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Supporting information for

Trifunctional Mesoporous Silica-Based, Highly Active Catalyst for One-Pot, Three-Step Cascade Reactions

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1. Materials and reagents

Toluene, tetraethoxysilane (TEOS), 3-aminopropyltriethoxysilane (APTS, 99%), 3-marcaptopropyltriethoxysilane (MPTS, 95%), hexamethyldisilazane (HMDS), benzaldehyde dimethyl acetal was purchased from Sigma-Aldrich, and they used as received without further purification. Anhydrous ethanol and hydrochloric acid solution (~36 wt. %) were obtained from Fisher-Scientific. The triblock co-polymer Pluronics-123 ($(PEO)_{20}(PPO)_{70}(PEO)_{20}$) was obtained from BASF.

2. Characterization methods

Thermogravimetric analyses (TGA) of the materials were performed using a Q50 Thermogravimetric Analyzer (TA Instruments) at a temperature ramp of 10 °C/min from room temperature to 700 °C under a flow of nitrogen gas. The BET gas adsorption–desorption measurements were carried out with Micromeritics Tristar 3000 volumetric adsorption analyzer after degassing the samples at 160 °C for 12 h prior to measurements. Transmission electron microscopy (TEM) images were taken with a JEOL 2011 microscope operated at 200 kV. The samples for TEM imaging were prepared by dispersing the materials in ethanol, and then placing a few drops of the dispersion on carbon-film-covered copper grids and letting them to dry under ambient conditions. Solid-state ^{13}C CP-MAS and ^{29}Si MAS NMR spectra were obtained using a 300 MHz Brüker Avance NMR spectrometer. For ^{29}Si MAS NMR experiments, 8.0 kHz spin rate, 5 s recycle delay, 10 ms contact time, $\pi/2$ pulse width of 5.6 μs, and 10000-20000 scans using TPPM 1H decoupling were employed. For ^{13}C CP-MAS NMR experiments, 8.0 kHz spin rate, 5 s recycle delay, 1.5 ms contact time, $\pi/2$ pulse width of 4.8 μs, and 10,000 scans using TPPM ^1H decoupling were employed. Solution ^1H and ^{13}CNMR spectra were obtained using a Brüker DPX-300 NMR spectrometer.

3. Synthesis of the trifunctional catalysts

A. Synthesis of SBA-15 and Cap-SBA-15. SBA-15 was synthesized by following the original procedure reported by Stucky and co-workers,[1] with a minor modification.[2] A solution of 12 g of Pluronics-123, 313 g Millipore water and 72 g HCl (~36 wt. %) was prepared and stirred vigorously at 40 °C until all the Pluronic-123 was dissolved. After adding 25.6 g of TEOS, the solution was stirred at 45 °C for 24 h. The solution was then kept under static conditions at 80 °C in oven for another 24 h to age. The resulting reaction mixture was filtered, and the precipitate was washed with copious amount of water and dried under ambient conditions. This produced as-synthesized SBA-15 mesostructured material. To graft the external surface of the mesostructured material with methyl groups, 4.0 g of this as-synthesized SBA-15 was suspended in a solution containing 30 mL of HMDS and 300 mL of toluene. The solution was then mildly stirred for 8 h at room temperature in order to functionalize the external Si-OH groups of the as-synthesized SBA-15 with $-Si(CH_3)_3$ (or -Me) groups. The solid sample was recovered by filtration, washed with toluene and ethanol (2x10 mL in each case), and then let to dry under ambient conditions. This resulted in SBA-15 material containing -Me functional groups on its outer surfaces. It was then calcined in a tube furnace at 350 ºC for 5 h under the flow of air to remove the Pluronics 123 templates from its mesopores, without compromising the grafted -Me groups. The resulting mesoporous SBA-15, whose external surfaces were capped with -Me groups but still had free -Si-OH groups in its mesopores, was denoted as Cap-SBA-15.

B. Synthesis of amine-functionalized SBA-15 (APTMS-SBA-15). The Cap-SBA-15 synthesized above was dried in an oven for 12 h at 80 °C before being grafted with organoamine groups. The well-dried Cap-SBA-15 (2 g) was stirred in a solution of 2 mL of APTS in 150 mL of toluene for 6 h at 80 °C to graft its mesoporous channel surfaces with primary amine groups. After filtration and washing with anhydrous ethanol (3x10 mL), the resulting sample was left to dry under ambient conditions. These procedures gave the amine-functionalized SBA-15 material, labelled as NH_2-SBA-15.

C. Synthesis of SH-NH_2-SBA-15. The Cap-NH_2SBA-15 synthesized above was dried in an oven for 12 h at 80 °C before being grafted with amine groups. The well-dried Cap-NH_2SBA-15 (1.5 g) was stirred in a solution of 3-marcaptopropyltriethoxysilane (MPTS) (1.5 mL) in 150 mL of toluene for 6 h at 80 °C to graft its mesoporous channel surface with organothiol groups. After filtration and washing with anhydrous ethanol (3x10 mL), the resulting material was left to dry under ambient conditions. These procedures produced the thiol and amine co-functionalized SBA-15 material labelled as SH-NH_2-SBA-15.

D. Oxidation of -SH groups in SH-NH_2-SBA-15 to -SO_3H groups. In order to convert the thiol groups SH-NH_2-SBA-15 to sulfonic acids, 2 g of the above-synthesized SH-NH_2-SBA-15 was dispersed in a solution containing acetic acid (50.0 mL) and 30 % H_2O_2 (40.0 mL) and stirred at 100 ºC for 6 h. The dispersion was filtered, and the solid product was washed with distilled water and let to dry overnight at room temperature. The resulting material was named as SO_3H-NH_2-SBA-15.

E. Loading Pd nanoparticles into SO_3H-NH_2-SBA-15. The SO_3H-NH_2-SBA-15 material (500 mg) was dispersed in 20 mL of distilled water via sonication. Then, 500 μL of 0.05 M aqueous solution of K_2PdCl_4 was slowly added, and the mixture was stirred at room temperature for 30 min to let Pd(II) ions anchor onto the NH_2 groups of SO_3H-NH_2-SBA-15. Then, 1000 μL of 1 M $NaBH_4$ (aq) solution was added. This caused the solution to change its color from yellowish to black, indicating the transformation of the Pd(II) ions to Pd(0) or Pd nanoparticles. The solid material was separated by filtration and washed twice with 3 x 20 mL distilled water and dried at room temperature in a desiccator. These procedures finally led to the organosulphonic acid, amine and Pd nanoparticles co-functionalized SBA-15 material, or the trifunctional catalyst denoted as Pd-SO_3H-NH_2-SBA-15.

4. Synthesis of the control (or monofunctional) catalysts

The corresponding three monofunctional (control) catalysts, namely amine-functionalized SBA-15 (APTMS-SBA-15), sulphonic acid-functionalized SBA-15 (SO_3H-SBA-15), and Pd-nanoparticles functionalized SBA-15 (Pd-SBA-15), were prepared, and the catalytic activity of their physical mixture toward the tandem reaction was tested. To prepare the three catalysts the following procedures were employed.

A. Synthesis of amine-functionalized SBA-15 (APTMS-SBA-15). The Cap-SBA-15 synthesized above was dried in an oven for 12 h at 80 °C before being grafted with organoamine groups. From the well-dried Cap-SBA-15, 0.3 mg material was taken and stirred in a solution of 0.3 mL of APTS in 50 mL of toluene for 6 h at 80 °C to graft its mesoporous channel surfaces with primary amine groups. After filtration and washing with anhydrous ethanol (3x10 mL), the resulting sample was left to dry under ambient conditions. These procedures gave the amine-functionalized SBA-15 material, labelled as NH_2-SBA-15.

B. Synthesis of to -SO_3H functionalized SBA-15. The Cap-SBA-15 synthesized above was dried in an oven for 12 h at 80 °C before being grafted with amine groups. The well-dried CapSBA-15 (0.3 g) was stirred in a solution of 3-marcaptopropyltriethoxysilane (MPTS) (0.2 mL) in 150 mL of toluene for 6 h at 80 °C to graft its mesoporous channel surface with organothiol groups. After filtration and washing with anhydrous ethanol (3x10 mL), the resulting material was left to dry under ambient conditions. These procedures produced the thiol-functionalized SBA-15 material labelled as SH-SBA-15.

Subsequently, the -SH groups in SH-SBA-15 were oxidized to -SO_3H groups. In order to convert the thiol groups SH-SBA-15 to sulfonic acids, 0.2 g of the above-synthesized SH-SBA-15 was dispersed in a solution containing acetic acid (20 mL) and 30% H_2O_2 (10 mL) and stirred at 100 ºC for

6 h. The dispersion was filtered, and the solid product was washed with distilled water and let to dry overnight at room temperature. The resulting material was named as SO_3H-SBA-15.

C. Synthesis of Pd nanoparticles containing Cap-SBA-15. The Cap-SBA-15 material (300 mg) was dispersed in 20 mL of distilled water via sonication. Then, 300 μL of 0.05 M aqueous solution of K_2PdCl_4 was slowly added, and the mixture was stirred at room temperature for 30 min. Then, 500 μL of 1 M $NaBH_4$ (aq) solution was added. This caused the solution to change its color from yellowish to black, indicating the transformation of the Pd(II) ions to Pd(0) or Pd nanoparticles. The solid material was separated by filtration and washed twice with 3 x 20 mL distilled water and dried at room temperature. These procedures finally led to Pd nanoparticles-functionalized SBA-15 material (Pd-SBA-15).

D. Catalytic activity. The catalytic property of the physically mixed, three monofunctional catalysts toward the one-pot, cascade deacetylation-Henry-hydrogenation reactions was then tested (Scheme S1). To carry this out, 50 mL three-necked round-bottom flask was charged with benzaldehyde dimethyl acetal (0.01 mol), water (0.02 mol), catalyst (30 mg (SO_3H-SBA-15, NH_2-SBA-15 and pd-SBA-15 10 mg each) and nitromethane (10 mL). The reaction mixture was stirred at 90 ºC for desired time in oil bath under balloon pressure or 50 mL Parr reactor in 2 bar H_2 pressure (see Table S1).

FT-IR spectra

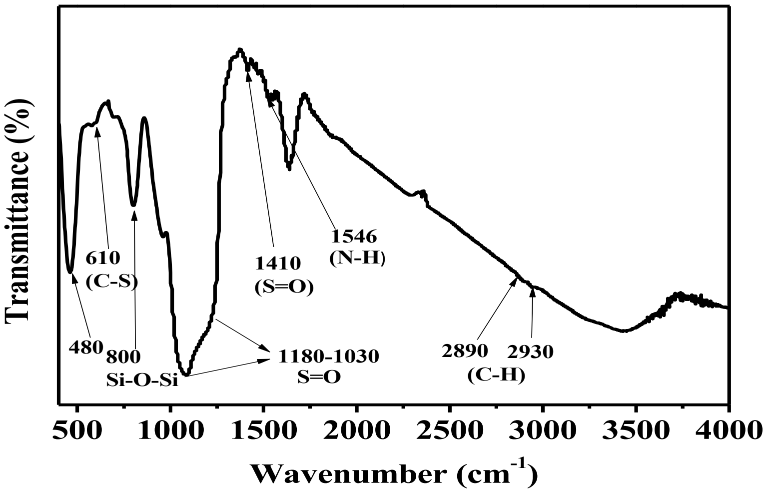


Fig S1. FT-IR spectra of SO_3H-NH_2-SBA-15.

Solid-state NMR spectra of the trifunctional catalyst and its parent materials

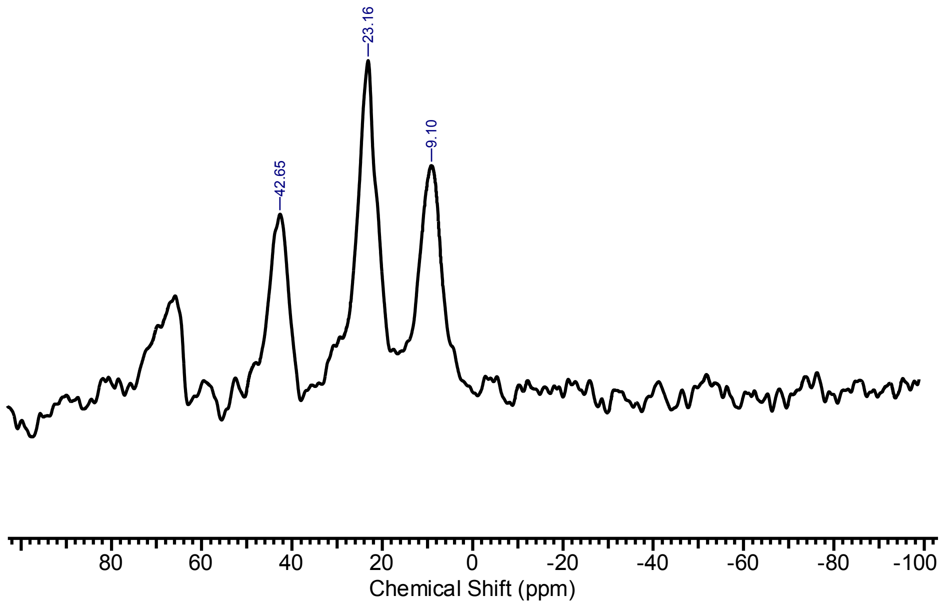


Fig. S2. Solid-state ^{13}C CP-MAS NMR spectrum of NH_2-SH-SBA-15.

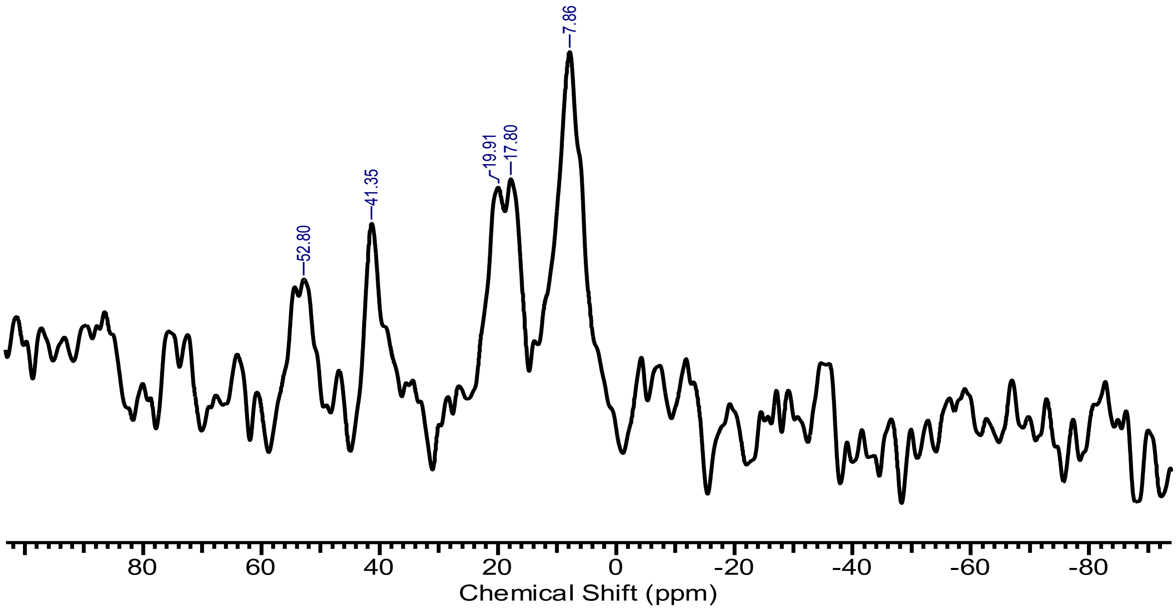


Fig. S3. Solid-state ^{13}C NMR spectrum of NH_2-SO_3H-SBA-15.

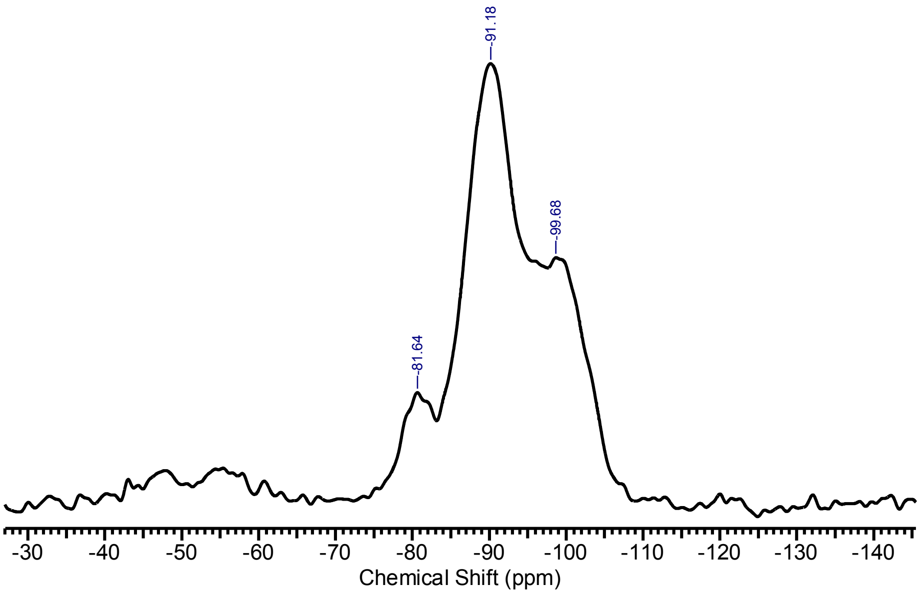


Fig. S4. Solid-state ^{29}Si MAS NMR spectrum of Pd-SO_3H-NH_2-SBA-15.

Nitrogen gas adsorption/desorption isotherms of the trifunctional catalyst and its control samples

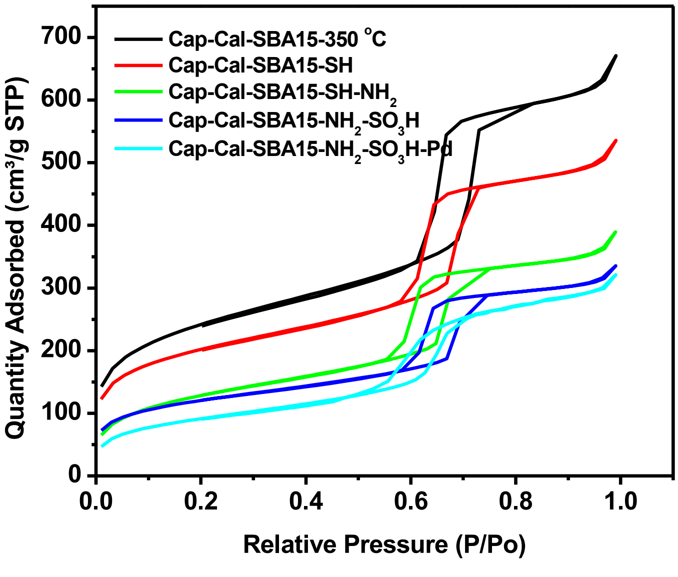
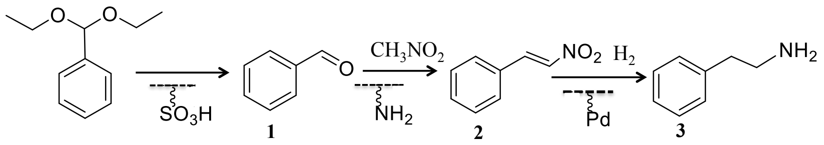


Fig. S5. Nitrogen gas adsorption/desorption isotherms of the trifunctional catalyst and its parent (reference) materials.



Scheme S1. A one-pot, three-step cascade deacetylation, Henry and hydrogenation reactions catalyzed by a trifunctional catalyst.

Table S1. Catalytic performances of the physical mixture of the three monofunctional catalysts in the one-pot, three-step cascade reactions comprised deacetylation, Henry and hydrogenation.[a]

Entry	**Reaction in**	**Time (h)**	**Conversion** (%)	**Selectivity (%)**		
				1	2	3
1[a]	Round bottom flask	2	68	78	20	2
		10	76	56	34	10
2[b]	Parr reactor	10	78	44	~ 0	66

[b] **Reaction conditions:** benzaldehyde dimethyl acetal: 0.01 moles; water: 0.02 mole; catalyst: A + B + C = 30 mg; temperature: 90 ºC; nitromethane: 10 mL (0.16 mol); [a] Reaction was performed in round-bottom flask with H_2 in balloon. [b] reaction was performed in a Parr reactor at 2 bar H_2 pressure.

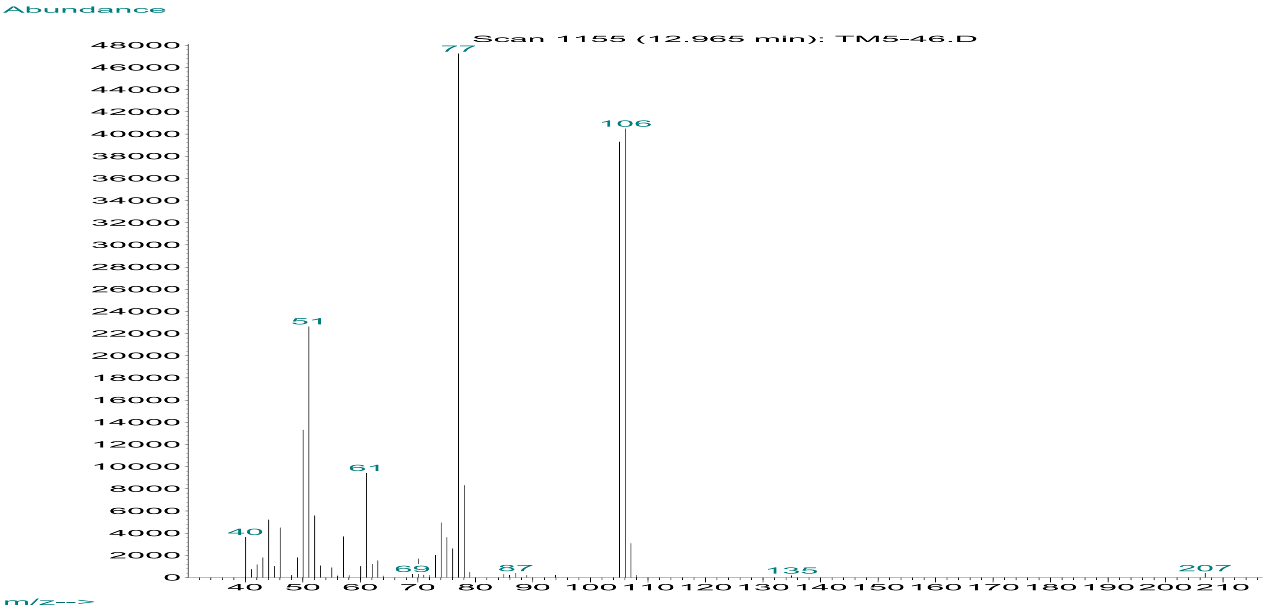
Table S2. Recyclability studies for three-step in one-pot tandem reaction catalyzed by the trifunctional catalyst[a].

Entry	Cycle	Conversion (%)	% Selectivity		
			1	**2**	**3**
1	0	~100	0	7	93
2	1	~100	0	8	92
3	2	~100	0	11	89
4	3	~100	0	14	86
5	4	~100	0	16	84

[a] **Reaction conditions:** benzaldehyde dimethyl acetal (0.01 mole), water (0.02 mole), catalyst Pd-SO_3H-NH_2-SBA-15 (30 mg), nitromethane (10 mL or 0.16 mol) temperature = 90 ºC; reaction was performed in a Parr reactor under 2 bar H_2 pressure, and reaction time = 10 h.

SGC-MS spectra of product

1. Benzaldehyde



2. *β*-Nitrostyrene

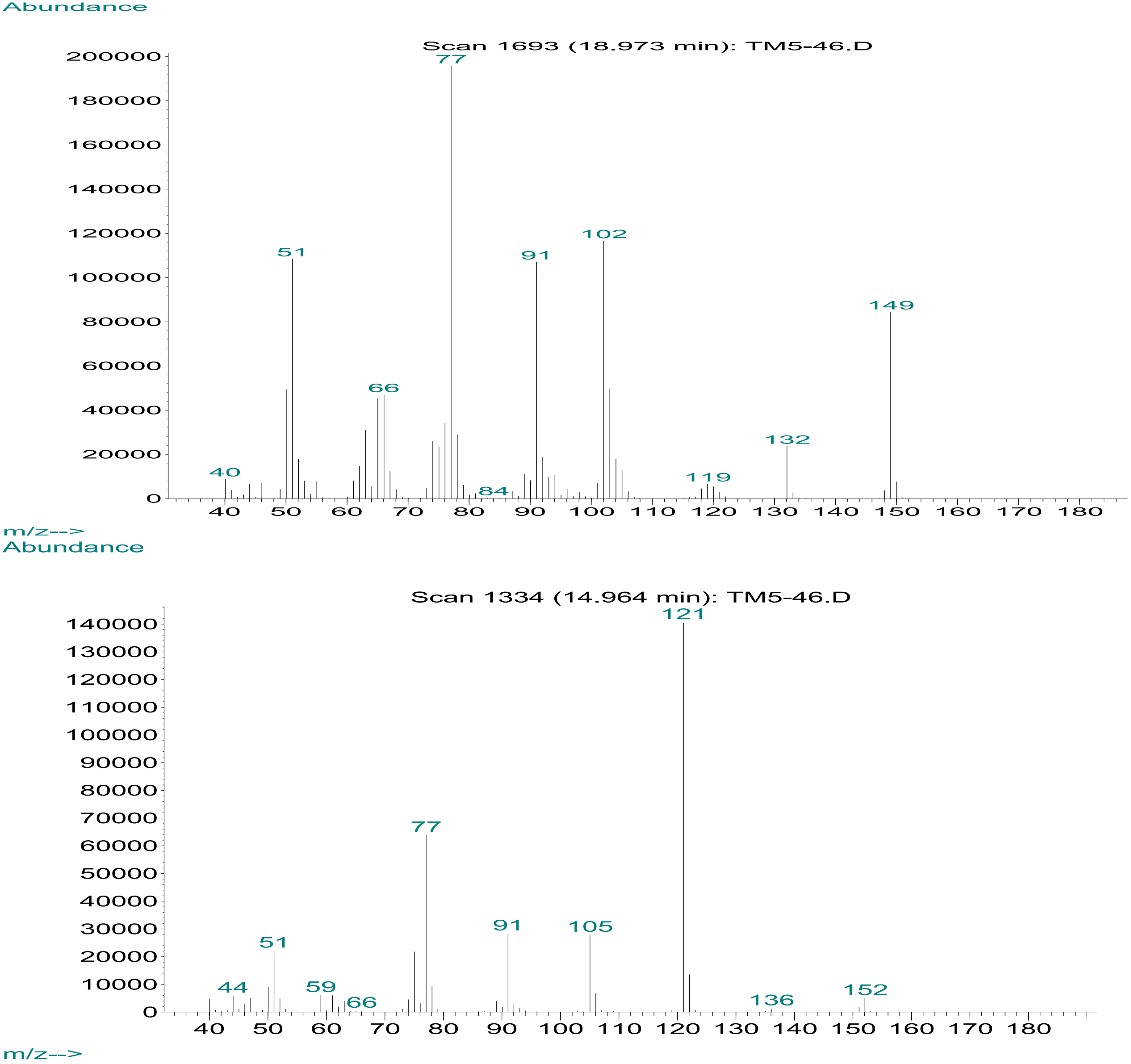


Fig. S6. GC-MS spectra and results of the different reaction products.

References for Supporting Information

[1] D. Y. Zhao, J. L. Feng, Q. S. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, G. D. Stucky, *Science* **1998**, *279*, 548–552.

[2] Y. Xie, S. Quinlivan, T. Asefa, *J. Phys. Chem. C* **2008**, *112*, 9996–10003.