Electronic Supplementary Information for

Chiral Environment of Catalytic Sites in the Chiral Metal-Organic Frameworks

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Preparation of (*R*)-**KUMOF-1**(1)

Preparation of (*R*)-**KUMOF-1**(1) by Filtration of (*R*)-**KUMOF-1**(2)

A reaction mixture was prepared by dissolving $Cu(NO_3)_2\cdot 3H_2O$ (7.2 mg, 0.030 mmol) and (*S*)-2,2'-dihydroxy-6,6'-dimethylbiphenyl-4,4'-dicarboxylic acid ((*R*)-**KUBP**, 10 mg, 0.033 mmol) with a solvent mixture of DMF/MeOH (1.5 / 1.5 mL) in a small vial (4 mL). *N*,*N*-dimethylaniline (1.0 mL) was put in a larger (20 mL) vial, and into the vial, the vial containing the reaction mixture was placed without capping. When the tightly-capped larger vial was heated at 65 ºC for 1 day, blue cubic crystals were obtained as a product in 35 % yield based on the used ligand. The blue crystals were washed with a solvent mixture of DMF/MeOH (3 / 3 mL) three times and filtered through glass filter (50 µm). The filtered crystal was collected and rinsed with dry dichloromethane.

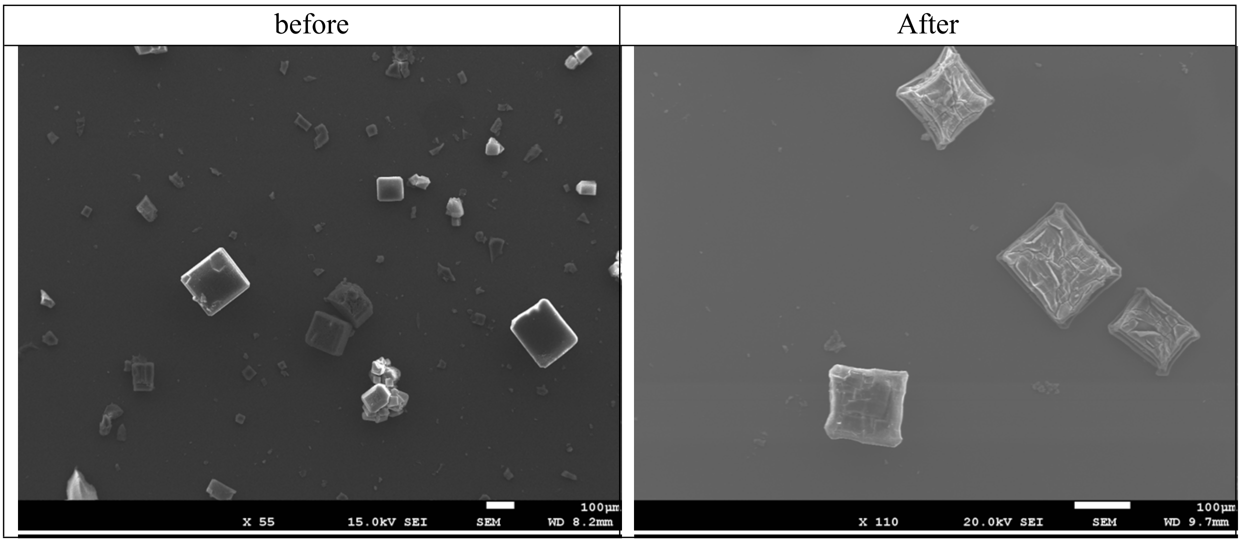


Figure S1. SEM images of the (*R*)-**KUMOF-1(2)** as-prepared and (*R*)-**KUMOF-1(1)** after filtration.

Synthesis of micrometer-size KUMOF-1

- Preparation of (*R*)-**KUMOF-1** (3) with microwave

*Synthesis of (R)-**KUMOF-1**(3) with microwave*

KUBP (2,2'-dihydroxy-6,6'-dimethyl-[1,1'-biphenyl]-4,4'-dicarboxylic acid) (0.24 mg, 0.0008 mmol), $Cu(NO_3)_2 \cdot 3H_2O$ (0.2 mg, 0.0008 mmol), and 4 mL of solvent (DMF : MeOH = 1 : 1, v/v) were loaded in a 10 mL cell and sealed with a PTFE cap. The mixture was reacted in a microwave reactor (CEM Discover) at 65 ℃ with 100 psi and 50 W. After 20 min, the blue crystal was collected via filtration and washed with hot DMF several times.

*TGA of (R)-**KUMOF-1**(3)*

Thermogravimetric Analysis (TGA) of (*R*)-**KUMOF-1**(3)**:** Thermogravimetric analyses were carried out at a ramp rate of 10 ^oC/min in a N_2 flow using a Scinco TGA N-1000 instrument. Sample (~14.14 mg) was loaded and the temperature was increased by 10 °C/min from 25 °C to 500 °C. The first weight loss (– 63.5 %) is due to the evaporation of DMFs. The second step (–29.1 %) is for the decomposition of the (*R*)-**KUMOF-1**(2) and the residue is attributed to CuO.

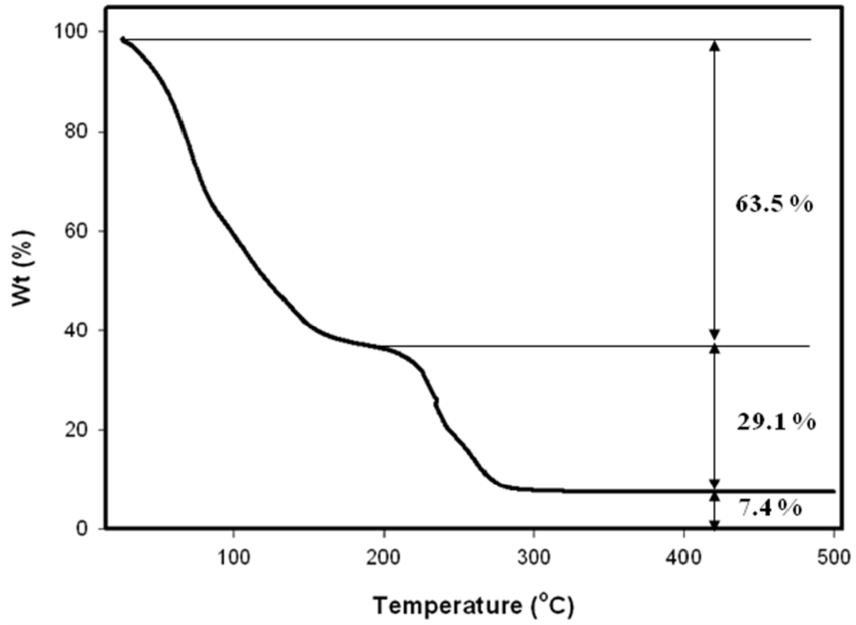


Figure S2. TGA thermogram of the (*R*)-**KUMOF-1** as-prepared.

*XRPD of (R)-**KUMOF-1**(3)*

PXRD data were recorded using Cu Kα (λ = 1.5406 Å) on a Rigaku Ultima III diffractometer with a scan speed of 2°/min and a step size of 0.02°. The X-ray powder diffraction (XRPD) data of the evacuated (*R*)-**KUMOF-1**(3) were obtained as it is and after solvent exchange. The occluded solvents in the MOF crystals were replaced by continuous washing with relatively inert solvent, such as dichloromethane. For example, the blue crystals were collected and rinsed with dry dichloromethane

(3 × 5 mL) to remove DMF and MeOH and soaked in dry dichloromethane for 3 days. The PXRD study confirmed that the MOF structure was intact.

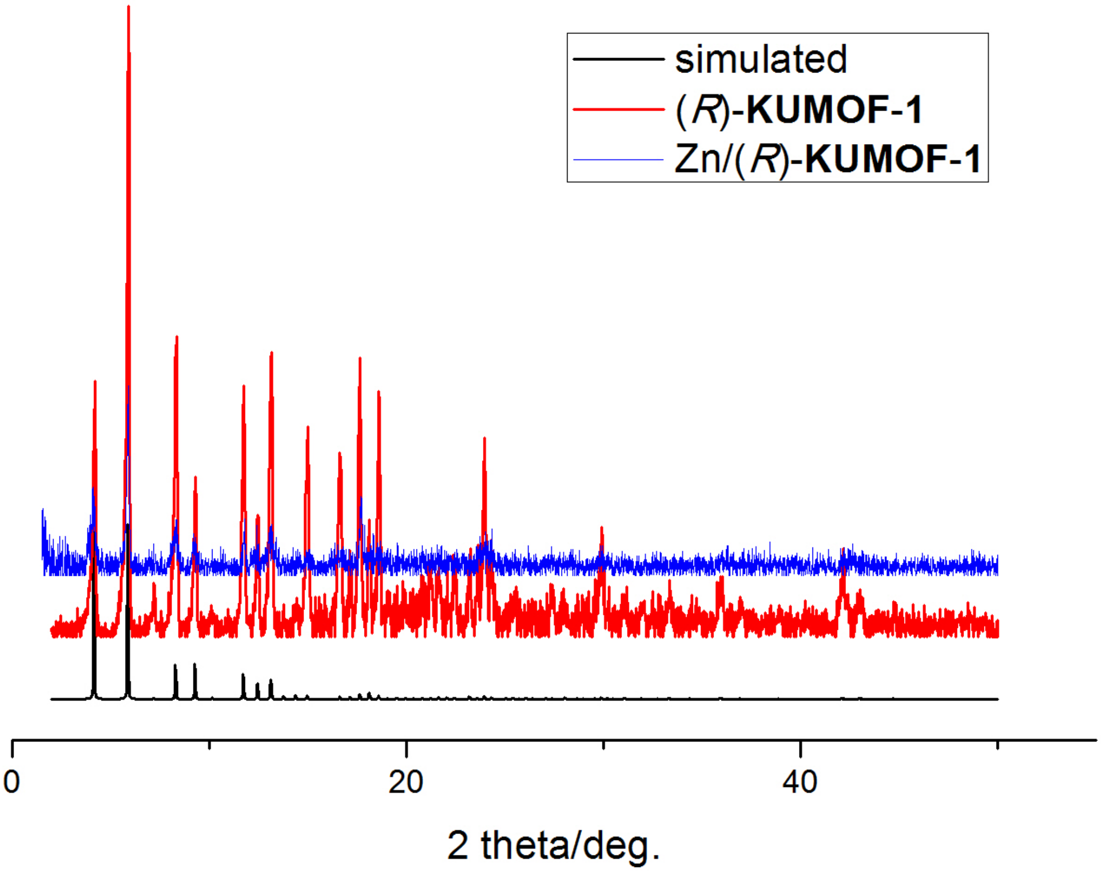


Figure S3. PXRD of *(R)-**KUMOF-1**(3)*

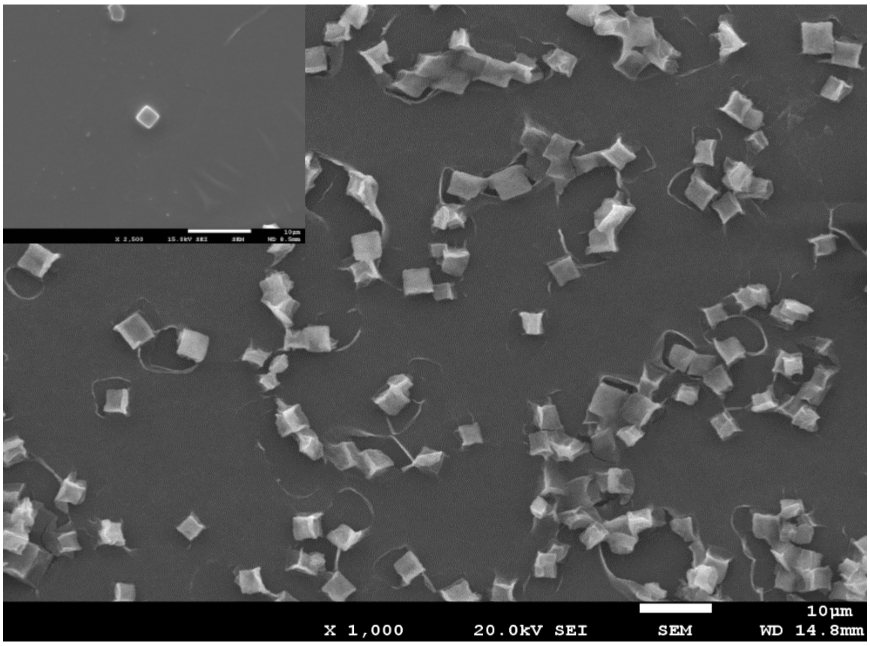
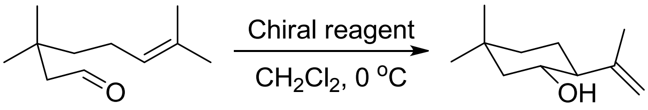


Figure S4. SEM image of *(R)-**KUMOF-1**(3)*

General reaction of enantioselective carbonyl-ene reaction



■ Reaction quenched at various time interval

To a suspension of (*R*)-**KUMOF-1** (102 mg, 0.27 mmol) in dichloromethane (1 mL) was added dimethyl zinc (0.4 mL, 2 M in dichloromethane, 0.80 mmol) at -78 °C. The resultant mixture was shaken for 3 h at this temperature. To this mixture was added a solution of **7** (15 mg, 0.089 mmol) in dichloromethane (0.1 mL) at -78 °C. The reaction mixture was warmed to 0 °C and shaken for a given period at this temperature. Then the supernatant was removed and the resultant crystalline materials were washed with dichloromethane (3 mL) and treated with aqueous solution of 6 N HCl (3 mL), and the organic materials were extracted with dichloromethane (3mLx3). The combined organic layer was dried over $MgSO_4$. After filtration of in soluble materials, the filterate was concentrated *in vacuo* and the residue was purified by flash chromatography (*n*-hexane/ethyl acetate 5:1) to give **8**. Ee was determined after transformation **8** to **S1**.

- After 1h 1.65 mg 11 % yield, 0 % *ee*
- After 2h 4.5 mg 30 % yield, 11 % *ee*
- After 3.5h 9.3 mg 62 % yield, 24 % *ee*
- After 12h 13.8 mg 92 % yield, 50 % *ee*

■ Reactions with different amount of substrate at a given amount of MOF catalyst

To a suspension of (*R*)-**KUMOF-1** (102 mg, 0.27 mmol) in dichloromethane (1 mL) was added dimethyl zinc (0.4 mL, 2 M in dichloromethane, 0.80 mmol) at -78 °C. The resultant mixture was shaken for 3 h at this temperature. To this mixture was added a solution of **7** (a given amount) in dichloromethane (0.1 mL) at -78 °C. The reaction mixture was warmed to 0 °C and shaken for 12 h at this temperature. Then the supernatant was removed and the resultant crystalline materials were washed with dichloromethane (3 mL) and treated with aqueous solution of 6 N HCl (3 mL), and the organic materials were extracted with dichloromethane (3mLx3). The combined organic layer was dried over $MgSO_4$. After filtration of in soluble materials, the filterate was concentrated *in vacuo*. The reaction products were analyzed by GC. Ee was determined after transformation **8** to **S1**.

- 0.1 equivalent of substrate **8** 1.5 mg 91 % yield, 0 %*ee*
- 0.5 equivalent of substrate **8** 7.5 mg 90 % yield, 17 %ee
- 1.0 equivalent of substrate **8** 15 mg 89 % yield, 50 %*ee*

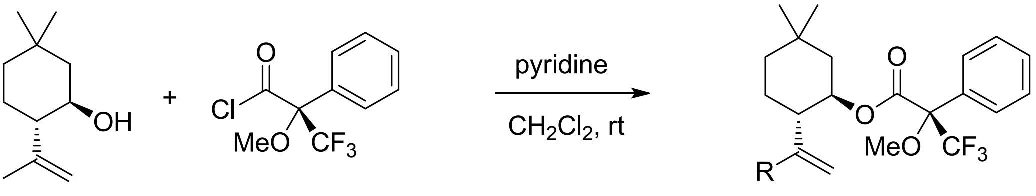
■ Reactions with different crystal size of MOF catalyst

To a suspension of (*R*)-**KUMOF-1** (102 mg, 0.27 mmol) in dichloromethane (1 mL) was added dimethyl zinc (0.4 mL, 2 M in dichloromethane, 0.80 mmol) at -78 °C. The resultant mixture was shaken for 3 h at this temperature. To this mixture was added a solution of **7** (15 mg, 0.089 mmol) in dichloromethane (0.1 mL) at -78 °C. The reaction mixture was warmed to 0 °C and shaken for 12 h at this temperature. Then the supernatant was removed and the resultant crystalline materials were washed with dichloromethane (3 mL) and treated with aqueous solution of 6 N HCl (3 mL), and the organic materials were extracted with dichloromethane (3mLx3). The combined organic layer was dried over $MgSO_4$. After filtration of in soluble materials, the filterate was concentrated *in vacuo* and the residue was purified by flash chromatography (*n*-hexane/ethyl acetate 5:1) to give **8**. Ee was determined after transformation **8** to **S1**.

- Micro sized (*R*)-**KUMOF-1**(3) 92 % yield, 0 % *ee*
- (*R*)-**KUMOF-1**(2) 89 % yield, 50 % *ee*
- (*R*)-**KUMOF-1**(1) 91 % yield, 70 % *ee*

■ Preparation of Mosher ester of **8** and ee Determination

Compound **8** was treated with (*S*)-(-)-MTPA-Cl and pyridine in dichloromethane to give its Mosher ester **S1**, which would be a diastereomeric mixture and would be subjected to gas chromatography for determining optical purity.



8   **S1**

Scheme S1. Transformation of product **9** into a diastereomeric mixture of Mosher's esters

(2*S*)-(1*S*,2*R*)-5,5-Dimethyl-2-(prop-1-en-2-yl)cyclohexyl 3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (**S1**) and its diastereomeric excess

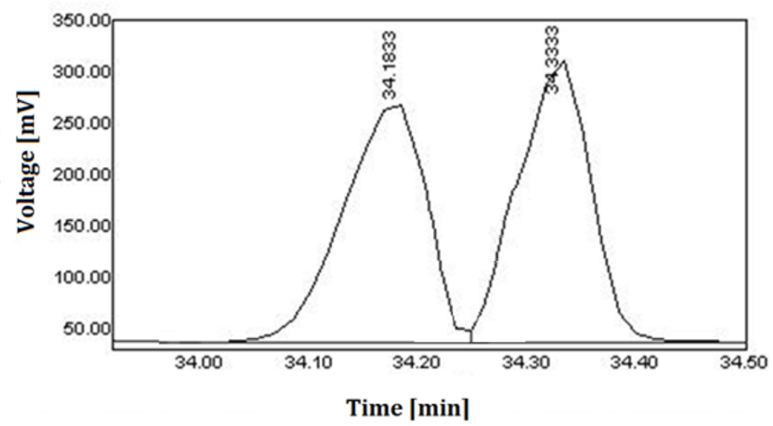
A mixture of **8** (5 mg, 0.030 mmol), pyridine (0.03 mL, 0.37 mmol) and (*S*)-(-)-α-methoxy-(α-trifluoromethyl)phenylacetyl chloride ((*S*)-(-)-MTPA-Cl: 36 μL, 0.20 mmol) in dichloromethane (1 mL) was stirred for 1 h in the presence of a catalytic amount of 4-dimethylamlnopyridine at room temperature. The mixture was poured into l N HCl (3 mL) and extracted with dichloromethane. The combined organic layer was concentrated in vacuo and the residue was purified by flash chromatography to give **S1** (7.5 mg, 65% yield). The diastereomeric ratio of MTPA esters was measured to be 60:40 by GC (180 ^{o}C) (t, = 34.31 and 34.48 min).

TLC (*n*-Hexane: ethyl acetate, 84:16 v/v): R_f = 0.4; Yield: 45%

GC Data

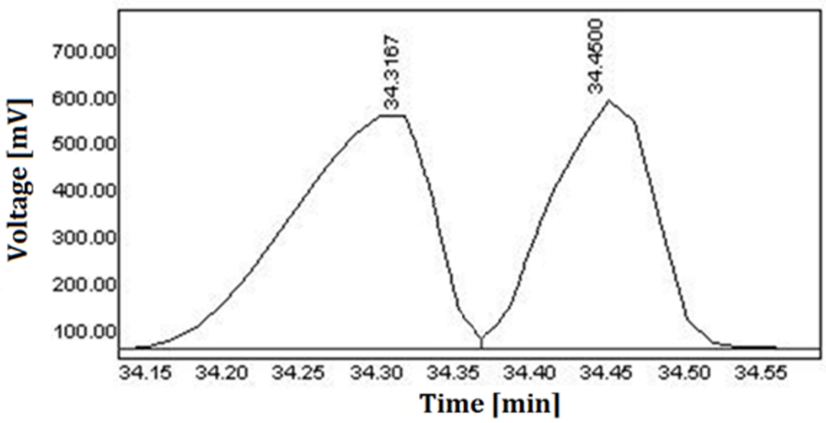
GC Analysis [CP-Chirasil-Dex CB Column, 25m, 0.25mm, 0.25μm, flow rate 1.4ml/min]

◆ After 1h 1.65 mg 11% yield, 0% *ee*



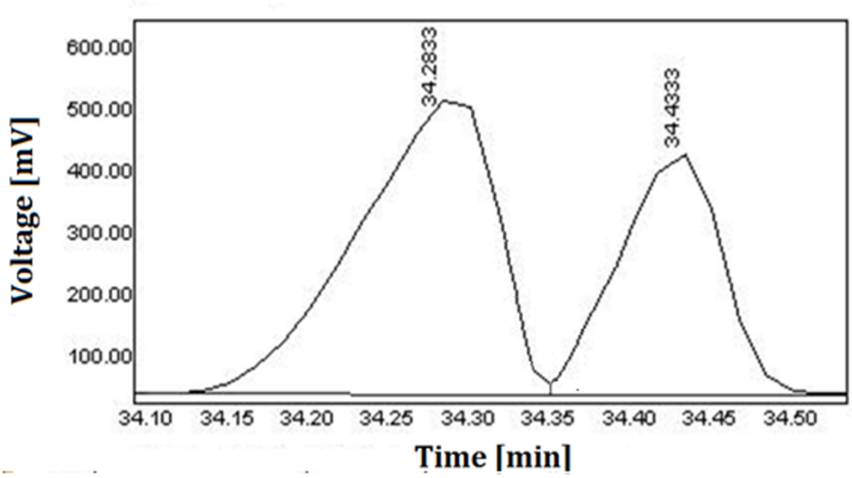
#	RT	Area[mV*sec]	Area ratio[%]
1	34.1833	1300.3597	50.17
2	34.3333	1291.7653	49.83
total		2592.1250	

◆ After 2h 4.5 mg 30%yield, 11% *ee*



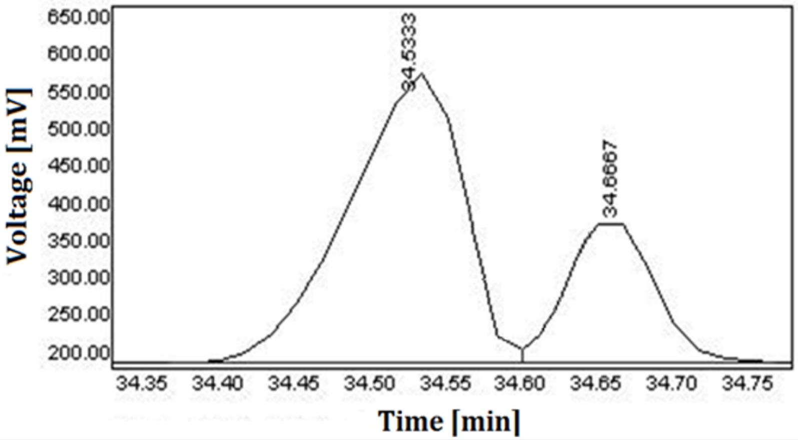
#	RT	Area[mV*sec]	Area ratio[%]
1	34.3167	3357.0183	55.59
2	34.4500	2682.0500	44.41
total		6039.0684	

- After 3.5h 9.3 mg 62%yield, 24% *ee*



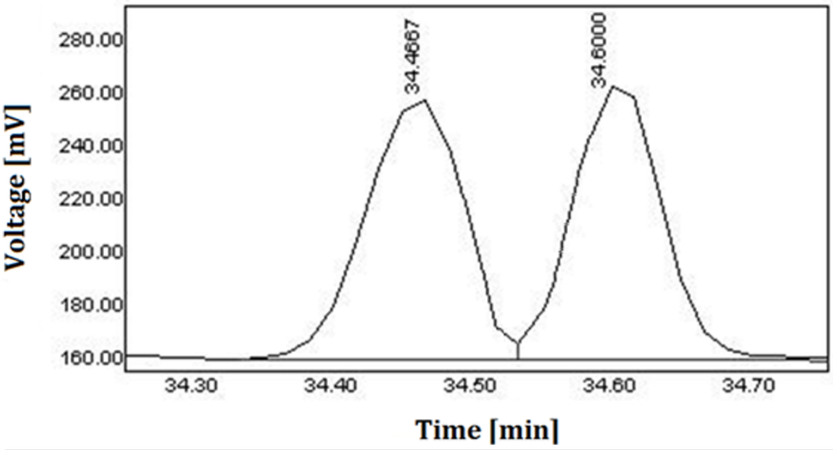
#	RT	Area[mV*sec]	Area ratio[%]
1	34.2833	2966.0024	61.89
2	34.4333	1826.5814	38.11
total		4792.5840	

- After 12h 13.8 mg 92%yield, 50% *ee*



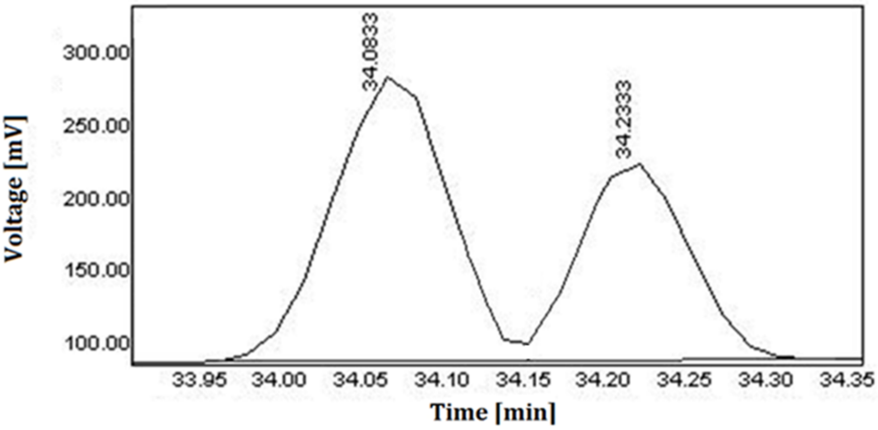
#	RT	Area[mV*sec]	Area ratio[%]
1	34.5333	1389.1079	75.72
2	34.6667	445.3715	24.48
total		1834.4795	

◆ 0.1 equivalent of substrate **8** 1.5 mg 91% yield, 0% *ee*



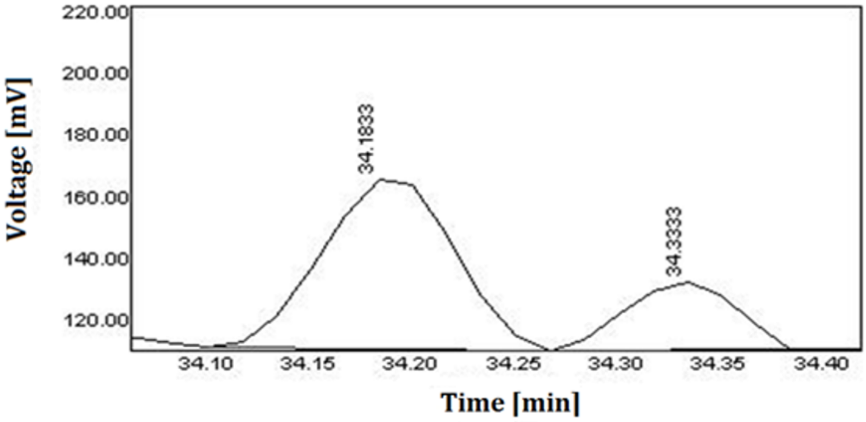
#	RT	Area[mV*sec]	Area ratio[%]
1	34.4667	500.1718	49.48
2	34.6000	510.7631	50.52
total		1010.9349	

◆ 0.5 equivalent of substrate **8** 7.5 mg 90% yield, 17% *ee*



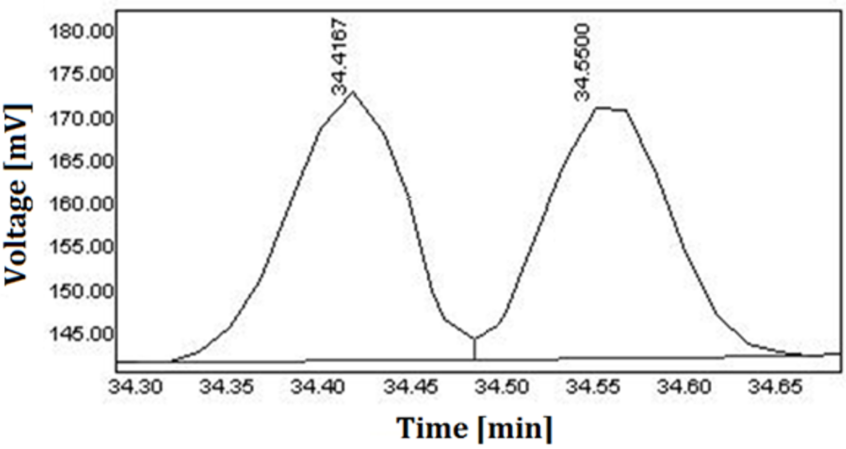
#	RT	Area[mV*sec]	Area ratio[%]
1	34.0833	652.0044	58.33
2	34.2333	465.6969	41.67
total		1117.7013	

◆ 1.0 equivalent of substrate **8** 15 mg 89% yield, 50% *ee*



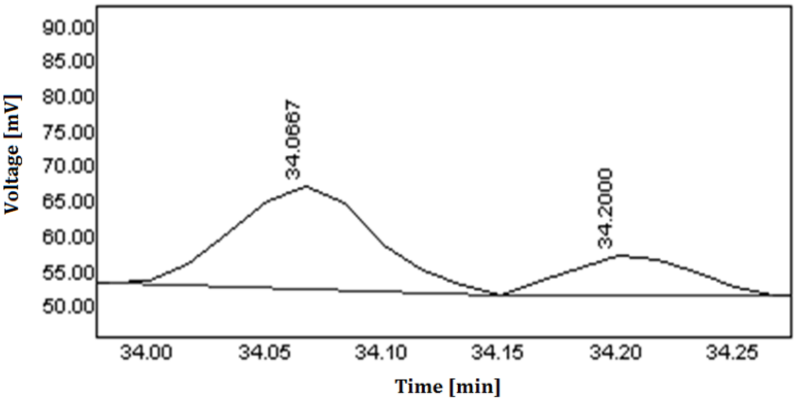
#	RT	Area[mV*sec]	Area ratio[%]
1	34.1833	248.0011	75.38
2	34.3333	81.0053	24.62
total		329.0064	

◆ Micro sized (*S*)-KUMOF-1 92% yield, 0% *ee*



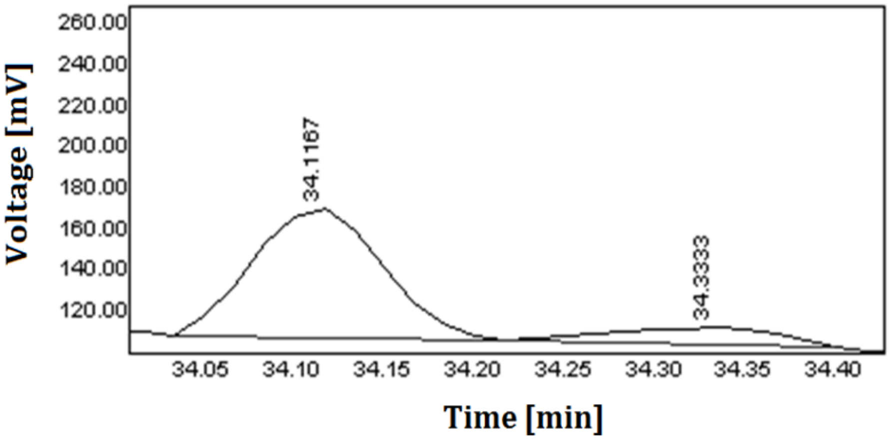
#	RT	Area[mV*sec]	Area ratio[%]
1	34.4167	147.2035	50.14
2	34.5500	146.3953	49.86
total		293.5988	

◆ (*S*)-KUMOF-1 89% yield, 50% *ee*



#	RT	Area[mV*sec]	Area ratio[%]
1	34.0667	61.2081	74.47
2	34.2000	20.9833	25.53
total		82.1914	

◆ (*S*)-KUMOF-1 91% yield, 70% *ee*



#	RT	Area[mV*sec]	Area ratio[%]
1	34.1167	315.4463	85.39
2	34.3333	53.9721	14.61
total		369.4184	