Supporting Information

Novel synthesis of bifunctional catalysts with different microenvironments

Experimental

Materials. The triblock copolymer P_{123}, poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) [(PEG-PPG-PEG); average molecular weight 5800], 3-mercaptopropyltrimethoxysilane (**MPTS**) and 3-aminopropyltriethoxysilane (**APS**) were obtained from Aldrich. Bis(triethoxysilyl)ethylene (**BTSE**, 95 %) was obtained from Gelest Inc. The oxidizing agents aqueous H_2O_2 (30 – 35 %, Wako), tert-butylhydroperoxide solution anhydrous (TBHP, 5.5 M in decane, dried over molecular sieve 4A, Fluka), 3-chloroperbenzoic acid (77 %, Aldrich) and $NaHSO_3$ (99 %, Sigma-Aldrich) were obtained commercially. Ammonia solution (28 % aqueous), NaCl (99.5 %), HCl (2M aqueous) and NaOH (2M aqueous) were purchased from Wako chemicals.

Preparation of hybrid materials. The hybrid **PMES–NH_2** and **PMES–SH** were synthesized by co-condensation of **BTSE** with either **MPTS** or **APS**. In a typical synthesis of **PMES–NH_2**, 3.0 g of P_{123} was added to 67 mL of ion-exchanged water and 45 mL of 4M HCl and dissolved by stirring at room temperature. To the above solution, 4.3 g **BTSE** and 0.69 g **MPTS** (or) 0.66 g **APS** was added and the contents were stirred at 40 °C for 24 h. The resulting white precipitate was aged at 100 °C for 24 h and the solid product was separated, washed thoroughly with water, and ethanol. The oligomeric surfactant was removed by refluxing 1 g of as-synthesized material with 200 mL of ethanol and 5 mL of 4M HCl solution for 20 h. The surfactant-extracted solid was filtered,

washed with copious amount of water and ethanol, and finally dried under vacuum 10^{-3} Torr in decicator.

Sulfonation of PMES–NH_2 using $NaHSO_3$. In a typical reaction, 1 g of silica was mixed with 60 mL of 2 M $NaHSO_3$ solution in round bottom flask. The flask was fitted with water condenser which is attached to a 2 liter O_2 balloon and the content was vigorously stirred using a magnetic stirrer at 70 °C for period of 24 h. The desired material was obtained after ion-exchange with 1M HCl followed by adjusting the pH to neutral conditions.

Epoxidation of PMES–SH. In a typical epoxidation reaction, 250 mg of **PMES–SH** was suspended in 6 mL of dry acetonitrile in a 30 mL sample bottle. To the above mixture 50 mg of 2M NaOH solution was added under stirring at room temperature and then the content was effectively cooled to 0 °C using freezing mixture (ice/NaCl). Then 1.5 mL of tert-butylhydroperoxide solution (TBHP, decane solution) was added and the contents were stirred vigorously using a magnetic stirrer for 5 h. After the reaction, the solid was filtered, washed thoroughly with acetonitrile and ethanol and finally dried under vacuum at 10^{-3} Torr for 3 h. Thus obtained hybrid material was further treated with ammonia solution at room-temperature to give the required bifunctional catalysts. The bifunctional material was obtained after ion-exchange with 1M HCl followed by adjusting the pH to neutral conditions.

Screening of Bifunctional activity. The one-pot deacetalization of benzaldehyde dimethyl acetal and nitroaldol condensation reactions (Hendry reaction) was performed in a two-necked glass reactor fitted with a water condenser at 90 °C under vigorous stirring. A typical reaction involves 2 mmol of benzaldehyde dimethyl acetal, 5 mL nitromethane and PMES-SO_3H-NH_2-A (22 mg, 0.025 mmols SO_3H, 0.028 mmols), and the reaction was carried out in the absence of any co solvents. The reaction progress was made by analyzing the products at various times with a capillary gas chromatograph (Shimadzu 14A, OV–1 columns with flame ionization detectors). The products were identified by GC–MS splitting pattern as well as from authentic samples and in some cases the mixture was distilled off to obtain pure products and analyzed through GC–MS and ^{1}H NMR.

Characterization. Powder X-ray diffraction (PXRD) patterns were measured on a MAC Science diffractometer with CuKα radiation (50 kV, 200 mA) from 0.7° to 8° (2θ) in 0.01 steps at a scan speed of 1°(2θ) min^{-1}. Porosimetry measurements (N_2 isotherms) were obtained on a Quantachrome Autosorb-1 sorptometer at –196° C. Prior to measurement, all samples were outgassed at 60° C and 10^{-4} Torr for 3 h. Brunauer-Emmett-Teller (BET) surface areas were calculated from the linear section of the BET plot (P/P_0 =0.05–0.2). Pore-size distributions were determined using the Barrett-Joyner-Halenda (BJH) method from the adsorption branch of the isotherms. The ^{29}Si MAS NMR and ^{13}C CP MAS NMR spectra were recorded on a Bruker AMX-400 spectrometer at 59.62 MHz and 75.47 MHz for ^{29}Si and ^{13}C, respectively. Their chemical shifts were referenced to tetramethylsilane and glycine, respectively. Raman spectra were obtained

using the 532 nm laser line with a Jasco micro-Raman system NRS-3300 equipped with holographic notch filter, 600 grooves/mm holographic grating, a 100X-microscope objective, and a peltier cooled (–50° C) CCD detector. FTIR spectra were recorded on a Shimadzu FTIR-8100 spectrometer using KBr pellet method. Transmission electron microscope (TEM) observation was made with JEOL-2000EX II operating at 200 kV. Analysis of the organic material present in the solid was carried out using a Perkin-Elmer 2400 CHN analyzer.

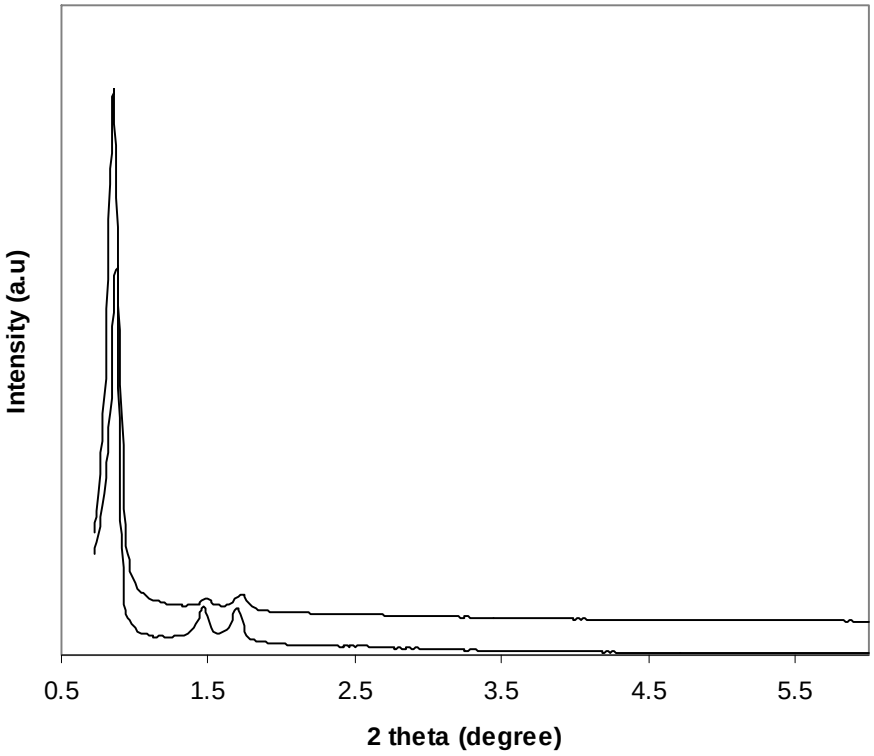


Figure S1. Small-angle X-ray diffraction of **PMES–SH** (bottom) and **PMES–NH_2** (top).

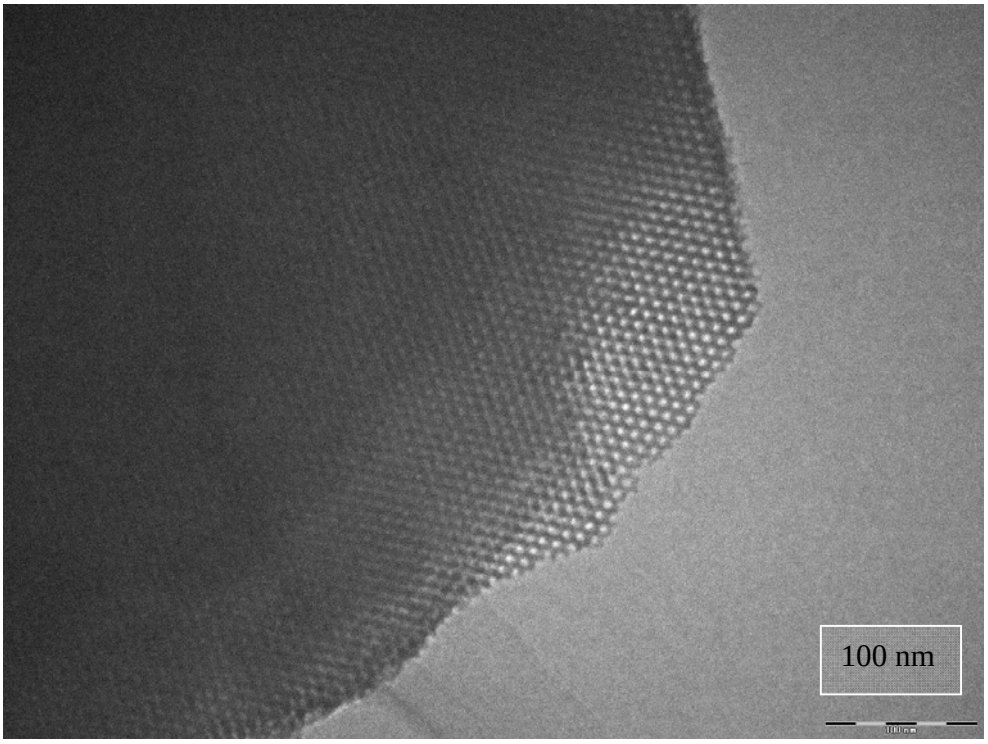
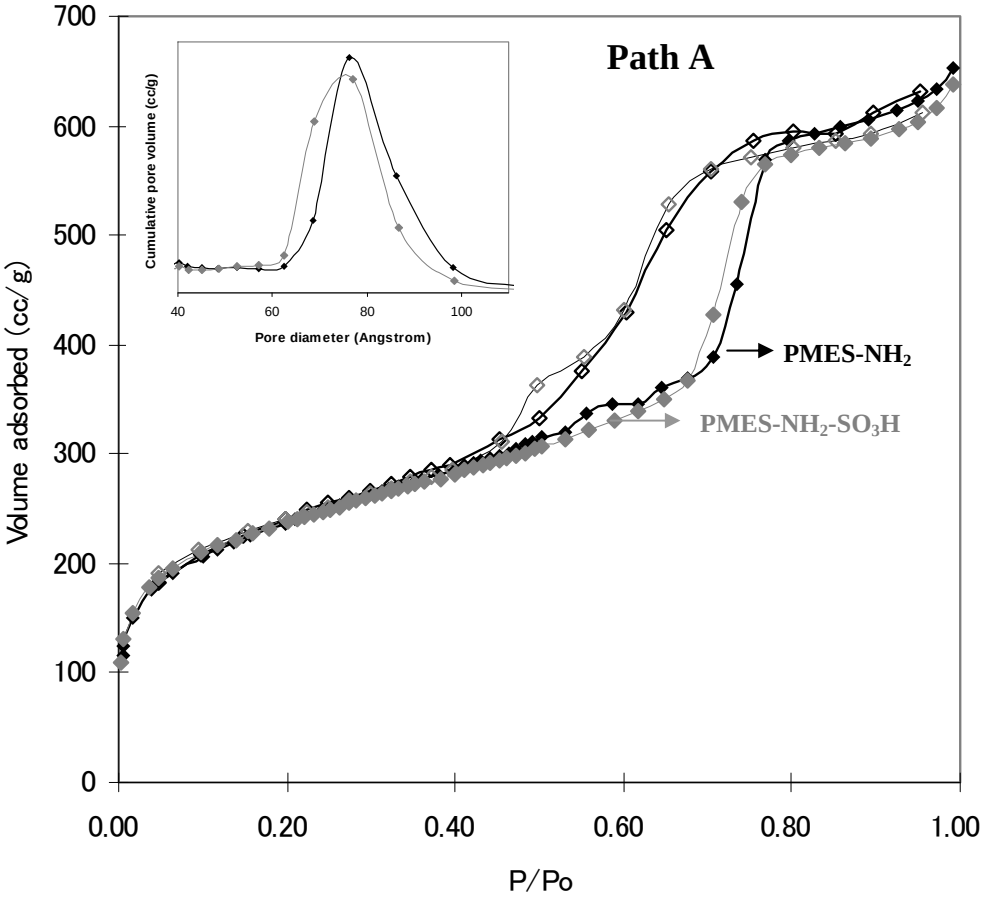


Figure S2. TEM image of **PMES–SH**.


Path A
Volume adsorbed (cc/g)
P/Po
0
100
200
300
400
500
600
700
0.00
0.20
0.40
0.60
0.80
1.00
Cumulative pore volume (cc/g)
Pore diameter (Angstrom)
40
60
80
100
PMES-NH2
PMES-NH2-SO3H

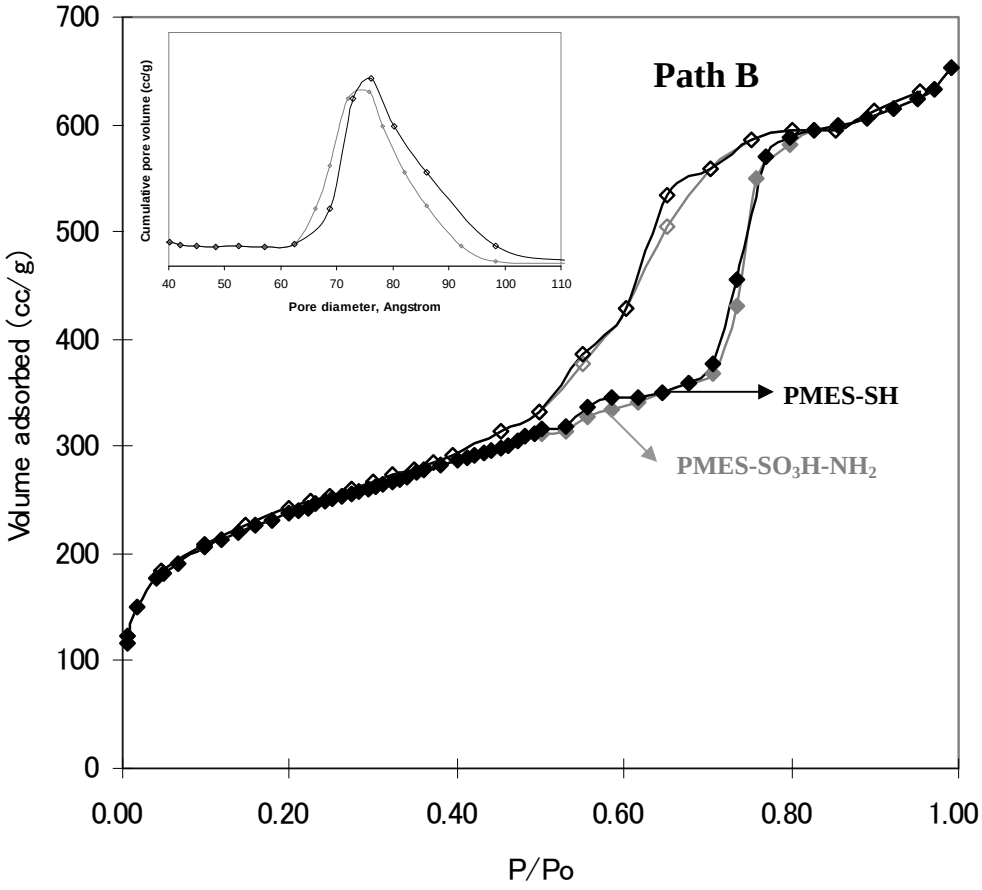


Figure S3. Nitrogen adsorption/desorption isotherms of: PMES-NH_2 and PMES-NH_2-SO_3H (**path A**); PMES-SH and PMES-SO_3H-NH_2 (**path B**).

Table S4. Structural Properties of PMO-NH_2 and PMO-SH before and after functionalization.

PMES	$S_{BET}/m^2.g^{-1}$	$V/mL.g^{-1}$	D/nm	d(100)/nm	Wall thickness/nm
PMES–NH_2 (path-A)	855	1.12	7.9	11.0	4.3
PMES–NH_2–SO_3H (path-A)	803	1.02	7.45	10.3	3.4
PMES–SH (path-B)	797	1.01	7.8	11.2	4.5
PMES–SO_3H–NH_2 (path B)	738	0.97	7.4	10.4	3.5

Table S5. Effect of reaction temperature over the addition of $NaHSO_3$ across ≡Si–C=C–Si≡

Reaction temperature, °C	Amount of $–SO_3H$ (mmols/g)[a]
40	0.91
50	0.98
65	1.13
75	1.15

[a] Sulfonic acid content was estimated by potentiometric acid-base titration after liberating the proton with NaCl.

Table S6. Optimization of bifunctional catalyst preparation with respect to various epoxidizing reagents.

Generally, epoxidation of ≡Si–C=C–Si≡ follows the electrophilic mechanism and existence of two silicon atoms in conjugated position makes them electron deficient. In order to reverse the electrophilic to nucleophilic pathway, we have carried out epoxidation reactions under mild basic medium with various oxidants under optimized reaction temperature and reaction time.

Oxidants	Amount of $-SO_3H$ (mmols/g)[a]	Amount of $-NH_2$ (mmols/g)[b]
H_2O_2	0.90	0.77
TBHP	1.15	1.31
m-CPBA	0.94	1.03
m-CPBA + TEA	0.97	1.004

[a] Sulfonic acid content was estimated by potentiometric acid-base titration.

[b] Estimated by elemental analysis.

TBHP = *tert*-butyl hydroperoxide (anhydrous)

m-CPBA = *m*-chloroperbenzoic acid

m-CPBA + TEA = *m*-chloroperbenzoic acid + triethylamine

Table S7. Optimization of bifunctional catalyst preparation with respect to pH.

pH of reactants	Amount of $-SO_3H$ (mmols/g)[a]	Amount of $-NH_2$ (mmols/g)[b]
7.0	0.95	0.86
8.0	1.09	1.21
8.5	1.24	1.17
9.0	1.1	0.93

[a] Sulfonic acid content was estimated by potentiometric acid-base titration.

[b] Estimated by elemental analysis.

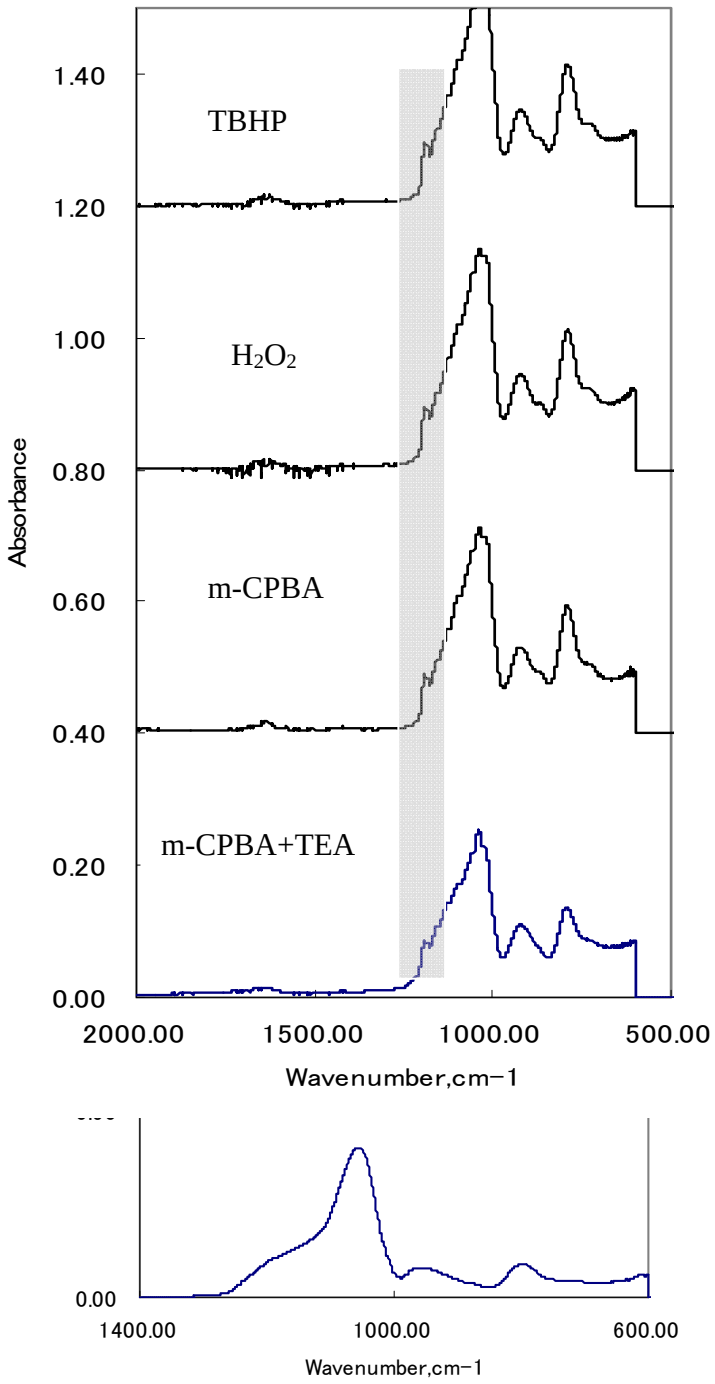


Figure S8. Observation of epoxide stretching vibrational mode at 1190 cm^{-1} for various epoxidizing reagents. The bottom FTIR spectrum shows ethylenesilica before oxidation.

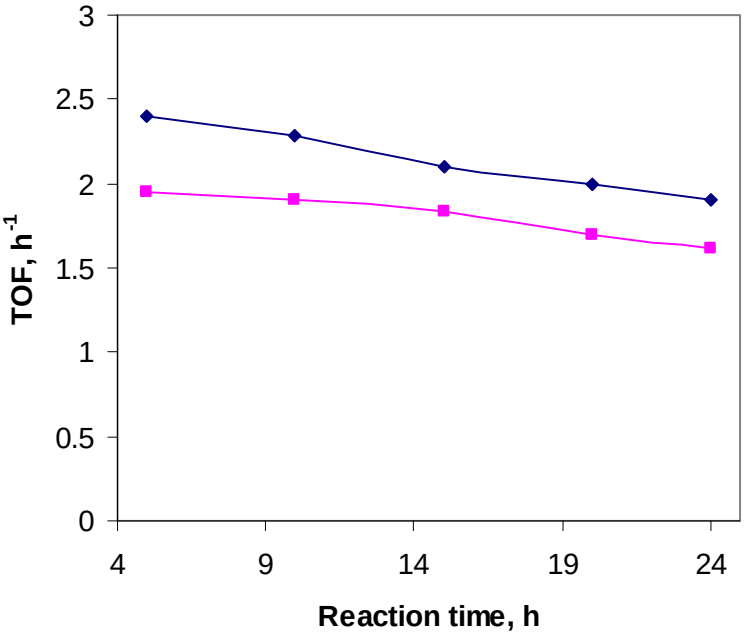


Figure S9. Variation in the intrinsic rate towards condensation between benzaldehyde and nitromethane under identical experimental conditions: **PMES-NH_2** with amino groups in the hydrophilic part (top) and **PMES-NH_2** with amino groups in the hydrophobic part (bottom).

Table S10. Catalyst stability and resusability towards one-pot deacetalization and Henry reaction.[a]

Entry	Catalyst	Conv.of **1** [%]	**2** [%]	**3** [%]
1	PMES-SO_3H-NH_2-**A**	100	1.7	98.3
2	PMES-SO_3H-NH_2-**A**	100	1.6	98.4
3	PMES-SO_3H-NH_2-**A**	100	1.9	98.1
4	PMES-SO_3H-NH_2-**A**	100	2.2	97.8
5	PMES-SO_3H-NH_2-**B**	100	23.5	76.5
6	PMES-SO_3H-NH_2-**B**	100	22.6	77.4
7	PMES-SO_3H-NH_2-**B**	100	22.1	77.9
8	PMES-SO_3H-NH_2-**B**	100	22.4	77.6

[a] Reaction conditions: Benzaldehyde dimethyl acetal (2 mmol), CH_3NO_2 (5 mL), Catalyst (22 mg), temperature 90 °C and reaction time 24 h.