Electronic Supplementary Material (ESI) for RSC Advances.

Supporting materials

Novel Non-hydrolytic Templated Sol-Gel Synthesis of Mesoporous Aluminosilicates and Their Use as Aminolysis Catalysts

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Table 1S. Crystallographic data of structure **1**

Crystal data	
Chemical formula	$C_{16}H_{46}AlNO_5Si_4$
M_r	471.88
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	120
a, b, c (Å)	17.8823 (3), 19.5954 (3), 17.8056 (3)
β (°)	100.948 (2)
V (Å^3)	6125.72 (18)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.24
Crystal size (mm)	0.12 × 0.12 × 0.10
Data collection	
Diffractometer	AFC11 (Right): Eulerian 3 circle diffractometer
T_{min}, T_{max}	0.891, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	72044, 11625, 9324
R_{int}	0.039
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.610
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.049, 0.142, 1.04
No. of reflections	11625
No. of parameters	677
No. of restraints	639
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.66, −0.52

Computer programs: *CrystalClear*-SM Expert 2.0 r15 (Rigaku, 2011), *CrysAlis PRO*, Agilent Technologies, Version 1.171.37.35 (release 13-08-2014 CrysAlis171 .NET) (compiled Aug 13 2014,18:06:01), *SHELXL2014*/7 (Sheldrick, 2014).

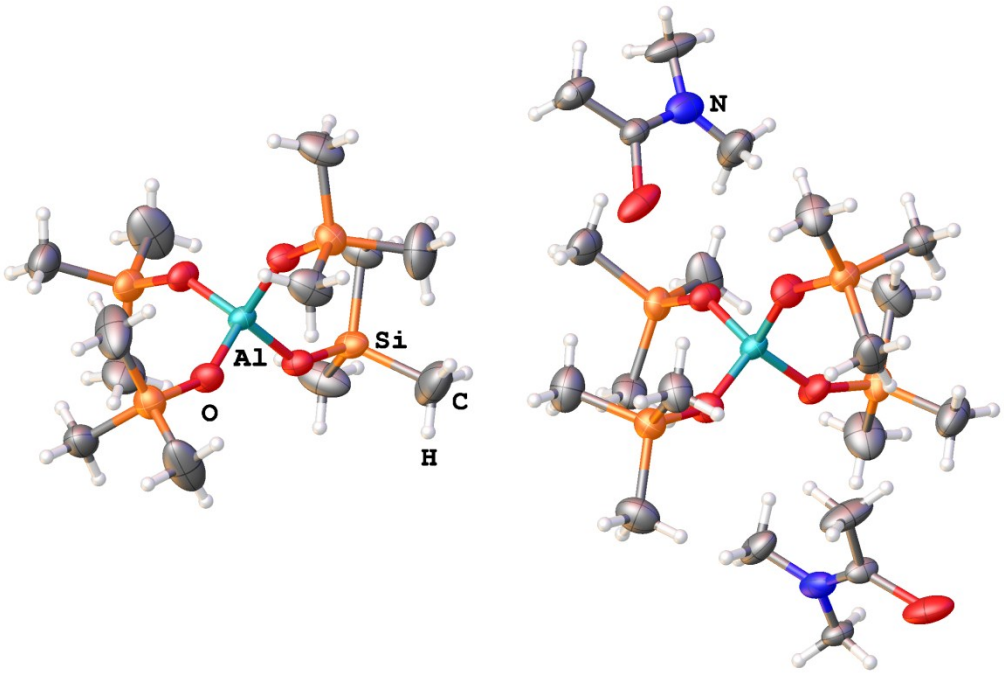

Fig. 1S Crystal structure of $[Me(C)OHNMe_2]^+$ $[Al(OSiMe_3)_4]^-$ (**1**). The temperature ellipsoids are displayed at 50% probability level. Only the first parts of disordered moieties are displayed for clarity.

The structure was solved using *SHELXT* program and refined (full matrix least-squares refinement on F^2) using *SHELXL* program. Both symmetrically independent cation fragments were disordered; the correct orientation of each part was selected according to electron densities at terminal positions, the largest densities were assigned to oxygen atoms. The electroneutrality condition requires the dimethylacetamide to be protonated; however relevant hydrogen atoms could not be located in the difference Fourier map. The protonation of Me_2N– fragments is unlikely, because the observed electron density at the position of disordered cations is rather planar. Also the refinement with protonated oxygens did not lead to a reasonable model and the location of proton remains uncertain. One Me_3Si- moiety of one anionic fragment was also refined as disordered. Disordered fragments were treated by geometrical similarity restraints and by ADP restraints and the sum occupancies of relevant fragments were set to 1. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms (of methyl and hydroxyl groups) were placed at calculated positions and refined as riding and rotating, with their U_{iso} set to 1.5 U_{eq} of carrier atom.

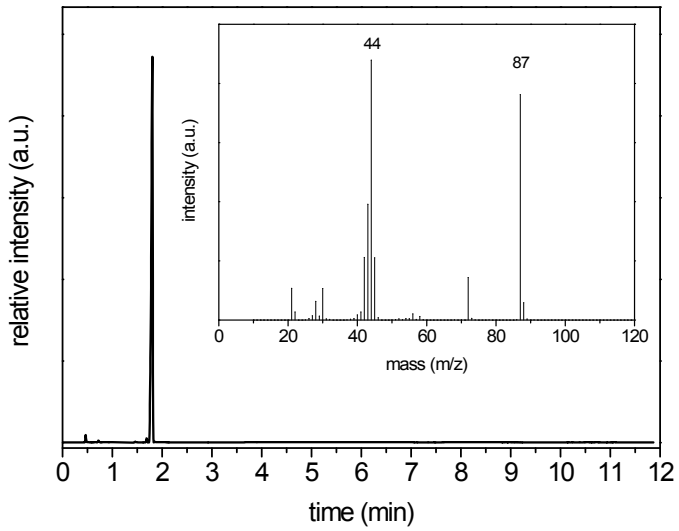

Fig. 2S GC-MS of byproducts separated from templated sol-gel reaction SiAlF2. The inset represents mass spectrum of N,N-dimethylacetamide (r.t. 1.8 min)

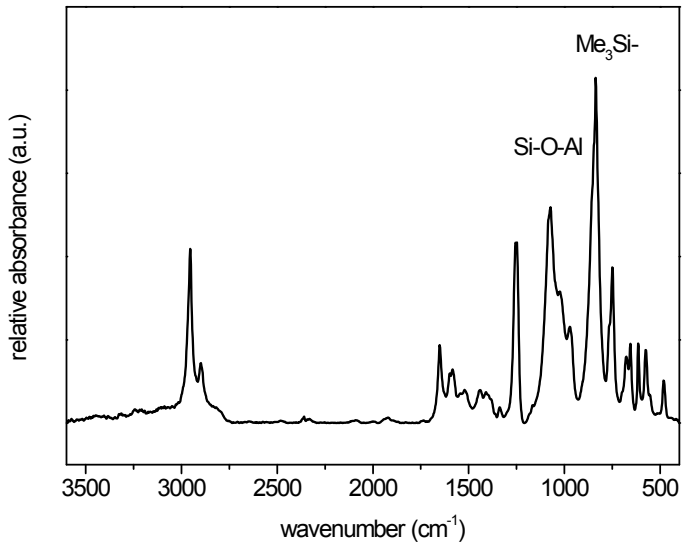

Fig. 3S IR spectra of $[Me(C)OHNMe_2]^+$ $[Al(OSiMe_3)_4]^-$ (**1**)

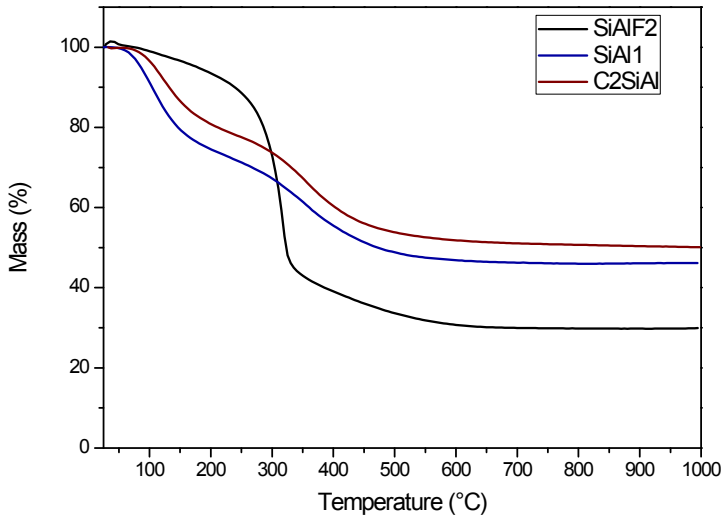

Fig. 4S TG curves of aluminosilicate xerogels

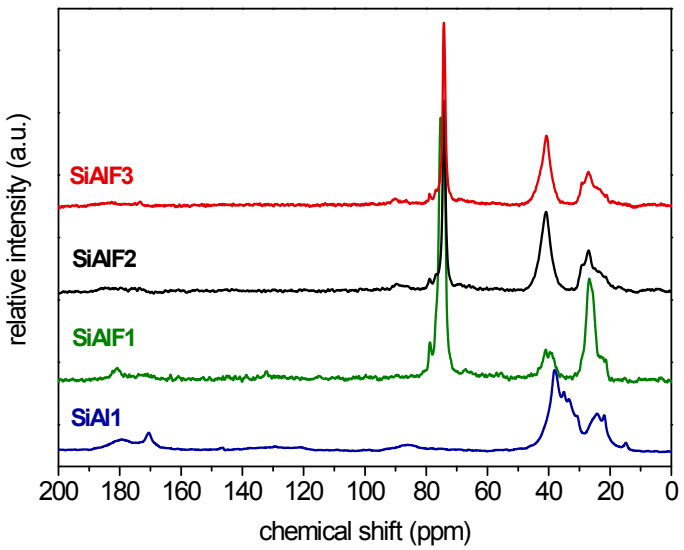

Fig. 5S ^{13}C CPMAS NMR spectra of dried aluminosilicate xerogels. The signals represent residual organic groups and copolymer template

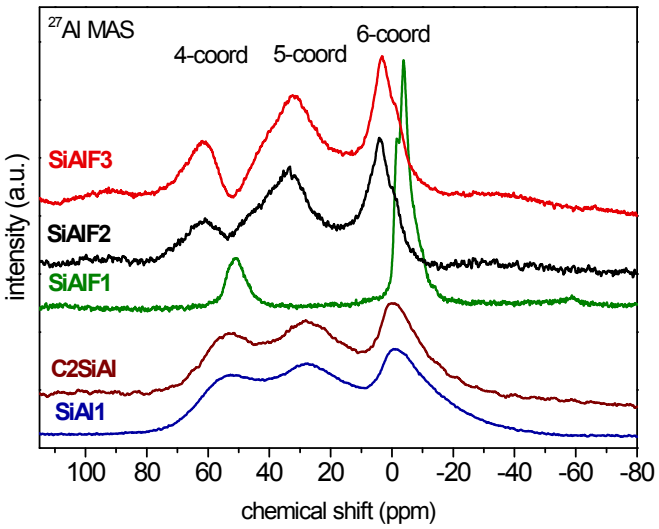

Fig. 6S ^{27}Al MAS NMR spectra of dried aluminosilicate xerogels

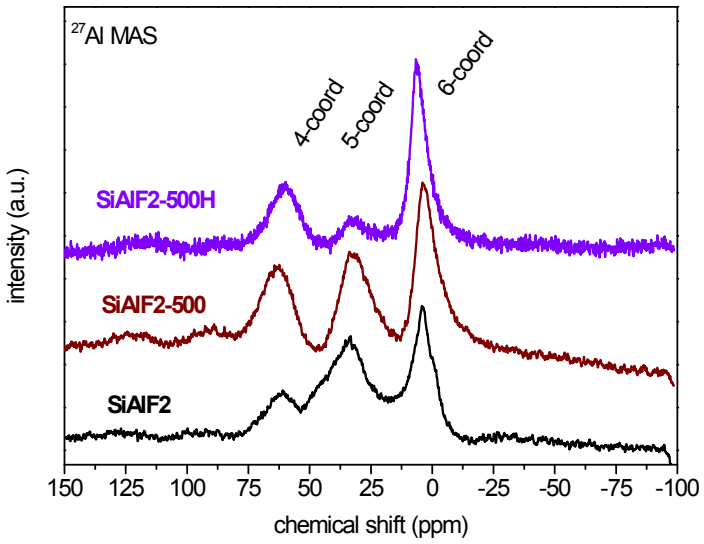

Fig. 7S ^{27}Al MAS NMR spectra of SiAlF2, SiAlF2-500, and SiAlF2-500H xerogel after treatment in boiling water

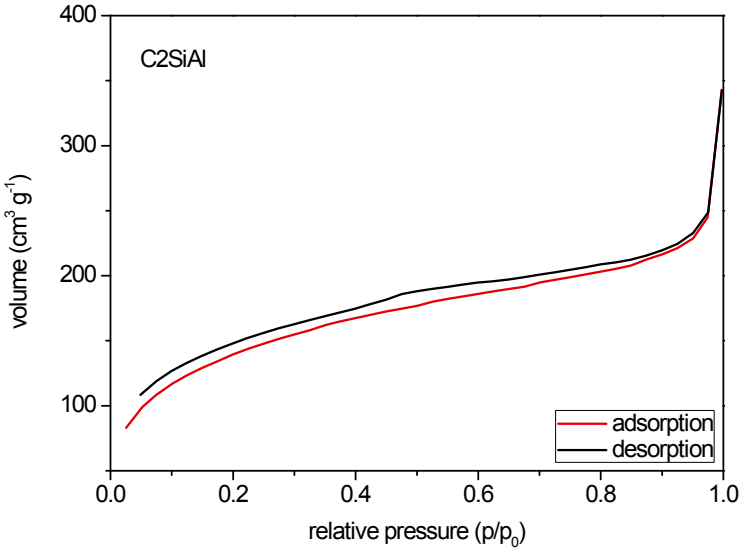

Fig. 8S N_2 Adsorption/desorption isotherm of the dried sample prepared from $(AcO)_3Si(CH_2)_2Si(OAc)_3$

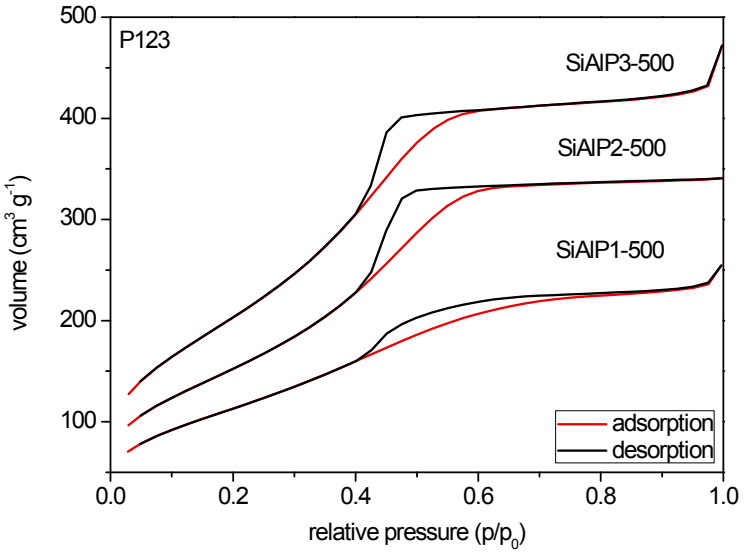

Fig. 9S N_2 Adsorption/desorption isotherms of the calcined aluminosilicate xerogels prepared with P123 template

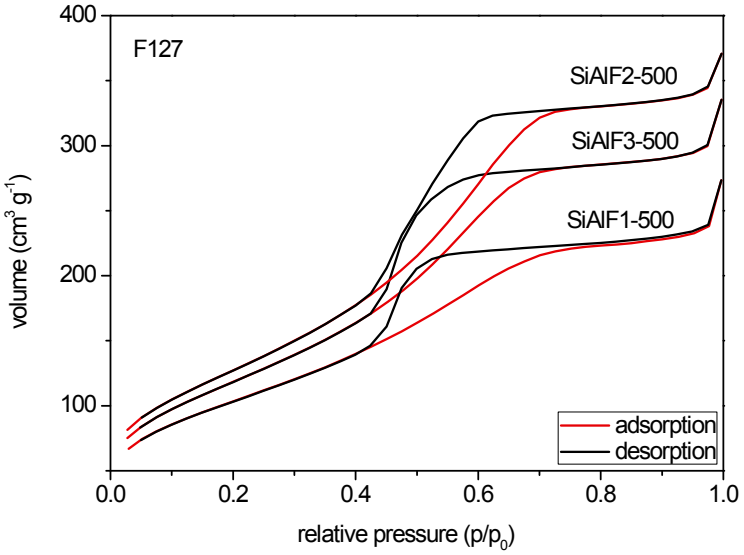

Fig. 10S N_2 Adsorption/desorption isotherms of the calcined aluminosilicate xerogels prepared with F127 template

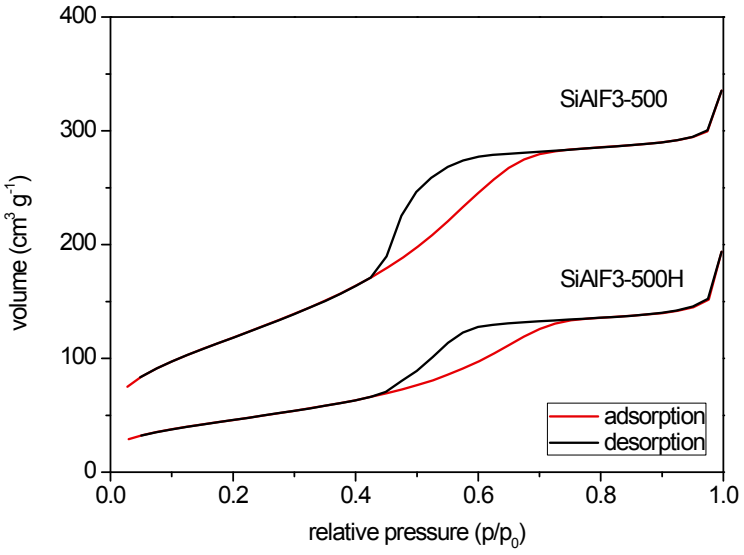

Fig. 11S N_2 Adsorption/desorption isotherms of the calcined sample SiAlF3-500 and water treated sample SiAlF3-500H

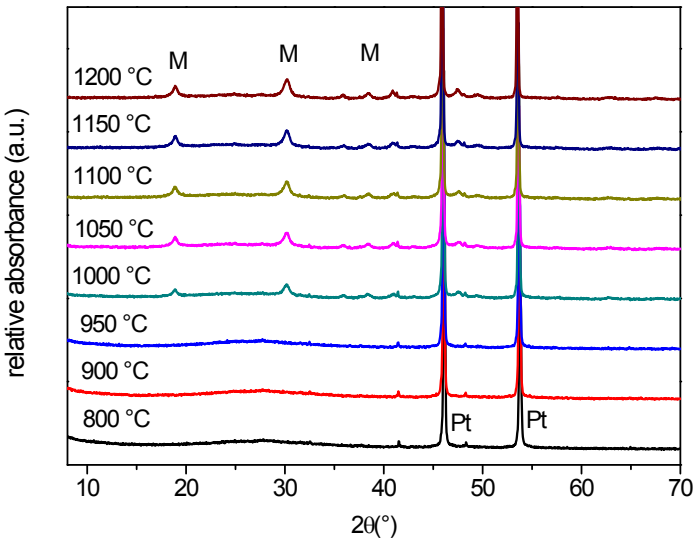

Fig. 12S High temperature powder XRD of calcined aluminosilicate (SiAlF2-500). Diffractions labeled as M are attributed to mullite.

Catalysis

Aminolysis of styrene oxide

Conditions: 25 mg of calcined aluminosilicate xerogel, 5 mmol of substrates, 5 cm^3 of toluene, 50 °C.

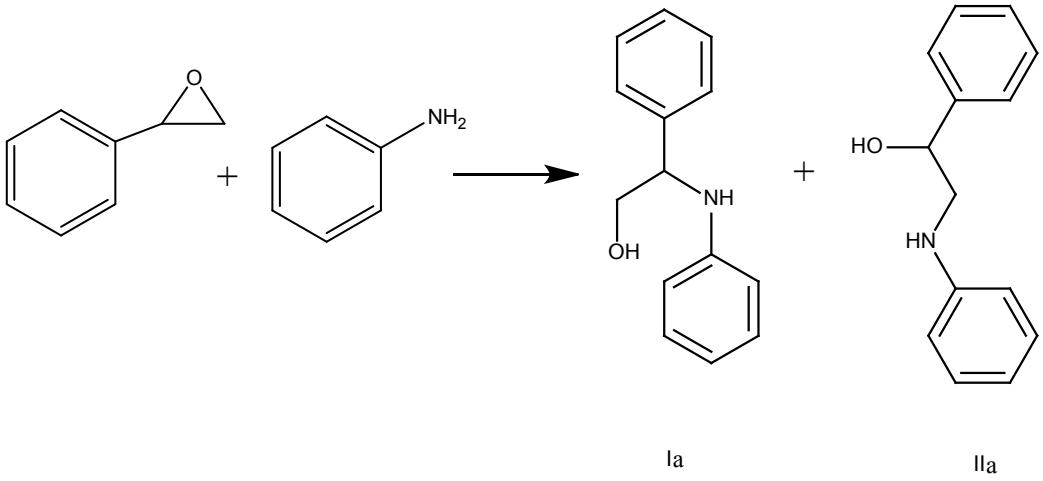

Fig. 13S Aminolysis of styrene oxide with aniline

Alcoholysis of styrene oxide

Conditions: 25 mg of calcined aluminosilicate xerogel, 5 mmol of substrates, 5 cm^3 of toluene, 50 °C.

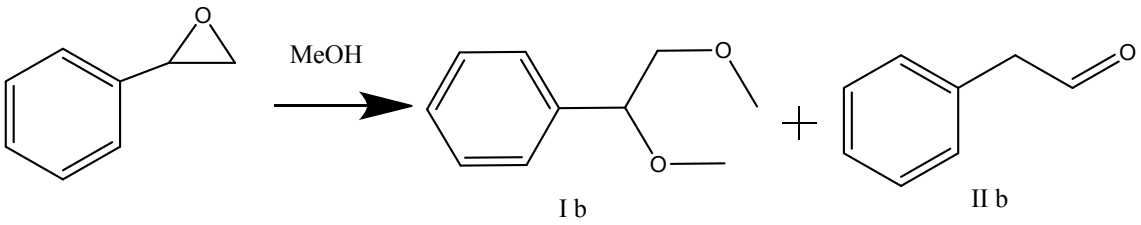

Fig. 14S Alcoholysis of styrene oxide with MeOH

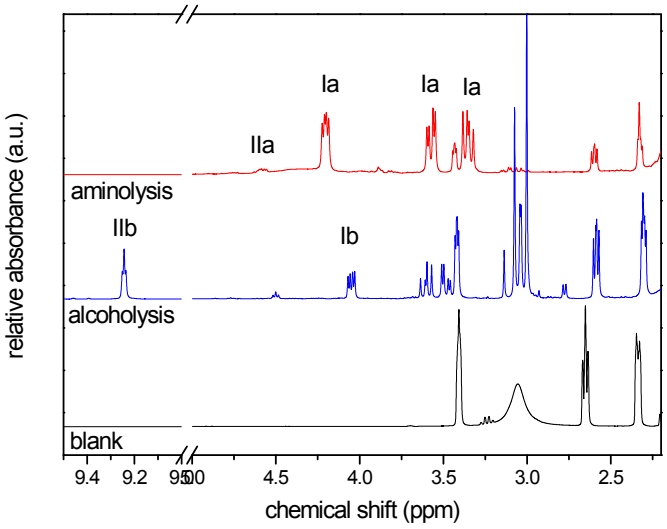

Fig. 15S ^{1}H NMR spectra of catalytic reaction mixtures after alcoholysis (blue) and aminolysis (red) of styrene oxide with aniline. The bottom spectrum represents blank reaction.

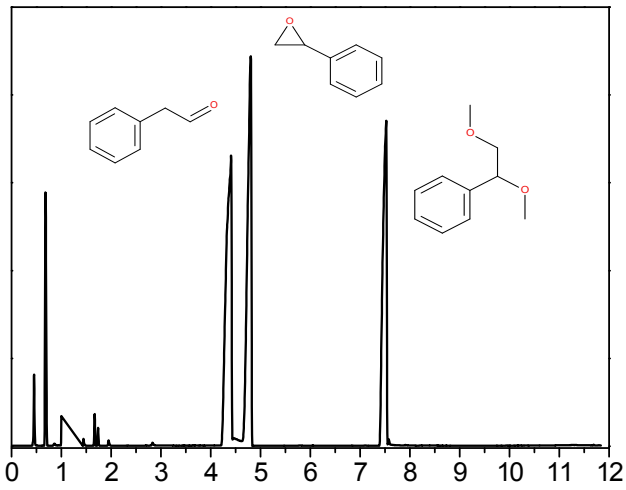

Fig. 16S GC chromatogram of alcoholysis reaction mixture