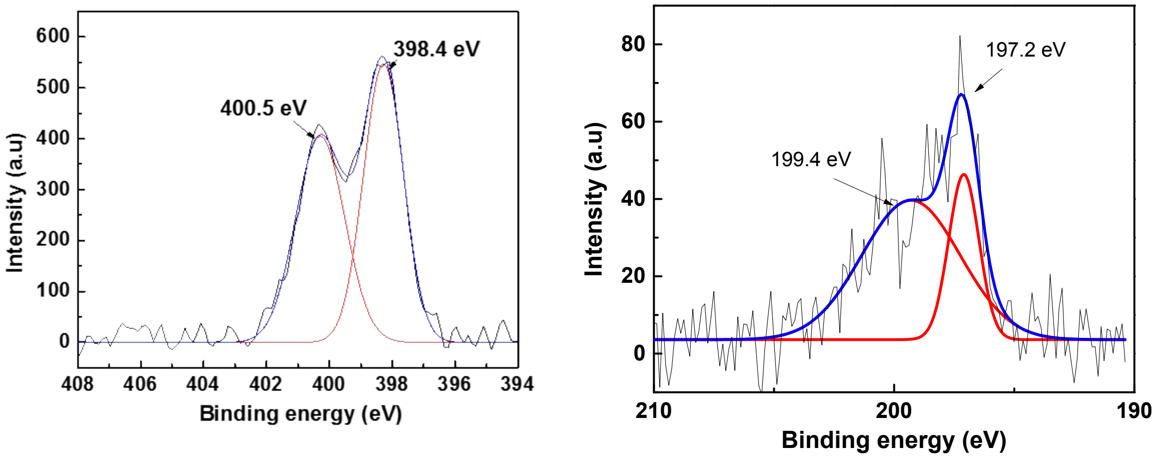


Figure S8: X-ray photoelectron N 1s spectrum of **2** (left) and Cl 2p spectrum of **2** (right)

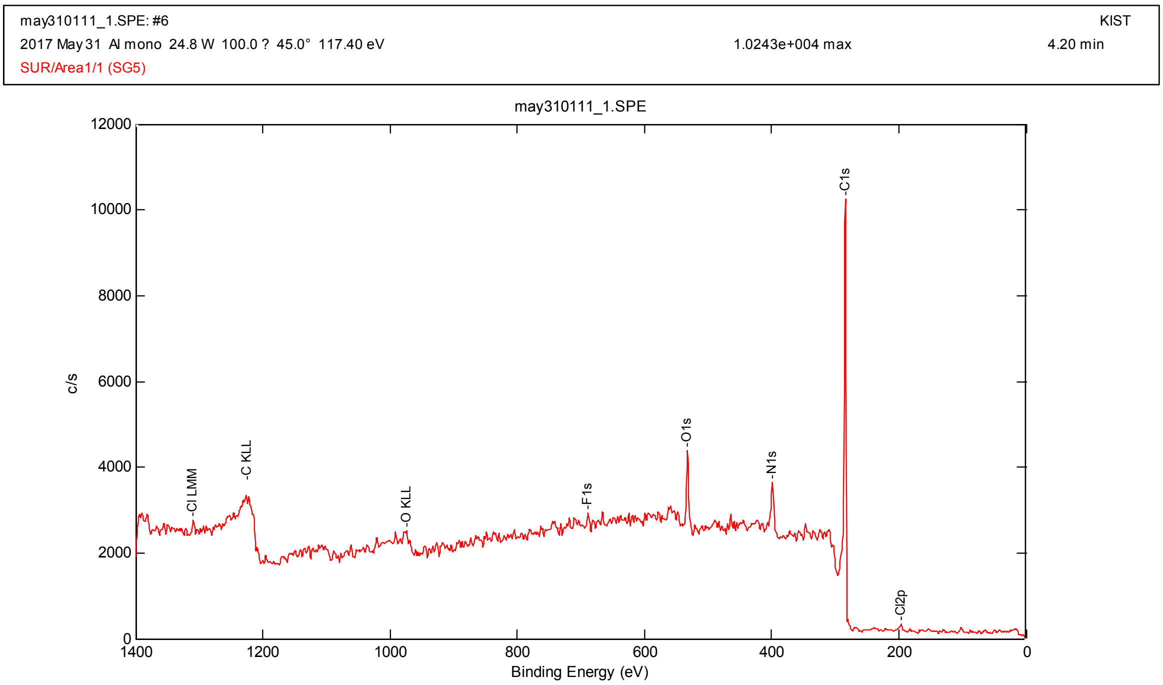


Figure S8-1: X-ray photoelectron spectrum of **2** no Br peak was shown.

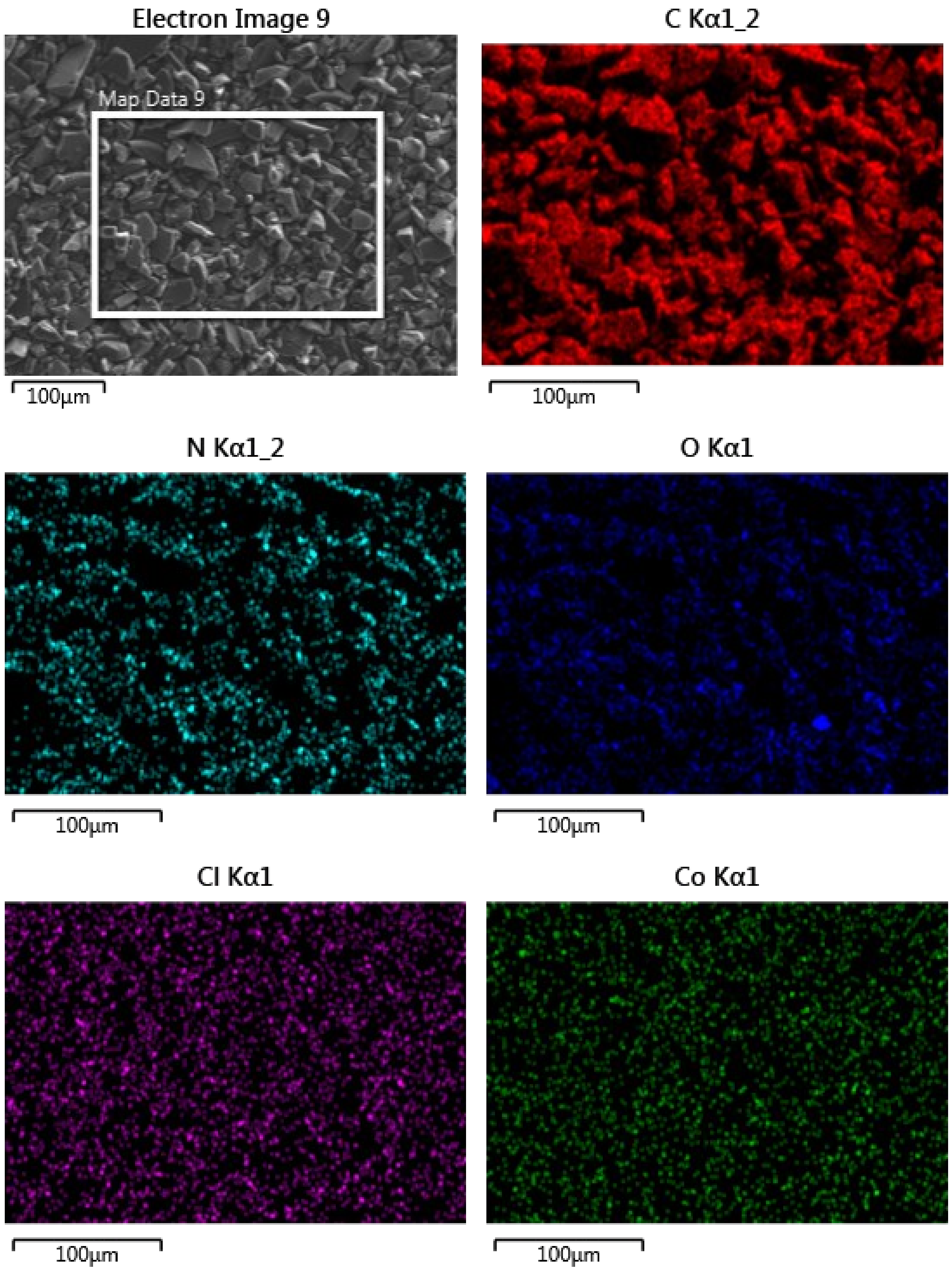


Figure S9. SEM image and EDS mapping of **3**.

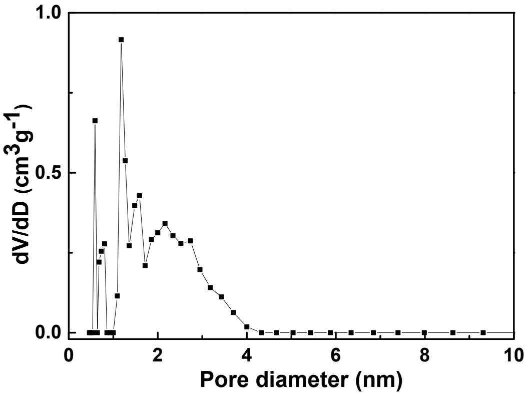


Figure S10. NL-DFT pore distribution of **3**.

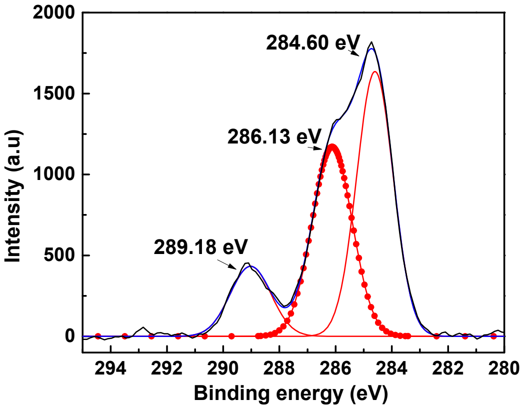


Figure S11: X-ray photoelectron C1s spectrum of **$KCo(CO)_4$**

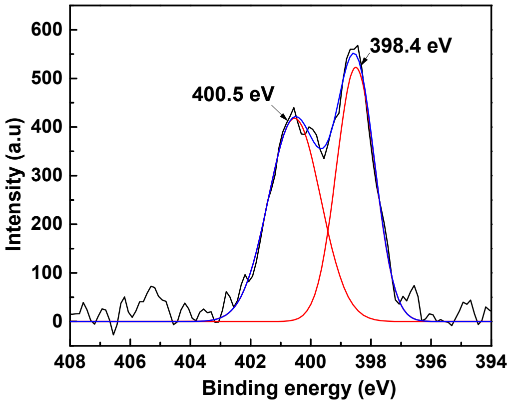
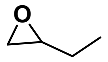
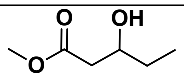
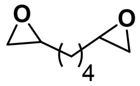
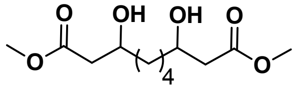
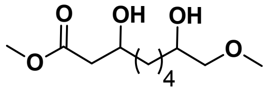
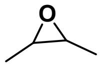
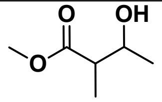


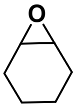
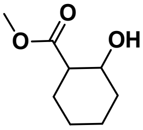
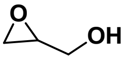
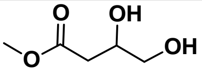
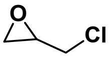
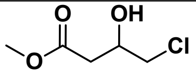
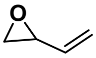
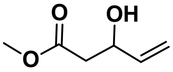
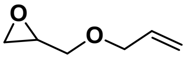
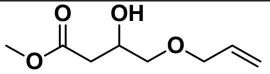
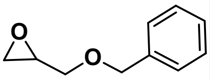
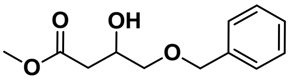
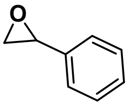
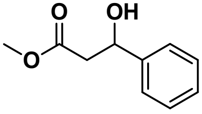
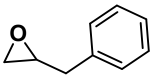
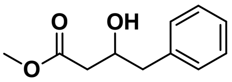
Figure S12: X-ray photoelectron N 1s spectrum of **3**

Table S2. CHN analysis

Compound	Carbon	Hydrogen	Nitrogen
Theoretical values for 3	51.13	3.73	15.56
3	50.79	3.73	16.14
4	71.55	2.55	9.59
5	76.77	3.11	8.76

Table S3. Results for the ring-opening carbonylation of epoxides using catalyst **3**[a]

Entry	**Epoxide**	**Epoxide/5**	**Conversion**[b]	***β*-hydroxyester**	**TON**
S1		**55**	**>99(89)**		**50**
S2		**55**	**>99(69:24)**	 	**38** **13**
S3		**15**	**>71(82)** [c]		**10**

S4		**15**	**94(89)**[c]		**14**
S5		**10**	**63(87)**[c]		**6**
S6		**15**	**78(84)** [c]		**13**
S7		**10**	**73(91)**[c]		**7**
S8		**20**	**95(81)**[c]		**19**
S9		**20**	**>99(86)**		**20**
S10		**20**	**>75(73)**[c]		**15**
S11		**30**	**>99(80)**		**24**

[a]Reaction performed in 2.5 mL of MeOH, CO pressurized at room temperature and heated to 75 °C. [b]Determined by ^{1}H-NMR spectroscopy with naphthalene as an internal standard. [c]Remaining were an unreacted epoxide. TON calculated based on the ester product.

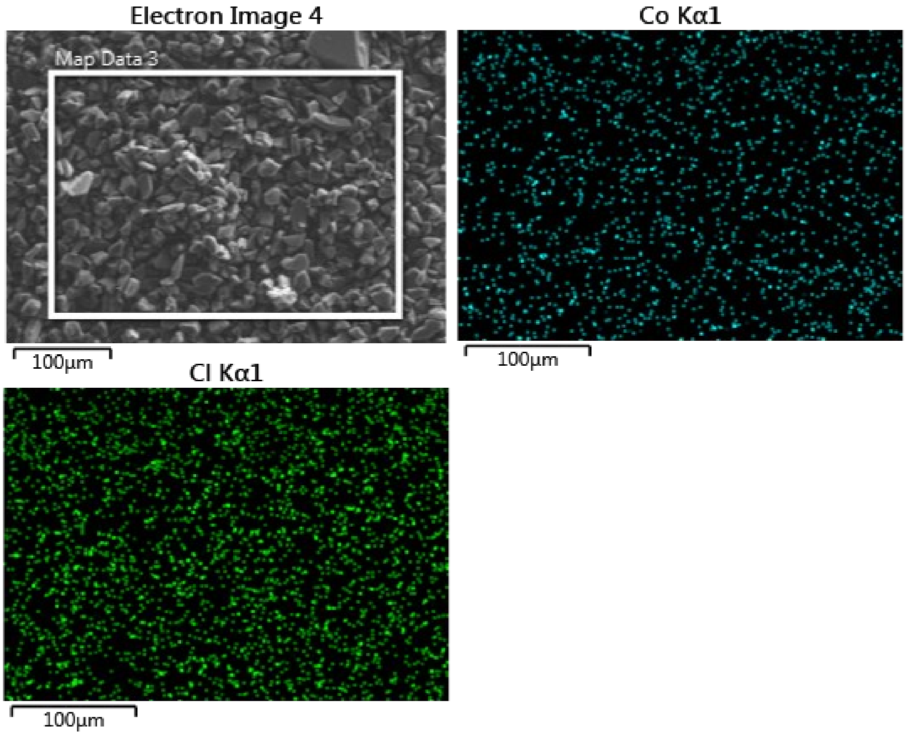


Figure S13. SEM image and EDS mapping of recycled catalyst **3**.

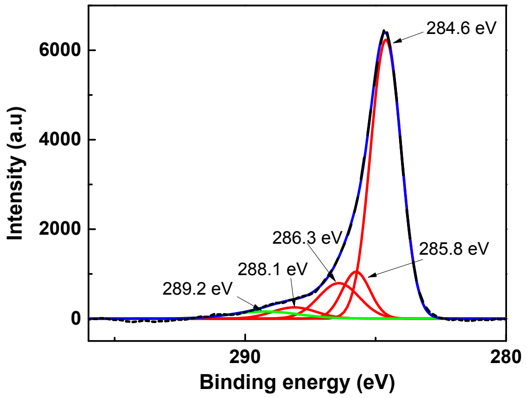


Figure S14: X-ray photoelectron C 1s spectrum of recycled catalyst **3**

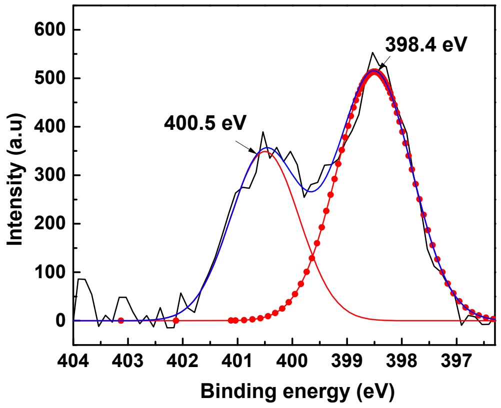


Figure S15: X-ray photoelectron N 1s spectrum of recycled catalyst **3**

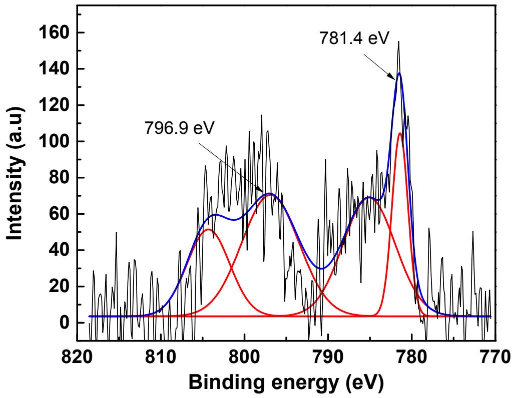


Figure S16: X-ray photoelectron Co spectrum of recycled catalyst **3**

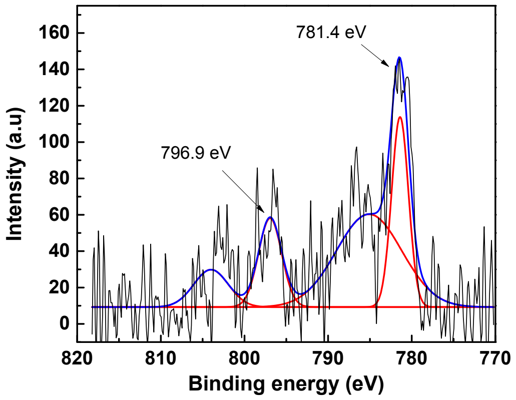


Figure S17: X-ray photoelectron Co spectrum of recycled catalyst **3** (after fifth run).

Table S4. Reproducibility of recycling experiments using 5[a].

Cycle	Time (h)	Conversion (%)[b]	Selectivity (%)[b]		
			MHB	**1-MP**	**Acetone**
1	24	>99	92	3	5
2	24	97	92	4	4
3	24	95	90	4	6

[a]Reaction performed in 2.5 mL of MeOH using pressurized CO at room temperature and heated to 75 °C. S/C ratio = 60/1. [b]Determined by ^{1}H-NMR spectroscopy with napthelene as internal standard.

The results demonstrate that the selectivity for MHB is similar to that of the first batch, with little variation in the selectivity for the side products.

NMR spectrum

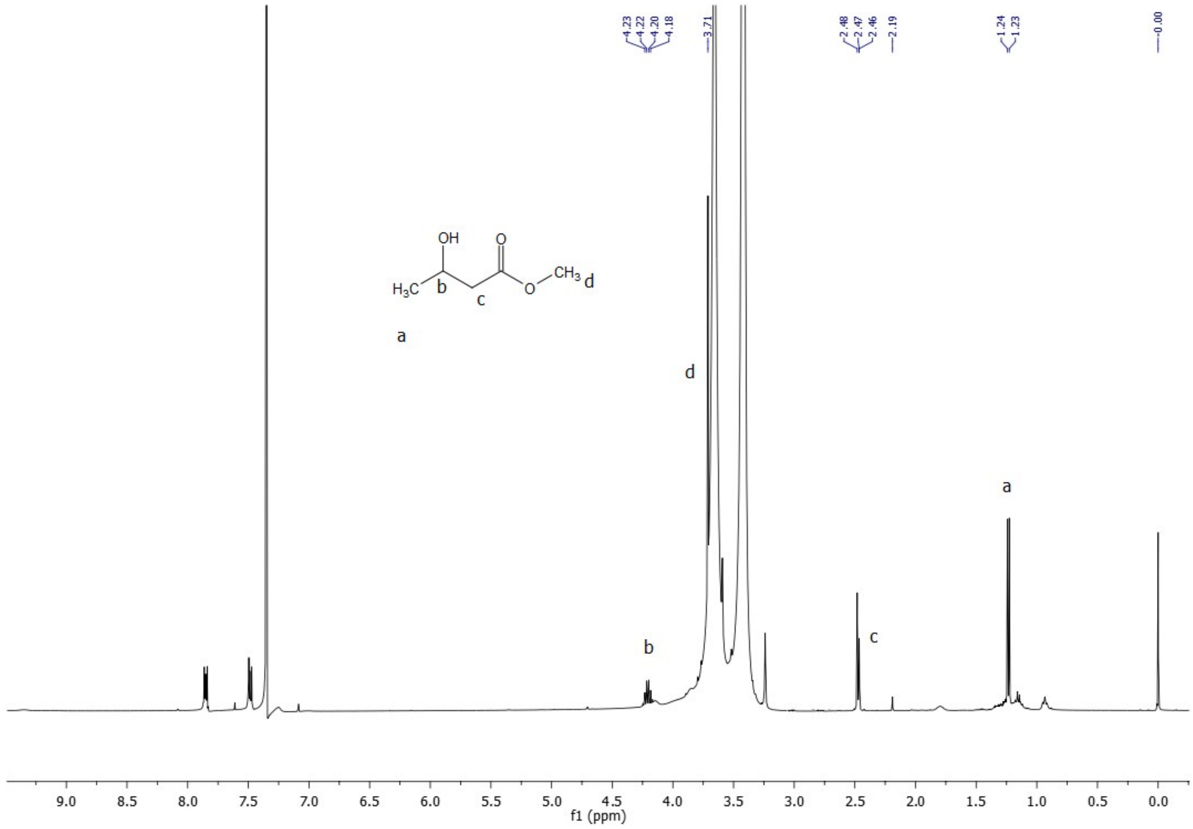


Figure S18. ^{1}H-NMR spectrum of table-1, entry-4.

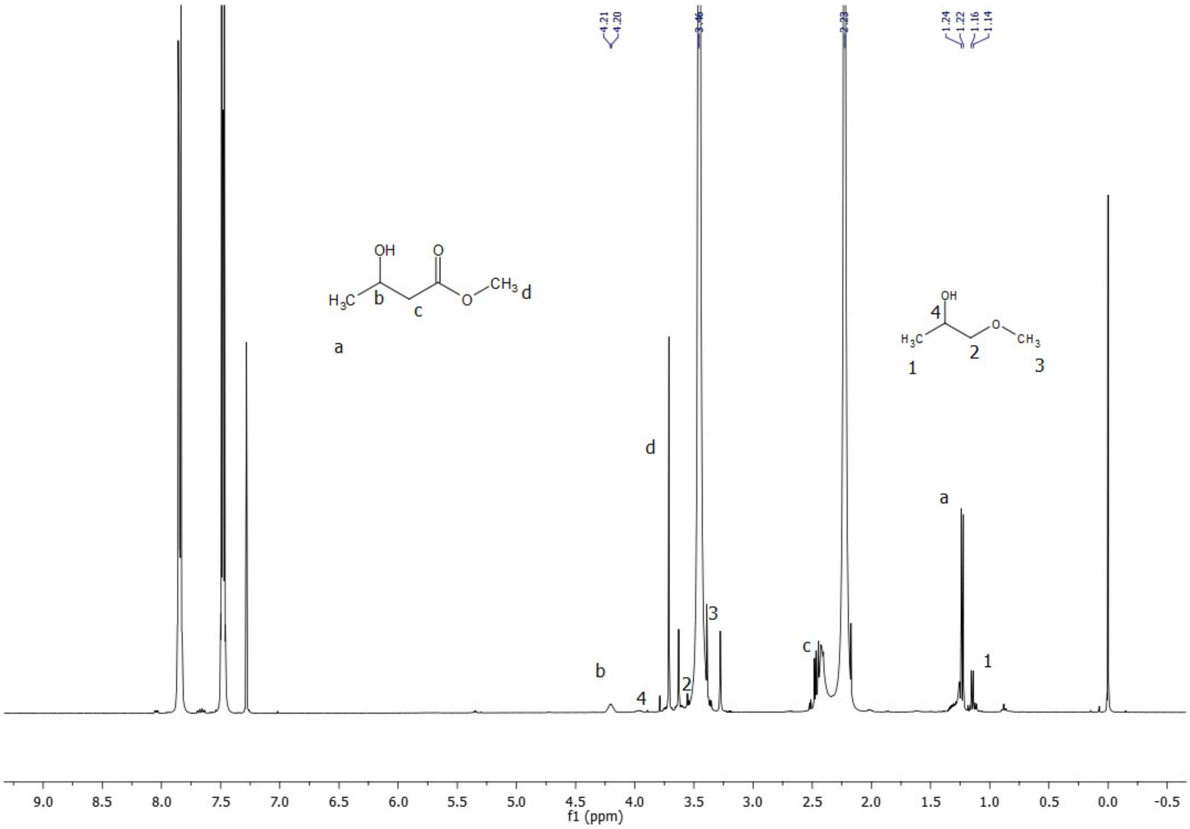


Figure S19. ^{1}H-NMR spectrum of table-1, entry-5.

References

1 S. Rajendiran, K. Park, K. Lee and S. Yoon, *Inorg Chem*, 2017, **56**, 7270-7277.