Electronic Supporting Information

Chemoselective Epoxidation of Cholesterol Derivatives on a Surface-Designed Molecularly Imprinted Ru-Porphyrin Catalyst

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Acknowledgements

The authors thank Prof. Stephan Irle, Assoc. Prof. Daisuke Yokogawa, and Assist. Prof. Yu Hijikata at Nagoya University, and Prof. Kazunari Yoshizawa and Assist. Prof. Takashi Kamachi at Kyusyu University for valuable suggestions regarding DFT calculations, Prof. Masato Kitamura and Assistant Prof. Shinji Tanaka at Nagoya University for the methods of epoxide product isolation, Prof. Kentaro Tanaka and Assoc. Prof. Yasuyuki Yamada at Nagoya University for the methods of epoxide product isolation and ESI-TOF MS measurements, and Mr. K. Oyama at Nagoya University for HR EI MS measurements.

Experimental Section

Materials and instruments

Chemicals were purchased from commercial sources (Wako Chemicals, Kishida Chemicals, Tokyo Chemical Industry, Sigma-Aldrich, Shin-Etsu Chemical, Gelest Inc., and Santa Cruz Biotechnology) and used without further purification unless noted. SiO_2 (Aerosil 300, 300 m^2 g^{-1}) was purchased from Nippon Aerosil Cd. Ltd. For flash column chromatography to isolate the products, neutral SiO_2 (Wakogel 60N 38~100 μn), SiO_2 functionalized with NH (Chromatorex NH-DM2035), and SiO_2 functionalized with diol (Chromatorex DIOL-MB100-40/75) were used.

The ^{1}H and ^{13}C liquid-state NMR spectra were measured on an ECA600 spectrometer (JEOL) at 293 K operating at 600 MHz and 150 MHz, respectively. Tetramethylsilane (Me_4Si) was used as an internal standard. FT-IR spectra of the samples were recorded on a FT/IR-4200 spectrometer (JASCO) operating at room temperature. A Ru porphyrin complex with four (triethoxysilyl)-propyl-carbamate moieties (**1**, 1 mg) and potassium bromide (KBr, 100 mg) were mixed by a mortar and a pestle, and pressed into a disk in an IR cell, and then a FT-IR spectrum was recorded. Template (**2**, 4 mg) was pressed into a disk in an IR cell, and then a FT-IR spectrum was recorded. MALDI-TOF MS spectra of the samples were recorded on an AXIMA-CFR Plus (Shimadzu) and Ultraflex III (Bruker Daltonics). 2-(4-Hydroxyphenylazo)-benzoic acid (HABA) was used as a matrix, and Insulin chain B oxidized was used as a control sample. ESI-TOF MS spectra were recorded on a LCT Premier XE (Waters) systems and microTOF-QII (Bruker Daltonics). UV-vis spectrum was measured on a V-550 spectrometer (JASCO). The concentration of sample solution in dichloromethane was 2.5×10^{-6} mol L^{-1}. HR EI MS spectra were measured on a JMS-T100GCV (JEOL) mass spectrometer.

Synthesis of Ru porphyrin complex with four four (triethoxysilyl)-propyl-carbamate moieties (1) and the template (2)

Synthesis of ruthenium 5,10,15,20-tetrakis(4-hydroxyphenyl)porphyrin[1]

5,10,15,20-Tetrakis(4-hydroxyphenyl)porphyrin (0.802 g, 1.18×10^{-3} mol) and triruthenium dodecacarbonyl (0.801 g, 1.25×10^{-3} mol) were dissolved in 1,3,5-trichlorobenzene (200 mL) and the solution was stirred for 92 h at 443 K under N_2. The solution was subjected to silica gel column chromatography with hexane and ethyl acetate/hexane (2:1, v/v) and the product was obtained. Yield: 0.878 g (1.09×10^{-3} mol, 92%). ^{1}H NMR (600 MHz, methanol-d_4): δ = 7.16 (m, 8H), 7.92 (dd, 4H), 8.02 (dd, 4H), 8.69 (s, 8H).

Synthesis of a Ru porphyrin complex 1

Reaction vessel was dried up and ruthenium 5,10,15,20-tetrakis(4-hydroxyphenyl)porphyrin (0.350 g, 4.34×10^{-4} mol) and 3-(triethoxysilyl)propyl isocyanate (0.800 mL, 3.23×10^{-3} mol, 7.44 eq.) were dissolved in dry acetone (20 mL), and the solution was stirred at 333 K under an N_2 atmosphere. After 72 h and 168 h, 3-(triethoxysilyl)propyl isocyanate (0.400 mL, 1.62×10^{-3} mol, 3.73 eq.) was added, respectively. After monitoring that the reaction was completed by MALDI-TOF MS, the solvent was evaporated *in vacuo*. Hexane (10 mL) was added to the obtained red residue, the suspension was treated with an ultrasonic bath, and supernatant was removed. This process was repeated 9 times until the viscosity of the residue was removed. Then, hexane (10 mL) and several drops of dichloromethane were added to the residue, the suspension was treated with an ultrasonic bath, and the supernatant was removed. This process was repeated 10 times, and ruthenium porphyrin complex (**1**) was obtained. Yield: 0.691 g (3.86×10^{-4} mol, 89%). ^{1}H NMR (600 MHz, methanol-d_4): δ = 0.75 (t, 8H), 1.25 (t, 24H), 1.76 (m, 8H), 3.89 (q, 24H), 7.43 (m, 8H), 8.06 (dd, 4H, H_o or $H_{o'}$), 8.17 (dd, 4H), 8.67 (s, 8H); ^{13}C NMR (150 MHz, methanol-d_4): δ = 8.6, 18.8, 24.4, 44.8, 59.6, 121.0, 122.3, 132.6, 136.0, 141.1, 145.4, 152.4, 157.5, 181.8; FT-IR (KBr disc/cm^{-1}) ν_{max} = 1390, 1442, 1495, 1528, 1639, 1724, 1746, 1937, 2886, 2927, 2974, 3338; MALDI-TOF MS (matrix : HABA) : *m/z* : 1767.67 [M-CO+H]$^+$ (calcd. for $C_{84}H_{113}O_{20}N_8RuSi_4$ 1767.61).

Synthesis of 3β-acetoxy-6-nitrocholest-5-ene[2]

Cholesteryl acetate (25.3 g, 5.89×10^{-2} mol) was added to a mixture of acetic acid (72 mL) and fuming nitric acid (20 mL) and stirred at room temperature for 2 h, then the solution was added to distilled water cooled in an ice bath. The mixture was washed with distilled water and filtered. This process was repeated 4 times until the viscosity of the solid disappeared and the pH of water was increased to around 4. The solid was then recrystallized with ethanol (155 mL) and the product was obtained. Yield: 7.45 g (1.57×10^{-2} mol, 27%). ^{1}H NMR (600 MHz, chloroform-*d*): δ = 0.67 (s, 3H), 0.85 (d, 3H), 0.86 (d, 3H), 0.90 (d, 3H), 2.46 (m, 1H), 2.76 (m, 1H), 4.63 (m, 1H); ^{13}C NMR (150 MHz, chloroform-*d*): δ = 11.8, 18.7, 19.7, 21.0, 21.3, 22.6, 22.8, 23.9, 24.2, 27.0, 28.0, 28.1, 31.1, 31.6, 33.3, 35.8, 36.1, 36.2, 37.8, 39.3, 39.5, 42.3, 49.0, 56.0, 56.1, 72.0, 137.4, 146.7, 170.1; FT-IR ν_{max} = 1034, 1236, 1365, 1467, 1523, 1744, 2869, 2949.

Synthesis of 3β-acetoxy-6β-nitrocholestane[3]

3β-Acetoxy-6-nitrocholest-5-ene (4.03 g, 8.51×10^{-3} mol) was added to dry ethanol (200 mL) and sodium borohydride (1.36 g, 3.59×10^{-2} mol) was added under an N_2 atmosphere. After stirring the solution for 30 min, a saturated aqueous solution of ammonium chloride was added. Distilled water (200 mL) was added, the

reaction mixture was extracted with dichloromethane (4 × 60 mL), dried with Na_2SO_4, then the solvent was evaporated under vacuum and the product was obtained. Yield: 3.86 g (8.11×10^{-3} mol, 95%). ^{1}H NMR (600 MHz, chloroform-*d*): δ = 0.72 (s, 3H), 0.79 (s, 3H), 0.86 (d, 3H), 0.87 (d, 3H), 0.91 (d, 3H), 2.37 (d, 1H), 4.36 (m, 1H), 4.66 (m, 1H); ^{13}C NMR (150 MHz, chloroform-*d*): δ = 12.4, 13.2, 18.8, 21.2, 21.5, 22.7, 23.0, 24.0, 24.1, 27.3, 28.2, 28.3, 31.1, 32.3, 34.2, 35.9, 36.2, 38.8, 39.6, 39.9, 42.8, 46.5, 54.5, 56.2, 56.3, 73.5, 84.4, 170.8.

Synthesis of 3β-acetoxy-6β-aminocholestane (template, 2)[4]

To a dry reaction vessel containing dry THF (34 mL) and dry methanol (34 mL) was added 3β-acetoxy-6β-nitrocholestane (3.79 g, 7.97×10^{-3} mol) under an N_2 atmosphere. Ammonium formate (3.48 g, 5.52×10^{-2} mol) and Pd/C (0.461 g, 4.39×10^{-4} mol) were added to the solution and stirred at room temperature for 24 h, then diethyl ether (160 mL) was added and the solution was filtered. After the solvent was evaporated *in vacuo*, a minimum amount of chloroform was added to dissolve the obtained white residue, and hexane (volume: 10 times to the added chloroform) was added. The total volume of solution was reduced to around half by evaporation, and the suspension was cooled in ice bath. **2** was obtained as a white solid. Yield: 2.28 g (5.12×10^{-3} mol, 64%). Elemental analysis: Calcd. (%) for $C_{29}H_{51}NO_2 \cdot H_2O$: C: 75.11, H: 11.52, N: 3.02, Found. C: 75.29, H: 11.26, N: 2.79; ^{1}H NMR (600 MHz, chloroform-*d*): δ = 0.68 (s, 3H), 0.86 (d, 3H), 0.87 (d, 3H), 0.89 (s, 3H), 3.03 (m, 1H), 4.70 (m, 1H); ^{13}C NMR (150 MHz, chloroform-*d*): δ = 12.3, 16.1, 18.8, 21.2, 21.6, 22.7, 23.0, 24.0, 24.5, 27.6, 28.2, 28.4, 30.5, 31.8, 34.6, 35.7, 36.0, 36.3, 38.5, 39.7, 40.0, 42.8, 46.3, 54.6, 56.2, 56.4, 62.9, 74.1, 170.8; FT-IR: 1027, 1246, 1278, 1364, 1381, 1446, 1467, 1706, 1735, 2868, 2951, 3375, 3427; ESI-TOF MS (positive, chloroform): *m/z*: Calcd. for $C_{29}H_{51}NO_2$: 446.40 $[M+H]^+$, Found. 446.40.

Preparation of molecularly imprinted Ru porphyrin catalyst

Preparation of SiO_2-supported Ru porphyrin complex A and removal of coordinating CO ligand

SiO_2 (Aerosil 300, 6 g) was calcined at 573 K for 3 h, and was kept under vacuum prior to the attachment of **1**. The precalcined SiO_2 was suspended in dry toluene (130 mL) under an N_2 atmosphere, and a dry toluene solution (50 mL) of **1** (0.354 g, 1.97×10^{-4} mol) was added. The suspension was refluxed at 393 K for 24 h. The obtained sample was collected in a thimble filter tube inside a Schenk tube and then dried under vacuum for 12 h, which is denoted as **A**. The loading of Ru was estimated by XRF (Ru: 0.31 wt%).

A (4 g) was ground into a fine powder and placed in a two-neck quartz cell under Ar atmosphere (inside the glove box). Toluene (50 mL) was added to the powder. The suspension was stirred while gently bubbling with Ar gas saturated with dry toluene vapor, and was exposed to the light from a high-pressure Hg lamp (Spectra-Physics Arc Lamp Housing Model 66902, 500 W Hg Lamp Model 66142) (Power: 400 W, no cutoff) for 72 h in a water bath. Dry toluene was occasionally added in order not to dry the solvent up inside the cell. After the complete removal of CO ligand monitored by FT-IR, the solvent was removed under vacuum and **B** was obtained. The loading of Ru was estimated by XRF (Ru: 0.31 wt%).

A and **B** with high Ru loading (denoted as **A-HL** and **B-HL**, Ru: 0.49 wt%, XRF) were prepared in a similar method. For **A-HL**, SiO_2 (3 g) and **1** (0.353 g, 1.96×10^{-4} mol) were used. For **B-HL**, **A-HL** (1.5 g) and toluene (20 mL) were used, and irradiation was conducted in a similar way for 86 h.

Coordination of the template 2 to B to prepare C

Under an N_2 atmosphere, the template (**2**) (0.820 g, 1.84×10^{-3} mol, 20 eq of Ru) was added to **B** (3 g, Ru: 9.20×10^{-5} mol) in dry toluene (60 mL). The mixture was stirred at 298 K for 4 h. The obtained solid sample was collected in a thimble filter tube and dried under vacuum for 12 h. The obtained sample is denoted as **C**. The loading of Ru was estimated by XRF (Ru: 0.31 wt%). The amount of coordinated **2** was estimated by HPLC analysis of unreacted **2** in the filtrate (see Supporting Information pp. S10).

Stacking of SiO_2-matrix overlayers on C to prepare D

Under an N_2 atmosphere, **C** (0.25 g) was suspended in dry dichloromethane (8 mL). The solution of tetramethoxysilane ($Si(OCH_3)_4$, TMOS) (1.22 mL, 8.27×10^{-3} mol) and distilled H_2O (0.58 mL, 3.22×10^{-2} mol) in dry dichloromethane (8 mL) were added to the suspension, and the mixture was stirred for 3 h. Then, dichloromethane was removed under vacuum. The closed reactor was heated at 383 K for 24 h (hydrolysis-polymerization), and then evacuated at 373 K for 3 h. The obtained sample is denoted as **D**. The hydrolysis-polymerization was also performed at 363 K and 373 K.

Several basic organosilanes, (3-(2-imidazolin-1-yl)-propyltriethoxysilane (**3**), *N*,*N*-dimethylaminopropyltrimethoxysilane (**4**), 3-aminopropyltrimethoxysilane (**5**), *N*-(*N*-acetylleucyl)-3-aminopropyltriethoxysilane (**6**), and (*R*)-*N*-triethoxysilylpropyl-*o*-quinineurethane (**7**) (The chemical structures are listed in the Supporting Information pp. S15.) were added to the solution of TMOS and H_2O, respectively. The added amount of organosilane was adjusted to be either 1 or 0.1 wt% to TMOS. The loading of Ru was estimated by XRF.

Removal of the template 2 to prepare E

Under an N_2 atmosphere, trifluoroacetic acid (CF_3COOH, 10 μL, 1.3×10^{-4} mol) was added to a suspension of **D** (0.50 g) in dry toluene (6.4 mL). The mixture was stirred at 298 K for 30 min, stopped stirring, and the supernatant was collected. This operation was repeated four times, and the solid sample was collected in a thimble filter tube, washed with dry toluene (5 mL × 3), and dried under vacuum. The obtained sample is denoted as **E**. The loading of Ru was estimated by XRF.

The supernatant was evaporated, and toluene (20 mL) was added. This solution was neutralized by saturated sodium carbonate aqueous solution (sat. Na_2CO_3 aq. 20 mL) using a separation funnel for three times. Then the organic phase was evaporated, and tetrahydrofuran/methanol = 1/9 (v/v) (10 mL) was added, and the solution was analyzed by HPLC (see Supporting Information pp. S10).

Catalyst characterization

XRF: XRF was measured on a JSX-1000S spectrometer (JEOL) operating at room temperature. The loading of Ru was estimated from the Ru/Si peak intensity ratio of Ru K_α and Si K_α fluorescence lines (Net counts were used.). Samples for standard curves were prepared as follows. SiO_2 (Aerosil 300) was impregnated with di-μ-chlorobis[(*p*-cymene) chlororuthenium] by using dichloromethane. The Ru loading was adjusted to 0.25, 0.5, 0.75, 1.0, 1.5, and 2.0 wt%, respectively. Samples were ground well by mortar and pestle, and 20 mg of mixture was pressed (2 MPa) into a pellet disk, and this disk was used for measurement.

Fourier-transform infrared spectroscopy (FT-IR): FT-IR spectra of the samples were recorded on a FT/IR-4200 spectrometer (JASCO) operating at room temperature. The solid samples were pressed into disks in a glove box and FT-IR spectra were recorded in an IR cell without exposure to air.

Solid-state nuclear magnetic resonance (NMR) spectroscopy: The ^{13}C and ^{29}Si solid-state (SS) NMR spectra were recorded on a JNM-ECX400 spectrometer (JEOL) operating at 100.6 and 79.5 MHz, respectively, under a magic angle spinning (MAS) condition. For ^{13}C NMR, a cross-polarization (CP) method was used, and the samples were spun at 10 kHz and 8 kHz using 6 mm zirconia rotors. The relaxation decay, the contact time, and the scan number were 0.5 s, 5.0 ms, and 1,000,000, respectively. Hexamethylbenzene (δ = 17.17 ppm, ^{13}C) was used as an external standard for calibrating the chemical shifts. For ^{29}Si NMR, a single-pulse detection method was used and the samples were spun at 7 kHz using 6 mm zirconia rotors. The relaxation decay, the contact time, and the scan number were 15 s, 5.0 ms, and 15,000, respectively. 3-(Trimethylsilyl)propionic acid sodium salt (TMSP) (δ = 1.5 ppm, ^{29}Si) was used as an external standard for calibrating the chemical shifts. ^{29}Si Solid-state MAS NMR difference spectra of **D-C** and **E-C** were curve-fitted with three Gaussian peaks (Q_2, Q_3, and Q_4).

UV/vis spectroscopy: Diffuse reflectance (DR) UV/vis spectra for solid samples were measured on a V-550 spectrometer (JASCO). A solid sample was enclosed in a quartz cell under Ar and DR-UV/vis spectra were recorded by using an integrating sphere.

X-ray photoelectron spectroscopy (XPS): XPS was measured using an ECSA3057, (ULVAC Phi.) at a base pressure of 1×10^{-7} Pa. The X-ray source and power were Al K_α (1486.7 eV) and 350 W, respectively. Narrow multiplex scans were recorded with 11.75 eV pass energy and 0.1 eV step size. A charge neutralization function was employed to compensate for charge built up on solid samples by X-ray irradiation. Samples were ground by mortar and pestle, and 10 mg of mixture was pressed (2~5 MPa) into a pellet disk, and the disk was attached to a cell holder by carbon tape. The background of each spectrum was subtracted by Shirley method using Origin software (ver. 8). Binding energies were referenced to those of Si 2p as 103.4 eV. The peak intensities of the spectra were normalized by the peak area of Si 2p XPS spectra.

X-ray absorption fine structure (XAFS): XAFS spectra at the Ru K-edge were measured in transmission mode at the NW10A station of the Photon Factory at KEK-IMSS (Tsukuba, Japan). The energy and current of electrons in the storage ring were 6.5 GeV and 60 mA, respectively. X-rays from the storage ring were monochromatized using a Si(311) double-crystal monochromator. **1** diluted with boron nitride, **A**, **B**, and **C** were measured in transmission mode, and ionization chambers filled with pure Ar and Kr gas were used to monitor the incident and transmitted X-rays, respectively. **D** and **E** were measure in fluorescence mode, and an ionization chamber filled with Ar and Kr gas, and a 19-channeled multi solid state detector (MSSD) were

used to monitor the incident, transmitted, and fluorescence X-rays, respectively. Ru powder diluted with boron nitride and pelletized into a disk was used as a reference. All samples were enclosed in an XAFS cell sealed with a carbon cap inside a glovebox without exposure to air. All samples were measured at 20 K under vacuum.

Ru K-edge XAFS spectra were analyzed with ATHENA and ARTEMIS using IFEFFIT (ver. 1.2.11).[5] Threshold energy was tentatively set at the inflection point of the Ru K-edge (22119.3 eV),[6] and background was subtracted by the Autobk method and the spline smoothing algorithm in ATHENA.[7] The k^3-weighted extended XAFS (EXAFS) oscillations (k: 30–180 nm^{-1} for Ru powder and 30–160 nm^{-1} for Ru catalysts) were Fourier transformed into R-space. Curve-fitting analysis was carried out in R-space. The fitting parameters for each shell were the coordination number (CN), interatomic distance (R), Debye–Waller factor (σ^2: mean-square displacement), and correction-of-edge energy (ΔE_0). Multiple scattering effects were assumed in the analysis of Ru–C and Ru···O (CO) in **1** and **A** (The CN of Ru···O (CO) was fixed to the same value of Ru–C (CO).), and in the analysis of Ru···C (porphyrin) and Ru···C(N) (porphyrin) in **1**, **A**, and **B** (The CN of Ru···C(N) (porphyrin) was fixed to the doubled value of Ru···C (porphyrin).), respectively, during the curve-fitting analyses. The CN of Ru···C (porphyrin) was fixed to the doubled value of Ru–N (porphyrin), and the CN of Ru···C' (porphyrin) was fixed to the same value of Ru–N (porphyrin), respectively, during the curve-fitting analyses. The ΔE_0 and σ^2 of Ru–C (CO) and Ru···C (CO/porphyrin), Ru–O (CO) and Ru···O (CO), and Ru–N (template) and Ru–N (porphyrin) were restrained to be the same values in the curve-fitting analyses, respectively. The value of S_0^2 was estimated by the EXAFS curve-fitting of Ru powder, and was fixed to be 1 in the whole curve-fitting analyses. The phase shifts and backscattering amplitudes for Ru–C (CO), Ru···O (CO), Ru···O(C) (CO), Ru···C(O)(C) (CO), Ru–N (template, porphyrin), Ru···C (porphyrin), Ru···C(N) (porphyrin), and Ru···C' (porphyrin) were calculated with FEFF8[8] code using structural parameters obtained from the crystal structures of (tetraphenylporphinato)-(carbonyl)-(pyridine) ruthenium (ii) toluene solvate and (5,10,15,20-tetraphenylporphyrinato)-(diphenylmethyleneamido)-hydroxy-ruthenium (iv).[9]

Density functional theory (DFT) calculation: DFT calculation for the coordinate structure of the template (**2**) to **1** was performed to model the structure of the SiO_2-attached Ru-porphyrin complex cooridated with **2** (**C**). Initial structure was prepared with GaussView 5.0. General function was B3LYP[10], basis function of Ru was LanL2DZ[11], and basis function of C, H, N, O, Si was 6-31g(d)[12]. CPMC[13] was utilized as solvent effect and parameter of dichloromethane was used. The structures of **1** ($Si(OEt)_3$ was changed to $Si(OMe)_3$ to reduce calculation load) and **2** were initially optimized respectively, and combined them to optimize the structure of **C** (Fig. S5). Coordinates of the Ru-porphyrin part of **1** and **2** were free and coordinate of the isocyanate part of **1** was fixed. Calculation was perfomed by Gaussian 09, Rev. C. 01[14].

Quantitative analyses of the coordinated template on SiO_2-supported Ru porphyrin by high performance liquid chromatography (HPLC):

2 (20 eq, 25 eq, and 29 eq. to Ru) was added to a suspension of **A** or **B** (50 mg, Ru: 0.33 wt%, 1.6×10^{-3} mmol) in dry toluene (1 mL), respectively, in an N_2 atmosphere. The suspensions were stirred for 4 h at 298 K, and they were filtered. The filtrates were evaporated, and tetrahydrofuran/methanol = 1/9 (v/v) (1 mL) was added. In this way, the amount of **2** that was not attached to **A** or **B** was measured by HPLC (JASCO LC-2100Plus series with an InertSil NH_2 (4.6 I.D. × 250 mm) column (YMC Co. Ltd.)). The eluent solvent was tetrahydrofuran/methanol = 1/9 (v/v) with the flow rate of 0.6 mL min^{-1}, and **2** was monitored at 254 nm using

a UV/vis detector. A standard curve of **2** from seven concentrations (8.53, 19.8, 23.6, 29.6, 33.9, 37.9, 48.0 mM) was prepared for the quantitative analysis of **2** (Fig. I). The experiments were conducted three times for each batch. The amount of the template coordinated to the Ru porphyrin was estimated by the subtraction of the amount of the template attached on **B** from that attached on **A**, which corresponds to the subtraction of the amount of the template detected in the supernatant of **A** from that detected in the supernatant of **B**. Same experiments were conducted on **A-HL** and **B-HL** (50 mg, Ru: 0.49 wt%, 2.4×10^{-3} mmol) with **2** (15 eq, 20 eq, and 25 eq. to Ru).

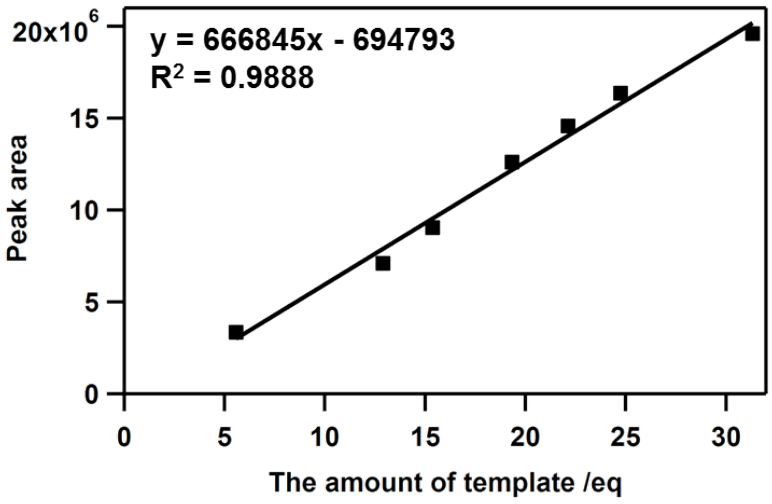


Fig. I. Standard curve to estimate the amount of the template (**2**) by HPLC.

Catalytic reactions

Oxidation of cholesterol derivatives on catalysts: Cholesterol derivatives (4.0×10^{-2} mmol) and 2,6-dichloropyridine N-oxide (79 mg, 0.48 mmol) were added to catalyst (50 mg for **E**, Ru: 8.0×10^{-4} mmol) in a Schlenk tube in an N_2 atmosphere (101.3 kPa). After the addition of chloroform (0.75 mL) the reaction mixture was stirred at 333 K for 24 h. The Ru concentration was kept at 1.1×10^{-3} mol L^{-1}, and the molar ratio of Ru/cholesterol derivatives/2,6-dichloropyridine N-oxide was 1/50/600. After the reaction, the suspension was filtered and the solvent was evaporated. The scale was doubled for the reaction of **B** (50 mg, Ru: 1.6×10^{-3} mmol). As for the reaction of **1**, 10 mg (Ru: 5.6×10^{-3} mmol) of **1** was used.

Estimation of conversion, C_5=C_6 epoxide selectivity, C_5=C_6 epoxide yield, and β-epoxide selectivity by ^{1}H NMR: For the standard scale reaction (cholesterol derivatives: 4.0×10^{-2} mmol), dimethyl terephthalate (used as an internal standard: 4.0×10^{-2} mmol) and chloroform-*d* (0.7 mL) were added to the residue. The mole of dimethyl terephthalate was adjusted to be the same as the initial mole of cholesterol derivatives. Integrated intensities of one H_6 proton at cholesterol derivatives were compared to that of four aromatic ring protons (δ = 8.1 (s, 4H)) of dimethyl terephthalate, and then converted to the amount of each cholesterol derivative.

Conversion % = (initial amount of cholesterol derivative - residual amount of cholesterol derivative) / (initial amount of cholesterol derivative) × 100.

C_5=C_6 Epoxide selectivity % = (amount of C_5=C_6 epoxide) / (initial amount of cholesterol derivative - residual amount of cholesterol derivative) × 100.

C_5=C_6 Yield % = (amount of C_5=C_6 epoxide) / (initial amount of cholesterol derivative) × 100 = (Conversion %) × (C_5=C_6 Epoxide selectivity %) / 100.

β-Epoxide selectivity % = (amount of β-epoxide) / (amount of α-epoxide + amount of β-epoxide) × 100.

Heterogeneity test: The reaction was conducted using the above procedure, but the reaction was stopped at 6 h. The suspension was quickly filtered, and the filtrate was collected and stirred at 333 K for 12 h or 24 h in an N_2 atmosphere (101.3 kPa). After the reaction, the solvent was evaporated, and the ^{1}H NMR analysis was performed in a similar way.

Catalyst recycling test: The reaction was conducted using the above procedure. After the reaction, the suspension was filtered and **E** was washed with chloroform (15 mL). The catalyst was collected and the reaction was performed using the same method.

Isolation of products:

Cholesterol-5α,6α-epoxide and Cholesterol-5β,6β-epoxide: The products were separated by flash column chromatography (neutral SiO_2, eluent: ethyl acetate-hexane (1:2 v/v)). The R_f values of both products were same (0.21). Yield: 92%. ^{1}H NMR (600 MHz, chloroform-*d*): δ = 0.5~2.1, 2.90 (d, $H_{6\alpha}$, 1H), 3.06 (d, $H_{6\beta}$, 1H), 3.69 (m, $H_{3\beta}$, 1H), 3.91 (m, $H_{3\alpha}$, 1H); ^{13}C NMR (150 MHz, chloroform-*d*): δ = 11.74, 11.83, 15.90, 17.03, 18.62, 18.65, 20.63, 21.98, 22.53, 22.79, 23.79, 23.82, 24.03, 24.17, 27.98, 28.05, 28.13, 28.81, 29.68, 29.76, 29.88, 31.03, 31.08, 32.38, 32.60, 34.84, 35.70, 35.73, 36.12, 37.21, 39.40, 39.48, 39.82, 39.86, 42.23, 42.27, 42.32, 42.54, 51.32, 55.85, 56.20, 56.22, 56.84, 59.27, 62.91, 63.70, 65.67, 68.70, 69.40; HR EI MS: *m/z*: Calcd. for $C_{27}H_{46}O_2$: 402.3498 $[M]^{+\bullet}$, Found. 402.3493.

Pregnenolone-5α,6α-epoxide and Pregnenolone-5β,6β-epoxide: The products were separated by flash column chromatography (SiO_2 functionalized with NH, eluent: ethyl acetate-hexane (2:1 v/v)). The R_f values of both products were same (0.32). Yield: 71%. ^{1}H NMR (600 MHz, chloroform-*d*): δ = 0.5~2.3, 2.49 (dd, $H_{17\alpha,\beta}$, 2H), 2.91 (d, $H_{6\alpha}$, 1H), 3.07 (d, $H_{6\beta}$, 1H), 3.70 (m, $H_{3\beta}$, 1H), 3.91 (m, $H_{3\alpha}$, 1H); ^{13}C NMR (150 MHz, chloroform-*d*): δ = 13.09, 13.22, 15.89, 17.05, 20.65, 21.96, 22.66, 22.77, 24.23, 24.35, 28.65, 29.75, 29.86, 30.99, 31.05, 31.43, 31.51, 32.41, 32.52, 34.87, 34.91, 37.24, 38.48, 38.84, 39.79, 42.14, 42.49, 43.87, 43.92, 51.20, 56.34, 56.99, 59.04, 62.81, 63.36, 63.45, 63.67, 65.62, 68.62, 69.34, 209.34, 209.41; HR EI MS: *m/z*: Calcd. for $C_{21}H_{32}O_3$: 332.2351 $[M]^{+\bullet}$, Found. 332.2347.

Dehydroepiandosterone-5α,6α-epoxide and Dehydroepiandosterone-5β,6β-epoxide: The products were separated by flash column chromatography (SiO_2 functionalized with NH, eluent: ethyl acetate-hexane (2:1 v/v)). The R_f values of both products were same (0.31). Yield: 59%. ^{1}H NMR (600 MHz, chloroform-*d*): δ = 0.5~2.3, 2.45 (m, $H_{16\alpha,\beta}$, 4H), 2.95 (d, $H_{6\alpha}$, 1H), 3.13 (d, $H_{6\beta}$, 1H), 3.71 (m, $H_{3\beta}$, 1H), 3.92 (m, $H_{3\alpha}$, 1H); ^{13}C NMR (150 MHz, chloroform-*d*): δ = 13.46, 13.55, 15.91, 17.06, 19.98, 21.27, 21.67, 21.72, 27.71, 29.46, 29.51, 30.97, 31.03, 31.07, 31.46, 31.50, 32.39, 35.00, 35.08, 35.69, 35.72, 37.23, 39.73, 42.05, 42.78, 47.46, 47.60, 51.17, 51.47, 51.82, 58.73, 62.96, 63.28, 65.65, 68.54, 69.27, 220.59, 220.84; HR EI MS: *m/z*: Calcd. for $C_{19}H_{28}O_3$: 304.2038 $[M]^{+\bullet}$, Found. 304.2045.

Methylandrostenediol-5α,6α-epoxide and Methylandrostenediol-5β,6β-epoxide: The products were separated by flash column chromatography (SiO_2 functionalized with NH, eluent: ethyl acetate-hexane (2:1 v/v)). The R_f values of both products were same (0.27). Yield: 52%. ^{1}H NMR (600 MHz, chloroform-*d*): δ = 0.6~2.1, 2.91 (d, $H_{6\alpha}$, 1H), 3.09 (d, $H_{6\beta}$, 1H), 3.70 (m, $H_{3\beta}$, 1H), 3.92 (m, $H_{3\alpha}$, 1H); ^{13}C NMR (150 MHz, chloroform-*d*): δ = 13.69, 13.82, 15.95, 17.10, 20.34, 21.63, 23.12, 23.18, 25.68, 25.82, 28.53, 30.61, 30.74, 31.05, 31.10, 31.20, 31.54, 32.38, 32.47, 34.92, 35.01, 37.24, 38.77, 38.93, 39.83, 42.20, 42.70, 45.23, 45.34, 50.40, 51.32, 51.41, 59.09, 62.91, 63.47, 65.72, 68.67, 69.40, 81.49, 81.63; HR EI MS: *m/z*: Calcd. for $C_{20}H_{32}O_3$: 320.2351 $[M]^{+\bullet}$, Found. 320.2357.

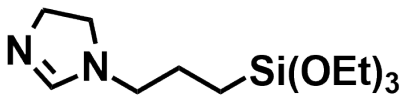
16-Dehydropregnenolone-5α,6α-epoxide and 16-Dehydropregnenolone-5β,6β-epoxide: The products were separated by flash column chromatography (SiO_2 functionalized with NH, eluent: ethyl acetate-hexane (2:1 v/v)). The R_f values of both products were same (0.30). Slight product decomposition was observed (Tailing of spots were observed.). Yield: 32%. ^{1}H NMR (600 MHz, chloroform-*d*): δ = 0.6~2.1, 2.93 (d, $H_{6\alpha}$, 1H), 3.09 (d, $H_{6\beta}$, 1H), 3.70 (m, $H_{3\beta}$, 1H), 3.91 (m, $H_{3\alpha}$, 1H), 6.68 (s, $H_{16\alpha,\beta}$, 2H); ^{13}C NMR (150 MHz, chloroform-*d*): δ = 15.63, 15.70, 15.91, 16.98, 20.36, 21.46, 27.10, 28.11, 28.22, 28.41, 31.08, 31.99, 32.21, 32.50, 34.24, 34.68, 34.91, 35.06, 35.09, 37.18, 39.81, 41.99, 42.20, 42.74, 46.02, 46.04, 51.78, 56.02, 56.30,

58.88, 63.12, 63.40, 65.83, 68.61, 68.67, 69.38, 144.10, 144.14, 155.18, 155.31, 196.70, 196.74; HR EI MS: *m/z*: Calcd. for $C_{21}H_{30}O_3$: 330.2195 $[M]^{+\bullet}$, Found. 330.2204.

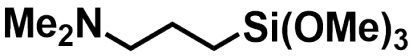
Stigmasterol-5α,6α-epoxide and Stigmasterol-5β,6β-epoxide: The products were separated by flash column chromatography (neutral SiO_2, eluent: ethyl acetate-hexane (1:1 v/v)). The R_f values of both products were same (0.35). Yield: 73%. ^{1}H NMR (600 MHz, chloroform-*d*): δ = 0.5~2.1, 2.90 (d, $H_{6\alpha}$, 1H), 3.05 (d, $H_{6\beta}$, 1H), 3.70 (m, $H_{3\beta}$, 1H), 3.91 (m, $H_{3\alpha}$, 1H), 4.98~5.03 (dd, $H_{23\alpha,\beta}$, 2H), 5.11~5.14 (d, $H_{22\alpha,\beta}$, 2H); ^{13}C NMR (150 MHz, chloroform-*d*): δ = 11.93, 12.04, 12.22, 15.92, 17.04, 18.97, 20.63, 21.07, 21.15, 21.98, 24.11, 24.25, 25.38, 28.73, 28.81, 28.84, 29.76, 29.88, 31.05, 31.10, 31.86, 32.40, 32.60, 34.87, 37.22, 39.30, 39.73, 39.87, 40.44, 42.17, 42.24, 42.59, 51.21, 51.23, 51.36, 55.63, 56.01, 56.33, 56.95, 59.26, 62.91, 63.68, 65.67, 68.74, 69.43, 129.32, 129.34, 138.20; HR EI MS: *m/z*: Calcd. for $C_{29}H_{48}O_2$: 428.3654 $[M]^{+\bullet}$, Found. 428.3646.

The chemical structures of basic organosilanes

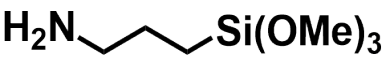
3-(2-imidazolin-1-yl)-propyltriethoxysilane (**3**)



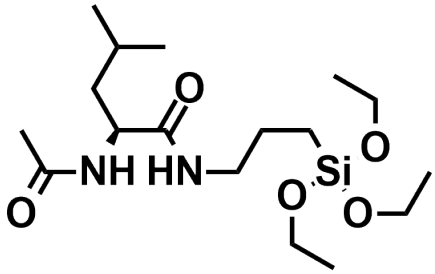
N,*N*-dimethylaminopropyltrimethoxysilane (**4**)



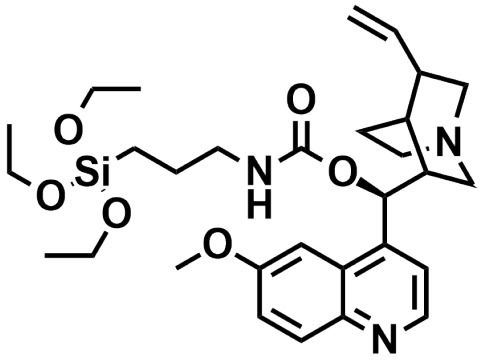
3-aminopropyltrimethoxysilane (**5**)



N-(*N*-acetylleucyl)-3-aminopropyltriethoxysilane (**6**)



(*R*)-*N*-triethoxysilylpropyl-*o*-quinineurethane (**7**)



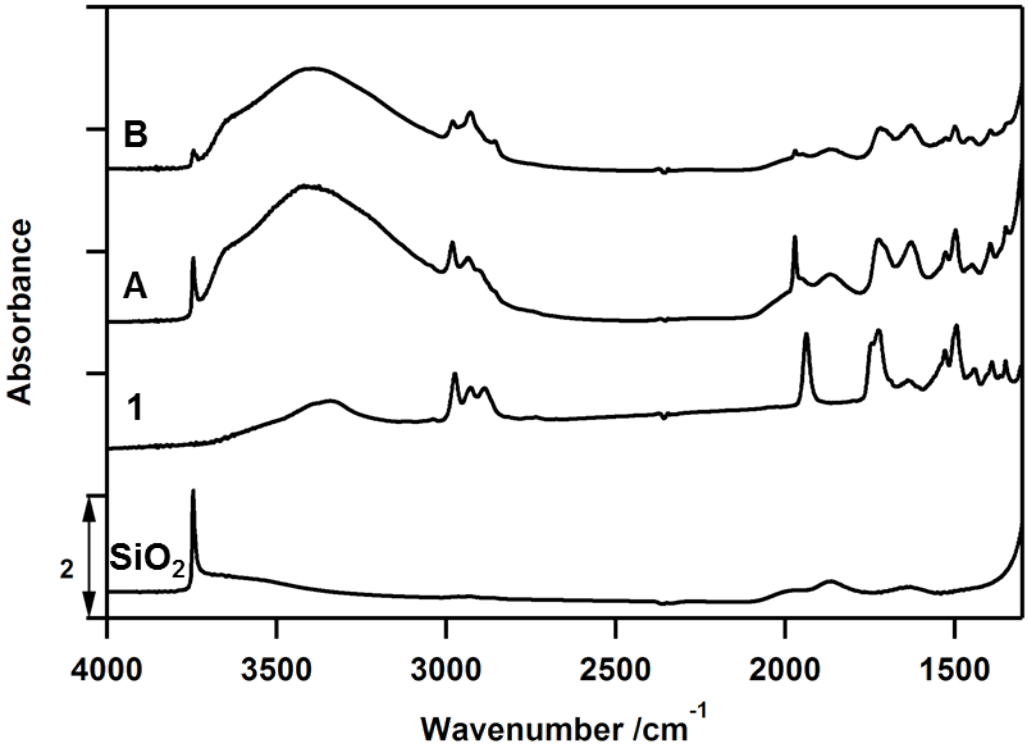


Fig. S1. FT-IR spectra of SiO_2, **1** (in KBr), **A**, and **B** (1300~4000 cm^{-1}).

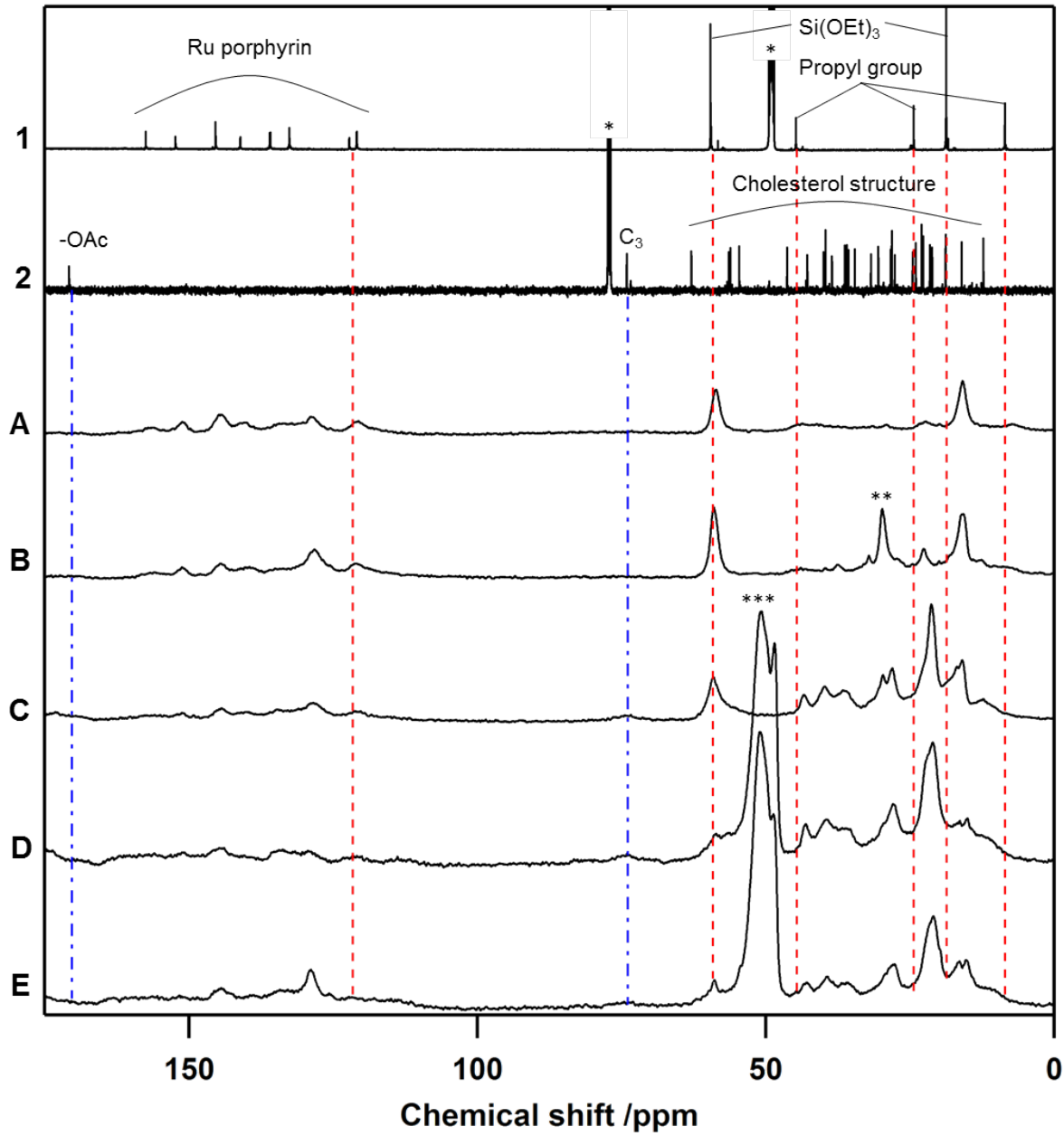


Fig. S2. ^{13}C liquid-state NMR spectra of **1** (in methanol-d_4) and **2** (in chloroform-*d*), and ^{13}C solid-state CP-MAS NMR spectra of **A**, **B**, **C, D**, and **E**. Red dotted lines were characteristic peaks attributed to **1** and blue dashed line were attributed to the template **2**. * and ** indicate solvent peaks, and *** indicates $Si(OCH_3)_x$ of unreacted TMOS.

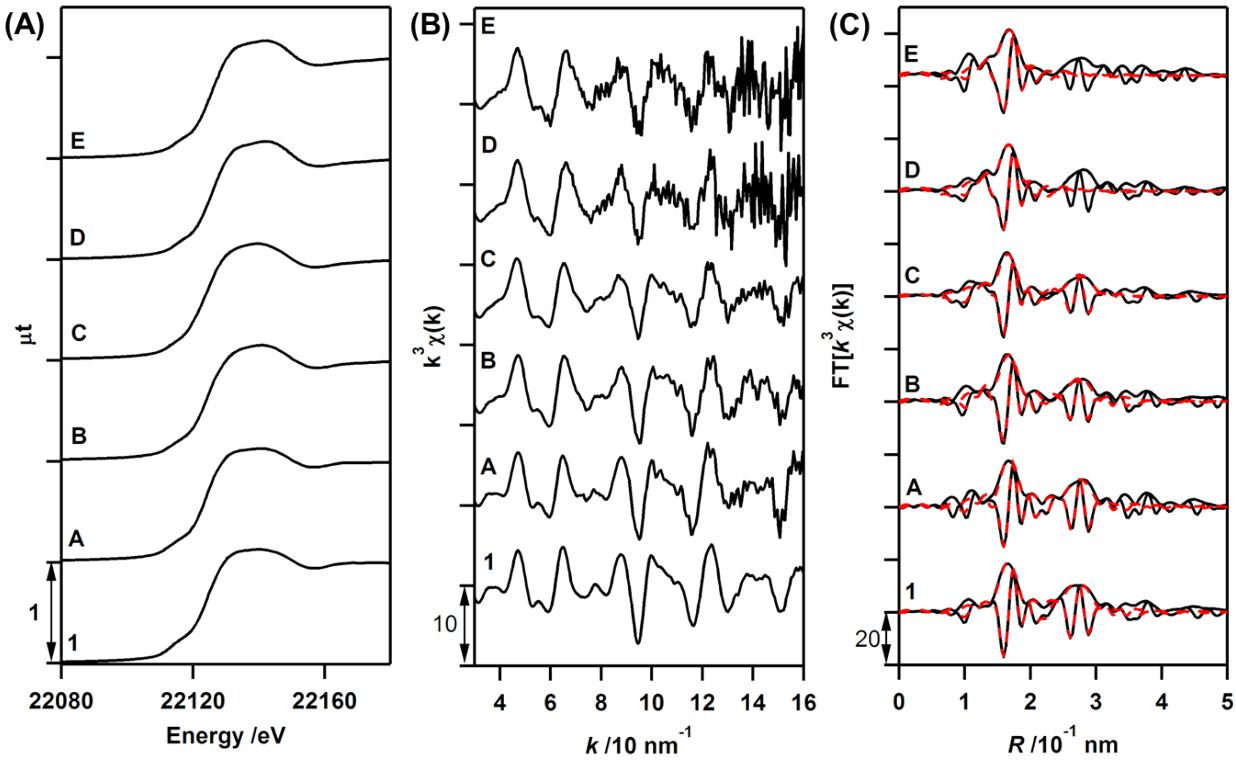


Fig. S3. (A) Normalized Ru K-edge XANES spectra, (B) k^3-weighted Ru K-edge EXAFS oscillations, and (C) their Fourier transforms (k = 30–160 nm^{-1}) for **1**, **A**, **B**, **C**, **D**, and **E** measured at 20 K. Black solid lines in (C) show observed data and red dashed lines show fitted data.

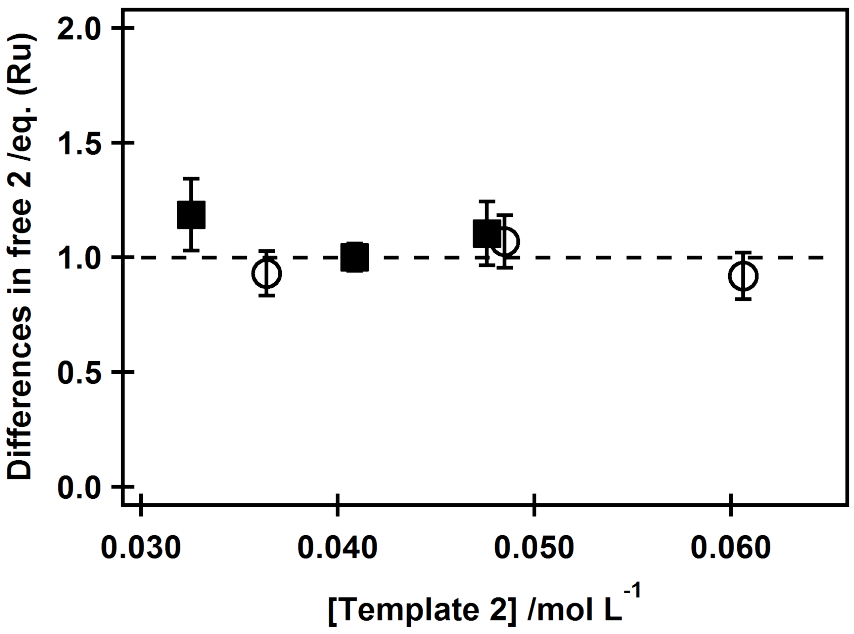


Fig. S4. Differences in free **2** in the supernatants of **A** and **B** per Ru (the amount of free **2** in the supernatant of **A** – that in the supernatant of **B**). ○: Data from **A** and **B**. ■: Data from **A-HL** and **B-HL**.

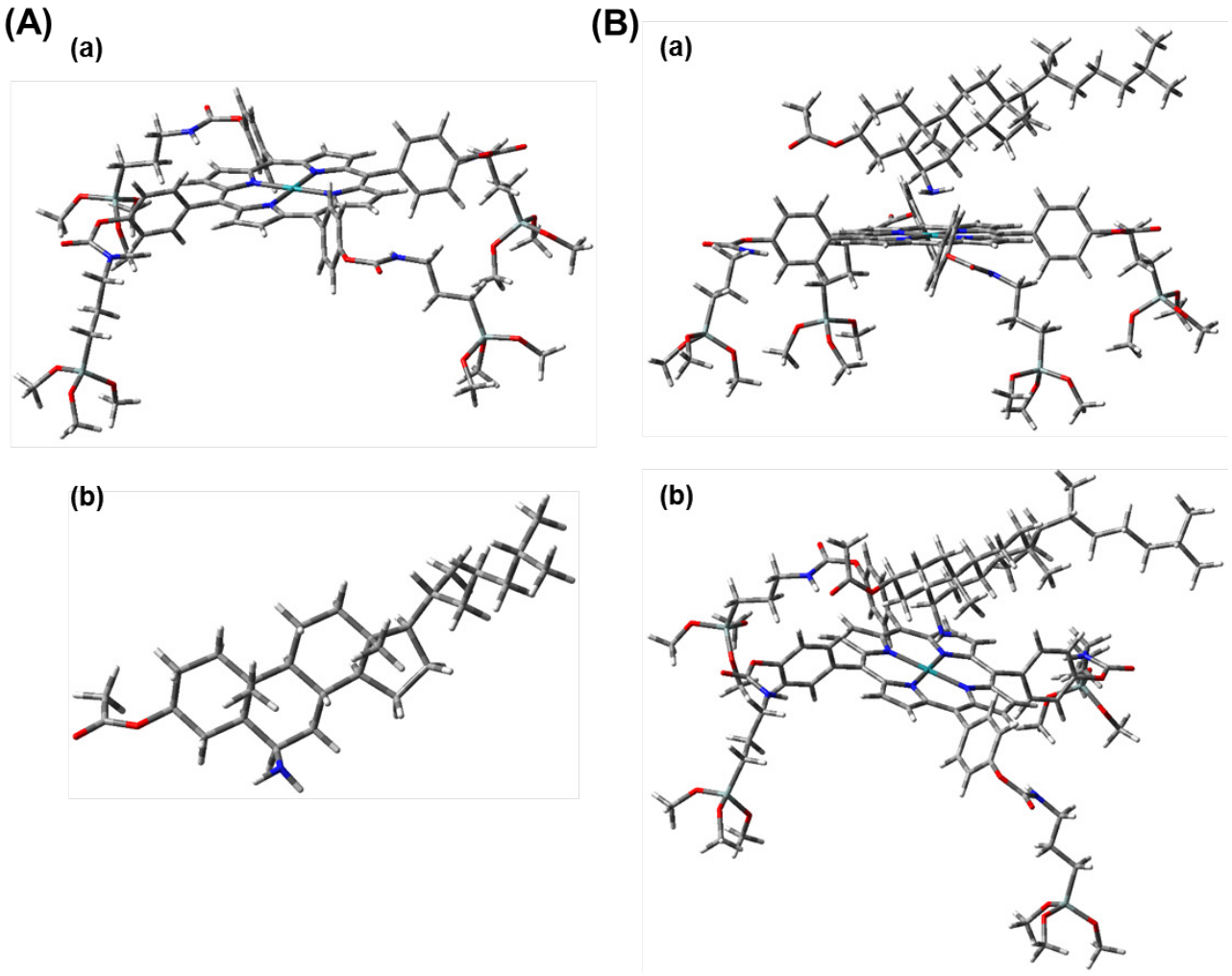


Fig. S5. (A) Optimized modeled structures of (a) **1** and (b) **2** at the DFT/B3LYP level. (Ru: green; C: gray; H: white; N: blue; O: red; Si: light blue), (B) Optimized modeled structure of **C** at the DFT/B3LYP level. (a) Side view, (b) top view (Ru: green; C: gray; H: white; N: blue; O: red, Si: light blue).

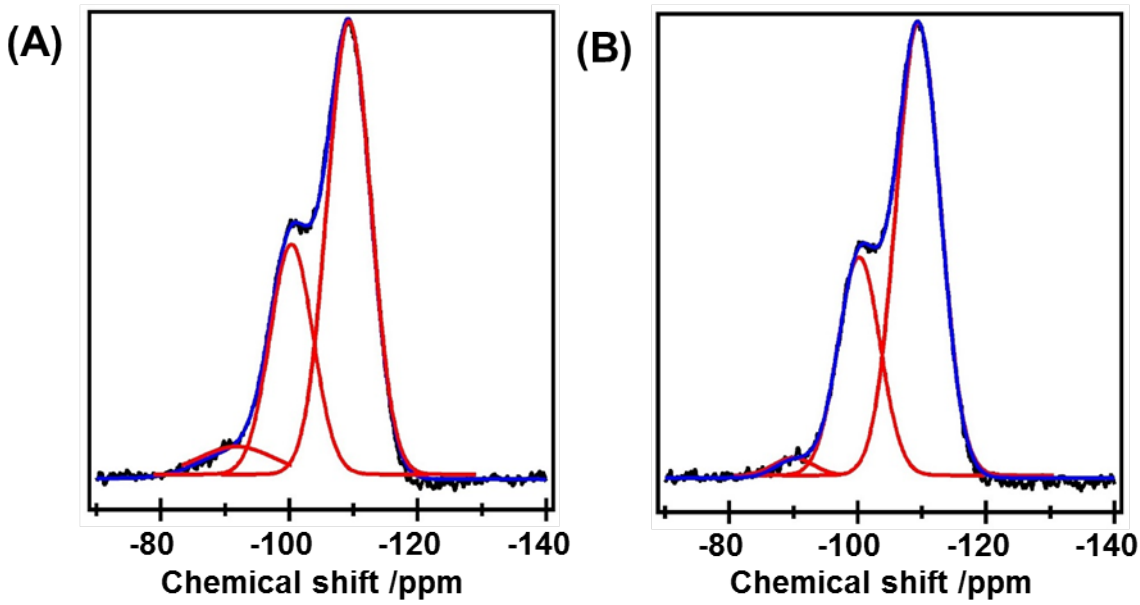


Fig. S6. Curve-fitting results of ^{29}Si solid-state MAS NMR difference spectra of (A) **D-C** and (B) **E-C**. Black lines: observed data; red lines: fitting curves for Q_2, Q_3, and Q_4; blue lines: fitted data.

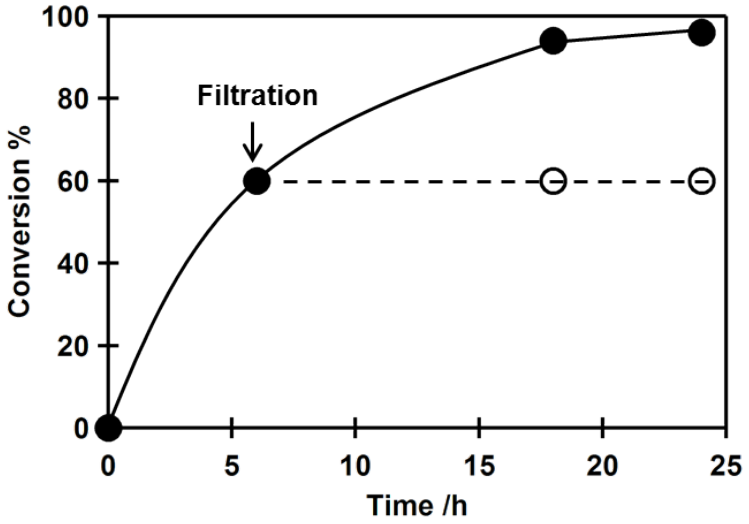


Fig. S7. Test of the heterogeneous nature of the molecularly imprinted catalyst **E** in the cholesterol epoxidation. Reaction conditions: Ru = 8.0×10^{-7} mol (1.1×10^{-3} mol L^{-1}), Ru/cholesterol/2,6-dichloropyridine N-oxide = 1/50/600 (molar ratio), chloroform (0.75 mL), 333 K. ●: Data of the reaction profile, ○: Data of the liquid phase after the filtration of the solid catalyst at 6 h. Conversion % = (initial amount of cholesterol derivative - residual amount of cholesterol derivative) / (initial amount of cholesterol derivative) × 100.

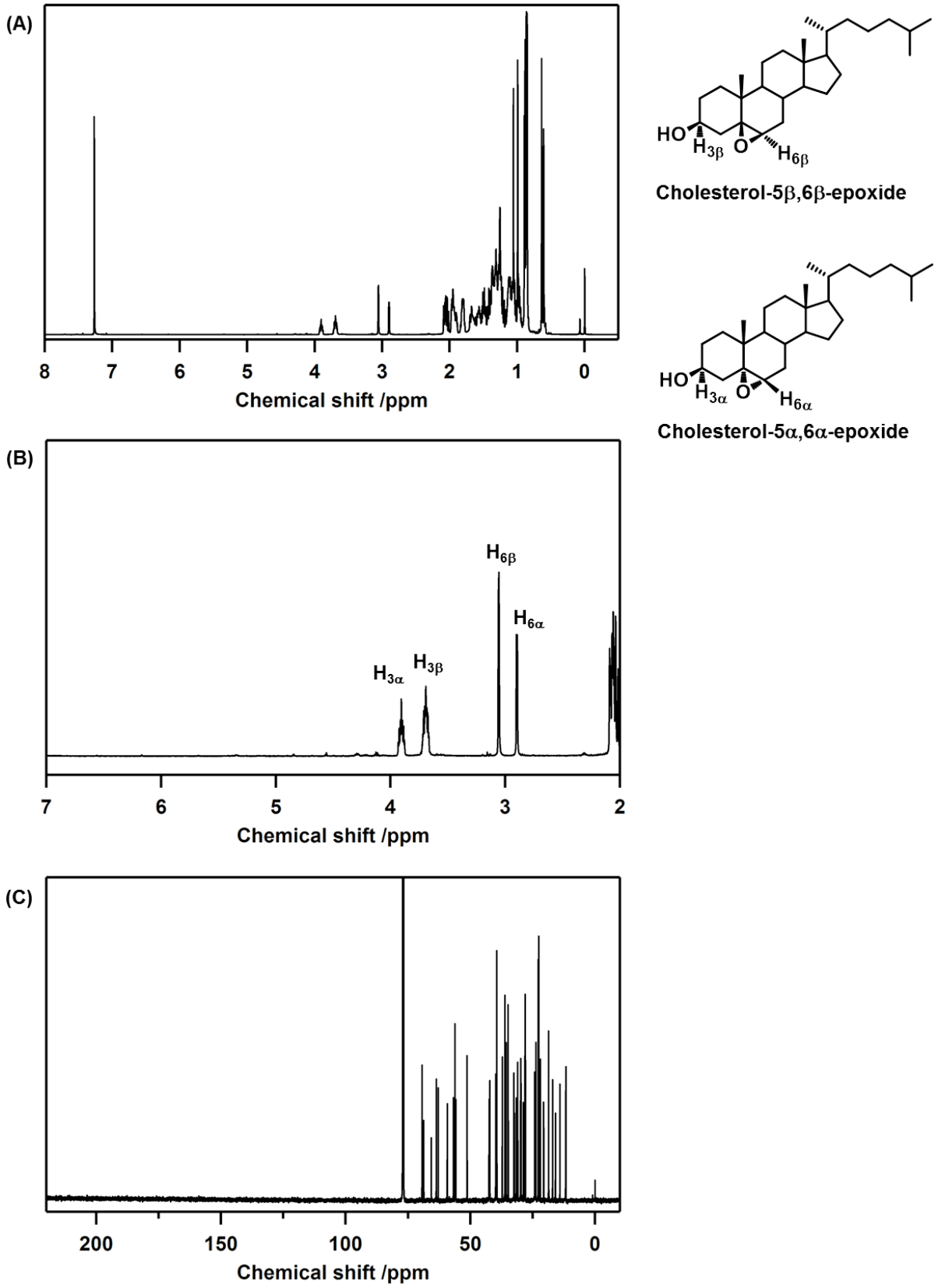


Fig. S8. (A) Whole range and (B) enlarged (2~7 ppm) ^{1}H NMR spectra (in chloroform-*d*), and (C) ^{13}C NMR spectrum (in chloroform-*d*) of isolated products (cholesterol-5α,6α-epoxide and cholesterol-5β,6β-epoxide) after catalytic epoxidation of cholesterol using the molecularly imprinted catalyst **E**.

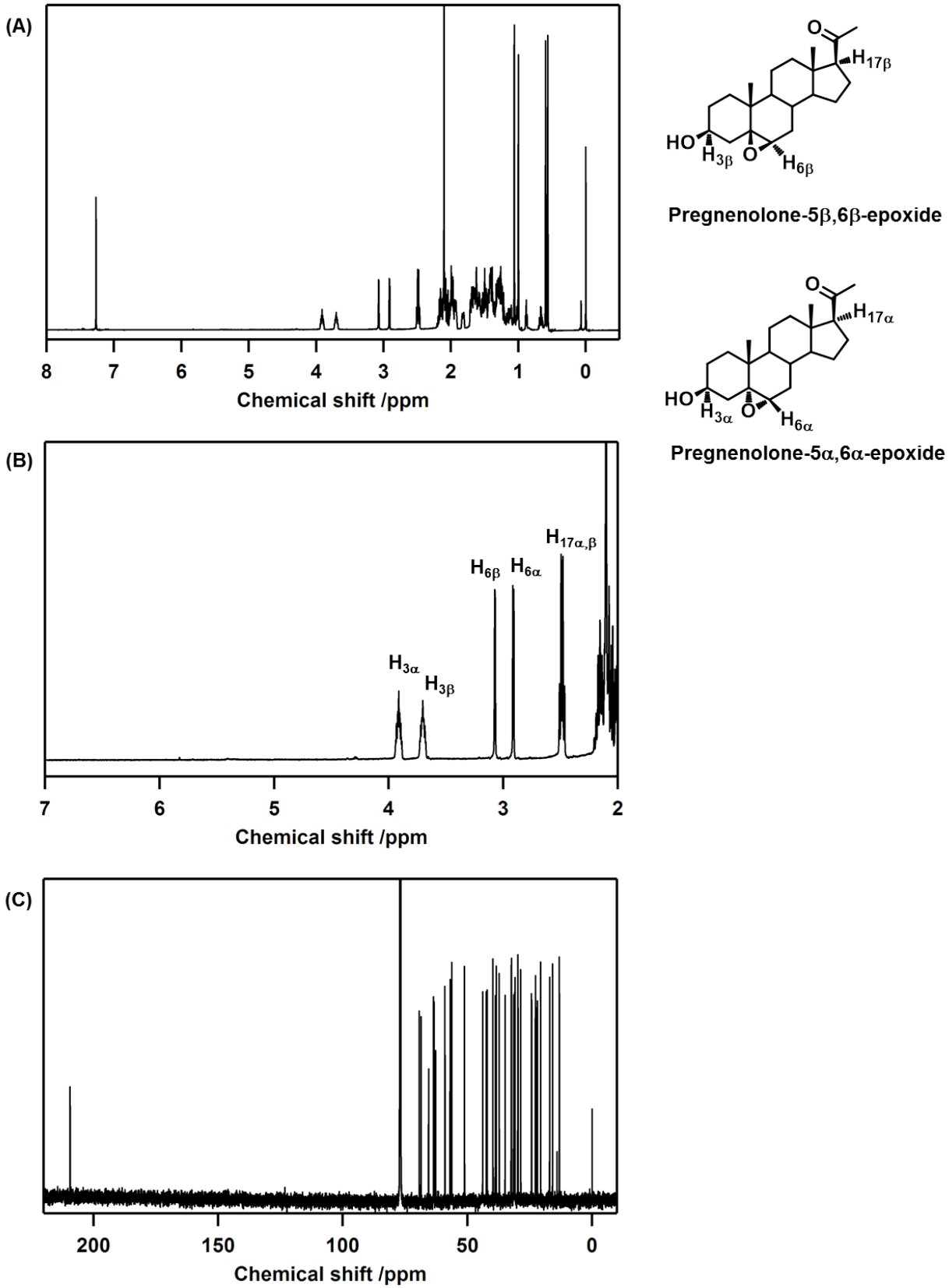


Fig. S9. (A) Whole range and (B) enlarged (2~7 ppm) ^{1}H NMR spectra (in chloroform-*d*), and (C) ^{13}C NMR spectrum (in chloroform-*d*) of isolated products (pregnenolone-5α,6α-epoxide and pregnenolone-5β,6β-epoxide) after catalytic epoxidation of pregnenolone using the molecularly imprinted catalyst **E**.

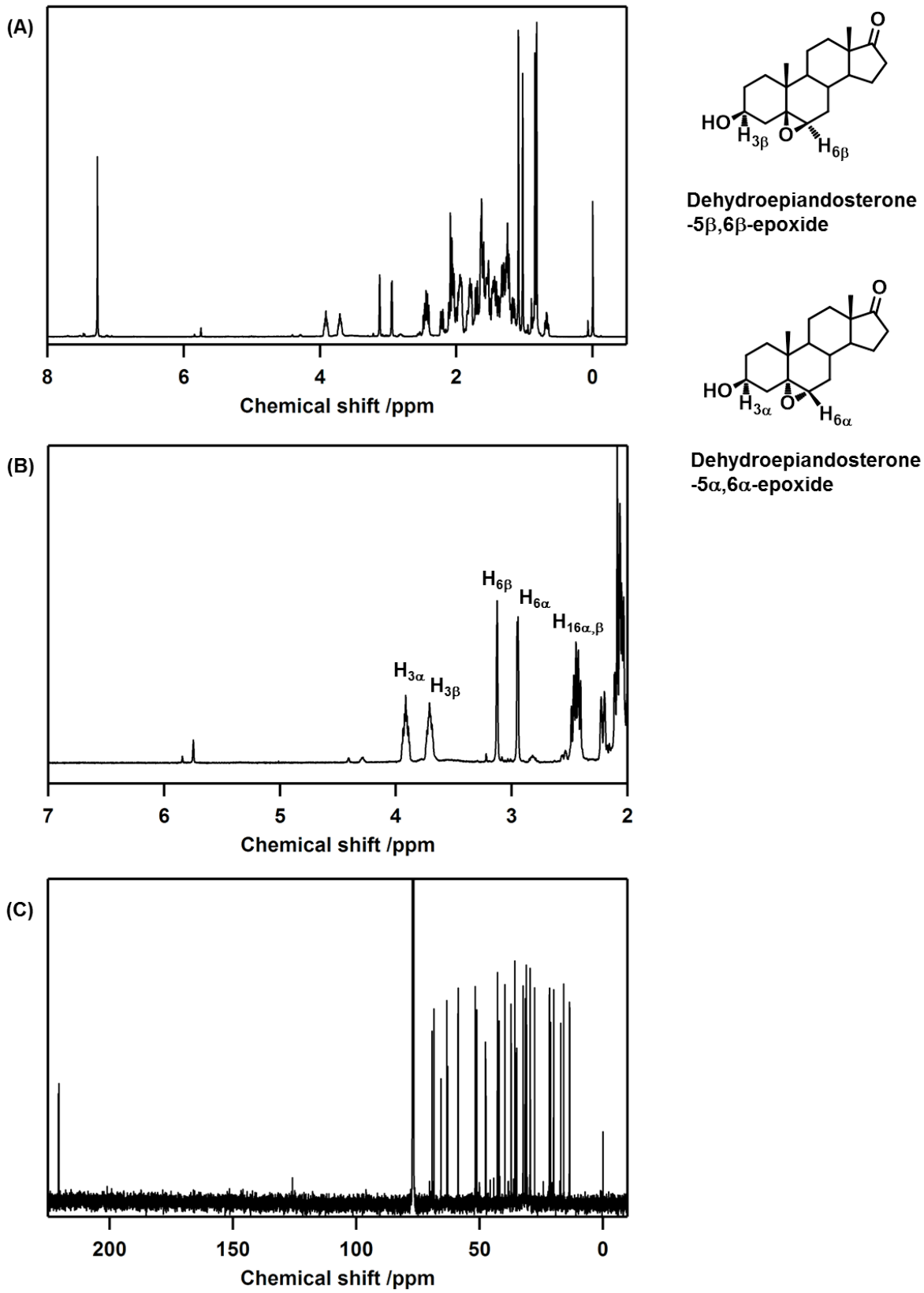


Fig. S10. (A) Whole range and (B) enlarged (2~7 ppm) ^{1}H NMR spectra (in chloroform-*d*), and (C) ^{13}C NMR spectrum (in chloroform-*d*) of isolated products (dehydroepiandrosterone-5α,6α-epoxide and dehydroepiandrosterone-5β,6β-epoxide) after catalytic epoxidation of dehydroepiandrosterone using the molecularly imprinted catalyst **E**.

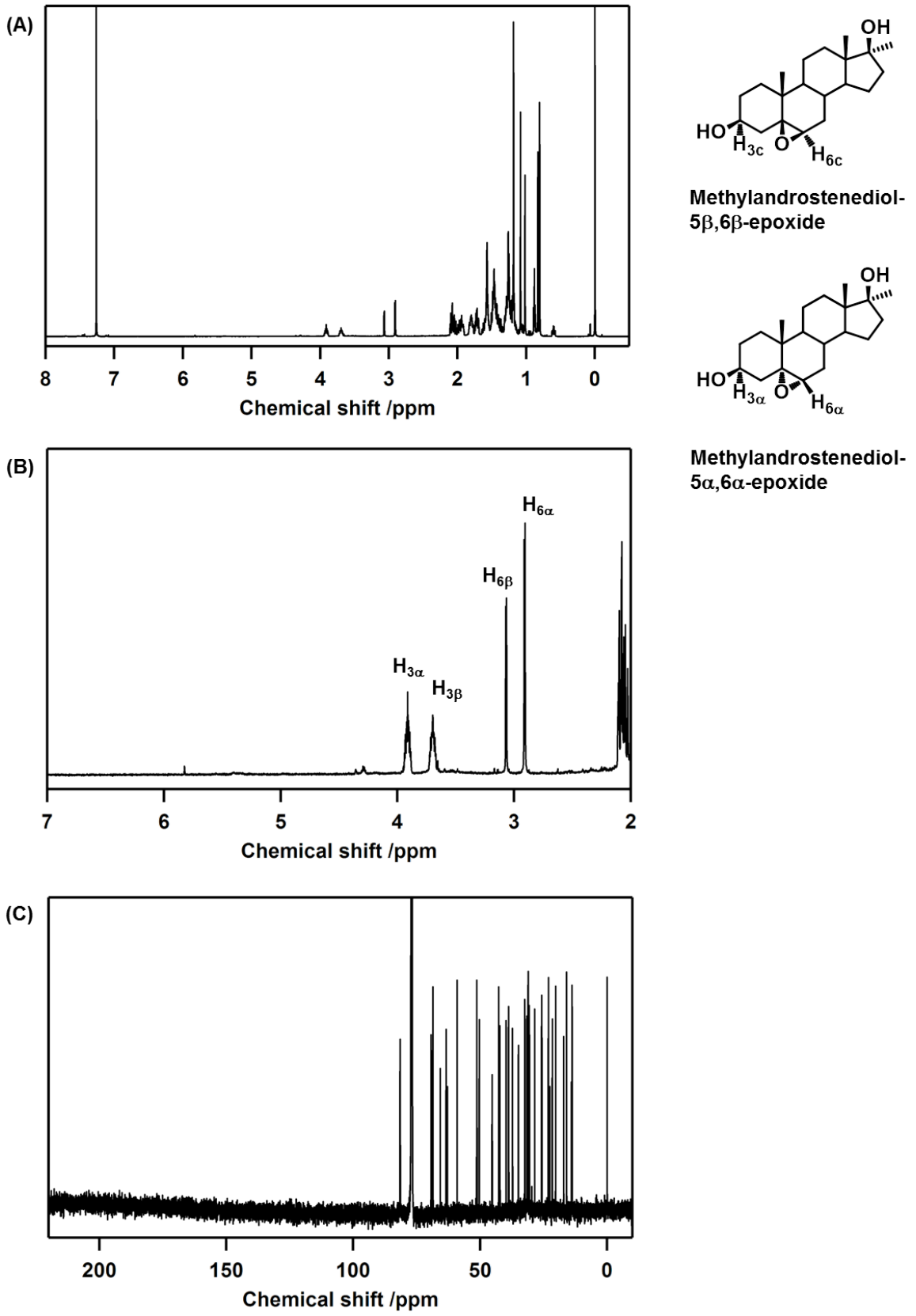


Fig. S11. (A) Whole range and (B) enlarged (2~7 ppm) ^{1}H NMR spectra (in chloroform-*d*), and (C) ^{13}C NMR spectrum (in chloroform-*d*) of isolated products (methylandrostenediol-5α,6α-epoxide and methylandrostenediol-5β,6β-epoxide) after catalytic epoxidation of methylandrostenediol using the molecularly imprinted catalyst **E**.

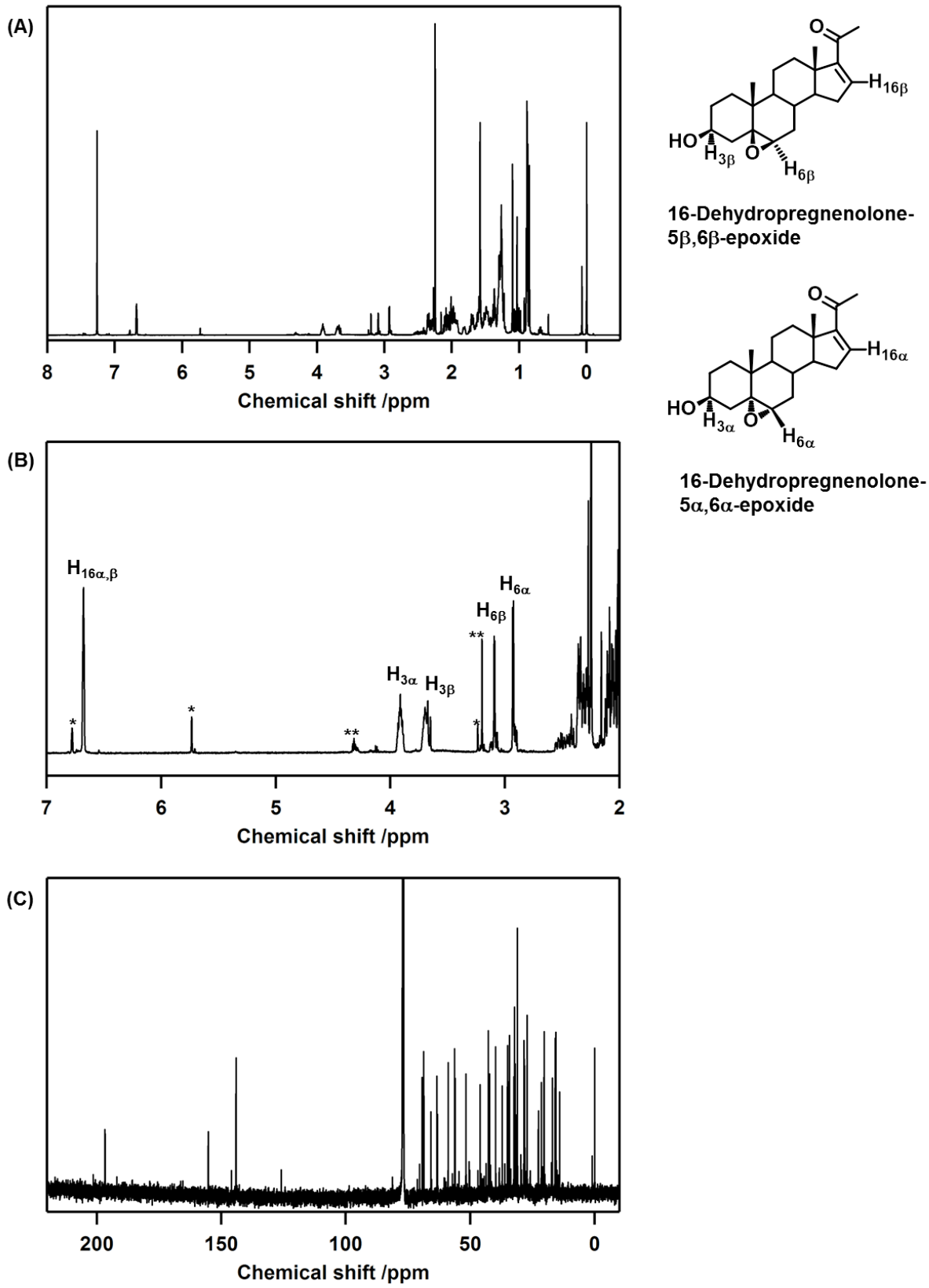


Fig. S12. (A) Whole range and (B) enlarged (2~7 ppm) ^{1}H NMR spectra (in chloroform-*d*), and (C) ^{13}C NMR spectrum (in chloroform-*d*) of isolated products (16-dehydropregnenolone-5α,6α-epoxide and 16-dehydropregnenolone-5β,6β-epoxide) after catalytic epoxidation of 16-dehydropregnenolone using the molecularly imprinted catalyst **E**. * is slightly decomposed species during isolation process. ** is impurity from initial reactant.

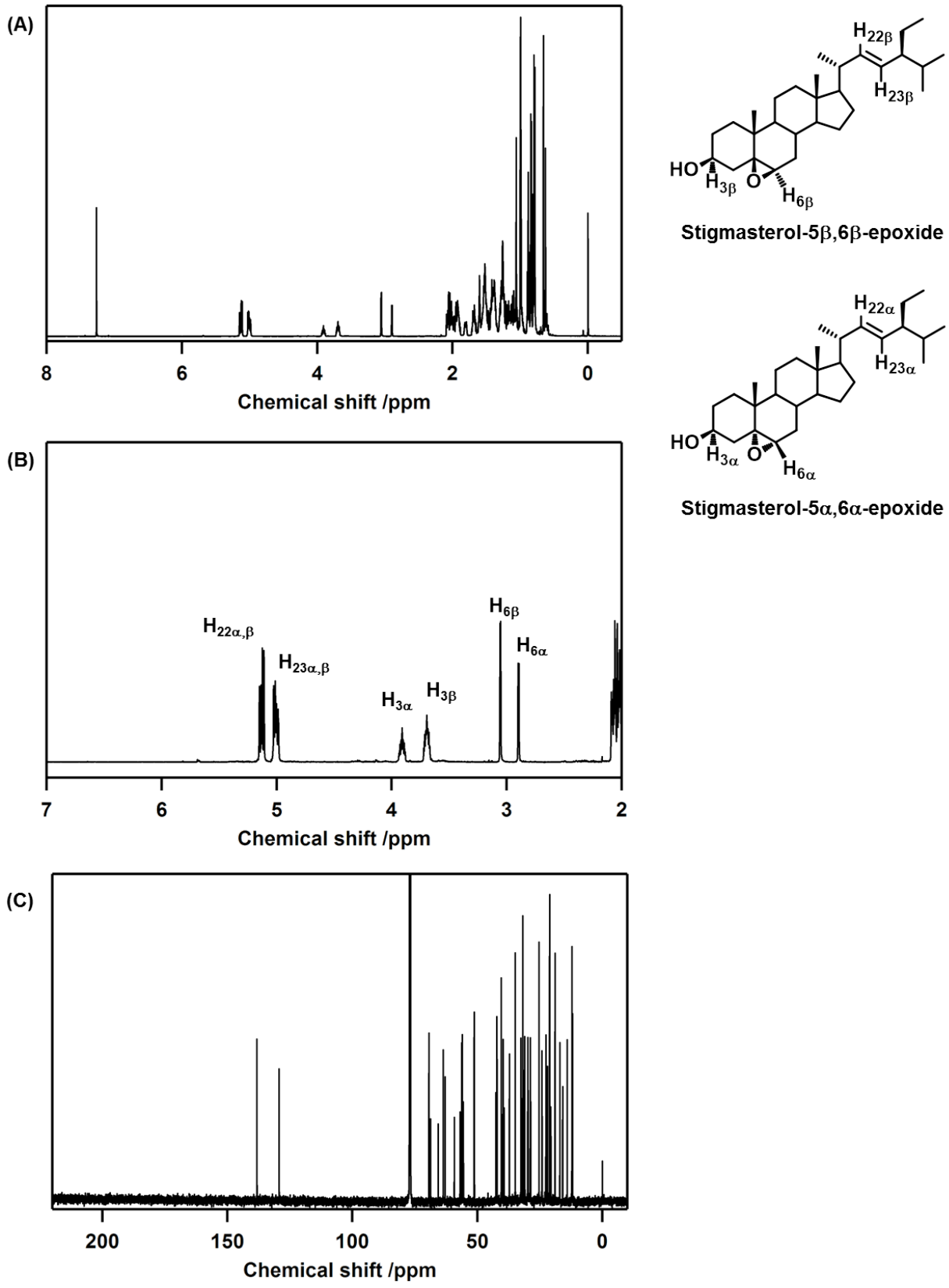


Fig. S13. (A) Whole range and (B) enlarged (2~7 ppm) ^{1}H NMR spectra (in chloroform-*d*), and (C) ^{13}C NMR spectrum (in chloroform-*d*) of isolated products (stigmasterol-5α,6α-epoxide and stigmasterol-5β,6β-epoxide) after catalytic epoxidation of stigmasterol using the molecularly imprinted catalyst **E**.

Table S1. Structural Parameters Obtained by Curve-Fitting Analysis of Ru K-edge EXAFS Measured at 20 K [a]

Shell	CN	R /nm	ΔE_0	σ^2 / 10^5 nm^2
		1 [b]		
Ru–C (CO)	1.1 ± 0.2	0.184 ± 0.002	0 ± 5	3 ± 2
Ru–N (porphyrin)	4.3 ± 0.9	0.205 ± 0.001	-3 ± 3	3 ± 1
Ru···O (CO)	1.1 ± 0.2	0.300 ± 0.005	3 ± 4	3 ± 4
Ru···O(C) (CO)	2.2 ± 0.5	0.300 ± 0.005	3 ± 4	3 ± 4
Ru···C(O)(C) (CO)	1.1 ± 0.2	0.300 ± 0.005	0 ± 5	3 ± 2
Ru···C (porphyrin)	8.6 ± 1.9	0.308 ± 0.002	0 ± 5	3 ± 2
Ru···C(N) (porphyrin)	17.2 ± 3.7	0.320 ± 0.006	0 ± 5	3 ± 2
Ru···C' (porphyrin)	4.3 ± 0.9	0.344 ± 0.004	0 ± 5	3 ± 2
		A [c]		
Ru–C (CO)	0.9 ± 0.3	0.187 ± 0.004	0 ± 5	3 ± 3
Ru–N (porphyrin)	3.7 ± 1.1	0.205 ± 0.001	-2 ± 4	2 ± 2
Ru···O (CO)	0.9 ± 0.3	0.301 ± 0.007	3 ± 7	2 ± 8
Ru···O(C) (CO)	1.8 ± 0.5	0.301 ± 0.007	3 ± 7	2 ± 8
Ru···C(O)(C) (CO)	0.9 ± 0.3	0.301 ± 0.007	0 ± 5	3 ± 3
Ru···C (porphyrin)	7.3 ± 2.1	0.308 ± 0.003	0 ± 5	3 ± 3
Ru···C(N) (porphyrin)	14.6 ± 4.2	0.322 ± 0.010	0 ± 5	3 ± 3
Ru···C' (porphyrin)	3.7 ± 1.1	0.344 ± 0.005	0 ± 5	3 ± 3
		B [d]		
Ru–N (porphyrin)	3.2 ± 0.6	0.206 ± 0.001	-1 ± 3	2 ± 1
Ru···C (porphyrin)	6.4 ± 1.2	0.309 ± 0.002	-1 ± 3	2 ± 1
Ru···C(N) (porphyrin)	12.8 ± 2.3	0.318 ± 0.004	-1 ± 3	2 ± 1
Ru···C' (porphyrin)	3.2 ± 0.6	0.343 ± 0.003	-1 ± 3	2 ± 1
		C [e]		
Ru–N (template)	0.9 ± 0.7	0.184 ± 0.003	-8 ± 6	3 ± 1
Ru–N (porphyrin)	4.2 ± 0.8	0.204 ± 0.002	-8 ± 6	3 ± 1
Ru···C (porphyrin)	8.3 ± 1.6	0.309 ± 0.002	-3 ± 4	3 ± 1
Ru···C(N) (porphyrin)	16.7 ± 3.2	0.320 ± 0.005	-3 ± 4	3 ± 1
Ru···C' (porphyrin)	4.2 ± 0.8	0.342 ± 0.003	-3 ± 4	3 ± 1
		D [f]		
Ru–N (template)	0.4 ± 0.6	0.186 ± 0.006	-1 ± 2	2 ± 1
Ru–N (porphyrin)	3.8 ± 1.0	0.206 ± 0.001	-1 ± 2	2 ± 1
		E [g]		
Ru–N (porphyrin)	3.2 ± 0.4	0.207 ± 0.001	2 ± 2	2 ± 1

[a] k = 30–160 nm^{-1}, S_0^2 was fixed to be 1. [b] R = 0.10–0.34 nm, R_f = 2.6%. [c] R = 0.10–0.34 nm, R_f = 3.5%. [d] R = 0.10–0.34 nm, R_f = 5.3%. [e] R = 0.10–0.34 nm, R_f = 5.4%. [f] R = 0.10–0.22 nm, R_f = 2.6%. [g] R = 0.12–0.22 nm, R_f = 1.0%.

Table S2. Curve Fitting Analysis of ^{29}Si solid-state MAS NMR difference spectra of **D-C** and **E-C**

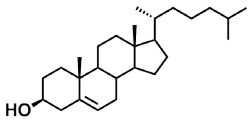
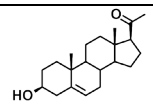
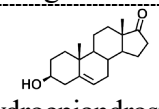
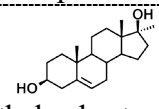
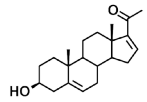
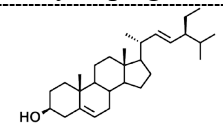
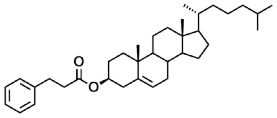
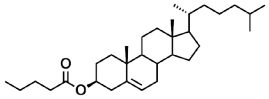
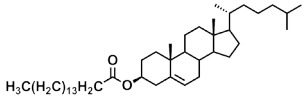
Sample	Q_2			Q_3			Q_4		
	Location (ppm)	Area	Ratio %	Location (ppm)	Area	Ratio %	Location (ppm)	Area	Ratio %
D-C	-91.8	1.76	6.5	-100.3	8.49	31.2	-109.3	17.0	62.3
E-C	-90.0	0.47	2.3	-100.2	6.25	30.7	-109.4	13.6	67.0

Table S3. Ru Loading of the Catalysts **E**

Catalyst	Temperature of the hydrolysis polymerization	Calculated SiO_2-matrix height [a]	Ru loading /wt%
E (363 K)	363 K	2.4 nm	0.12
E (373 K)	373 K	1.6 nm	0.15
E	383 K	2.1 nm	0.13
E (**3**-1 wt%)	383 K	2.1 nm	0.14
E (**4**-1 wt%)	383 K	1.6 nm	0.15
E (**5**-1 wt%)	383 K	1.4 nm	0.14
E (**6**-1 wt%)	383 K	2.4 nm	0.13
E (**7**-1 wt%)	383 K	2.4 nm	0.15
E (**4**-0.1 wt%)	383 K	1.8 nm	0.13

[a] Calculated height of the SiO_2-matrix overlayers was estimated by the density of SiO_2 (quartz, 2.2 g cm^{-3}).

Table S4. Complete Table for Selective Oxidation Performances of Cholesterol Derivatives [a]

Entry	Catalyst	Reactant	Yield of C_5=C_6 epoxide % [b]	β-Epoxide selectivity % [d]
1	---	 Cholesterol	0	–
2	**1**		30	33
3	**B**		23	26
4	**E** (363 K)		49	37
5	**E** (373 K)		68	32
6	**E**		95 (92[c])	57 (60[e])
7	**E** (**3**-1wt%)		0	–
8	**E** (**4**-1wt%)		4	42
9	**E** (**4**-0.1wt%)		82	51
10	**E** (**5**-1 wt%)		0	–
11	**E** (**6**-1 wt%)		35	43
12	**E** (**7**-1 wt%)		60	45
13	**B**	 Pregnenolone	~0	–
14	**E**		81 (71[c])	49 (49[e])
15	**B**	 Dehydroepiandrosterone	~0	–
16	**E**		73 (59[c])	49 (48[e])
17	**B**	 Methylandrostenediol	~0	–
18	**E**		76 (52[c])	50 (49[e])
19	**B**	 16-Dehydropregnenolone	~0	–
20	**E**		74 (32[c])	49 (49[e])
21	**B**	 Stigmasterol	~0	–
22	**E**		81 (73[c])	58 (60[e])
23	**E**	 Cholesterol hydrocinnamate	45	100
24	**E**	 Cholesterol *n*-valerate	38	87
25	**E**	 Cholesterol palmitate	49	100

[a] Reaction conditions: Ru = 1.1 × 10^{-3} mol L^{-1} in chloroform, Ru/reactant/2,6-dichloropyridine N-oxide = 1/50/600 (molar ratio), 333 K. 24 h. [b] Yield determined by ^{1}H NMR. Yield % = (amount of C_5=C_6 epoxide) / (initial amount of cholesterol derivative) × 100. [c] Isolated yield of C_5=C_6 epoxide. [d] β-Epoxide selectivity % = (amount of cholesterol-5β,6β-epoxide) / (amount of cholesterol-5α,6α-epoxide + amount of cholesterol-5β,6β-epoxide) × 100. [e] β-Epoxide selectivity % was also calculated from the ^{1}H NMR of the isolated products.

Table S5. Catalyst Recycling Results for the Selective Oxidation of Cholesterol with **E**

	Yield of C_5=C_6 Epoxide % [a]	β-Epoxide selectivity % [b]
Fresh	95	57
1st recycle	87	56
2nd recycle	85	57

Initial condition: Ru = 1.6×10^{-6} mol (1.1×10^{-3} mol L^{-1}), Ru/cholesterol/2,6-dichloropyridine N-oxide = 1/50/600 (molar ratio), chloroform (1.5 mL), 333 K. 24 h. [a] Yield determined by ^{1}H NMR. Yield % = (amount of C_5=C_6 epoxide) / (initial amount of cholesterol derivative) × 100. [b] β-Epoxide selectivity % = (amount of cholesterol-5β,6β-epoxide) / (amount of cholesterol-5α,6α-epoxide ＋ amount of cholesterol-5β,6β-epoxide) × 100.

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