Supporting information

Addtive and Base free Tandem Aerobic Oxidative Cleavage of Olefins to Esters using Bifunctional Mesoporous Copper Incorporated Al-SBA-15

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S1. Experimental section

S1.1 Physicochemical Methods

Powder X-ray diffraction (PXRD) data were obtained using a PANalytical Empyrean (PIXcel 3D detector) system equipped with Cu Kα (λ=1.54 Å) radiation. The operating voltage and current were 40 kV and 30 mA, respectively. A step size of 0.04˚ with a step time of 2 seconds was used for data collection. FTIR analysis of the samples was recorded on self-supporting wafers prepared as KBr pellets using a Perkin-Elmer GX FTIR spectrometer in the region of 400−4000 cm^{-1} with KBr in a 1:20 weight ratio. The morphology of the synthesized catalyst was obtained by Scanning Electron Microscopy (SEM) images which were recorded on a JEOL JSM 7100F microscope, using an accelerating voltage of 18 kV and a probe current of 102 A. Samples were prepared by dispersing in isopropyl alcohol (IPA), and a drop of the suspension added to the SEM copper grid. The transmission electron microscopy (TEM), high-resolution TEM observation was acquired on JEOL, JEM 2100 with an electron acceleration energy of 200 kV. The samples were ultrasonically dispersed in IPA for 30 min and deposited on the carbon coated Lacey 200 mesh Cu grid and dried overnight. Specific surface area and pore size analysis of the samples were measured by nitrogen adsorption at -196 ˚C using a sorptometer (ASAP-2010, Micromeritics). The samples were degassed under vacuum at 200 ˚C for 3h before measurements to expel the interlayer water molecules. The X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Fisher Nexsa spectrometer equipped with monochromatic Al Kα radiation of energy 1486.6 eV. The pass energy for the survey was set at 400 eV and the pass energy for the narrow scan was set at 50 eV. The dual-beam charge neutralization was used for both low-energy electrons and ions. The sample surface is at a 90° angle with the axis of the input lens. Further, the individual core-level spectra were checked for charging using C1s at 284.8 eV as standard and corrected if needed. The peak fitting of the individual core levels was done using Avantage software. Hydrogen Temperature Programmed Reduction (H_2-TPR) analysis data were obtained using Micrometrics® Autochem II 2920 instrument. In the U-shaped quartz tube, 0.1 g of sample was placed over a layer of quartz wool. The catalyst was purged first with helium flow for 2 h and then cooled to ambient temperature. The catalysts were then exposed to a 50 $mL.min^{-1}$ flow of 20% H_2 in helium as the temperature was linearly increased to 900 °C at a 10 $°C.min^{-1}$ ramping rate. The thermal conductivity detector (TCD) observed the changes in the effluent's H_2 concentration.

Temperature-Programmed Desorption (TPD) of CO_2 was also performed on the Micrometrics® Autochem II 2920 instrument. 0.1 g of sample was placed in the U-shaped quartz tube over a layer of quartz wool. First, 25 mL.min^{-1} of helium flow was introduced for 60 min at 200 °C with a 5 °C.min^{-1} ramp rate. Afterward, the sample was cooled in 50 mL.min^{-1} helium flow till 100 °C. For adsorption of NH_3 and CO_2, 40 mL.min^{-1} flow of CO_2 in helium was introduced into the reactor at 100 °C for 30 min. Then, 40 mL.min^{-1} of helium flow was fed for 60 min to get rid of physically adsorbed species. Finally, desorption was studied with 5 °C·min^{-1} heating rate until 850 °C. Gases were analyzed on a TCD, with helium used as a reference gas. The reaction mixture was collected and analyzed using a gas chromatography system equipped with FID as a detector (GC-7890B-Agilent) with HP-5 column, consisting of 5% diphenyl and 95% dimethyl polysiloxane capillary stationary phase and nitrogen as the carrier gas. The appropriate diluted reaction mixture with tetradecane as an internal standard and analyzed on GC and a gas chromatography-mass spectrometry (equipped with FID as a detector (GC-MS Shimadzu, QP-2010, Japan) with HP-5 column which consists of 5% diphenyl and 95% dimethyl polysiloxane capillary phase with helium as the carrier gas. The ramp rate of initially 50 ºC hold for 3 mins, 20 ºC ramp to 320 ºC with 20 mins hold).

S2. Catalysis synthesis and catalytic activity

S2.1 Synthesis of Co-Al-SBA-15

The Co-Al-SBA-15 was synthesized by simple impregnation methods. In a 50 mL polypropylene bottle, 0.2 g of Al-SBA-15 and 0.098 g $Co(NO_3)_2.6H_2O$ dissolved into 10 mL deionized water and constantly stirred for 24 h at 400 rpm. After 24 h, the water is evaporated through rota evaporation and dried at 80 °C overnight. Finally, the catalyst was calcined at 550 °C at 5 h (2 °C/min) and denoted 2Cu-Al-SBA-15, 5 Cu-Al-SBA-15, and 10 Cu-Al-SBA-15, respectively.

S2.2 Oxidation of styrene to benzaldehyde

In a 15 mL glass tube, 2.40 mmol of styrene, 0.025 g of Cu-Al-SBA-15, 1 mL GVL added and heated at different temperatures while stirring at 400 rpm for about 12 to 24 h. After the reaction, the reaction mixture is centrifuged to separate the catalyst. Further, the liquid product was analyzed by GC and GC-MS.

S2.3 Esterification of benzoic acid with different alcohols

In a 30 mL glass tube, 2.40 mmol of styrene, 0.025 g of Cu-Al-SBA-15, 1 mL solvent added and heated at different temperatures while stirring at 400 rpm for about 12 to 24 h. After the reaction, the reaction mixture is centrifuged to separate the catalyst. Further, the liquid product was analyzed by GC and GC-MS.

Conversion and selectivity calculated by GC

Conversion (%) = [(Initial mol%)-(Final mol%)/(Initial mol%)

Selectivity (%) = [(moles of product formed)/(moles of substrate consumed)]*100

S3. Aerobic oxidation of styrene to benzaldehyde using mesoporous silica materials

Table S1 Aerobic oxidation of styrene to benzaldehyde using mesoporous silica materials

Sr. No.	Catalyst	Oxidant Additives	Reaction conditions	Conv .(%)	Sel./yield of benzaldehyde(%)	Ref.
1	Cu-Mn/SBA-15	TBHP	Styrene (10 mmol), TBHP (40 mmol), Cu-Mn/SBA-15 (20 mg), acetonitrile (10 mL), 7 h at 80 °C.	97.3	20	1
2	HCS-50	H_2O_2	Styrene (1 mmol), H_2O_2 (1.0 g), HCS-50 (50 mg), 24 h at RT.	100	42.24%	2
3	Fe_3O_4@SiO_2@ mSiO_2-Fe	H_2O_2	Styrene (10 mmol), H_2O_2 (10 mmol), Fe_3O_4@SiO_2@mSiO_2-Fe (100 mg), acetonitrile (10 mL), 10 h at 60 °C.	52.8	84.9%	3
4	IMM-TMICl-Ni(II)	H_2O_2	Styrene (1 mol), H_2O_2 (4 mol), F IMM-TMICl-Ni(II) (500 mg), acetonitrile (8 g), 6 h at 70 °C.	36.8	93.6	4
5	V-SBA-16	TBHP	Styrene (2.6 mmol), TBHP (2.6 mmol), V-SBA-16 (50 mg), acetonitrile (10 mL), 24 h at 80 °C.	83.9	55.5	5
6	PMo11Co/SBA	O_2/IBA	Styrene (1 mmol), Air (10 ml/min), PMo11Co/SBA (10 mg), IBA (2 mmol), 1 h at 40 °C.	89	15	6
7	Ti-Fe-SBA-15	H_2O_2	Styrene (15 mmol), H_2O_2 (75 mmol), Ti-Fe-SBA-15 (100 mg), acetonitrile (16 mL), 12 h at 70 °C.	37	86	7
8	**10Cu-Al-SBA-15**	**O_2**	**Styrene (2.40 mmol), 10Cu-Al-SBA-15 (25 mg), 1 mL GVL and 1 atm O_2 at 120 °C for 24 h**	**100**	**6**	**This work**

HCS-50: Trivalent ceria–silica composite, IMM-TMICl-Ni(II): Ni^{2+}-containing ionic liquid (IL) 1-methyl-3-[(triethoxysilyl)propyl] imidazolium chloride (TMICl) immobilized on silica, IBA: isobutyraldehyde

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S3.1 One-pot two step oxidative esterification of olefins to esters using homogeneous/heterogeneous catalyst

Table S2 One-pot two step oxidative esterification of olefins to esters using homogeneous/heterogeneous catalyst

Sr. No.	Catalyst	Oxidant Additives	Reaction conditions	Conv .(%)	Sel./yield(%)	Ref.
1[a]	1,2-dibutoxyethane	O_2, N,N′-dicyclohexylcarbodiimide	Styrene (0.6 mmol), solvent (4 equiv), heat, O_2 balloon, 12 h. (Step-1) and MeOH (0.6 mmol), N,N′-dicyclohexylcarbodiimide (0.9 mmol) and 4-dimethylaminopyridine (0.3 mmol), 8 h at RT. (Step-2)	-	85	1
2[b]	Tubular carbon nitride	O_2 and HCl	Styrene: (0.5 mmol), TCN (10 mg), and HCl (0.3 mL, 37 wt% aqueous) in MeOH (2 mL) were irradiated with a 250 W Xe lamp under oxygen at RT for 10 h	-	77	2
3[c]	Fe-NC-900	TBHP	Styrene (0.25 mmol), Fe-NC-900 (10 mol%), K_2CO_3 (20 mol%), TBHP (2.2 equiv.), MeOH (4 mL), 1.0 MPa O_2, 48 h, 150 °C.	-	84	3
4[c]	**10Cu-Al-SBA-15**	**O_2**	**Styrene (2.40 mmol), 10Cu-Al-SBA-15 (0.25 g), 1 mL GVL and 1 atm O_2 at 120 °C for 24 h, 600 rpm (Step-1). Further, 1 mL of MeOH added without addition of O_2 for 24 h at 65 °C, 600 rpm.**	**100**	**66**	**This work**

[a]Homogeneous catalyst system, [b] photocatalytic conversion, [c]thermochemical catalytic conversion

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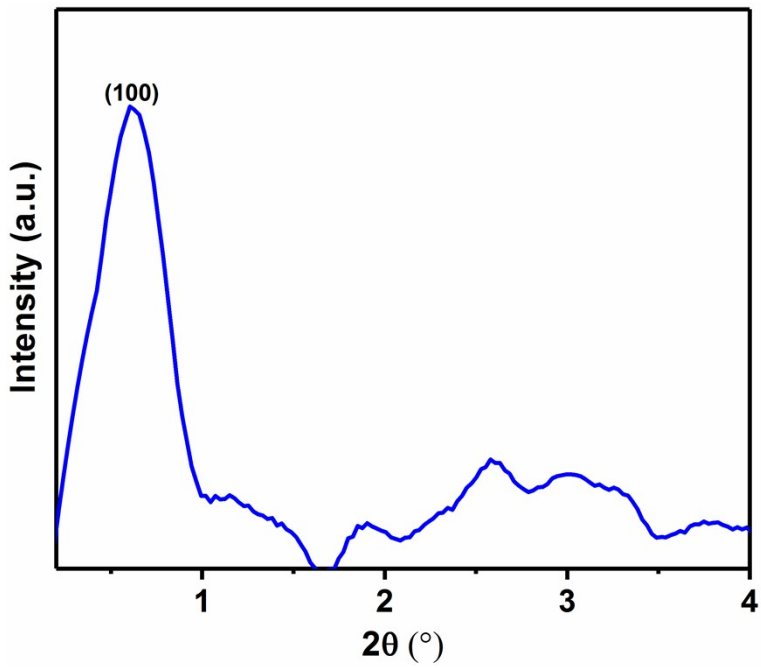

Fig. S1 Low angle PXRD spectra of Al-SBA-15

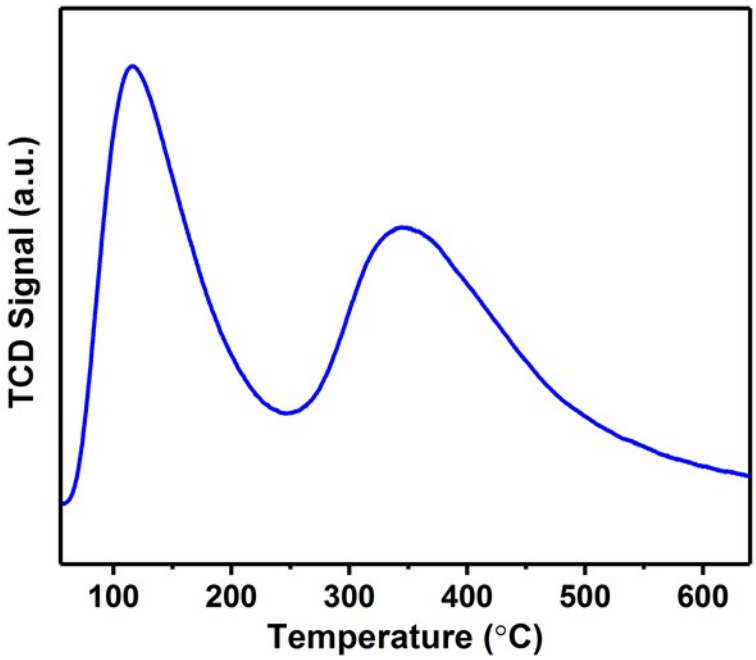

Fig. S2 CO_2-TPD spectrum of 10Cu-Al-SBA-15

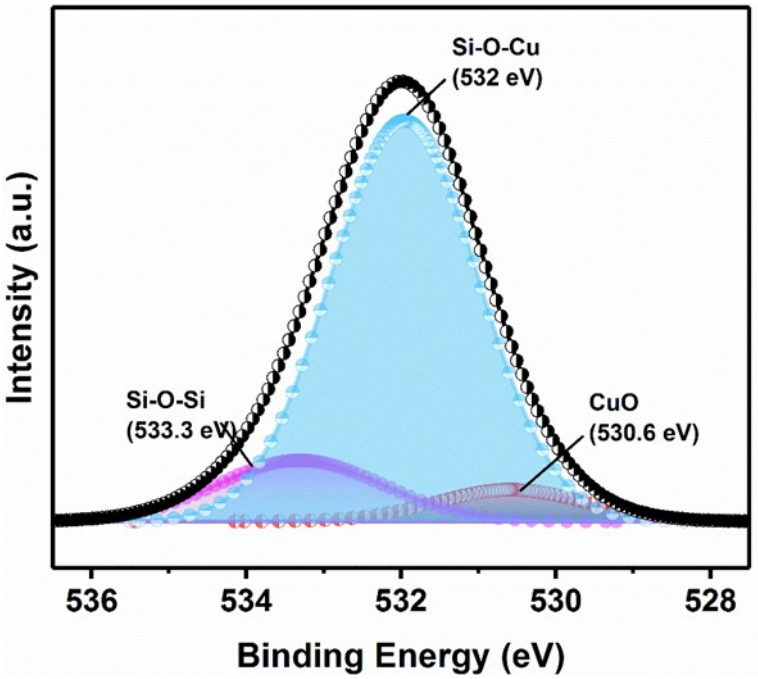

Fig. S3 High-resolution XPS spectra O 1s of the 10Cu-Al-SBA-15

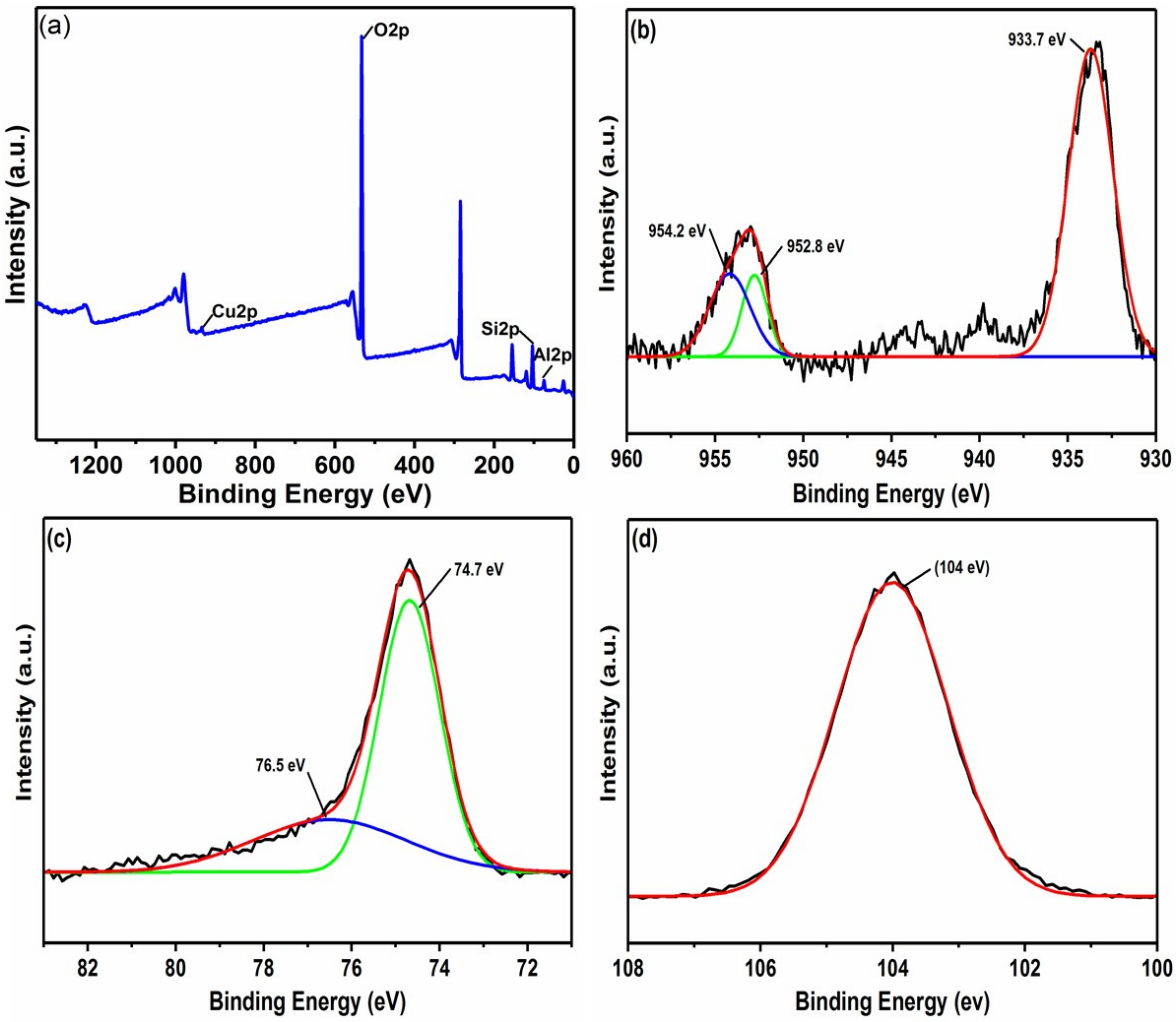

Fig. S4 (a) Survey spectra of the spent 10Cu-Al-SBA-15 catalyst. High-resolution XPS spectra (b) Cu 2p peak, (c) Al 2p peak, (d) Si 2p of the 10Cu-Al-SBA-15.

S4. GC-MS spectrum

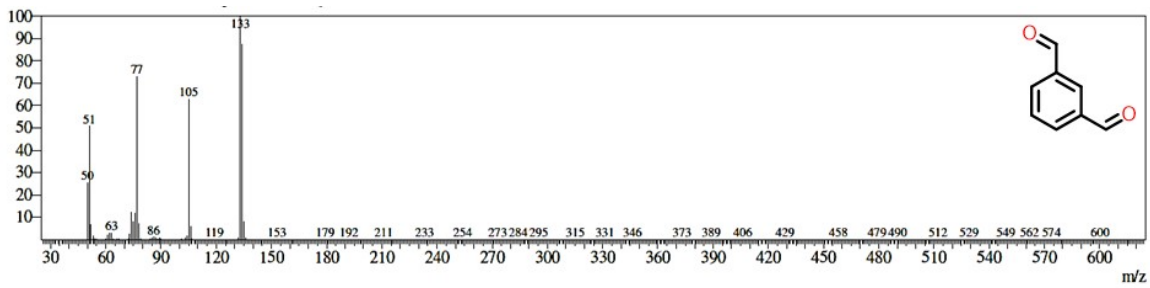

Fig. S5 GC-MS spectrum of isophthalaldehyde

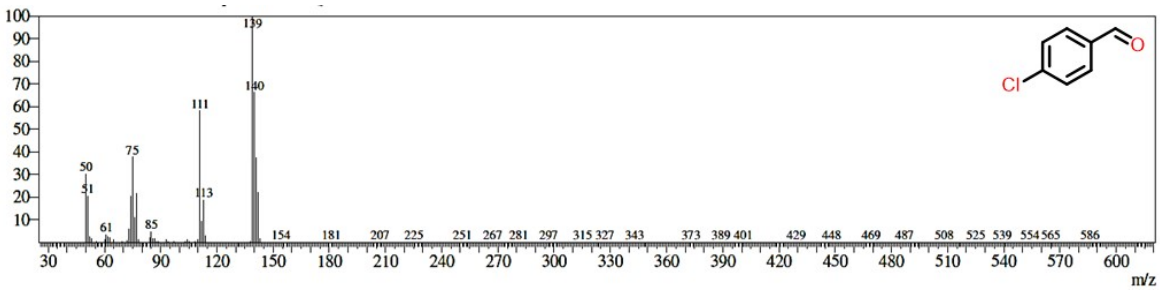

Fig. S6 GC-MS spectrum of 4-chlorobenzaldehyde

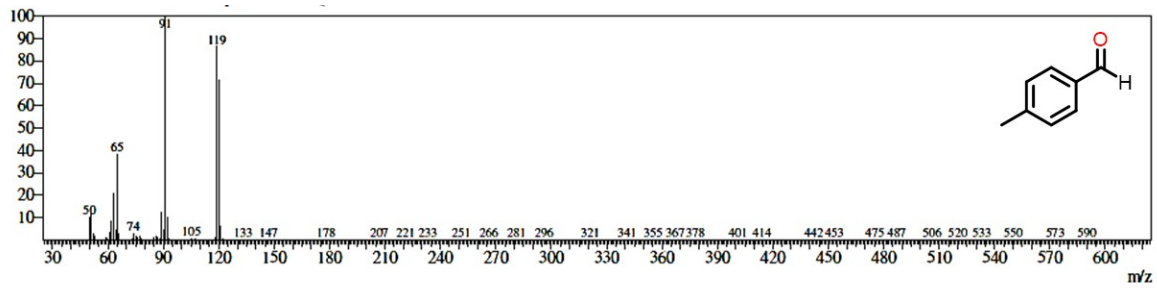

Fig. S7 GC-MS spectrum of 4-methylbenzaldehyde

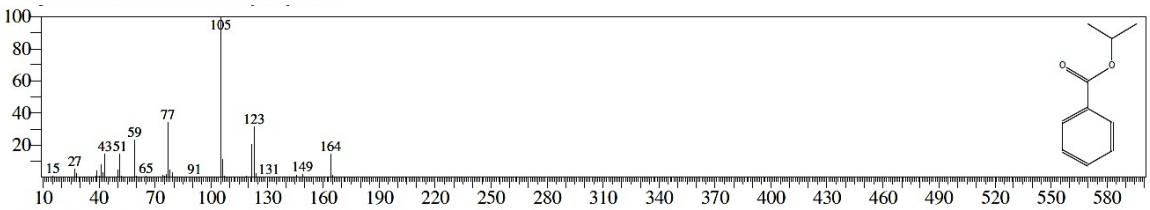

Fig. S8 GC-MS spectrum of isopropyl benzoate

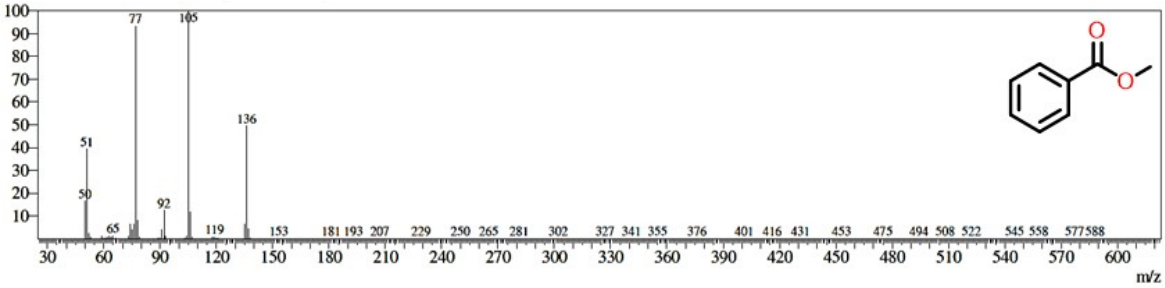

Fig. S9 GC-MS spectrum of methyl benzoate

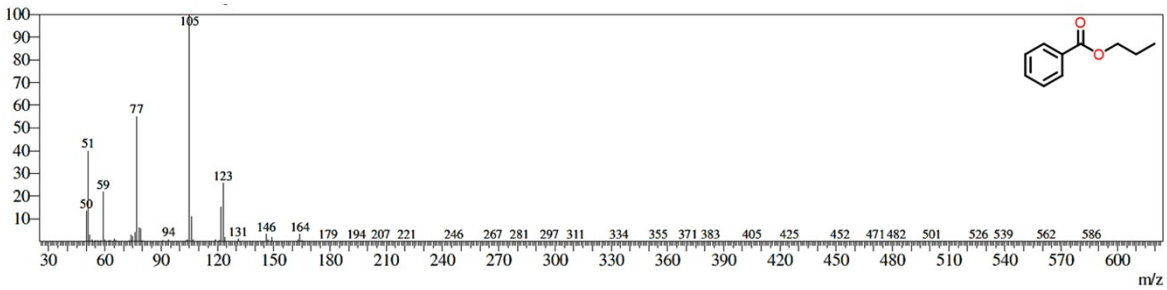

Fig. S10 GC-MS spectrum of propyl benzoate

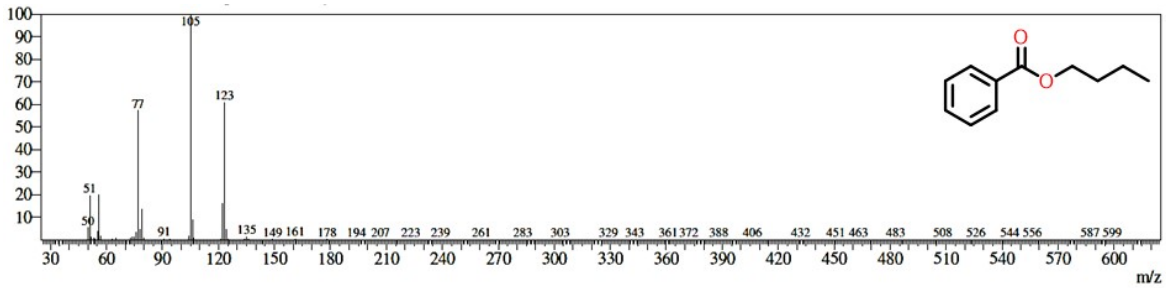

Fig. S11 GC-MS spectrum of butyl benzoate