Supporting Information

Gold Nanocluster Functionalized with Peptide Dendron Thiolates: Acceleration of the Photocatalytic Oxidation of an Amino Alcohol in a Supramolecular Reaction Field

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Contents

Experimental Section

General. All reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under a positive pressure of argon. The air- and moisture-sensitive liquids and solutions were transferred *via* syringes or a PTFE cannula. Analytical TLC was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator (Merck, #1.05715.0009). The TLC plates were visualized by exposure to UV light (254 nm), iodine vapor, and by immersion in a ninhydrin solution, followed by heating on a hot plate. Organic solutions were concentrated by rotary evaporation at *ca.* 30–400 mmHg. Flash column chromatography was performed on Merck silica gel 60 (spherical, neutral, 140–325 mesh).

Instruments. Proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on JEOL ECS-400NR (392 MHz) spectrometer. Proton chemical shift values are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the tetramethylsilane (δ 0.00). ^{13}C NMR spectra were recorded at 98.5 or 151 MHz: carbon chemical shift values are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of $CDCl^3$ (δ 77.0). Data are presented as: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, m = multiplet and/or multiplet resonances, br = broad), coupling constant in hertz (Hz), signal area integration in natural numbers, and assignment (*italic*). IR spectra were recorded on an ATR-FTIR spectrometer (FT/IR-spectrum One, PerkinElmer). Characteristic IR absorptions are reported in cm^{-1}. The high precision isotope peak intensities ratios were determined by fourier transformation-ion cyclotron resonance-mass spectrometry (FT-ICR-MS) coupled with electron spray

ionization (ESI) technique using a SolariX FT-ICR-MS spectrometer (Bruker Daltonics GmbH). UV−Vis absorption spectra were recorded on a Shimadzu UV-2700 spectrometer equipped with UNISOKU CoolSpek UV USP-203-B cryostat. Photoluminescence spectra were recorded at room temperature on a Horiba Jobin Yvon Fluorolog(r)-3 FL3-2iHR fluorescence spectrometer equipped with PMT (R2658 in the range of UV–Vis–NIR) and InGaAs (Symphony II IGA in the range of NIR-IR) photodetectors, and a 450 W xenon lamp. Photochemical reactions were carried out using Asahi Spectra MAX-303 and MAX-301 Xe light sources. Circular dichroism measurement was performed using JASCO J-820 spectrometer. The photo-irradiation power was measured by HIOKI optical power meter 3664. Optical rotation was measured on a JASCO DIP-370 digital polarimeter. Transmission electron microscopy (TEM) measurements were carried out using JEOL JEM-1011. TEM Samples were prepared by drying a drop of a $CHCl_3$ solution of metallic nanoparticles onto a copper grid coated with a carbon support film. Elemental analyses were carried out at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. Flash column chromatography was performed using Biotage SP-1 and Yamazen YFLC-AI-580.

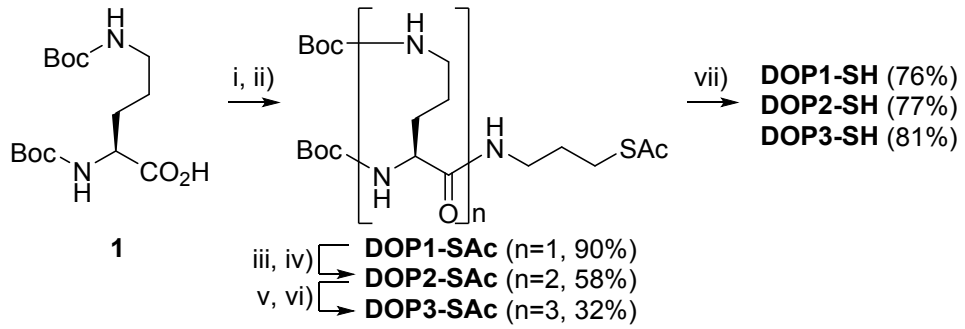
Materials. Materials were purchased from Wako, Tokyo Chemical Industry Co., Ltd., Nakalai tesque, Inc., and other commercial suppliers, and were used without further purification, unless otherwise noted. Sodium tetrahydrideborate ($NaBH_4$) and L-Ornithine hydrochloride were purchased from Nacalai tesque, Inc. Sodium hydrogen carbonate, sodium hydroxide, *N,N'*-dicyclohexylcalbodiimide (DCC), *N,N*-dimethyl-4-aminopyridine (DMAP), *S*-potassium thioacetate, diisopropylethylamine (DIEA), triethylamine (NEt_3), 1-hydroxybenzotriazole (HOBt), and trifluoroacetic acid were purchased from Wako. Methylene blue and 3-

bromopropylamine hydrobromide were purchased from Tokyo Chemical Industry Co., Ltd. (TCI). Tetrachloroauric(III) acid tetrahydrate ($HAuCl_4 \cdot 4H_2O$) was purchased from TANAKA KIKINNZOKU KOGYO K. K. Bis-*tert*-butyl dicarbonate was purchased from Apollo scientific Ltd. A coupling agent of 2-(1*H*-benzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate (HBTU) was purchased from peptide institute, Inc.

General procedure for photocatalytic oxidation of amino alcohols. A Schlenk-head NMR tube was charged with amino alcohol (6 μmol) and gold nanocluster (60 nmol). The NMR tube was purged with O_2 (1 atm). To the NMR tube were added solvent (600 μL) and a sealed glass capillary filled with 1,1,2,2-tetrachloroethane in $CDCl_3$ as an internal standard. The NMR tube was irradiated by an Asahi Spectra MAX-303 and MAX-301 xenon light sources from bottom. The photo-irradiation power was measured by HIOKI optical power meter 3664. The reaction process was monitored by ^1H NMR measurement on a JEOL ECS-400NR.

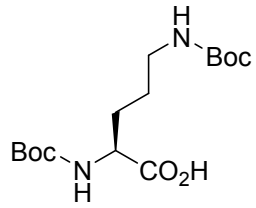
Time-course trace of $^1O_2$ probe reaction. The stock solution containing AuNCs (0.36 nmol) in $CHCl_3$ was added to 10 mm quarts cell for fluorescent measurement, then the solvent was removed under vacuum. To the quarts cell was added 60 μM 1,3-diphenylisobenzofuran (DPBF) solution in 3 mL of $CHCl_3$ or DMF and a magnetic stirring bar. The solution was purged with O_2 (1 atm) immediately prior to measurement. The quarts cell was put into a Shimadzu UV-2700 spectrometer equipped with a UNISOKU CoolSpeK UV USP-203-B temperature controller, and irradiated by an ASAHI SPECTRA MAX-303 (680 nm, c.a. 1 mW/cm^2) under stirring at 25 °C. The time-course reaction process was monitored by the disappearance of 418 nm absorption band of DPBF.

Scheme S1. Synthesis of Peptide Dendron Thiols



Conditions: i) 3-bromopropylamine hydrobromide (1.0 eq), NEt_3 (1.1 eq), DCC (1.2 eq), DMAP (0.1 eq), CH_2Cl_2, 0 °C to rt, 5 h; ii) KSAc (1.2 eq), acetone, 40 °C, 1 h; iii) TFA (20 eq), CH_2Cl_2, 0 °C to rt, 2 h, then HCl (20 eq), dioxane, rt, 1 h; iv) **1** (2.2 eq), HBTU (2.2 eq), HOBt (1.0 eq), NEt_3 (4.2 eq), CH_2Cl_2, rt, 20 h; v) TFA (40 eq), CH_2Cl_2, 0 °C to rt, 12 h, then HCl (40 eq), dioxane, rt, 1 h; vi) **1** (4.2 eq), HBTU (4.2 eq), HOBt (2.2 eq), NEt_3 (12 eq), CH_2Cl_2, rt, 24 h; vii) DIEA (2.0 eq), MeOH, rt, 12 h.

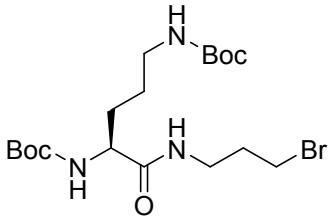
Boc-L-Orn(Boc)-OH



To a stirred solution of L-ornithine hydrochloride (5.8 g, 35 mmol) and sodium hydrogen carbonate (6.1 g, 73 mmol) in water (70 mL) was added dropwise a solution of di-*tert*-butyl dicarbonate (19 g, 87 mmol) in 1,4-dioxane (73 mL) and the resulting mixture was stirred at room temperature for 12 h. The mixture was concentrated under reduced pressure, diluted with H_2O and washed with hexane. The pH of the aqueous layer was reduced to c.a. 3 through addition of aqueous hydrochloric acid (0.5 M). The resultant precipitate was extracted with $CHCl_3$. The combined organic layer was dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure to afford Boc-L-Orn(Boc)-OH as colorless solid (10.9 g, yield 95%); $[\alpha]_D^{25} = -0.17$ (c=1.0 in MeOH); ^{1}H NMR (DMSO-d_6, 391.8 MHz): δ 12.4 (s, 1H, -COO*H*), 7.05 (d, J= 7.9 Hz, 1H, -CON*H*-),

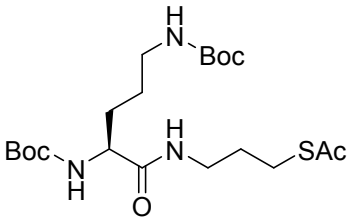
6.77 (t, J = 8.5 Hz, 1H, -CON*H*-), 3.85–3.80 (m, 1H, -NHC*H*(CH_2-)COOH), 2.88 (q, J = 6.3 Hz, 2H, -$CHCH_2CH_2CH_2$-), 1.68–1.41 (m, 4H, -$CHCH_2CH_2CH_2$-), 1.38 (s, 9H, -$C(CH_3)_3$), 1.37 (s, 9H, -$C(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 98.5 MHz): δ 174.1, 155.6, 80.2, 77.9, 73.6, 53.3, 28.3, 28.2, 26.2, 17.6; HRMS (ESI-FT-ICR): *m/z* calcd for $C_{18}H_{33}N_3O_5(H_2O)$: 390.25986 $[M+H]^+$; found: 390.25970.

DOP1-Br



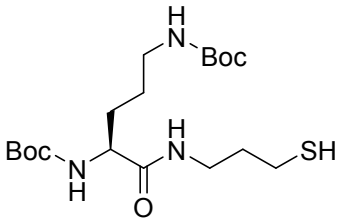
To a stirred solution of 3-bromopropylamine hydrobromide (10.7 g, 49 mmol) in CH_2Cl_2 (250 mL) was added DCC (10.1 g, 49 mmol), DMAP (600 mg, 4.9 mmol), and NEt_3 (6.8 mL, 49 mmol) and Boc-L-Orn(Boc)-OH (16.3 g, 49 mmol) at 0 ˚C. The mixture was warmed to rt and stirred for 4 h. The resulting mixture was filtered to remove urea and dried in vacuo. The residue was dissolved to $CHCl_3$, washed with 0.5 M aqueous hydrochloric acid (100 mL × 3), saturated aqueous sodium hydrogen carbonate (100 mL × 3), and Brine (30 mL × 3). The combined organic layer was dried over $MgSO_4$, filtered, and evaporated. The obtained residue was subjected to flash silica gel chromatography ($CHCl_3$:MeOH = 96:4) where major fraction was collected to afford **DOP1-Br** as white solid (24.4 g, yield 89%); IR (neat): 3344 (N–H), 2980 (C–H), 1681 (C=O), 1656 (C=O), 1367 (C–H), 761 (C–H) cm^{-1}; m.p. 133.9–139.9 ˚C; $[\alpha]_D^{25} = -1.18$ (c=1.0 in MeOH); ^{1}H NMR (391.8 MHz, $CDCl_3$): δ 6.72 (br, 1H, -CON*H*-), 5.17 (br, 1H, -CON*H*-), 4.70 (br, 1H, -CON*H*-), 4.22 (br, 1H, -NHC*H*(CH_2-)COOH), 3.47–3.41 (m, 2H, -C*H*$_2$Br), 3.37–3.29 (m, 3H, -CONHC*H*$_2$-), 3.10–3.02 (m, 1H, -CONHC*H*$_2$-), 2.11–2.04 (m, 2H, -CH_2C*H*$_2$$CH_2$Br), 1.96–1.92 (m, 1H, -NHCH(C*H*$_2$-)COOH), 1.60–1.50 (m, 3H, -NHC*H*(C*H*$_2$C*H*$_2$-)COOH), 1.44 (s, 18H, -C(C*H*$_3$)$_3$); ^{13}C NMR (98.5 MHz, $CDCl_3$): δ 172.5, 156.6, 155.8, 79.9, 77.0, 53.1, 39.1, 37.9, 32.2, 30.7, 28.3, 28.3, 26.6; HRMS (ESI-FT-ICR): *m/z* calcd for $C_{18}H_{34}BrN_3O_5Na$: 474.15740 $[M+Na]^+$; found: 474.15717; Anal. Calcd for $C_{18}H_{34}N_3O_5Br$: C, 47.79; H, 7.58; N, 9.29. Found: C, 47.76; H, 7.58; N, 9.32.

DOP1-SAc



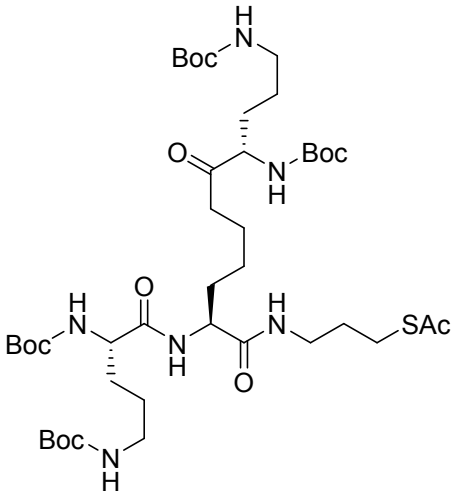
To a stirred solution of potassium thioacetate (5.80 g, 51.0 mmol) in acetone (150 mL) was added **DOP1-Br** (19.3 g, 43.0 mmol). The solution was stirred at rt for 1 h. The resulting mixture solution was filtered to remove NaBr salt and the filtrate was evaporated. The residue was diluted with $CHCl_3$ (150 mL), washed with water (100 mL × 3) and Brine (100 mL). The combined organic layer was dried over $MgSO_4$, filtered, and evaporated. The obtained residue was subjected to flash silica gel chromatography ($CHCl_3$:MeOH = 98:2), where major fraction was collected to afford **DOP1-SAc** as white solid (12.4 g, yield 65%); IR (neat): 3352 (N–H), 3323 (N–H), 2966 (C–H), 2935 (C–H), 1681 (C=O), 1649 (C=O), 1517 (N–H), 1388 (C–H), 670 (C–S) cm^{-1}; m.p. 52.6–56.3 ˚C; $[\alpha]_D^{25} = -0.70$ (*c*=1.0 in MeOH); ^{1}H NMR (391.8 MHz, $CDCl_3$): δ 6.68 (br, 1H, -CON*H*-), 5.15 (br, 1H, -CON*H*-), 4.69 (m, 1H, -CON*H*-), 4.20 (m, 1H, -CONHC*H*(CH_2-)CONH-), 3.36–3.23 (m, 3H, -CONHCH_2CH_2-), 3.13–3.05 (m, 1H, -CONHCH_2-), 2.89 (t, *J* = 7.2 Hz, 2H, -CH_2S-), 2.34 (s, 3H, -SCOCH_3), 1.85–1.75 (m, 3H, -CH_2-), 1.64–1.50 (m, 3H, -CH_2-), 1.44 (s, 18H, -C(CH_3)$_3$); ^{13}C NMR (98.5 MHz, $CDCl_3$): δ 196.3, 172.4, 156.4, 155.8, 79.2, 77.4, 53.6, 39.5, 37.8, 30.6, 30.3, 29.6, 28. 4, 28.4, 26.3, 26.3; HRMS (ESI-FT-ICR): *m/z* calcd for $C_{20}H_{37}N_3O_6S$: 470.22953 $[M+Na]^+$; found: 470.22892 Anal. Calcd for $C_{20}H_{27}N_3O_6S$: C, 53.67; H, 8.33; N, 9.39. Found: C, 53.93; H, 8.37; N, 9.38.

DOP1-SH



To a stirred solution of **G1-SAc** (4.0 g, 8.9 mmol) in methanol (180 mL) was added DIEA (6.2 mL, 35.6 mmol) at 0 ˚C and the mixture was stirred for 12 h. The resulting mixture was neutralized by HCl aq. The mixture was dried and dissolved in $CHCl_3$. The solution was washed with H_2O (50 mL × 3), Brine (50 mL), and dried over $MgSO_4$. The residue was evaporated and purified by flash silica gel chromatography ($CHCl_3$:MeOH = 97:3), where major fraction was collected to afford **DOP1-SH** as white solid (2.7 mg, yield 76 %); IR (neat): 3341 (N–H), 2979 (C–H), 2347 (C–H), 1681 (C=O), 1656 (N–H), 1516 (C=O), 1445 (C–N), 859 (N–H), 763 (C–H), 630 (C–S) cm^{-1}; m.p. 121.9–122.6 ˚C; $[\alpha]_D^{25} = -0.90$ (c=1.0 in MeOH); ^1H NMR (391.8 MHz, $CDCl_3$): δ 6.60 (br, 1H, -CON*H*-), 5.16 (br, 1H, -CON*H*-), 4.67 (m, 1H, -CON*H*-), 4.21 (m, 1H, -C*H*CH_2-), 3.49–3.27 (m, 5H, -C*H*$_2$$CH_2$$CH_2$SH, -CHC*H*$_2$C*H*$_2$-), 3.10–3.03 (m, 1H, -CHCH_2C*H*$_2$-), 2.54 (q, J = 7.1 Hz, 2H, -C*H*$_2$SH), 1.86–1.78 (m, 3H, -CONHC*H*$_2$-, -C*H*$_2$$CH_2$SH), 1.60–1.51 (m, 4H, -CHC*H*$_2$C*H*$_2$-) 1.47 (t, J = 8.2 Hz, 1H, -S*H*), 1.44 (s, 18H, -C(C*H*$_3$)$_3$); ^{13}C NMR (98.5 MHz, $CDCl_3$): δ 172.4, 156.6, 155.9, 79. 9, 79.3, 53.3, 39.3, 37.8, 33.6, 30.3, 28.5, 28.4, 26.5, 21.9. HRMS (ESI-FT-ICR): *m/z* calcd for $C_{18}H_{35}N_3O_5S$: 406.23702 $[M+Na]^+$; found: 406.23723; Anal. Calcd for $C_{18}H_{35}N_3O_5S\cdot(NaCl)_{0.13}$: C, 52.33; H, 8.54; N, 10.17. Found: C, 52.56; H, 8.49; N, 9.95.

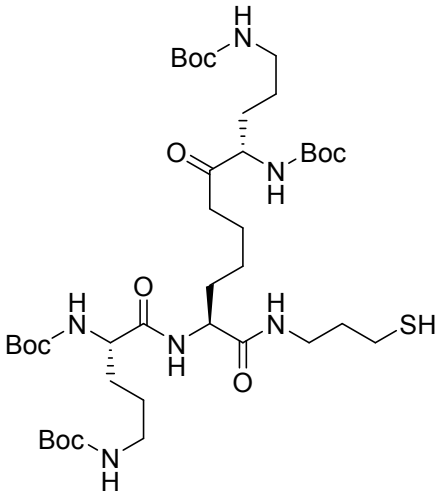
DOP2-SAc



To a stirred solution of **DOP1-SAc** (19.5 g, 44 mmol) in CH_2Cl_2 (150 mL) was added trifluoroacetic acid (40 mL, 880 mmol) at 0 ˚C. The reaction solution was stirred at rt for 24 h. The resulting mixture was evaporated and a solution (30 mL) of HCl (4.0 M) in 1,4-dioxane was added to the residue, generating a white solid. The solvent was removed by decantation and the precipitate was washed repeatedly with diethylether. The obtained solid was used for next reaction without further purification. The solid was dissolved in CH_2Cl_2 (225 mL) and NEt_3 (17.6 g, 174 mmol) was added to the mixture, followed by Boc-L-Orn(Boc)-OH (28.9 g, 87 mmol). The solution was stirred under Ar at 0 ˚C for 10 min. HBTU (33.0 g, 87 mmol) and HOBt (11.7 g, 87 mmol) were added to the solution and stirred at rt for 24 h. The resulting mixture was evaporated, dissolved in $CHCl_3$, and washed with saturated $NaHCO_3$ solution, 0.5 M HCl aqueous solution, and Brine. The organic layer was dried over $MgSO_4$, filtered, and evaporated. The obtained residue was purified by flash silica gel chromatography ($CHCl_3$:MeOH = 20:1), where major fraction was collected to afford **DOP2-SAc** as white solid (30.6 g, yield 80%); IR (neat): 3280 (N–H), 2972 (C–H), 1685 (C=O), 1642 (N–H), 1518 (C=O), 1451 (C–N), 865 (N–H), 780 (C–H), 629 (C–S) cm^{-1}; m.p. 75.0–78.0 ˚C; $[\alpha]_D^{25} = -1.76$ (c=1.0 in MeOH); ^1H NMR (391.8 MHz,

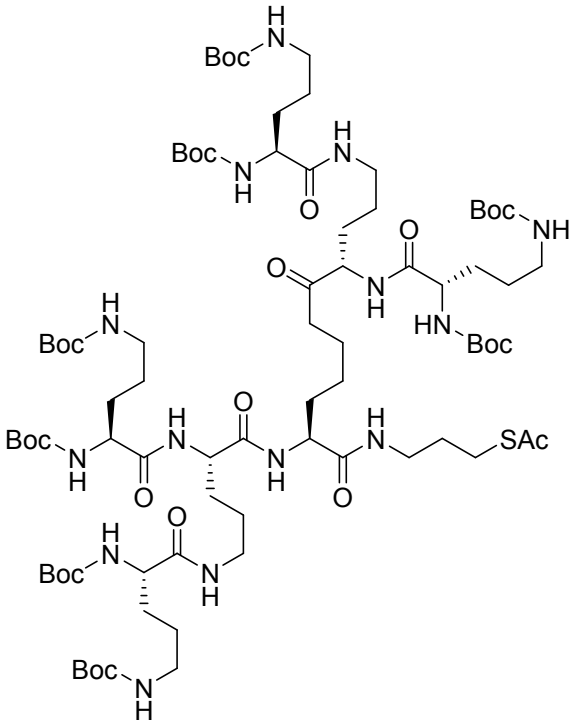
$CDCl_3$): δ 7.23 (m, 1H, -CON*H*-), 6.97 (s, 2H, -CON*H*-), 5.41 (br, 1H, -CON*H*-), 5.32 (br, 1H, -CON*H*-), 4.98 (br, 1H, -CON*H*-), 4.85 (br, 1H, -CON*H*-), 4.43 (br, 1H, -NHC*H*(CH_2-)CO-), 4.20 (br, 2H, -NHC*H*(CH_2-)CO-) 3.45 (br, 1H, -CH_2-), 3.35–3.28 (m, 2H, -CH_2C$H_2$$CH_2$S-), 3.26–3.21 (m, 2H, -CH_2-), 3.15 (br, 4H, -CH_2-), 2.90–2.86 (m, 2H, -CH_2S-), 2.34 (s, 3H, -SCOCH_3), 1.94–1.74(m, 6H, -CH_2-, -C$H_2$$CH_2$$CH_2$S-), 1.58 (br, 8H, -C$H_2$-), 1.43 (s, 36H, SCOC$H_3$); ^{13}C NMR (98.5 MHz, $CDCl_3$): δ 196.7, 172.9, 171.6, 156.6, 156.3, 156.2, 80.3, 80.1, 79.4, 79.3, 54.4, 53.8, 52.9, 39.9, 39.6, 38.6, 38.1, 31.1, 30.8, 30.2, 29.9, 29.6, 29.1, 29.0, 28.6, 28.5, 28.5, 26.5, 26.3, 26.1; HRMS (ESI-FT-ICR): *m/z* calcd for $C_{40}H_{73}N_7O_{12}S$: 898.4931 $[M+Na]^+$; found: 898.49208; Anal. Calcd for $C_{40}H_{73}N_7O_{12}S{\cdot}CH_4O$: C, 54.84; H, 8.40; N, 11.19. Found: C, 54.46; H, 8.37; N, 10.95.

DOP2-SH



To a stirred solution of **G2-SAc** (100 mg, 58 μmol) in methanol (5.0 mL) was added DIEA (40 μL, 230 μmol) at 0 ˚C and the mixture was stirred for 12 hours. The resulting mixture was neutralized by HCl aq, evaporated, and dissolved in $CHCl_3$. The solution was washed with 0.5 M HCl solution, Brine, dried over $MgSO_4$, and evaporated. The residue was purified by flash silica gel chromatography ($CHCl_3$: MeOH = 97:3), where major fraction was collected to afford **DOP2-SH** as white solid (80 mg, yield 82 %); IR (neat): 3313 (N–H), 2973 (C–H), 1690 (C=O), 1649 (N–H), 1518 (C=O), 1452 (C–N), 863 (N–H), 780 (C–H), 643 (C–S) cm^{-1}; m.p. 73.6–79.0 ˚C; $[\alpha]_D^{25} = -1.72$ (*c*=1.0 in MeOH); ^{1}H NMR (391.8 MHz, $CDCl_3$): δ 7.24 (br, 1H, -CON*H*-), 6.99 (br, 2H, -CON*H*-), 5.44 (m, 1H, -CON*H*-), 5.35 (m, 1H, -CON*H*-), 4.98 (m, 1H, -CON*H*-), 4.85 (m, 1H, -CON*H*-), 3.05 (t. *J* = 6.1 Hz, 8H, -C*H*$_2$-), 2.71 (t, *J* = 7.4 Hz, 4H, -C*H*$_2$-), 1.92–1.85 (m, 4H, -C*H*$_2$-), 1.82–150 (m, 28H, -C*H*$_2$-), 1.45–1.43 (m, 72H, -C(C*H*$_3$)$_3$); ^{13}C NMR (98.5 MHz, $CDCl_3$): δ 173.3, 173.0, 171.6, 156.4, 156.2, 156.1, 80.2, 80.0, 79.1, 77.3, 54.3, 53.7, 52.3, 53.0, 52.3, 52.1, 39.8, 39.6, 38.7, 37.7, 33.4, 10.4, 29.9, 29.7, 29.2, 28.5, 28.4, 26.2, 25.8, 21.8; HRMS (ESI-FT-ICR): *m/z* calcd for $C_{38}H_{71}N_7O_{11}S$: 856.48245 $[M+Na]^+$; found: 856.48068; Anal. Calcd for $C_{38}H_{71}N_7O_{11}\cdot 2H_2O$: C, 53.56; H, 8.64; N, 11.51. Found: C, 53.49; H, 8.44; N, 11.28.

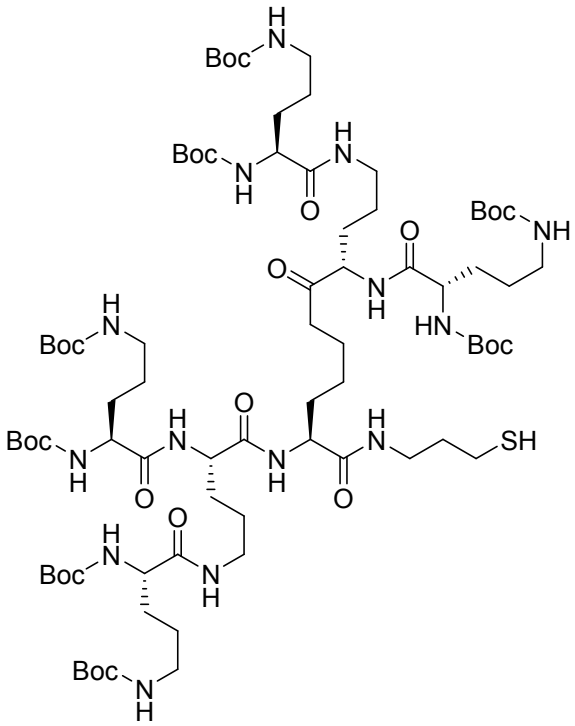
DOP3-SAc



To a stirred solution of **DOP2-SAc** (4.0 g, 4.6 mmol) in CH_2Cl_2 (50 mL) was added trifluoroacetic acid (21 g, 182 mmol) at 0 ˚C. The reaction solution was stirred at rt for 12 h. The resulting mixture was evaporated and a solution (30 mL) of HCl (4.0 M) in 1,4-dioxane was added to the residue, generating a white solid. The solvent was removed by decantation and the precipitate was washed repeatedly with diethylether. The obtained solid was used for next reaction without further purification. The solid was dissolved in 200 mL of CH_2Cl_2 and NEt_3 (3.2 mL, 18.4 mmol) was added to the mixture, followed by Boc-L-Orn(Boc)-OH (6.6 g, 20 mmol). The solution was stirred under Ar at 0 ˚C for 10 min. HBTU (7.6 g, 20 mmol) and HOBt (2.5 g, 18 mmol) were added to the solution and stirred at rt for 48 h. The resulting mixture was evaporated and dissolved in $CHCl_3$. The solution was washed with saturated $NaHCO_3$ solution, 1.0 M HCl, and Brine. The organic layer was dried over $MgSO_4$, filtered, and evaporated. The obtained residue was purified by flash silica gel chromatography ($CHCl_3$: MeOH

= 97:3), where major fraction was collected to afford **DOP3-SAc** as white solid (4.6 g, yield 58%); IR (neat): 3294 (N–H), 2976 (C–H), 1688 (C=O), 1643 (N–H), 1517 (C=O), 1452 (C–N), 866 (N–H), 780 (C–H), 629 (C–S) cm^{-1}; m.p. 138.6–144.2 ˚C; $[\alpha]_D^{25} = -1.54$ (c=1.0 in MeOH); ^1H NMR (391.8 MHz, $CDCl_3$): δ 7.36 (br, 8H, N*H),* 5.89–5.64 (br, 4H, N*H*), 5.29–5.04 (br, 3H, N*H*), 4.41 (br, 3H, -NHC*H*(CH_2)CO-), 4.42–4.24 (br, 7H, -NHC*H*(CH_2)CO-), 3.34–3.13 (m, 20H, -CH_2-), 2.88 (t, J = 6.7 Hz, 2H, -CH_2CH_2SCOCH_3), 2.33 (s, 3H, -SCOCH_3), 1.78–1.58 (m, 34H, -CH_2-), 1.42 (m, 108H, -C(CH_3)$_3$); ^{13}C NMR (98.5 MHz, $CDCl_3$): δ 196.6, 173.4, 173.0, 171.9, 156.4, 156.3, 80.1, 80.0, 79.3, 79.2, 54.7, 54.0, 54.0, 53.1, 52.9, 52.7, 40.1, 39.9, 39.8, 38.8, 38.3, 30.8, 30.4, 30.3, 30.1, 29.8, 29.5, 29.0, 28.5, 26.5, 26.3, 25.6; HRMS (ESI-FT-ICR): *m/z* Calcd for $C_{80}H_{145}N_{15}O_{24}S$: 1755.01998 $[M+Na]^+$; found: 1755.03798; Anal. Calcd for $C_{80}H_{145}N_{15}O_{24}S{\cdot}CH_4O$: C, 55.44; H, 8.43; N, 12.12. Found: C, 55.11; H, 8.51; N, 11.90.

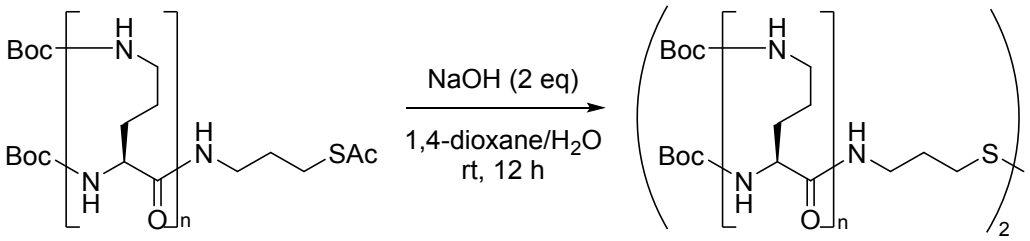
DOP3-SH



To a stirred solution of **DOP3-SAc** (2.0 g , 1.2 mmol) in methanol (20 mL) was added DIEA (820 μL , 4.7 mmol) at 0 ˚C and the mixture was stirred for 40 h. The resulting mixture was neutralized by HCl aq. The mixture was evaporated and dissolved in $CHCl_3$. The solution was washed with 0.5 M HCl, Brine, dried over $MgSO_4$, and evaporated. The residue was purified by flash silica gel chromatography ($CHCl_3$:MeOH = 95:5), where major fraction was collected to afford **DOP3-SH** as white solid (1.7 g, yield 83 %); IR (neat): 3280 (N–H), 2977 (C–H), 1685 (C=O), 1636 (N–H), 1515 (C=O), 1452 (C–N), 865 (N–H), 754 (C–H) cm^{-1}; m.p. 133.2–135.8 ˚C; $[\alpha]_D^{25} = -1.60$ (*c*=1.0 in MeOH); ^{1}H NMR (391.8 MHz, $CDCl_3$) δ 7.34 (br, 8H, N*H),* 5.80–5.61 (br, 4H, N*H*), 5.29–5.04 (br, 3H, N*H*), 4.41 (br, 3H, -NHC*H*(CH_2)CO-), 4.21 (br, 4H, -NHC*H*(CH_2)CO-), 3.34–3.13 (m, 20H, -CH_2-), 2.55 (q, *J* = 7.2 Hz, 2H, -CH_2CH_2SH), 1.97–1.53 (m, 35H, -CH_2- and -S*H*), 1.42 (m, 108H, -C(CH_3)$_3$); ^{13}C NMR (98.5 MHz, $CDCl_3$): δ 173.5, 173.1, 172.1, 172.0, 156.4, 80.1, 80.0, 79.2, 54.7, 54.5, 54.0, 52.9, 52.7, 41.2 40.1, 39.9, 39.8, 38.8, 38.7, 37.9, 33.5, 31.1, 30.4, 30.0, 29.8, 29.5, 29.3, 28.6, 28.5,

26.3, 25.7, 25.6, 21.9; HRMS (ESI-FT-ICR): *m/z* calcd for $C_{78}H_{143}N_{15}O_{23}S$: 1713.00942 $[M+Na]^+$; found: 1712.99971; Anal. Calcd for $C_{78}H_{143}N_{15}O_{23}S\cdot(NaCl)_{1.7}$: C, 52.32; H, 8.05; N, 11.73. Found: C, 52.25; H, 8.06; N, 11.47.

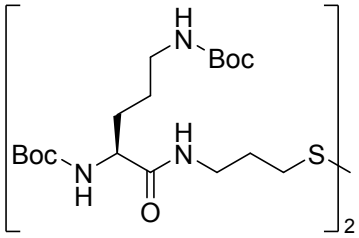
Scheme S2. Synthesis of Peptide Dendron Disulfides



DOP1-SAc (n=1)
DOP2-SAc (n=2)

[DOP1-S]$_2$ (n=1, 98%)
[DOP2-S]$_2$ (n=2, 50%)

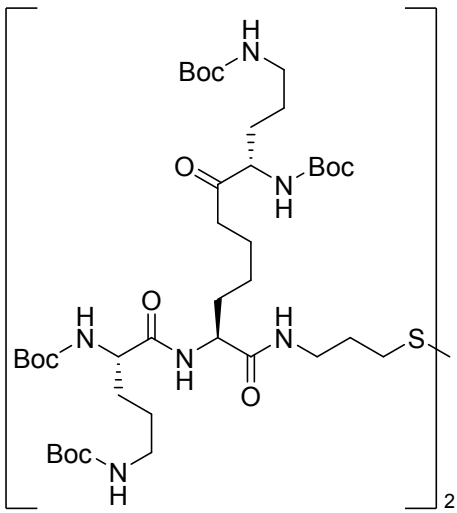
[DOP1-S]$_2$



To a stirred solution of **DOP1-SAc** (58.2 mg, 0.13 mmol) in THF (460 μL) was added aqueous sodium hydroxide solution (1 M, 260 μL). The solution was stirred at rt for 20 h. The resulting solution was concentrated to remove THF, then neutralized by 0.5 M aqueous HCl solution and extracted with chloroform (15 mL × 3). The combined organic layer was dried over $MgSO_4$, filtered, and evaporated. The obtained residue was subjected to flash silica gel chromatography ($CHCl_3$:MeOH = 95:5), where major fraction was collected to afford **[DOP1-S]$_2$** as white solid (48.9 mg, yield 98%); IR (neat): 3316 (N–H), 2976 (C–H), 1691 (C=O), 1659 (N–H), 1514 (C=O), 1453 (C–N), 865 (N–H), 754 (C–H) cm^{-1}; m.p. 60.3–63.0 °C; $[\alpha]_D^{25} = -1.34$ (c=1.0 in MeOH); ^{1}H NMR (391.8 MHz, $CDCl_3$): δ 7.05 (br, 1H, -CON*H*-), 5.54 (d, J = 6.3 Hz, 1H, -CHCON*H*-), 4.88 (br, 1H, -CON*H*-), 4.24 (br, 1H, -NHC*H*(CH_2-)CO-), 3.54–3.45 (m, 1H, -CONHCH_2-), 3.30-3.18 (m, 2H, -CONHCH_2-), 3.13–3.13-3.05 (m, 1H, -CONHCH_2-), 2.73 (t, J = 7.2 Hz, 2H, -CH_2CH_2S-), 1.94–1.87 (m, 2H, -

NHCH$_2$C*H$_2$*CH$_2$S-), 1.81–1.73 (m, 1H, -CHC*H$_2$*CH$_2$NH-), 1.67–1.53 (m, 3H, -CHC*H$_2$*C*H$_2$*NH-), 1.43 (s, 18H, -C(C*H$_3$*)$_3$); ^{13}C NMR (98.5 MHz, $CDCl_3$): δ 172.7, 156.3, 156.0, 79.7, 79.1, 39.47, 38.1, 36.3, 30.0, 29.1, 28.4, 28.3, 26.2; HRMS (ESI-FT-ICR): *m/z* calcd for $C_{36}H_{68}N_6O_{10}S_2$: 831.43305 $[M+Na]^+$; found: 831.43241; Anal. Calcd for $C_{21}H_{23}NO_2$·NaCl: C, 49.84; H, 7.90; N, 9.69. Found: C, 49.85; H, 7.86; N, 9.45.

[DOP2-S]$_2$



To a stirred solution of **DOP2-SAc** (50 mg, 57 μmol) in THF (1.0 mL) was added aqueous sodium hydroxide solution (1 M, 114 μL). The solution was stirred at rt for 48 h. The resulting solution was concentrated to remove THF, then neutralized by 0.5 M aqueous HCl solution and extracted with chloroform. The combined organic layer was dried over $MgSO_4$ and filtered. The obtained residue was subjected to flash silica gel chromatography ($CHCl_3$:MeOH = 95:5), where major fraction was collected to afford **[DOP2-S]$_2$** as white solid (23.6 mg, yield 50%); IR (neat): 3289 (N–H), 2977 (C–H), 1687 (C=O), 1643 (N–H), 1512 (C=O), 1450 (C–N), 864 (N–H), 755 (C–H) cm^{-1}; m.p. 104.3–105.1 ˚C; $[\alpha]_D^{25}$ = −1.24 (*c*=0.75 in MeOH); ^{1}H NMR (391.8 MHz, $CDCl_3$): δ 7.81 (br, 2H, -CON*H*-), 7.42 (br, 4H, -CON*H*-), 5.92 (br, 2H, -CON*H*-), 5.44 (br, 2H, -OCON*H*-), 5.03 (br, 2H, -OCON*H*-), 4.92 (br, 2H, -OCON*H*-), 4.46 (br, 4H, -NHC*H*(CH_2-)CO-), 4.28 (br, 2H, -NHC*H*(CH_2-)CO-), 3.78 (br, 2H, -C*H*$_2$-), 3.69 (br, 2H, -C*H*$_2$-), 3.50 (br, 2H, -C*H*$_2$-), 3.78 (br, 2H, -C*H*$_2$-), 3.15 (br, 8H, -C*H*$_2$-), 3.01 (br, 4H, -C*H*$_2$-), 2.80 (br, 4H, -C*H*$_2$-), 2.73 (br, 4H, -C*H*$_2$-), 1.79–1.55 (m, 24H, -C*H*$_2$-), 1.43–1.42 (m, 72H, -C(CH_3)$_3$-); ^{13}C NMR (98.5 MHz, $CDCl_3$): δ 173.3, 171.8, 156.6, 156.4, 156.2, 156.1, 80.3, 80.1, 79,2, 79.2, 54.3, 53.5, 40.1, 39.8, 38.8, 38.3, 35.3, 31.1, 30.1, 29.8, 29.3, 28.6, 28.6, 26.2, 26.0, 25.8; HRMS (ESI-FT-ICR):

m/z calcd for $C_{76}H_{140}N_{14}O_{22}S_2$: 1687.96002 $[M+Na]^+$; found: 1687.96778; Anal. Calcd for $C_{76}H_{140}N_{14}O_{22}S_2 \cdot (NaCl)_{1.5}$: C, 52.05; H, 8.05; N, 11.18. Found: C, 51.93; H, 8.12; N, 10.92.

Synthesis of DOPx-AuNCs.

Synthesis of DOP1-AuNC.

DOP1-SH (487 mg, 1.2 mmol) was added to a solution of $HAuCl_4 \cdot 4H_2O$ (113 mg, 0.24 mmol) in 24 mL of THF with very slow stirring (c.a. 60 rpm). After the solution turned from yellow to colorless, the resulting mixture was cooled to 0 ˚C. Then the stirring speed was increased to 1500 rpm, and an aqueous solution of $NaBH_4$ (90 mg, 2.4 mmol, freshly prepared with 3.6 mL ice-cold ultrapure water) was rapidly added all at once. The reaction was allowed to proceed under constant stirring at 0 ˚C for 1 h. After that, the ice bath was removed and the solution was warmed to 60 ˚C. The reaction was allowed to proceed for further 12 h. After the removal of precipitate by filtration, the solution was concentrated. The residue was purified by flash silica gel chromatography (gradient from $CHCl_3$: MeOH = 97:3 to 95: 5), where major fraction was collected to afford **DOP1-AuNC** as brown solid (33.7 mg, yield 29 %); IR (neat): 3302 (N–H), 2975 (C–H), 1687 (C=O), 1649 (N–H), 1513 (C=O), 1452 (C–N), 850 (N–H), 752 (C–H), 666 (C–S) cm^{-1}; HRMS (ESI-FT-ICR): *m/z* calcd for $Au_{25}(C_{18}H_{34}N_3O_5S)_{18}Cl$: 6120.06803 $[M+Cl]^{2-}$; found:6120.07953.

Synthesis of DOP2-AuNC.

DOP2-SH (1.0 g, 1.2 mmol) was added to a solution of $HAuCl_4 \cdot 4H_2O$ (100 mg, 0.24 mmol) in 23 mL of THF with very slow stirring (c.a. 60 rpm). The yellow solution turned colorless within a few fours. After the solution turned colorless, the resulting mixture was cooled to 0 ˚C. Then the stirring speed was increased to 1500 rpm, and an aqueous solution of $NaBH_4$ (91 mg, 2.4 mmol, freshly prepared with 3.6 mL ice-cold ultrapure water) was rapidly added all at once. The reaction was allowed to proceed under constant stirring at 0 ˚C for 1 h. After that, the ice bath was removed and the solution was warmed to 60 ˚C. The reaction was allowed to proceed for further 12 h. After the removal of precipitate by filtration, the solution was concentrated. The residue was purified by flash silica gel chromatography ($CHCl_3$: MeOH = 95:5), where major fraction was collected to afford **DOP2-AuNC** as brown solid (41 mg, yield 21 %); IR (neat): 3280 (N–H), 2977 (C–H), 1685 (C=O), 1636 (N–H), 1515 (C=O), 1452 (C–N), 865 (N–H), 754 (C–H) cm^{-1}; HRMS (ESI-FT-ICR): *m/z* calcd for $Au_{25}(C_{38}H_{70}N_7O_{11}S)_{18}Cl_3$: 5006.20738 $[M+3Cl]^{4-}$; found: 5006.20459.

Synthesis of DOP3-AuNC.

DOP3-SH (217 mg, 0.13 mmol) was added to the solution of $HAuCl_4 \cdot 4H_2O$ (17.6 mg, 0.043 mmol) in 4.4 mL THF with very slow stirring (c.a. 60 rpm) for 1 h at rt. Then the stirring speed was increased to 1500 rpm, and a solution of $NaBH_4$ (17 mg, 2.4 mmol, freshly prepared with 3.6 mL EtOH) was rapidly added all at once. The reaction was allowed to proceed under constant stirring at rt for 30 h. After that, the solution was warmed to 60 ˚C. The reaction was allowed to proceed for further 12 h. After the removal of precipitate by filtration, the

solution was concentrated. The residue was purified by preparative TLC ($CHCl_3$: MeOH = 95:5), where major band was collected to afford **DOP3-AuNC** as brown solid; IR (neat): 3279 (N–H), 2978 (C–H), 1688 (C=O), 1642 (N–H), 1518 (C=O), 1450 (C–N), 866 (N–H), 779 (C–H) cm^{-1}.

1-Phenyl-2-pyrrolidinyl-1-propanol (1)

This compound was synthesized according to the literature method.[1] To a 200 mL two-neck flask, 1-phenyl-1-propanol (4.07 g, 29.9 mmol) and *N*-bromosuccinimide (6.99 g, 39.3 mmol) were added on ice, and the mixture was stirred for 20 min, generating brown gas. After that, 1,4-dioxiane (60 mL) was added and the solution was stirred at room temperature for 25 min. Pyrrolidine (6.51 g, 91.5 mmol) was added dropwise and the solution was stirred at room temperature for 24 h and the solution color turned to orange. Saturated aqueous $NaHCO_3$ solution (100 mL) was added and the organic layer was extracted with ethyl acetate (60 mL × 5). The combined organic layer was dried over Na_2SO_4 and concentrated to give brown oil. The obtained brown oil was dissolved into MeOH (60 mL), then $NaBH_4$ (1.12 g, 29.543 mmol) was added on ice over an hour. After 1 h stirring on ice, the solution was warmed to room temperature and stirred for further 3 h. Water (70 mL) was added and the organic layer was extracted by ethyl acetate (70 mL × 3). The combined organic layer was dried over Na_2SO_4 and evaporated. The residual blown oil was purified by silica gel chromatography ($CHCl_3$/MeOH) to afford brown solid of **1** (2.26 g, 37%); ^{1}H NMR (391.8 MHz, $CDCl_3$): δ 7.30 (m, 5H, -C_6H_5), 5.03 (d, J =3.1 Hz, 1H, C_6H_5CH(OH)-), 2.90–2.60 (m, 4H, -NCH_2CH_2-), 2.52 (dq, J = 3.1, 6.7 Hz, 1H, -$NCHCH_3$), 1.83 (m, 4H, -NCH_2CH_2-), 0.81 (d, J = 6.7 Hz, 3H, -$CHCH_3$); ^{13}C NMR (391.8 MHz, $CDCl_3$): δ 128.15, 126.88, 125.9, 72.7, 65.5, 52.0, 23.7, 12.1. The formation of the product was confirmed by the correspondence to the reported spectral data.[2]

Hexahydro-3-methyl-2-phenylpyrrolo[2,1-*b*]oxazole (2)

^{1}H NMR (391.8 MHz, $CDCl_3$): δ 7.42–7.19 (m, 5H, -C_6H_5), 5.35 (dq, J = 1.8, 5.0 Hz, 1H, -(-O)CH(N-)(CH_2-)), 5.11 (d, J = 5.4 Hz, >C$H$$C_6H_5$), 3.52 (m, 1H, >C$H$$CH_3$), 3.26 (m, 1H, >N$CH_2CH_2$-), 2.81 (m, 1H, >N$CH_2CH_2$-), 2.21–1.90 (m, 2H, >$NCH_2CH_2$-), 2.00–1.76 (m, 2H, >$CCH_2$-), 0.72 (d, J = 7.18, 1H, –CH_3). The product was confirmed by the correspondence to the reported spectral data.[3]

N-(2-Hydroxy-1-methyl-2-phenylethyl)pyrrolidine *N*-oxide (3)

IR (neat): 3333 (O–H), 2958 (C–H), 2483 (N–O), 1670, 1450, 1024, 750, 702, 587, 427 cm^{-1}; m.p. 167.1–171.6 °C; ^{1}H NMR (391.8 MHz, $CDCl_3$): δ 7.40–7.25 (m, 5H, -C_6H_5), 5.59 (d, J = 1.8 Hz, 1H, >C*H*OH), 4.09 (m, 1H, >NOC$H_2$$CH_2$-), 3.57 (m, 1H, >NOC$H_2$$CH_2$-), 3.47 (m, 1H, >NOC$H_2$$CH_2$-), 3.22 (dd, J = 1.8, 6.7 Hz, 1H, >C*H*CH_3), 3.10 (m, 1H, >NOC$H_2$$CH_2$-), 2.59 (m, 2H, >NO$CH_2CH_2$-), 2.10 (m, 2H, >NO$CH_2CH_2$-), 1.31 (d, J = 6.7 Hz, 1H, -CH_3). ^{13}C NMR (391.8 MHz, $CDCl_3$) δ 140.8, 128.5, 127.5, 126.0, 76.8, 77.2, 68.7, 67.6, 21.9, 21,5. HRMS: *m/s* calced for $C_{13}H_{19}NO_2$: 222.14886 [M+H]; found: 222.14867; Anal. Calcd for $C_{13}H_{19}NO_2$: C, 70.56; H, 8.65; N, 6.33. Found: C, 67.09; H, 8.65; N, 6.44.

References

1. Guha, S.; Rajeshlumar, V.; Kotha, S. S.; Sekar, G. A Versatile and One-Pot Strategy to Synthesize α-Amino Ketones from Benzylic Secondary Alcohols Using *N*-Bromosuccinimide, *Org. Lett.* **2015,** *17,* 406–409.

2. Soai, K.; Yokoyama, S.; Hayasaka, T. Chiral *N,N*-Dialkylnorephedrines as Catalysts of the Highly Enantioselective Addition of Dialkylzincs to Aliphatic and Aromatic Aldehydes. The Asymmetric Synthesis of Secondary Aliphatic and Aromatic Alcohols of High Optical Purity, *J. Org. Chem.* **1991,** *56,* 4264–4268.

3. Sedelmeier, J.; Ley, S. V.; Baxendale, I. R.; Baumann, M. $KMnO_4$-Mediated Oxidation as a Continuous Flow Process, *Org. Lett.* **2010,** *12,* 3618–3621.

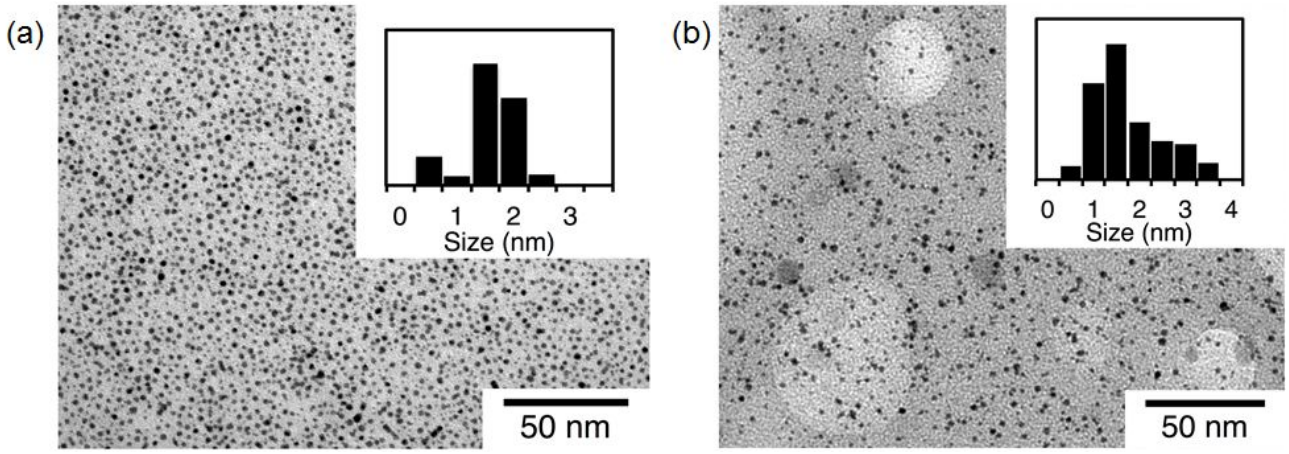


Figure S1. TEM images of (a) **DOP1-AuNP** and (b) **DOP2-AuNP**.

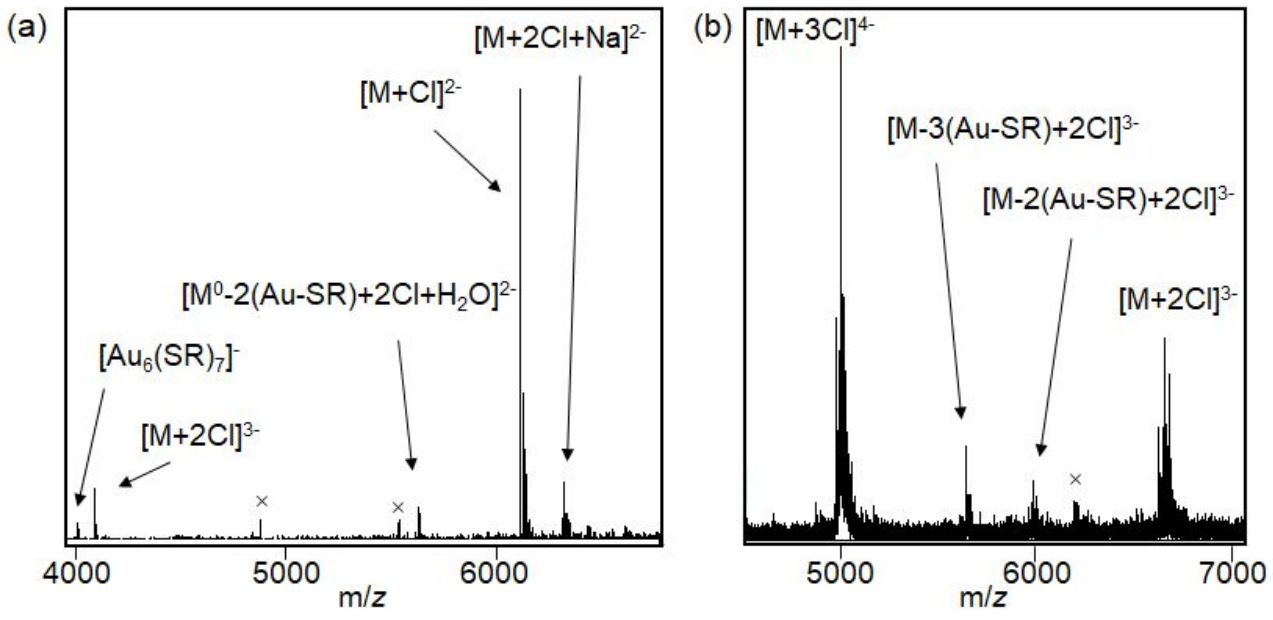


Figure S2. ESI-MS spectra of (a) **DOP1-AuNC** and (b) **DOP2-AuNC** with assignments of side peaks. X mark: noise signals.

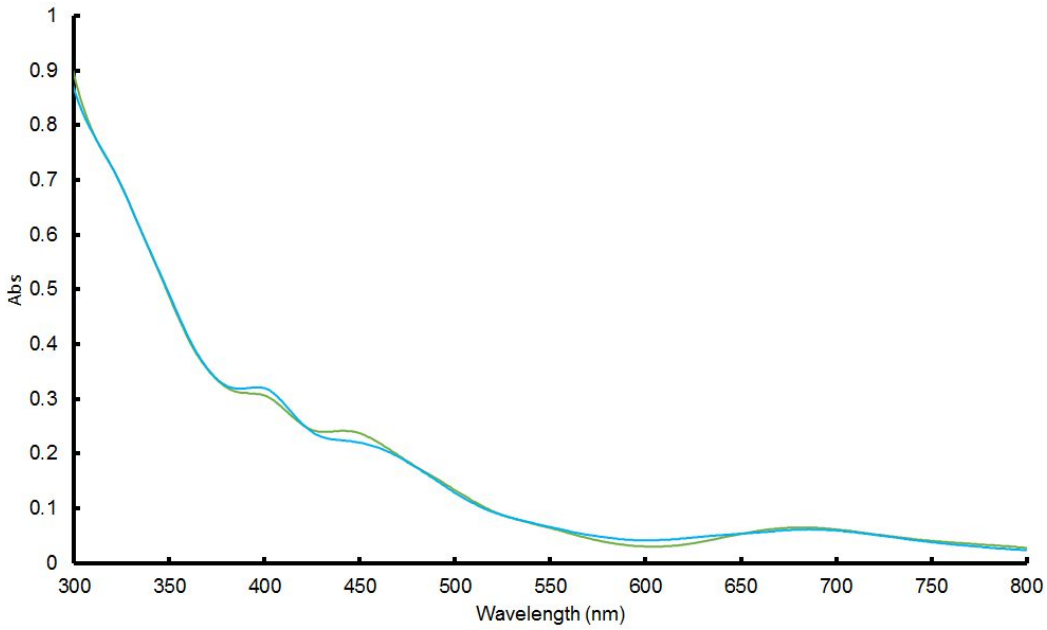


Figure S3. UV–Vis absorption spectra of **DOP1-AuNC** (0.1 mM in $CHCl_3$) under O_2 atmosphere before (green line) and after 5 h (blue line) irradiation of 680 nm light.

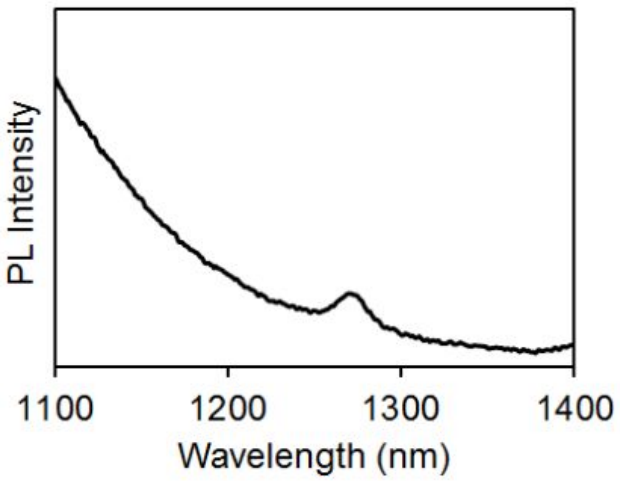
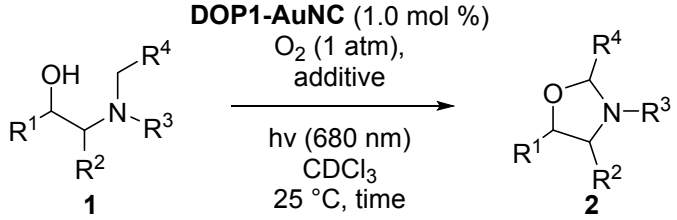
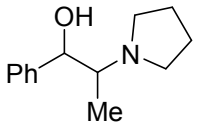
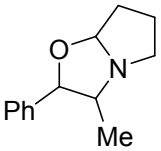
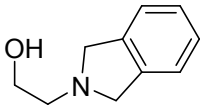
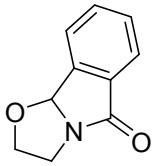
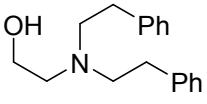
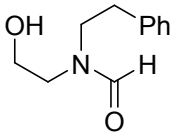
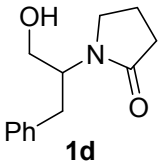


Figure S4. Photoluminescence spectrum of photo-generated $^1O_2$ (**DOP1-AuNC**: 28 μM in CCl_4, O_2: 1.0 atm, λ_{ex}: 680 nm).

Table S1. Photocatalytic Oxidation of Amino Alcohols with DOP1-AuNC



entry	substrate	additive	time (h)	light intensity (mW/cm^2)	product[a]
1	 **1a**	HQ (1 eq)	12	11.4	 **2a**: 89%
2	 **1b**	H_2O (5 eq)	70	5.7	 **2b**: 23%
3	 **1c**	H_2O (5 eq)	24	5.7	**2c**: n.d.  **7c**: 34%
4	 **1d**	H_2O (5 eq)	24	11.4	**2d**: n.d.

[a]Yields were determined by ^1H NMR using 1,1,2,2-tetrachloroethane as an internal standard. n.d.: not detected.

Time-course trace of photoreaction of DPBF.

The stock solutions of photosensitizer in $CHCl_3$ were prepared. This was then added to fluorescence cell containing 3 mL solution of 60 μM DPBF in each solvent and stirrer bar. The solutions were purged with O_2 immediately prior to measurement. The solutions were then irradiated with a Xe Lamp at 680 nm (~1.0 mW/1.2 cm^2, ASAHI SPECTRA, MAX-303) under stirring at 25 ˚C (UNISOKU, CoolSpeK UV USP-203-B). The spectra were recorded during the irradiation at regular intervals.

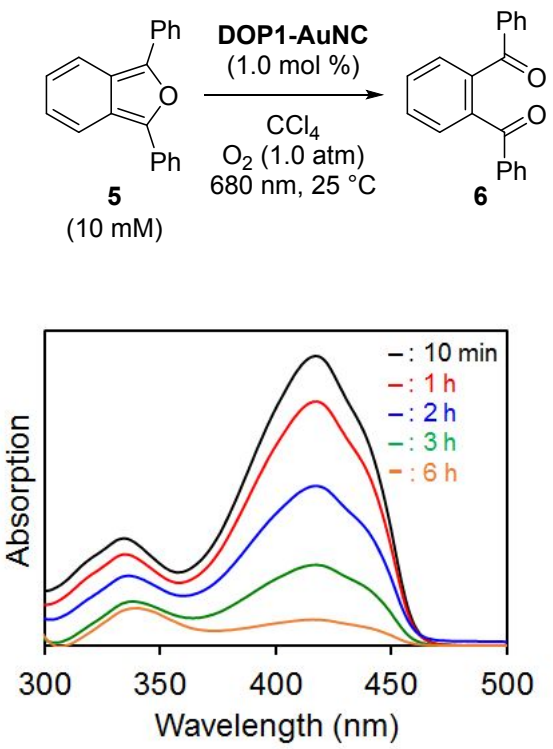


Figure S5. Time-course trace of UV-Vis absorption spectra of **5** under photocatalytic oxidation with **DOP1-AuNC** (**5**: 10 mM in CCl_4, **DOP1-AuNC**: 1.0 mol %, O_2: 1.0 atm, irradiation: 680 nm).

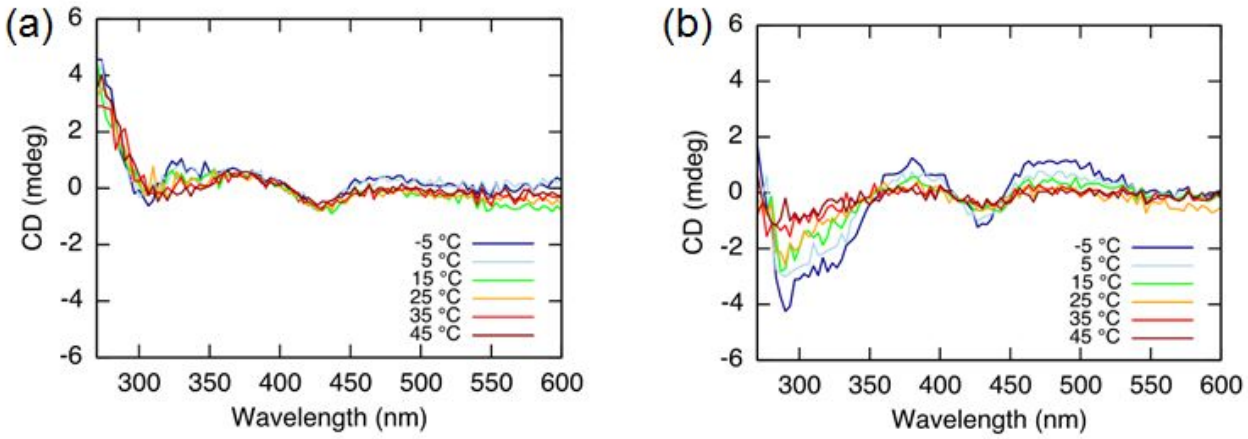


Figure S6. CD spectra of (a) **DOP1-AuNC** and (b) **DOP2-AuNC** (20 μM) in MeOH at −5, 5, 15, 25, 35, and 45 °C.

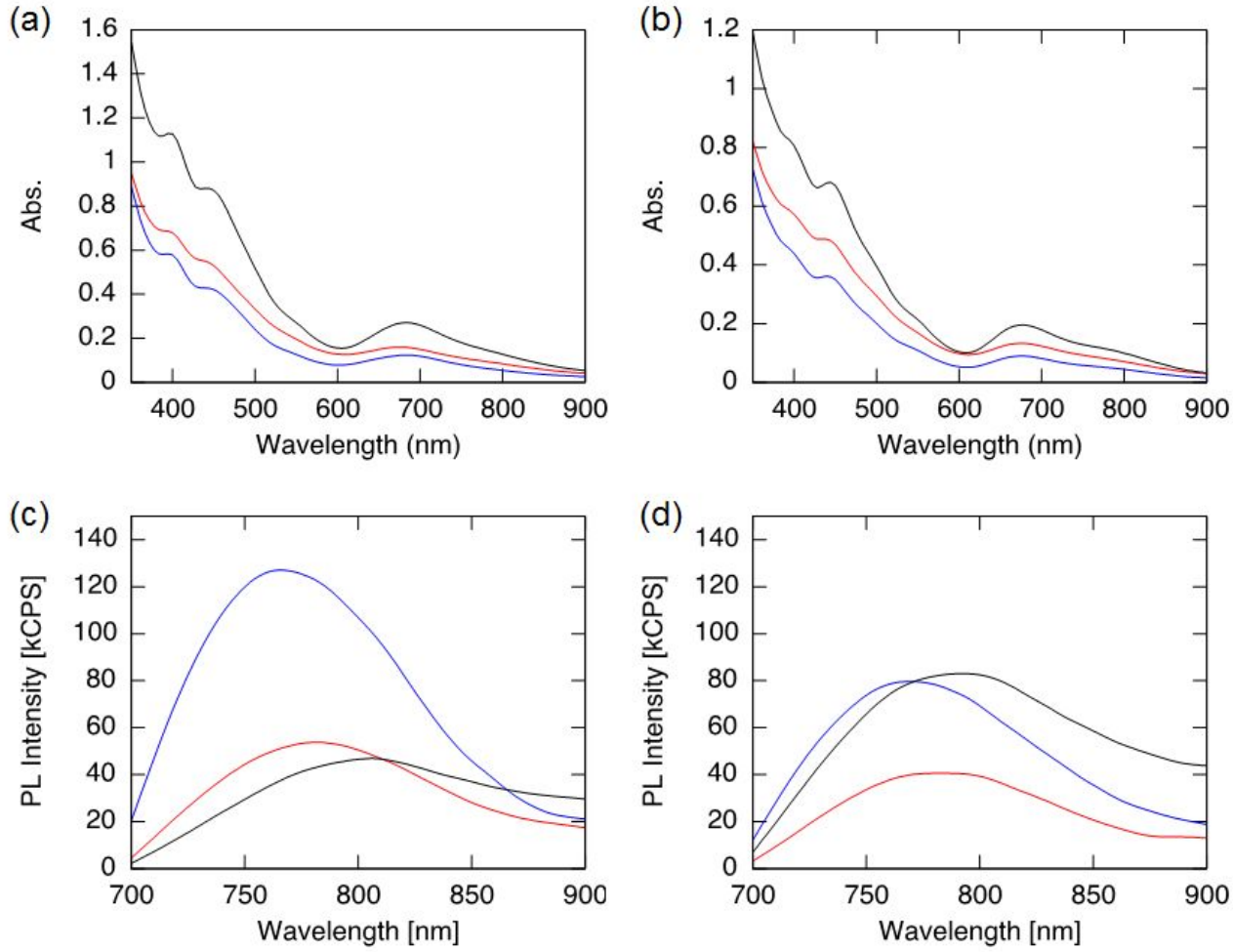


Figure S7. Absorption (a,b) and photoluminescence spectra (c,d) of **DOP1-AuNC** (blue line), **DOP2-AuNC** (red line), and **PET-AuNC** (black line) in $CHCl_3$ and DMF (20 uM).

Molecular Modeling of DOPx-AuNCs.

The molecular models of **DOP1-AuNC** (Figure S8) and **DOP2-AuNC** (Figure S9) were obtained by molecular mechanics (MMFF) calculation using Spartan '16 software, in which the reported crystal structure of $Au_{25}S_{18}$ core (Heaven, M. W.; Dass, A.; White, P. S.; Holt, K. M.; Murray, R. W. *J. Am. Chem. Soc.* **2008,** *130,* 3754-3755.) was used with all bonds strained.

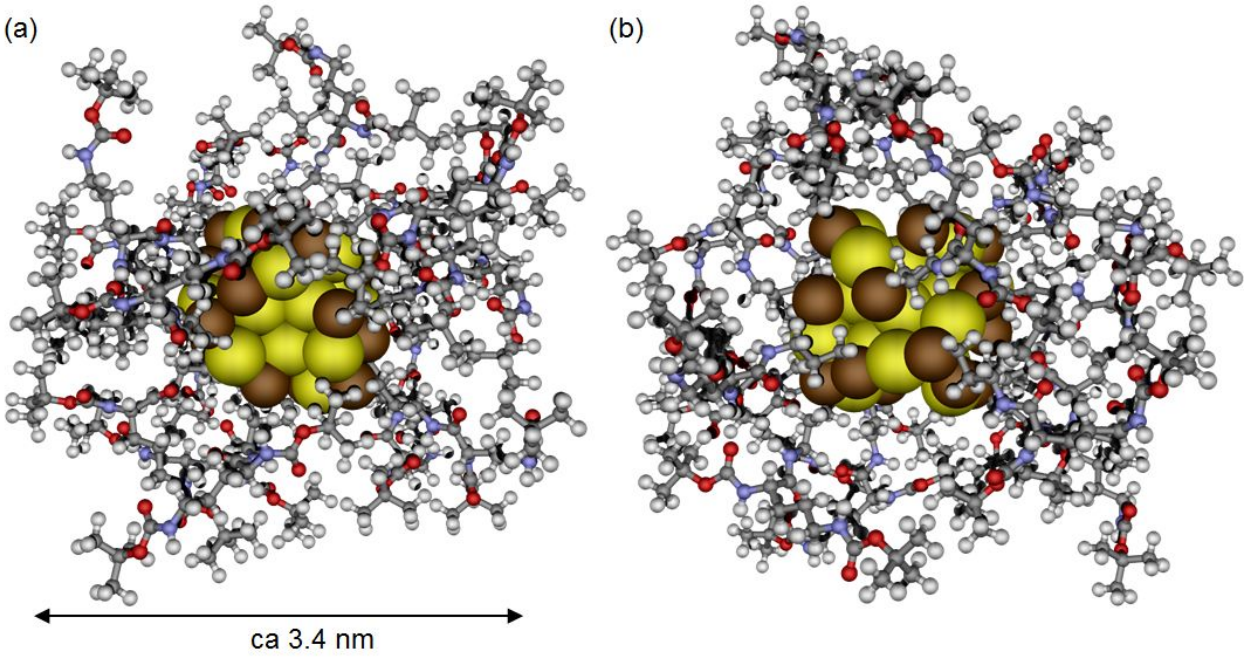


Figure S8. Molecular model of **DOP1-AuNC**. (a) Front view and (b) top view. Yellow: gold, brown: sulfur, red: oxygen, cyan: nitrogen, gray: carbon, and white: hydrogen.

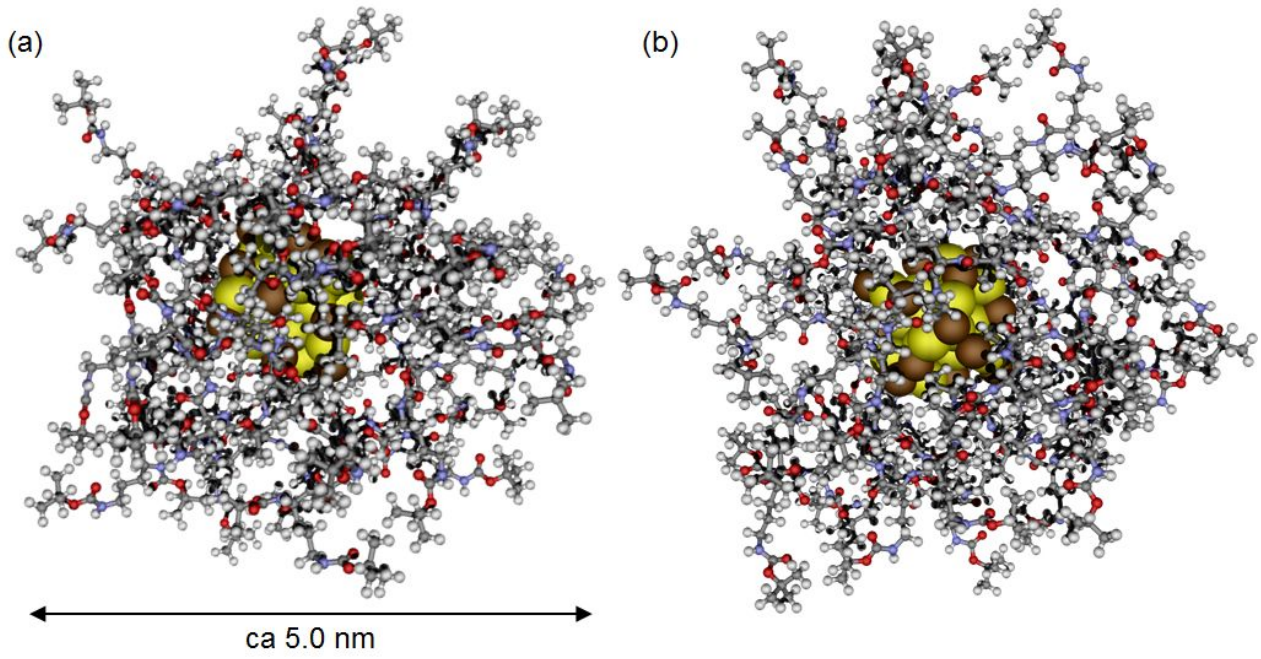


Figure S9. Molecular model of **DOP2-AuNC**. (a) Front view and (b) top view. Yellow: gold, brown: sulfur, red: oxygen, cyan: nitrogen, gray: carbon, and white: hydrogen.

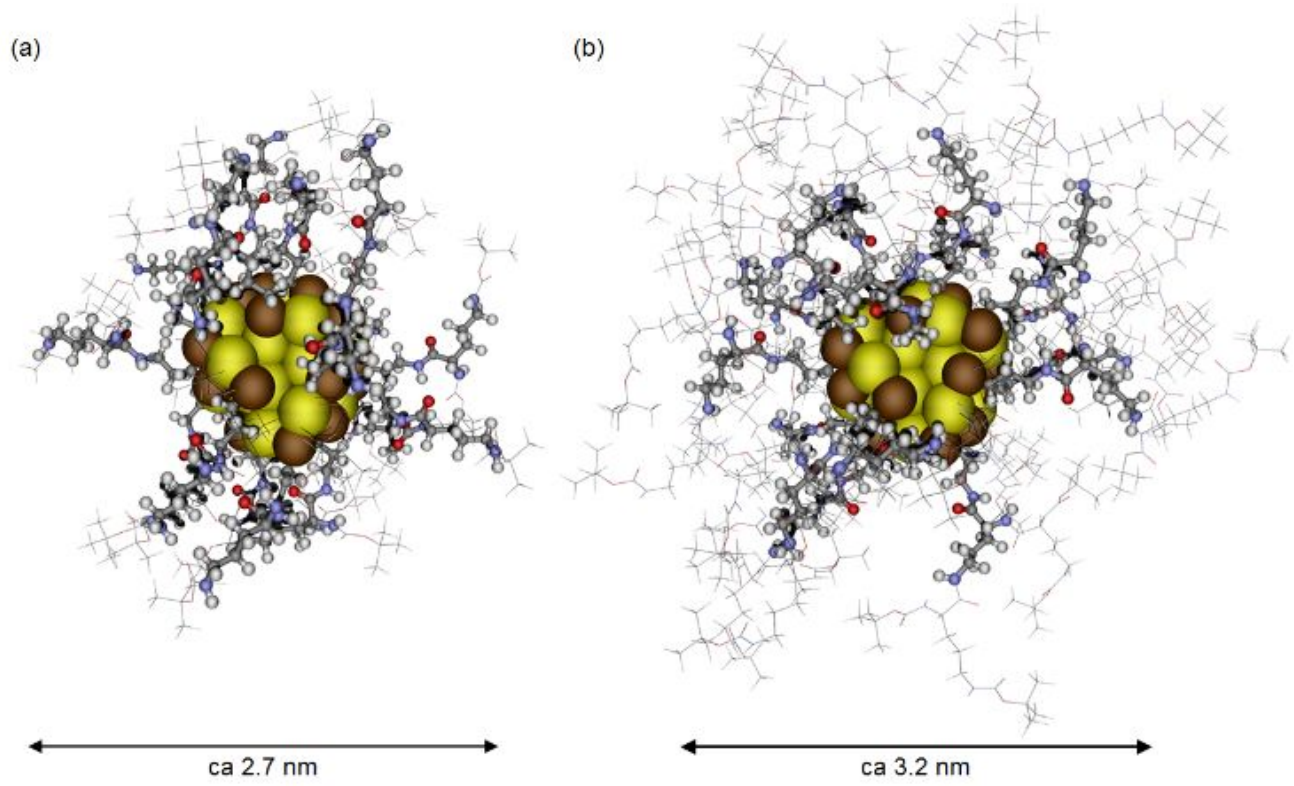


Figure S10. Molecular models of (a) **DOP1-AuNC** and (b) **DOP2-AuNC** in which 2nd generation moieties and Boc groups of ligands are shown as lines for clarity.

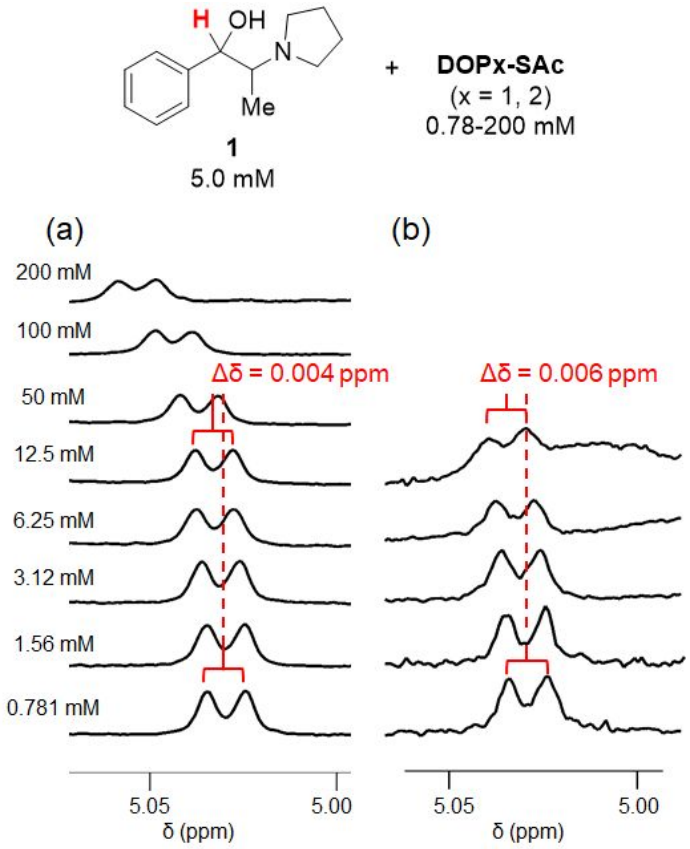


Figure S11. ^{1}H NMR chemical shift of benzylic proton of **1** (5.0 mM) in the existence of and variable concentration (200, 100, 50, 25, 12.5, 6.25, 3.12, 1.56, and 0.78 mM) of (a) **DOP1-SAc** or (b) **DOP2-SAc** in $CDCl_3$.

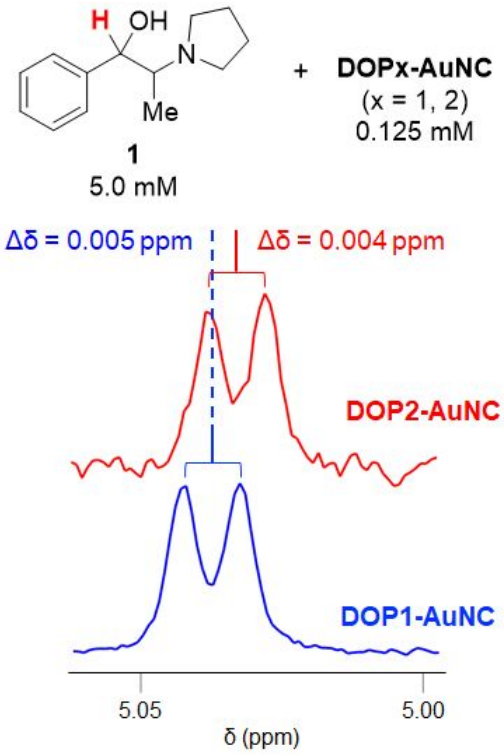


Figure S12. ^{1}H NMR chemical shift of benzylic proton of **1** (5.0 mM) in the existence of 0.125 mM of (a) **DOP1-AuNC** or (b) **DOP2-AuNC** in $CDCl_3$.

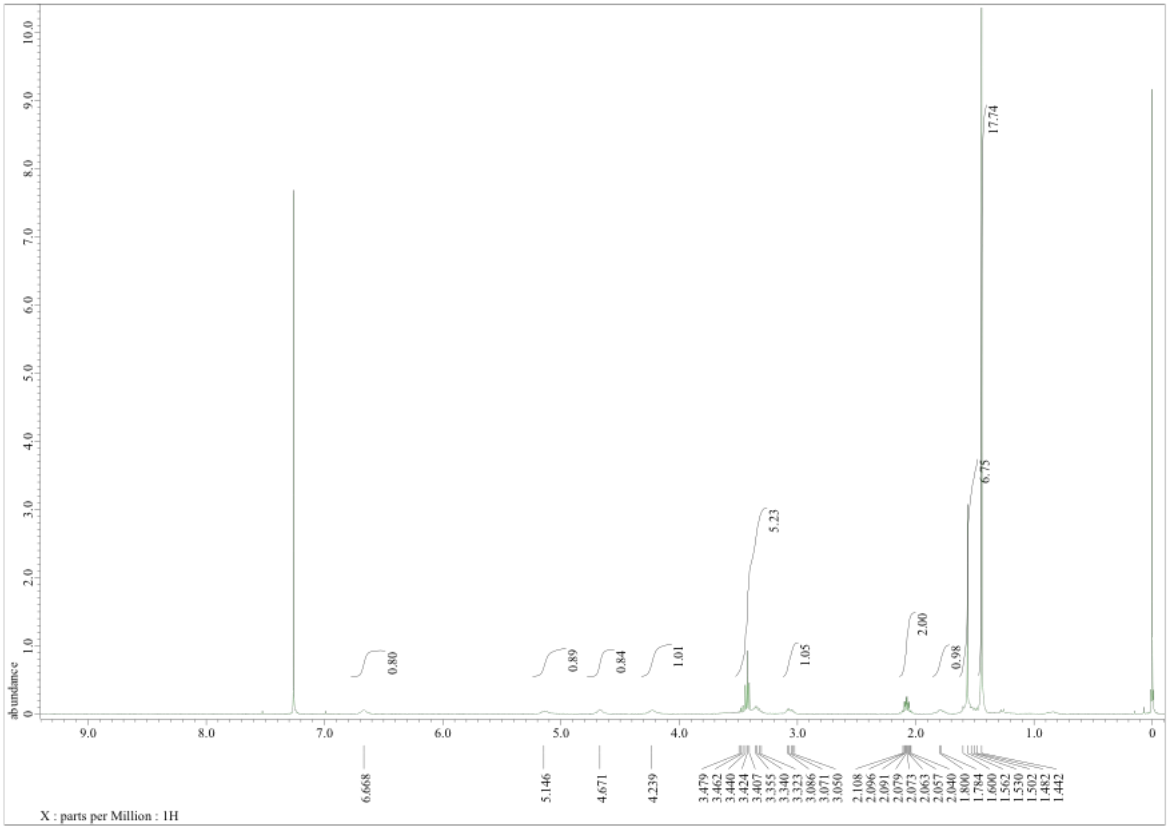


Figure S13. ^{1}H NMR spectrum of **DOP1-Br**.

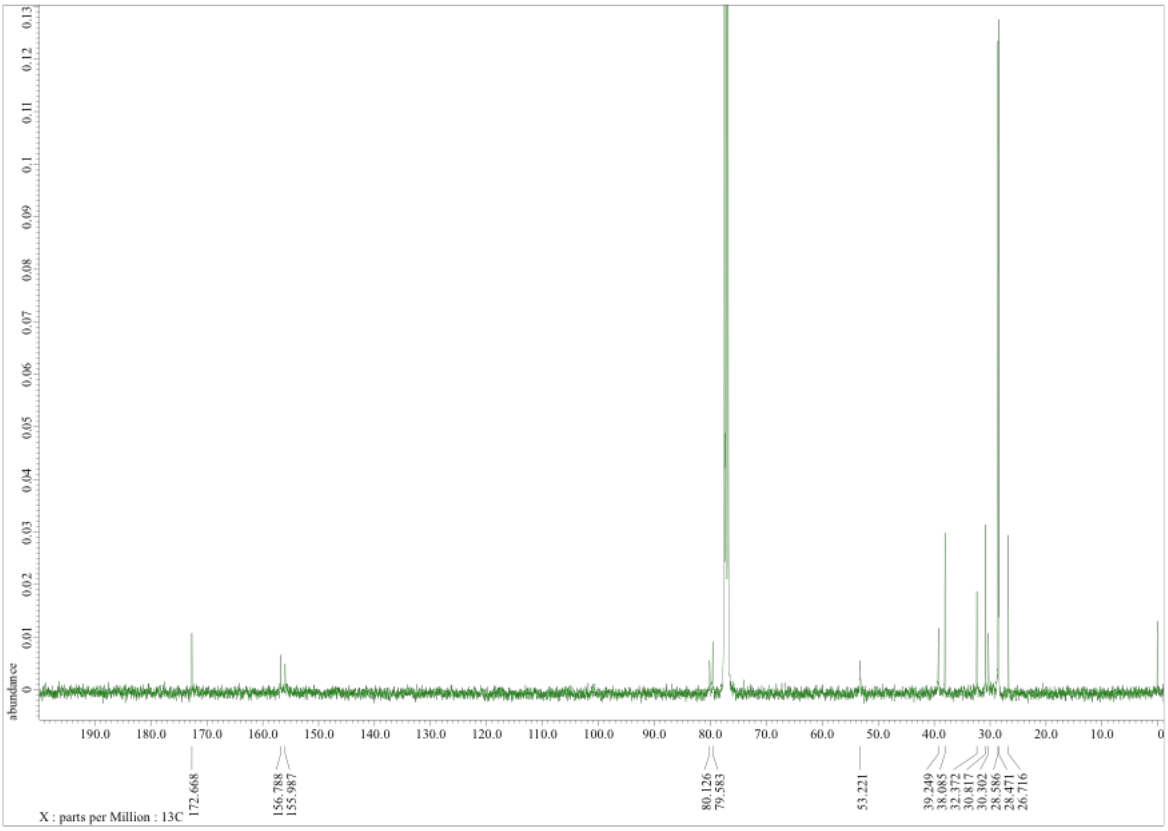


Figure S14. ^{13}C NMR spectrum of **DOP1-Br**.

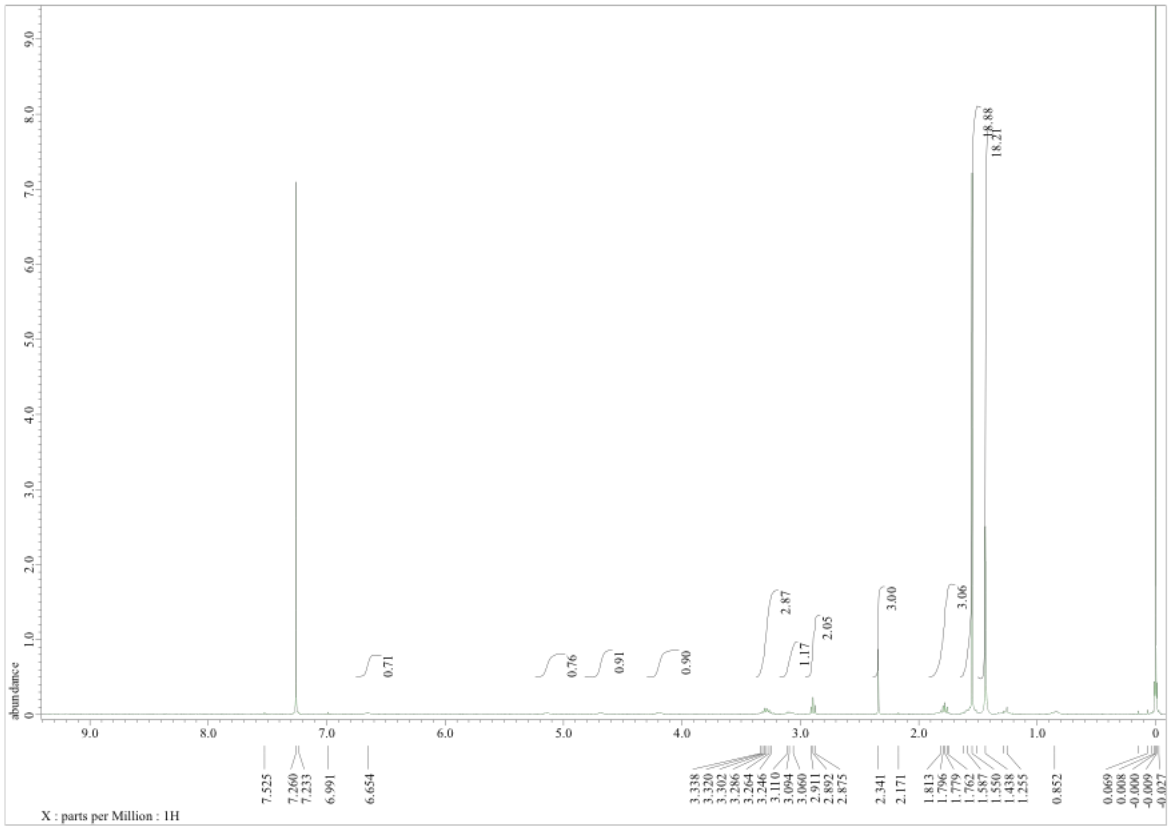


Figure S15. ^{1}H NMR spectrum of **DOP1-SAc**.

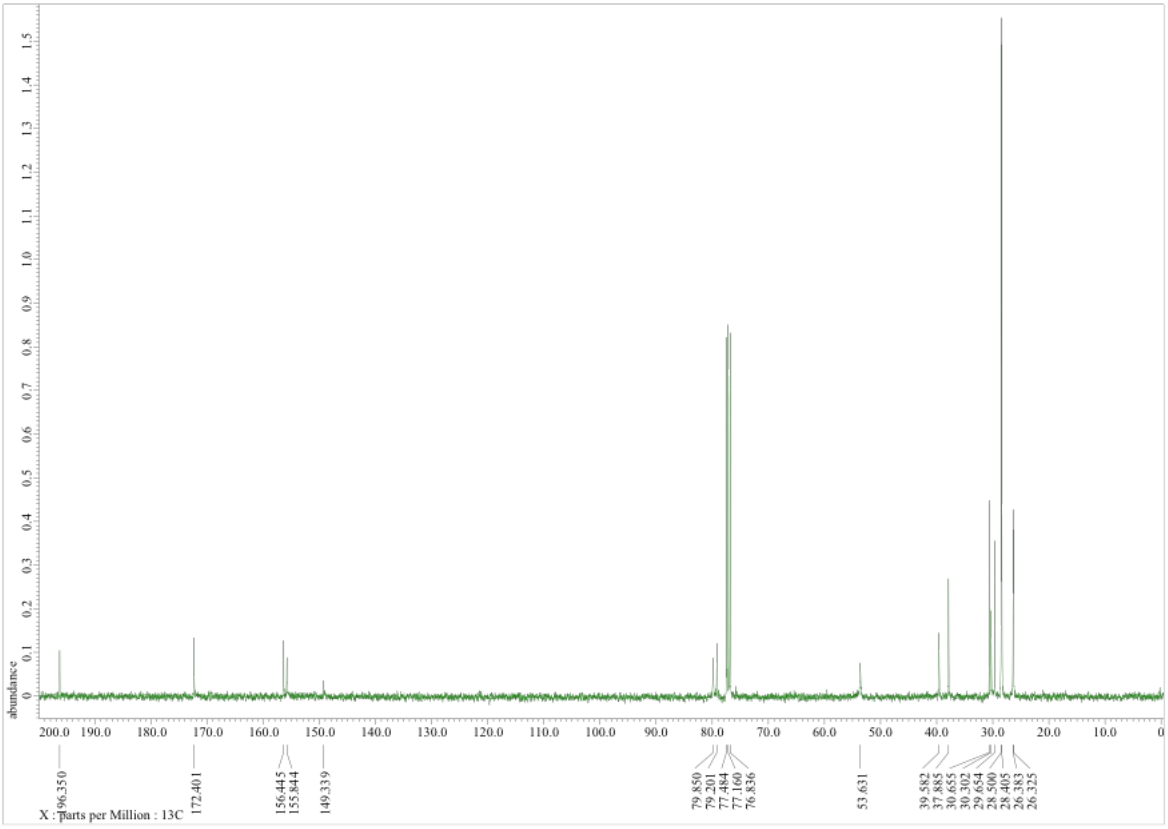


Figure S16. ^{13}C NMR spectrum of **DOP1-SAc**.

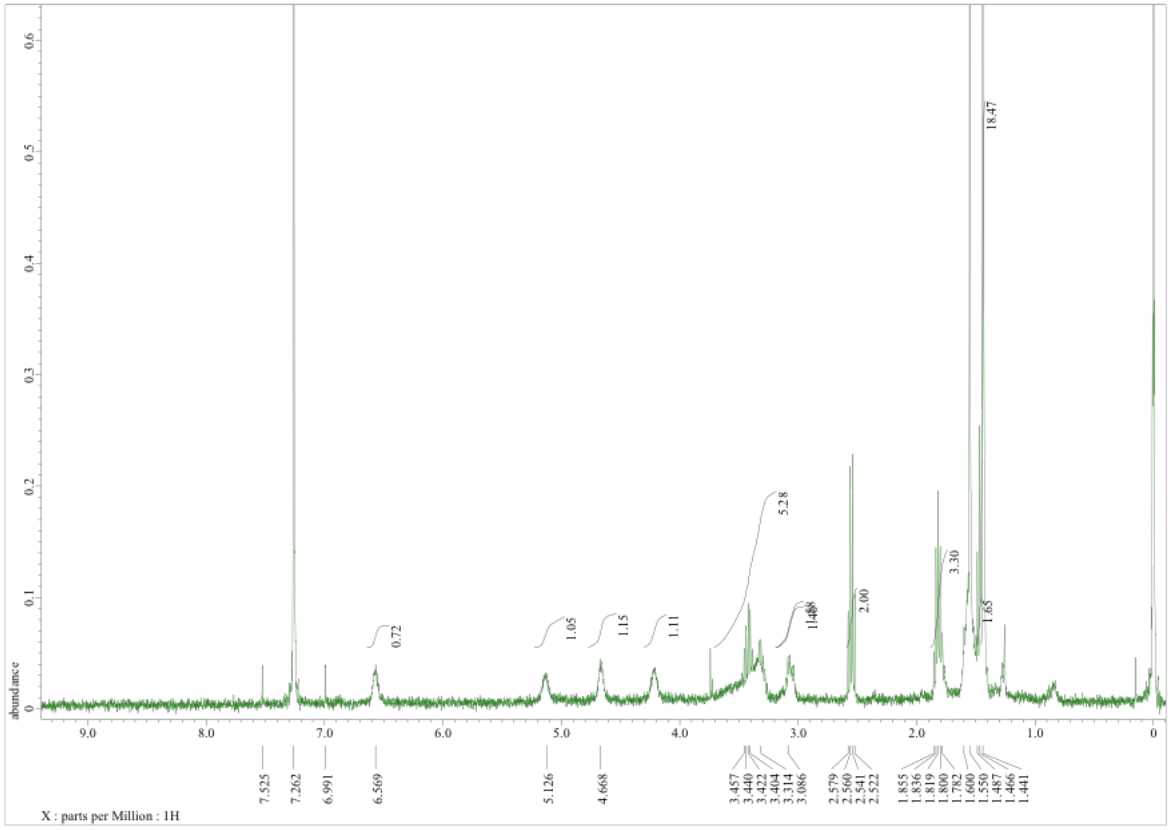


Figure S17. ^{1}H NMR spectrum of **DOP1-SH**.

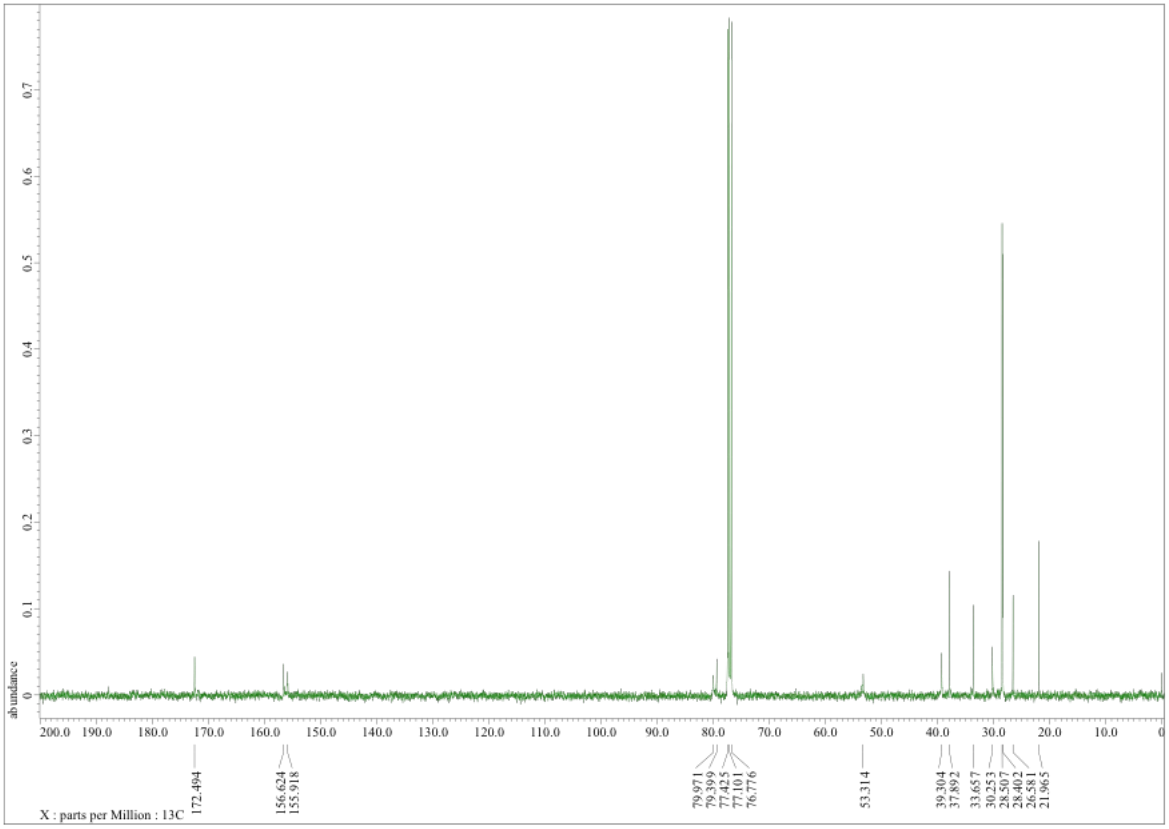


Figure S18. ^{13}C NMR spectrum of **DOP1-SH**.

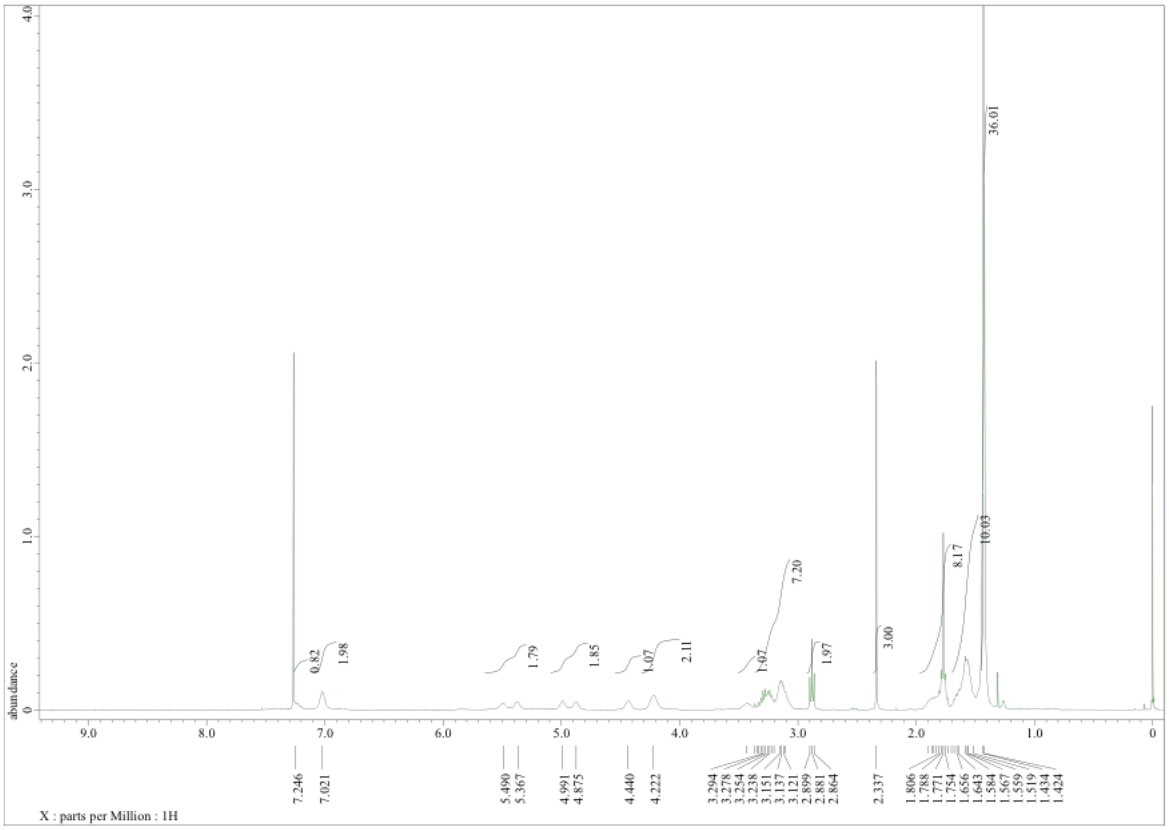


Figure S19. ^{1}H NMR spectrum of **DOP2-SAc**.

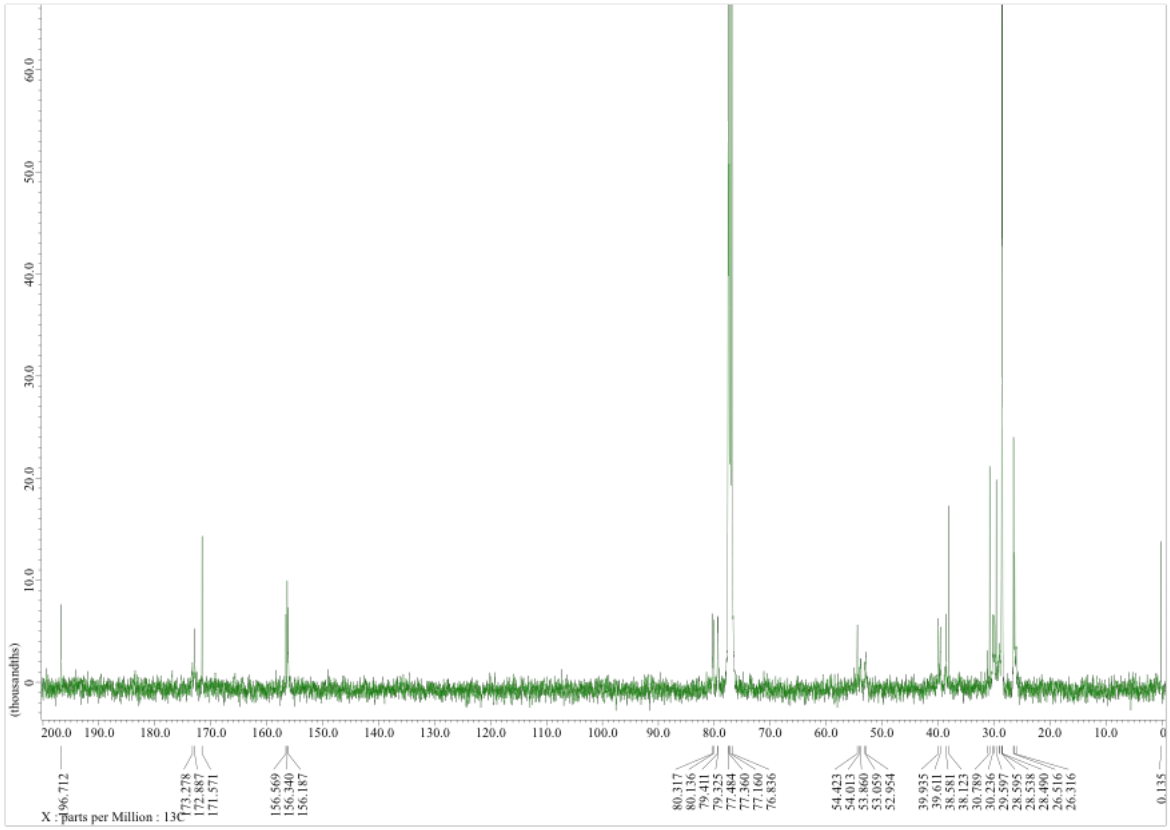


Figure S20. ^{13}C NMR spectrum of **DOP2-SAc**.

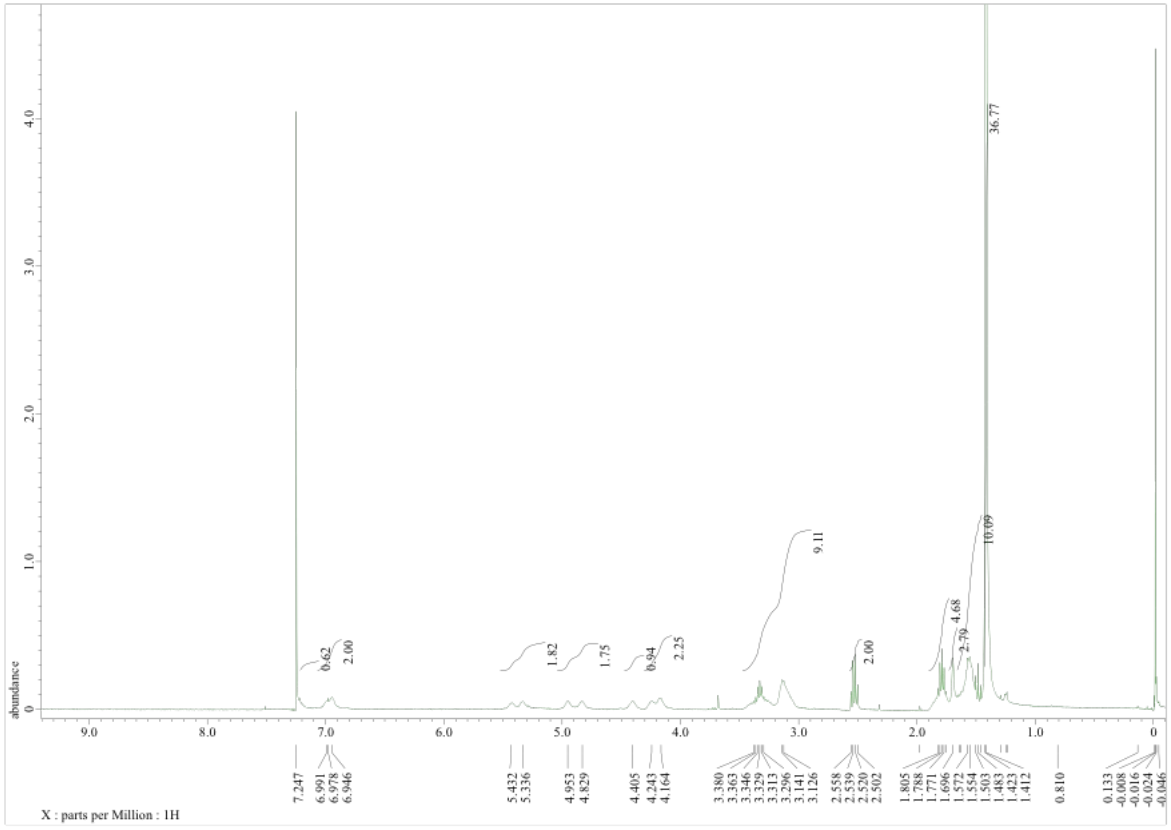


Figure S21. ^{1}H NMR spectrum of **DOP2-SH**.

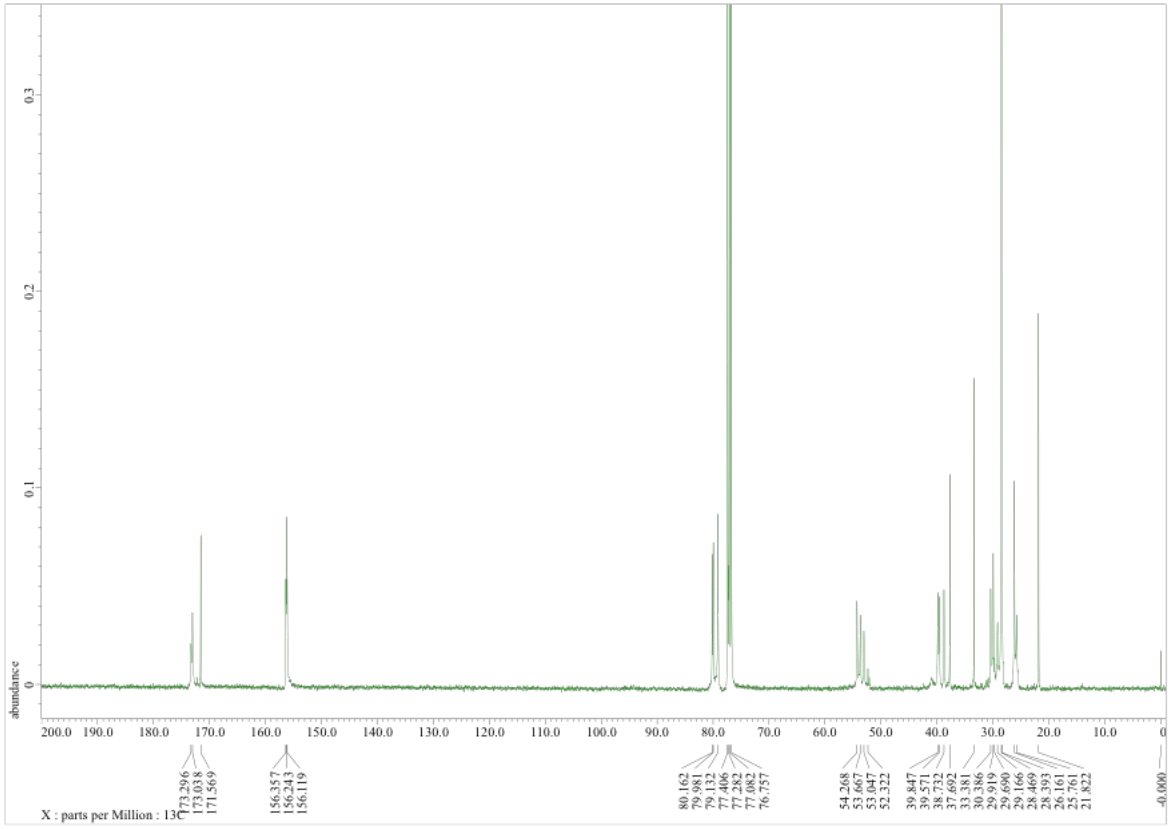


Figure S22. ^{13}C NMR spectrum of **DOP2-SH**.

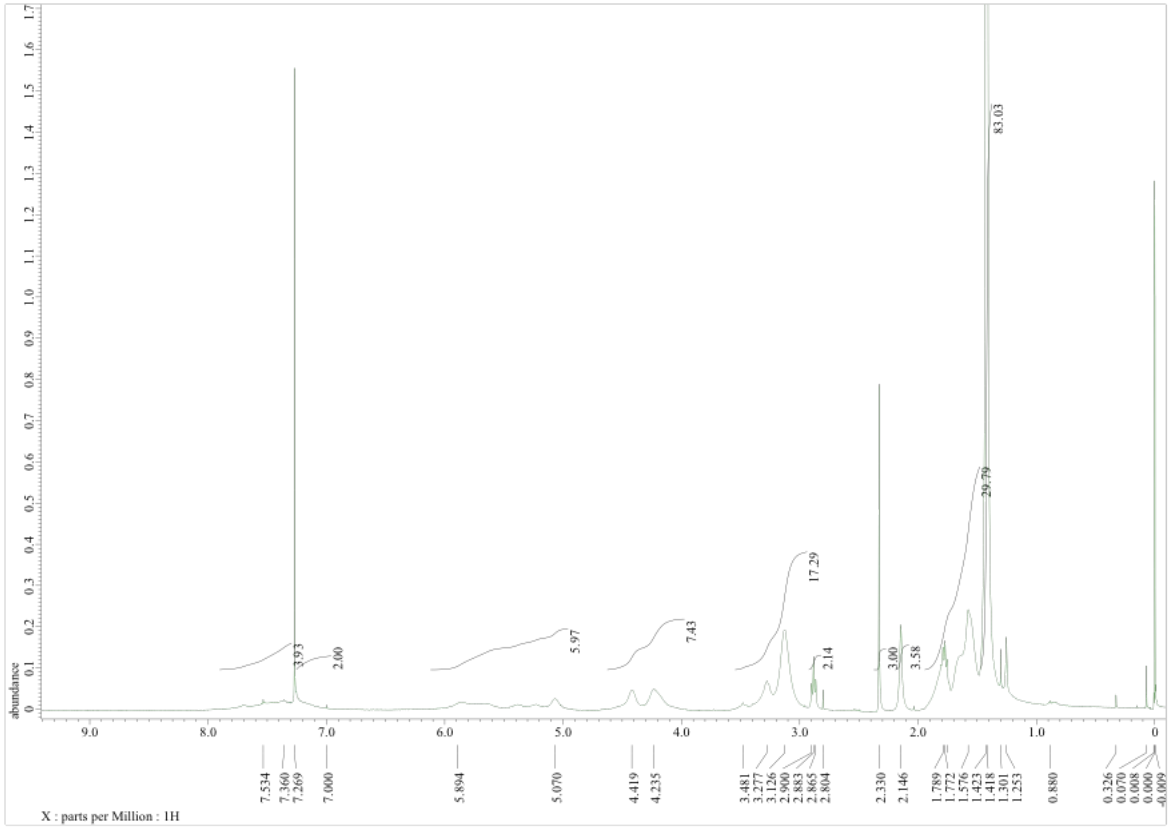


Figure S23. ^{1}H NMR spectrum of **DOP3-SAc**.

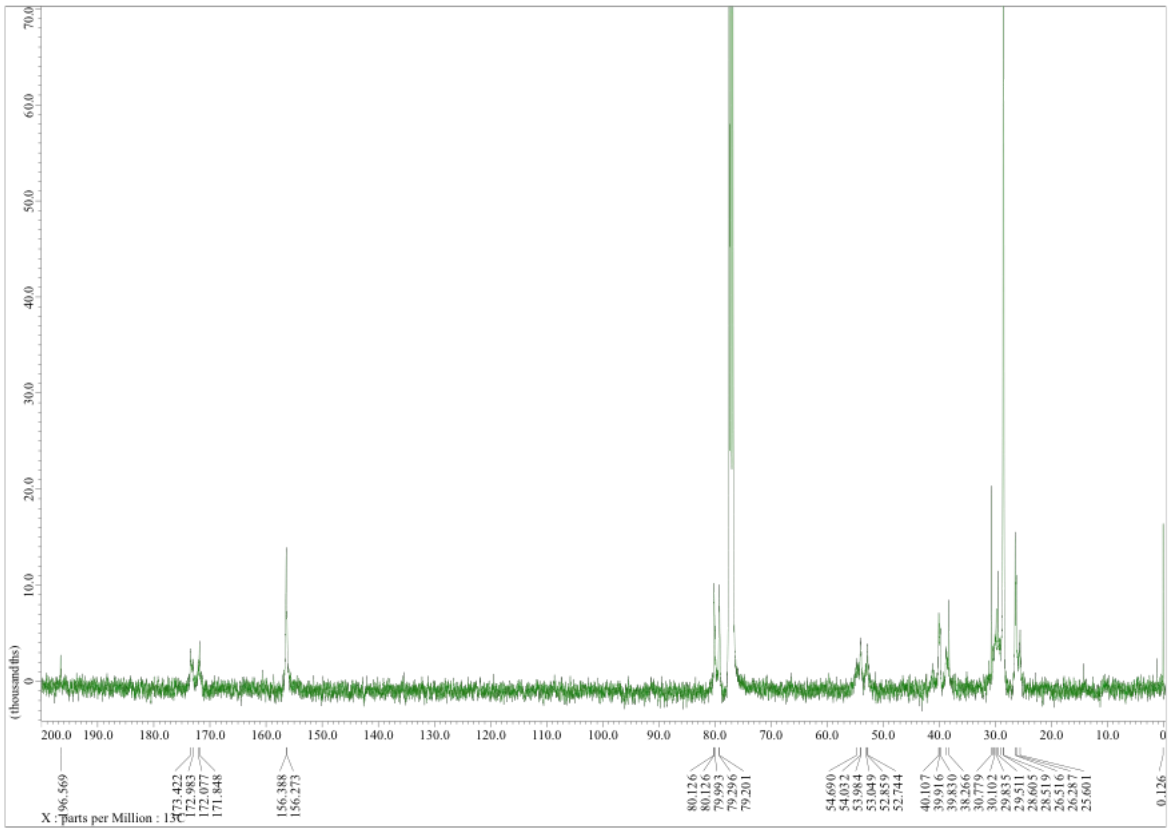


Figure S24. ^{13}C NMR spectrum of **DOP3-SAc**.

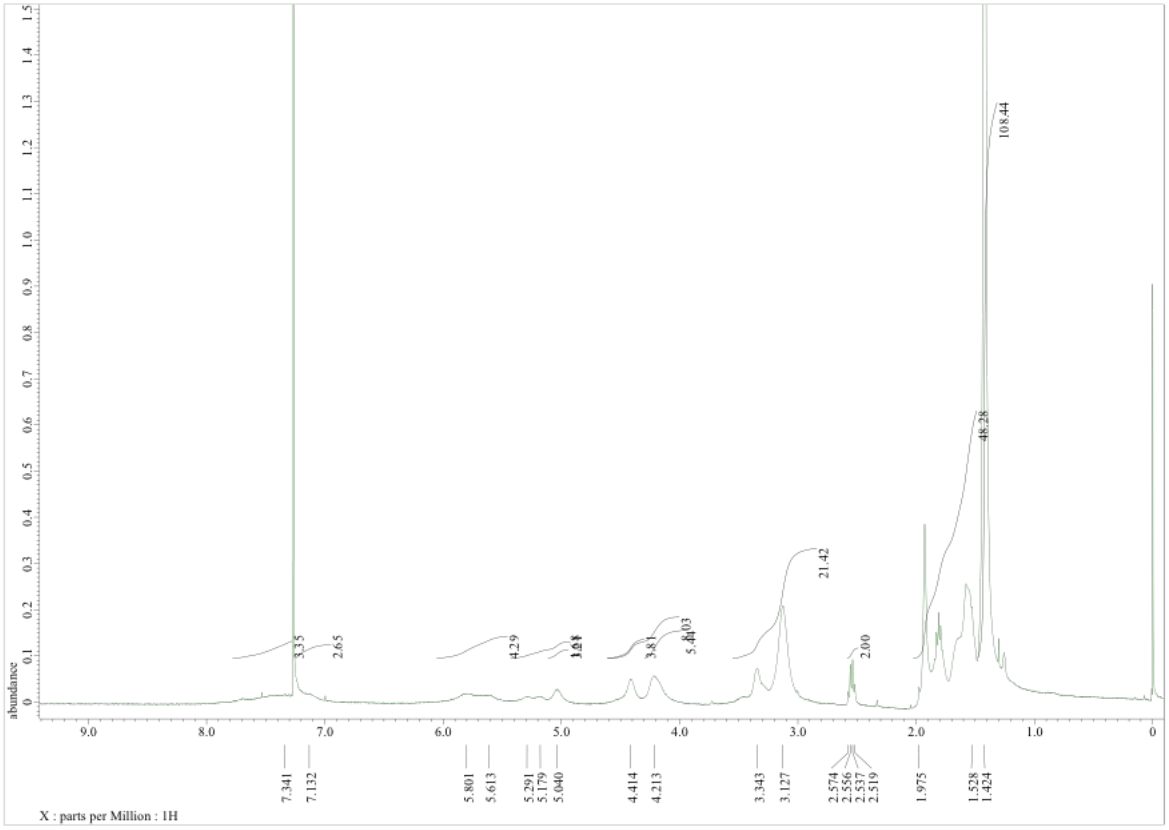


Figure S25. ^{1}H NMR spectrum of **DOP3-SH**.

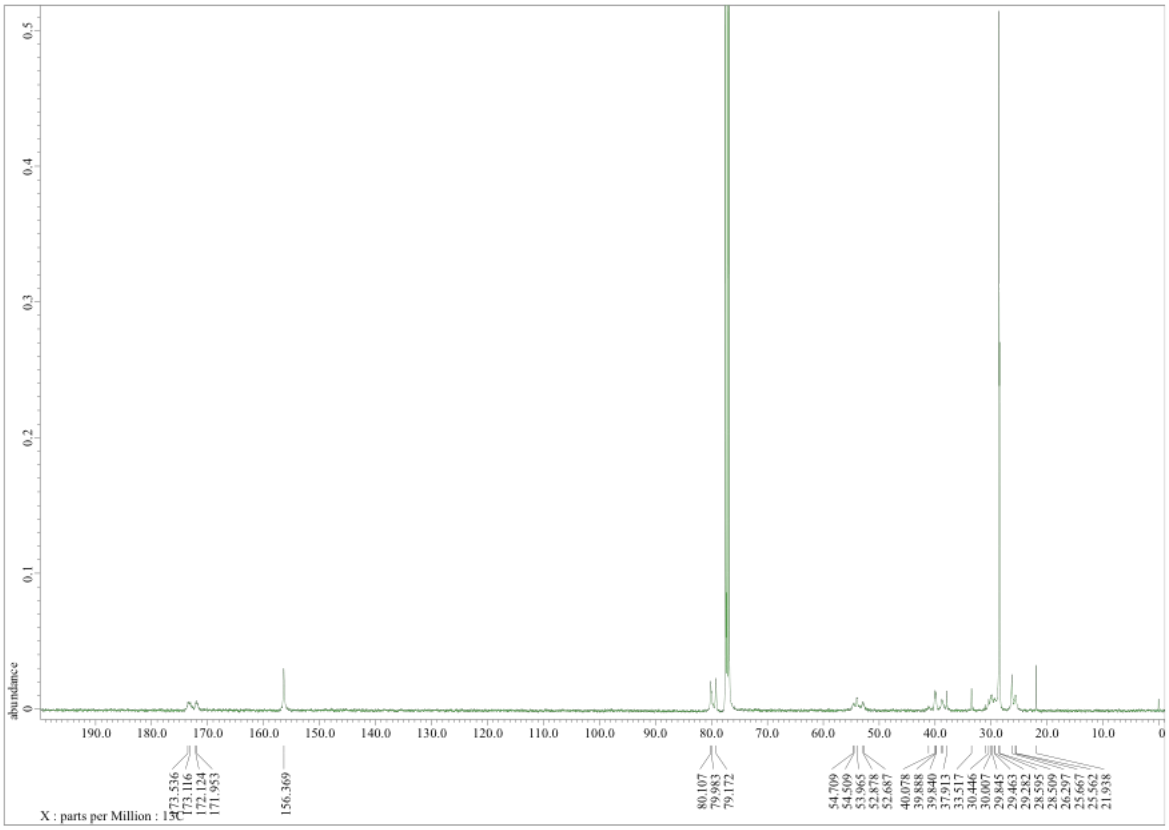


Figure S26. ^{13}C NMR spectrum of **DOP3-SH**.

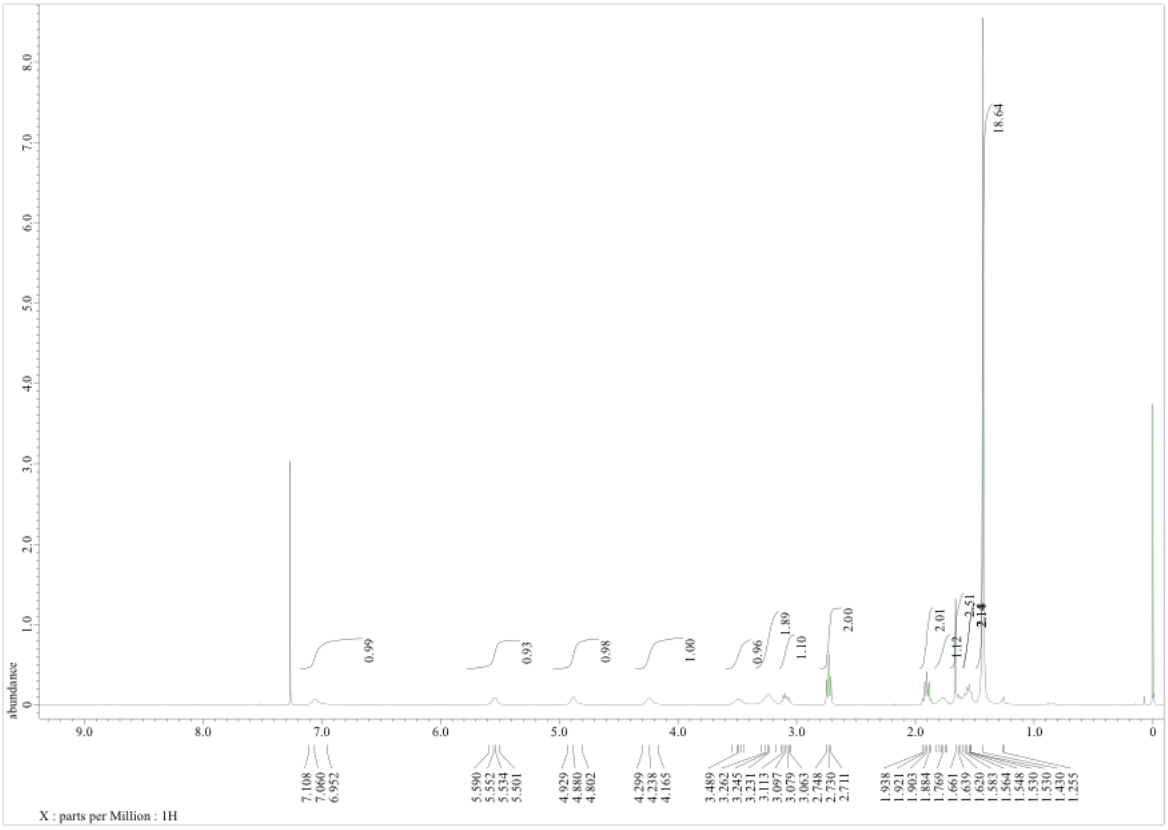


Figure S27. ^{1}H NMR spectrum of **[DOP1-S]$_2$**.

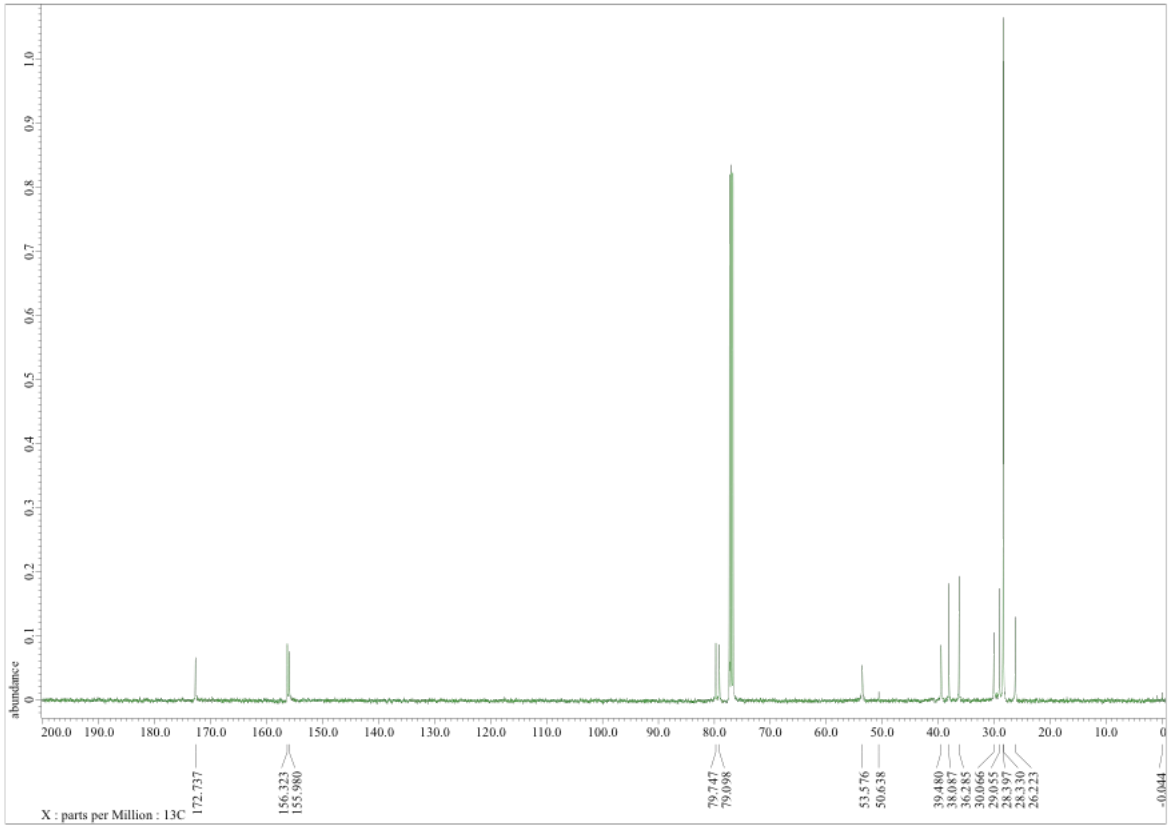


Figure S28. ^{13}C NMR spectrum of **[DOP1-S]$_2$**.

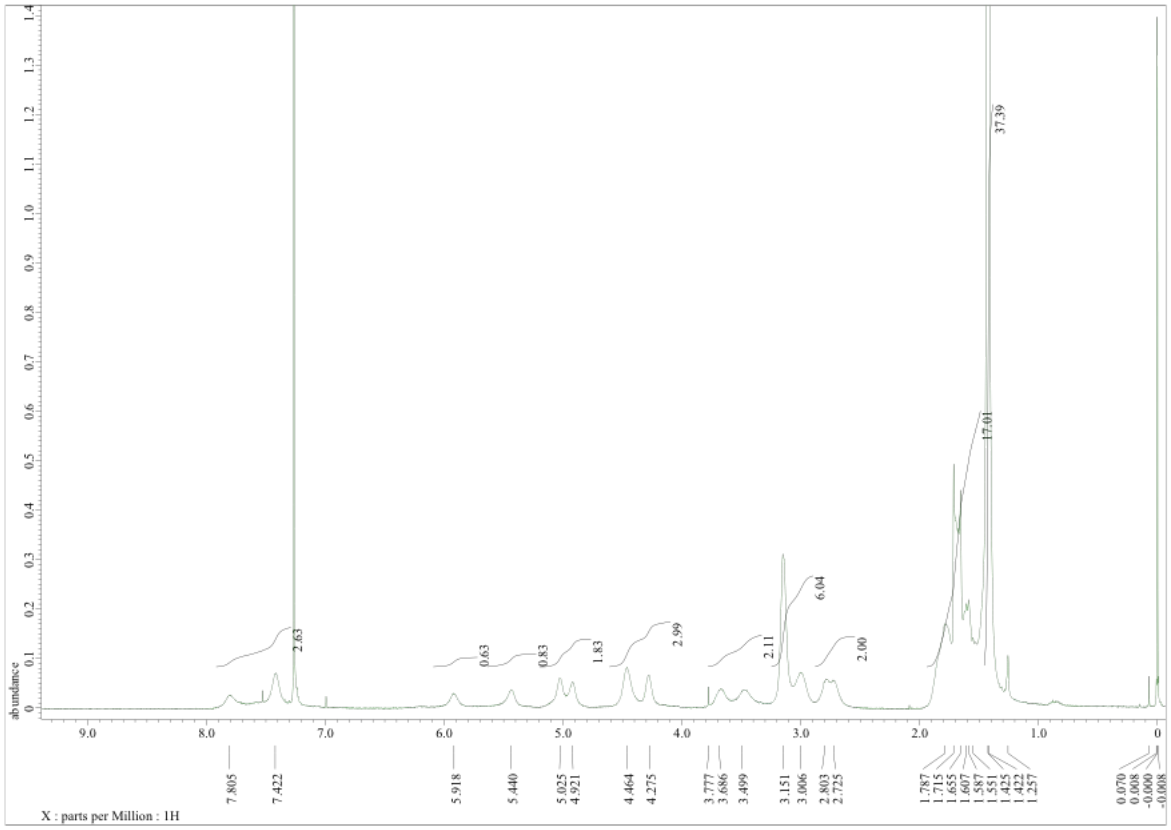


Figure S29. ^{1}H NMR spectrum of [**DOP2-S**]$_2$.

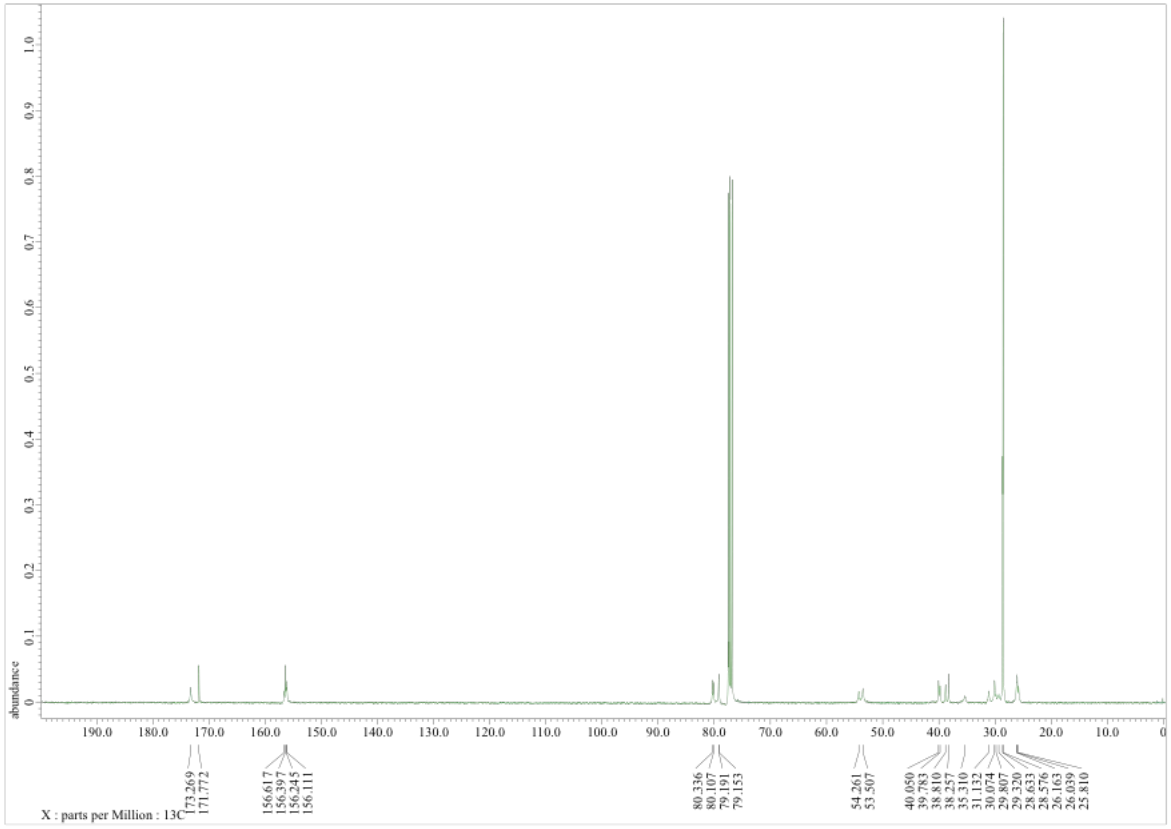


Figure S30. ^{13}C NMR spectrum of **[DOP2-S]$_2$**.

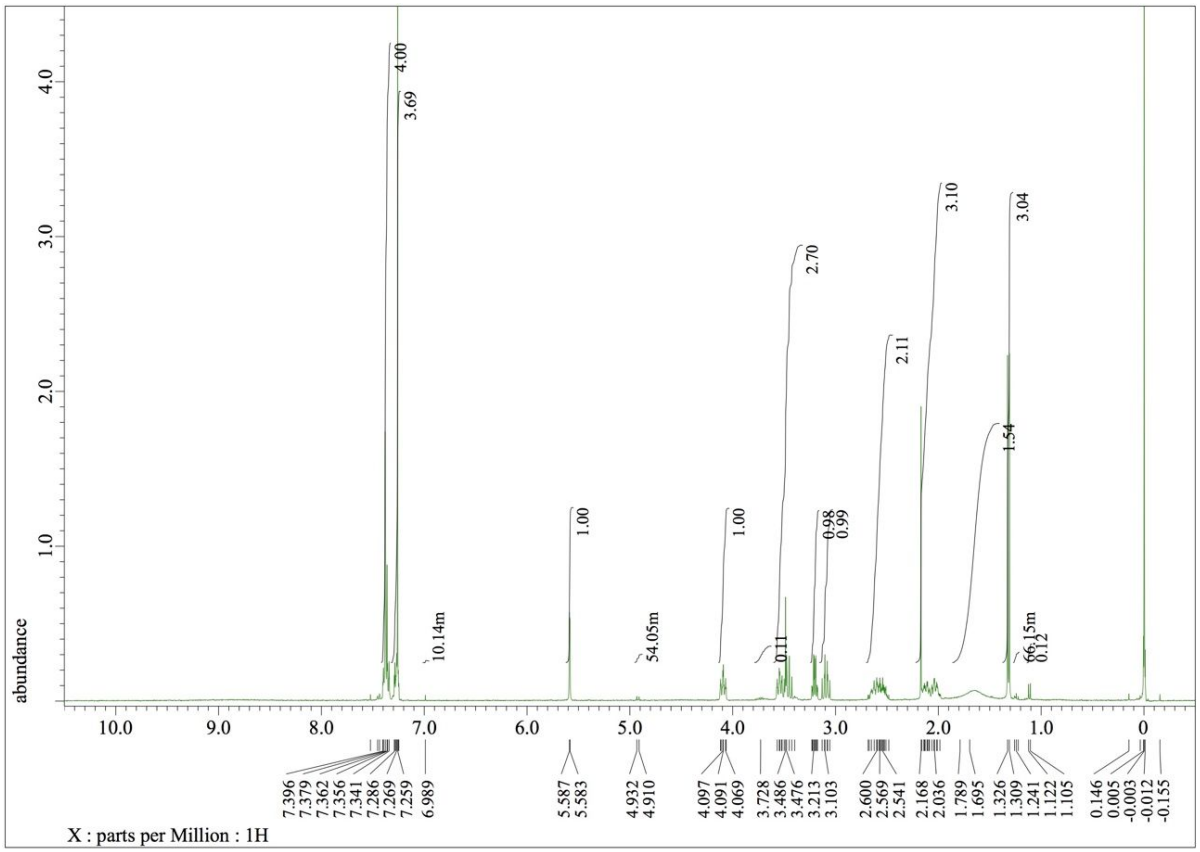


Figure S31. [1]H NMR spectrum of *N*-(2-hydroxy-1-methyl-2-phenylethyl)pyrrolidine *N*-oxide (**3**).

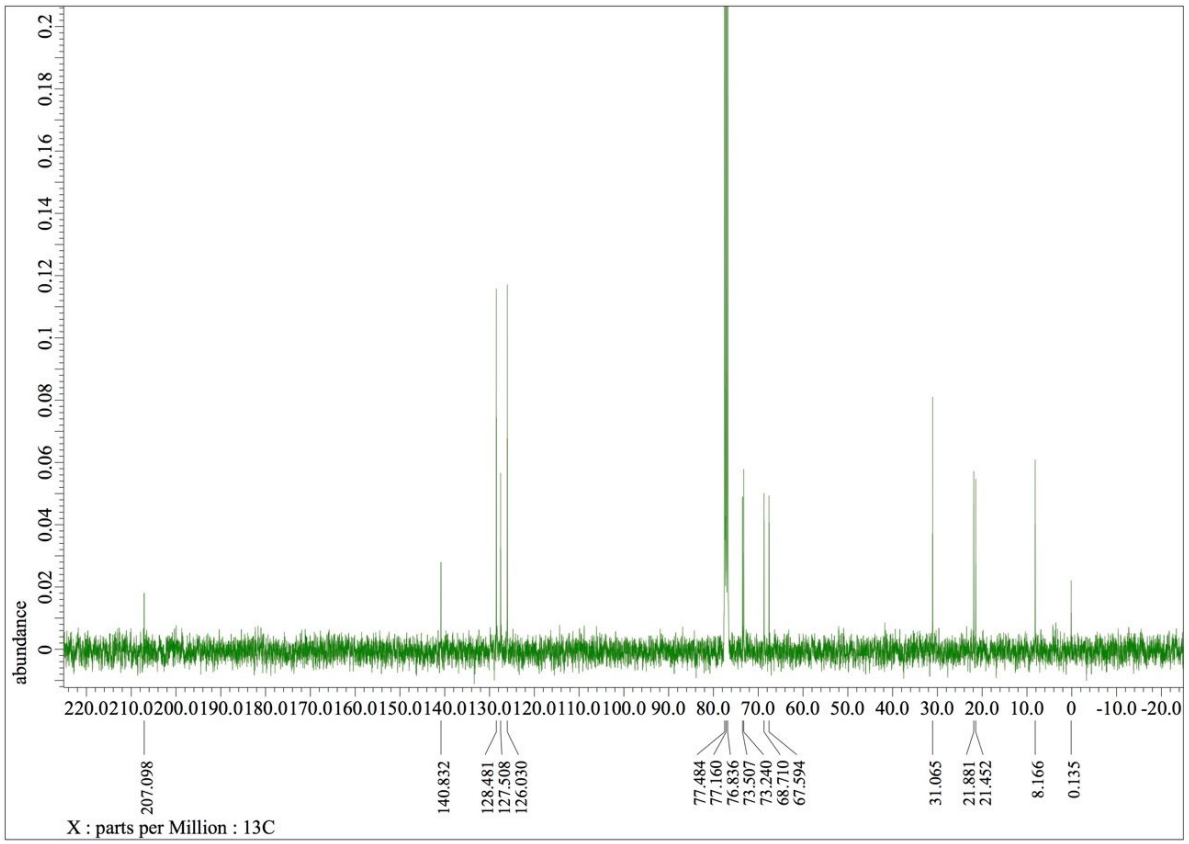


Figure S32. [13]C NMR spectrum of *N*-(2-hydroxy-1-methyl-2-phenylethyl)pyrrolidine *N*-oxide (**3**).