Supplementary Information

Compartmentalization of Incompatible Catalytic Transformations for Tandem Catalysis

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Contents

1. General

1.1 Materials

2-Nonyl-2-oxazoline (NOx, monomer **A**)[1], 2-(3-butenyl)-1,3-oxazoline (AlkeneOx, monomer **B**)[2], methyl 3-(oxazol-2-yl)propionate (EsterOx, monomer **C**)[3], alkene functionalized Co-porphyrin catalyst,[4] and amine functionalized Rh-TsDPEN catalyst[5] were synthesized based on adapted literature procedures. All reagents were purchased from standard suppliers and used as received unless otherwise stated. 2-Methyl-2-oxazoline, acetonitrile and chlorobenzene were distilled over CaH_2 and stored under dry argon and molecular sieves (4 Å). Methyltriflate was distilled over barium oxide and stored under dry argon at 4 °C. Dichloromethane was dried by passing through columns of activated alumina. Flash column chromatography was performed using silica gel 60 Å (230-400 mesh) from Sorbent Technologies.

1.2 Measurements

^{1}H NMR and ^{13}C NMR spectra were recorded at 25°C on a Bruker AC 600 MHz spectrometer. All chemical shifts are reported in parts per million (ppm) with reference to solvent residual peaks. Splitting patterns are reported as singlet (s), doublet (d), triplet (t), quartet (q) and unresolved multiplet (m).

IR-spectra were recorded on a Nicolet 6700 FT-IR spectrometer, equipped with a Smart iTR ATR accessory.

Gel-permeation chromatography (GPC) was carried out using a Shimadzu pump coupled

to a Shimadzu RI detector. A 0.03 M LiCl solution in *N*,*N*-dimethylformamide was used as eluent at a flow rate of 1 mL/min at 60 °C. A set of Polymer Standards columns (AM GPC gel, 10 μm, precolumn, 500 Å and linear mixed bed) was used. M_w^{app}, M_n^{app}, and $Đ$ represent the apparent weight-average molecular weight, apparent number-average molecular weight, and dispersity index, respectively. Commercially available poly(styrene) standards were used for calibration.

The thermal stability of polymers and micelles was investigated by TGA analysis, using a PerkinElmer Pyris1 TGA instrument with a heating rate of 10 °C min^{-1} from 50 °C to 650 °C under nitrogen, and by DSC analysis, using a PerkinElmer Pyris 1 DSC instrument with a heating rate of 5 °C min^{-1} from -20 °C to 200 °C .

Hydrodynamic diameters of the cross-linked and uncross-linked micelles were determined at 25 °C by dynamic light scattering (DLS) using a Protein Solution DynaPro instrument with a 663 nm laser module. SEM images were recorded on Carl Zeiss Merlin® Field Emission-Scanning Electron Microscope (FE-SEM). The accelerating voltage was 2 kv and the working distance was 3.9 mm. The SEM samples were prepared by depositing the sample methanol solution onto a piranha solution processed silicon wafer, followed by vacuum drying at room temperature. The particle size was measured by Zeiss FE-SEM built-in program SmartSEM User Interface.

Analytical gas chromatography (GC) was performed on a HP 6890 Series chromatograph equipped with a flame-ionization detector. A fused silica capillary column (30 m x 0.320

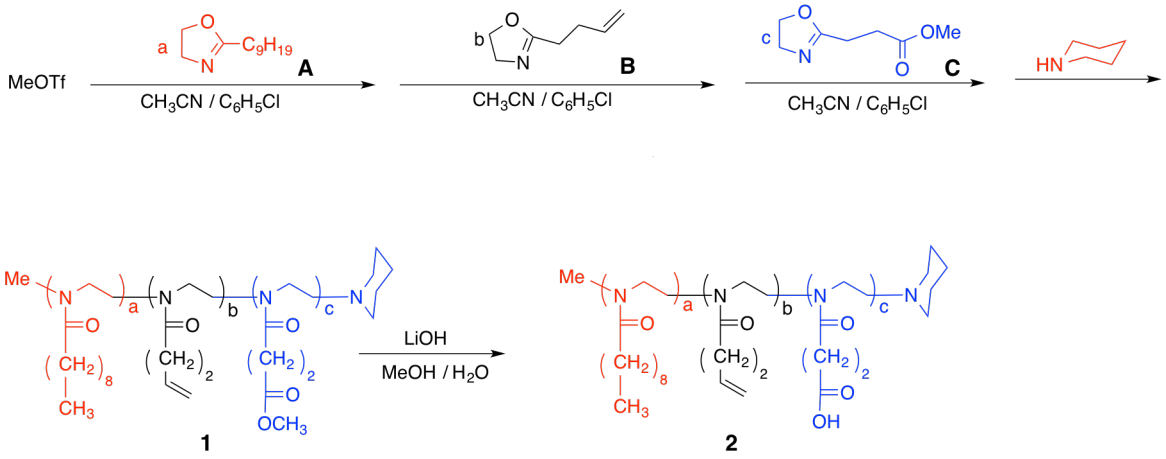
mm x 0.25 mm) wall-coated with DB-1 was used with helium gas carrier (25 psi column head pressure).

Analytical high performance liquid chromatography (HPLC) was performed on an Agilent 1200 series with a diode array detector. A Chiracel OD column (Chiral Technologies, Inc.) and a mixture of n-hexane and isopropanol (ratio at 92:8, flow rate at 0.6 mL/min) were used.

Elemental analysis (CHN) and inductively coupled plasma mass spectrometry (ICP-MS) were carried out by Robertson Microlit Laboratories, Inc.

2 Preparation

2.1 Polymer precursor



Scheme S1. Synthesis of amphiphilic triblock copolymer based on poly(2-oxazoline)

Polymer 1: A typical procedure for cationic ring opening polymerization was followed: Methyltriflate (28.29 µL, 0.25 mmol) was added to a solution of monomer **A** NOx (0.52 mL, 2.5 mmol) in chlorobenzene (1 mL) and acetonitrile (2 mL). The mixture was stirred for 28 h at 70 °C. The polymerization was monitored via ^{1}H NMR spectroscopy. After monomer **A** was completely consumed, monomer **B** AlkeneOx (0.32 mL, 1.25 mmol) and chlorobenzene (1 mL) was added to the polymer solution under an argon atmosphere. The mixture was stirred for eight hours at 70 °C. After monomer **B** was fully consumed, monomer **C** EsterOx (1.65 mL, 12.5 mmol) and acetonitrile (2 mL) were added. The solution was stirred at 70 °C for an additional 36 hours. After monomer C was fully consumed, the polymerization was terminated via the addition of piperidine (50 µL, 0.5mmol) and stirred at room temperature for four hours. The polymer was purified by dialysis against DCM and isolated by freeze-drying from dioxane.

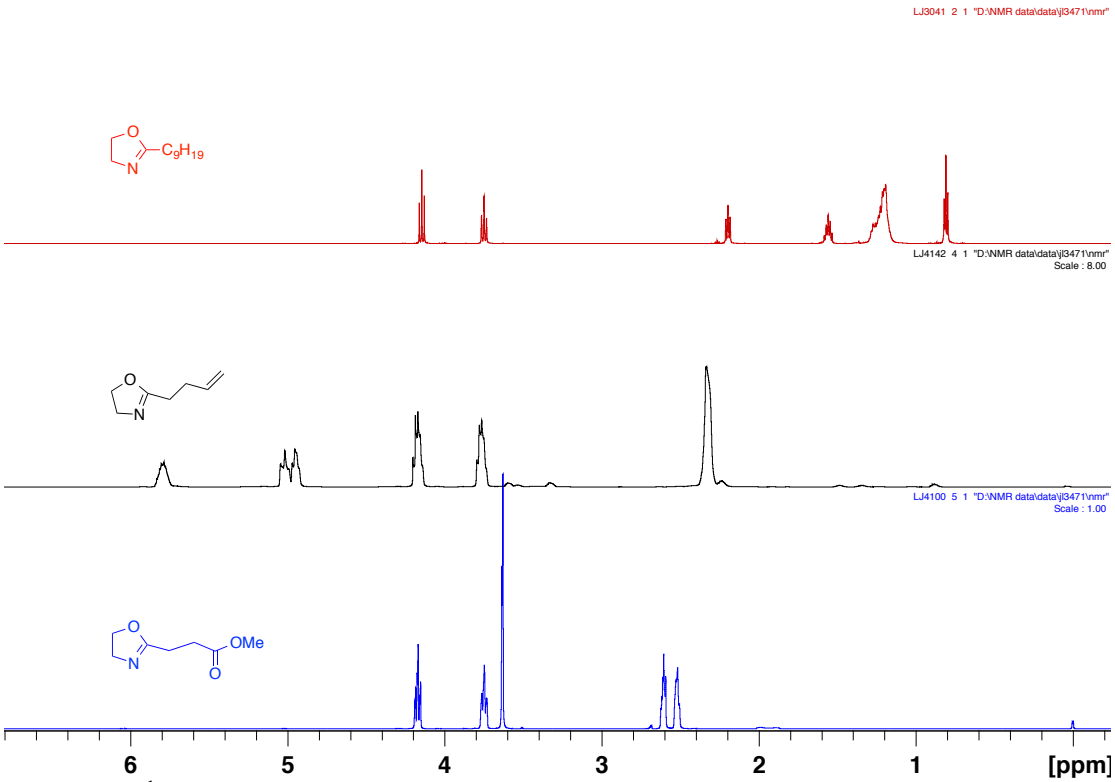


Figure S1. ^{1}H NMR spectrum of the three 2-substitute-2-oxazoline monomers.

The repeat units for **A** NOx (a=3), **B** AlkeneOx (b=4), and **C** EsterOx (c=28) were determined by ^{1}H NMR spectroscopy endgroup analysis (Figure S2).

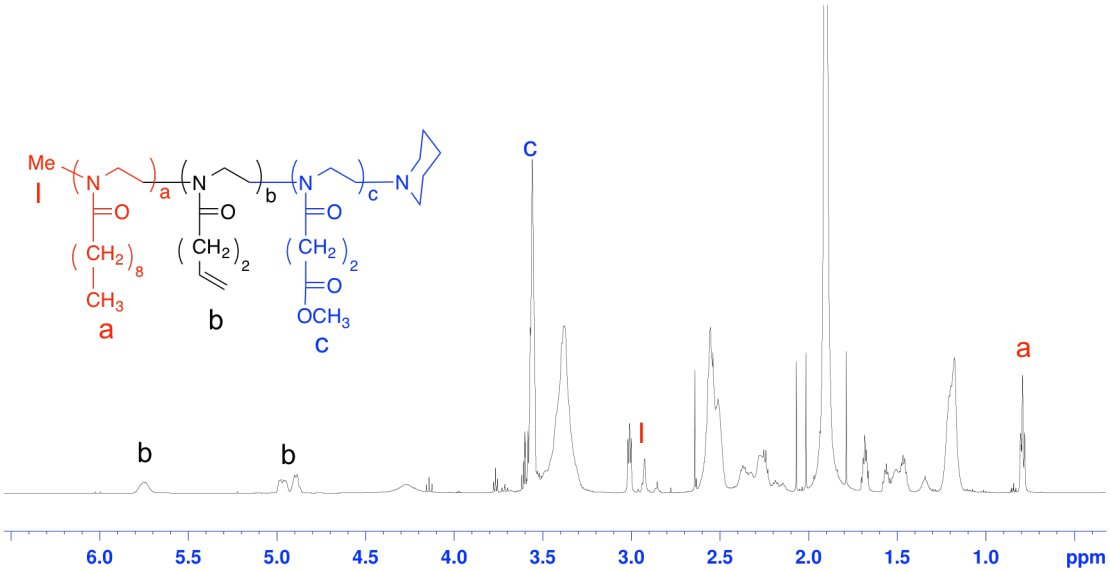


Figure S2. ^{1}H NMR spectrum of triblock copolymer **1**.

The molecular weight distributions were determined by GPC using DMF as the eluent: M_n^{app} = 5,500 g/mol, $Đ$ = 1.23 (Fig. S3). TGA analysis showed that the thermal weight loss of polymer **1** started around 240 °C. DSC analysis was performed from -20 °C to 200 °C at a heating rate of 5 °C min^{-1}, no detectable thermal transition was observed.

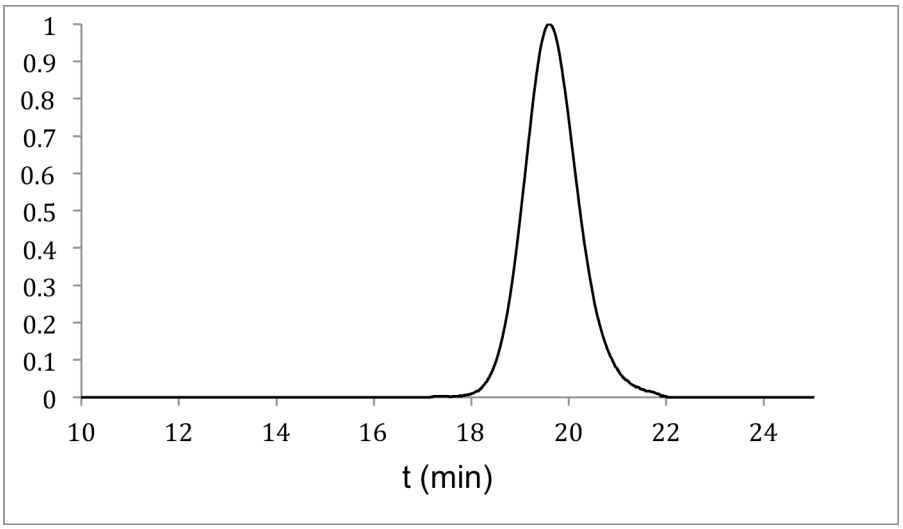


Figure S3. Normalized gel-permeation chromatogram of triblock copolymer **1**.

^{13}C-NMR ($CDCl_3$, 150 MHz, δ vs. TMS): 173.6, 172.1, 137.4, 123.5, 121.3, 119.3, 117.2, 115.4, 54.3, 51.7, 49.9, 47.5, 47.1, 46.3, 45.6, 45.1, 43.6, 43.2, 36.8, 33.6, 32.8, 32.1, 31.9, 29.5, 28.9, 27.5, 25.4, 24.9, 24.2, 23.1, 22.7, 22.4, 21.7, 14.1.

FTIR: ν = 3478, 2927, 2854, 1731, 1619, 1435, 1366, 1211, 1161, 1029, 992, 948, 848 cm^{-1}.

Polymer 2: Triblock copolymer **1** (200 mg) was dissolved in 20 mL methanol. Then, 20 mL of a 0.1 M LiOH solution was added. The mixture was stirred at 50 °C overnight. The solvent was removed under reduced pressure and the residue was redissolved in ten mL water. The solution was cooled to 0°C and neutralized with 0.1 M HCl. The polymer was purified by dialysis against water and dried by lyophilization. The disappearance of the ester peak in the ^{1}H NMR spectrum indicated completion of the methyl ester deprotection (Fig. S4). TGA analysis showed that the thermal weight loss of polymer **2** started around 240 °C. DSC analysis was performed from -20 °C to 200 °C at a heating rate of 5 °C min^{-1}, no detectable thermal transition was observed.

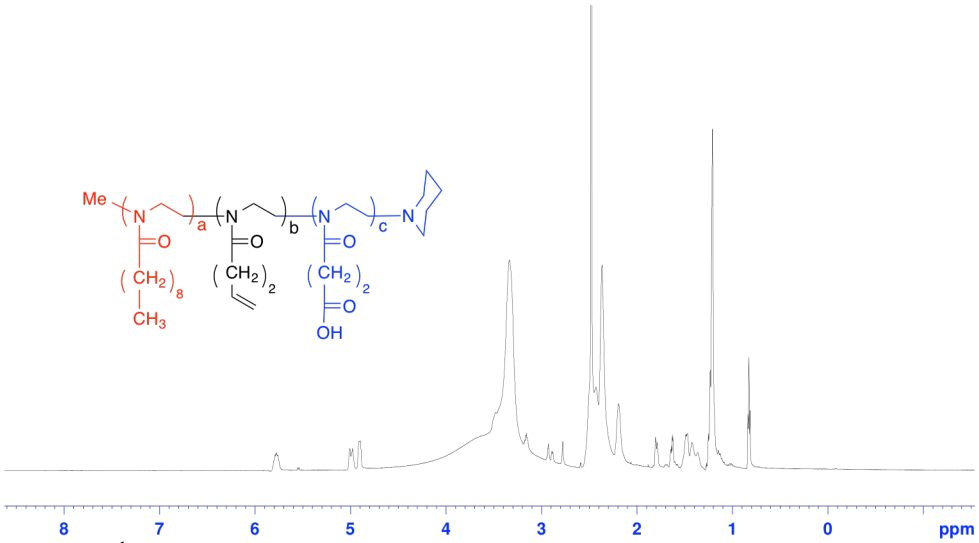
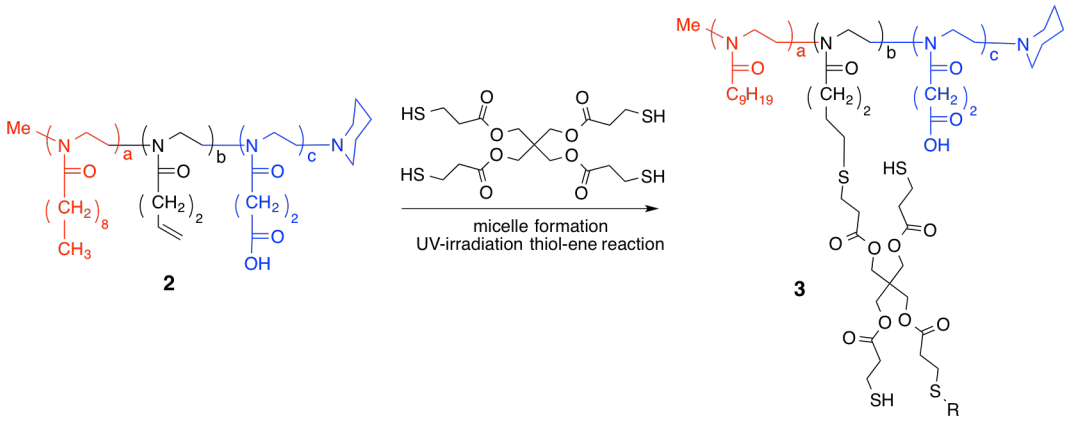


Figure S4. ^{1}H NMR spectrum of triblock copolymer **2** in D_6-DMSO.

^{13}C-NMR ($CDCl_3$, 150 MHz, δ vs. TMS): 173.6, 172.2, 137.4, 121.4, 119.2, 115.5, 54.3, 51.8, 50.0, 47.5, 47.1, 45.7, 45.1, 33.6, 32.8, 31.9, 29.5, 28.8, 27.6, 25.9, 25.4, 24.9, 24.2, 23.1, 22.7, 14.2.

FTIR: ν = 3445, 2925, 2854, 2540, 1721, 1610, 1419, 1209, 1167, 1029, 984, 947, 914, 836 cm^{-1}.

2.2 Cross-linking of the micelle assemblies



Scheme S2. Covalent cross-linking of micelle assemblies via thiol-ene chemistry.

Cross-linked micelle with two orthogonal functional handles (micelle 3): The amphiphilic triblock copolymer was dissolved in water with a concentration of 1 mg/mL. Pentaerythritol tetrakis(3-mercaptopropionate) (0.5 eq) was added to the micelle solution and the mixture was stirred at room temperature for two hours. The reaction was degassed via three freeze-pump-thaw cycles. The thiol-ene reaction was initiated by DMPA (0.1 eq) and irradiation with UV light (15W UVP Black Ray UV Bench Lamp XX-15L) while stirring for 24 hours at 4 °C. The reaction mixture was purified by dialysis and dried by lyophilization. As shown in Figure S5, the double bond proton signals disappeared after the cross-linking. TGA analysis showed that the thermal weight loss of micelle **3** started around 320 °C. DSC analysis was performed from -20 °C to 200 °C at a heating rate of 5 °C min^{-1}, no detectable thermal transition was observed.

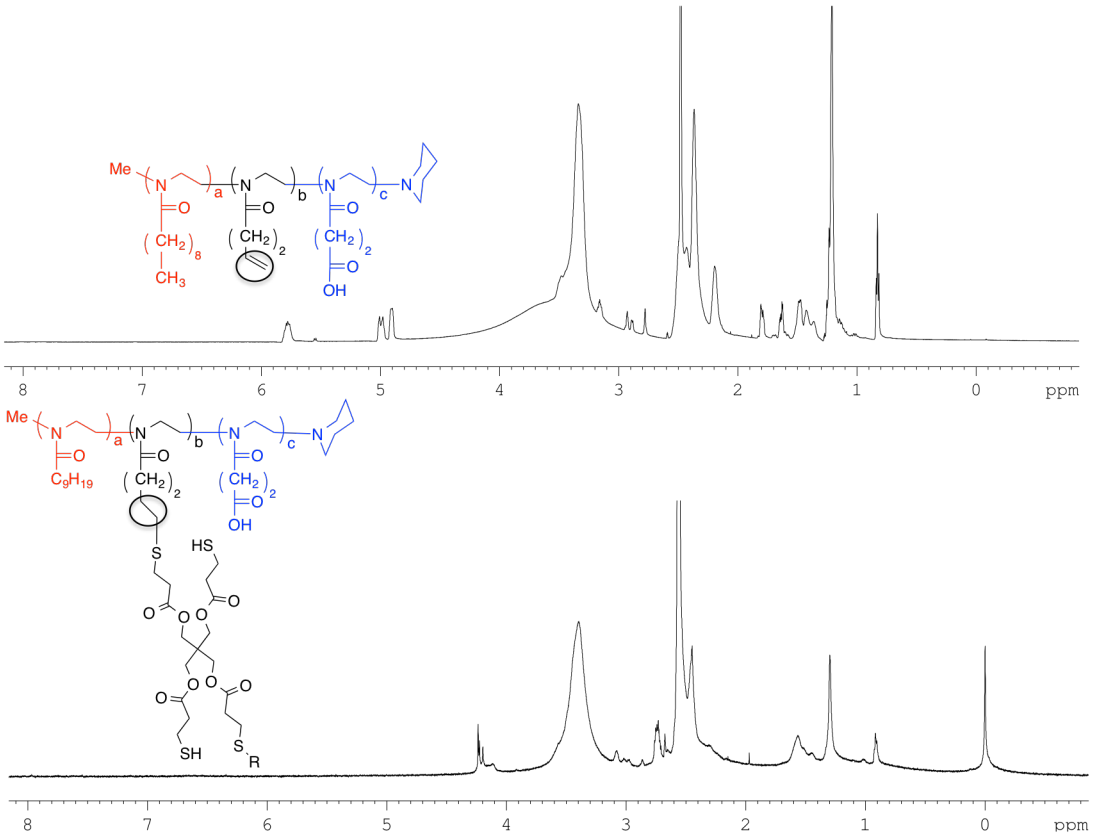
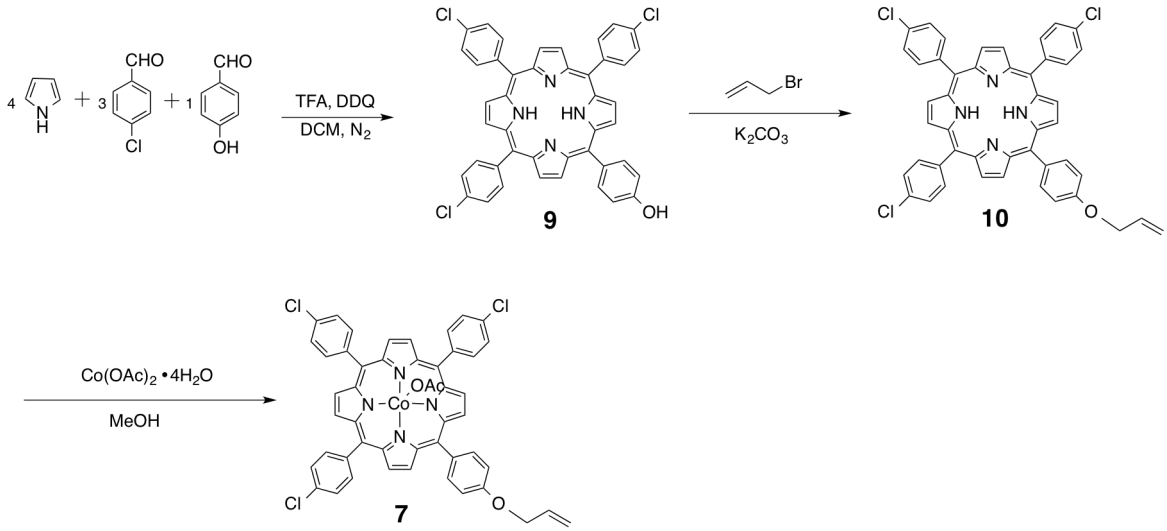


Figure S5. ^{1}H NMR spectrum of polymer 2 and cross-linked micelle **3**.

2.3 Alkene-functionalized cobalt catalyst



Scheme S3. Synthesis of alkene-functionalized Co-porphyrin catalyst.

Compound 9: 4-Chlorobenzaldehyde (0.4216 g, 3 mmol) and 4-hydroxylbenzaldehyde (0.122 g, 1 mmol) were dissolved in 500 mL of CH_2Cl_2 contained in a one L three-neck flask. The flask was covered with aluminum foil and purged with N_2 for ten minutes. Then, freshly distilled pyrrole (1.4mL, 4 mmol) was injected. The mixture was stirred for another ten minutes, and the reaction was initiated by the injection of TFA (0.56 mL, 8 mmol). After the reaction was stirred at room temperature for 1.5 hours, DDQ (0.68 g, 3 mmol) was added, and the reaction was stirred for an additional hour at room temperature and then neutralized with triethylamine (1.12 mL, 8 mmol). The crude mixture was purified with silica gel flash chromatography; elution with DCM removed all tetrarylporphyrin, and the desired A_3B porphyrin was then eluted with 20% EtOAc in DCM. Solvent was removed under vacuum, affording a purple solid in a yield of 132 mg, y = 18%.

^{1}H NMR ($CDCl_3$, 600 MHz, δ vs. TMS): 8.9 (d, J = 4.5 Hz, 2H), 8.8 (d, J =7.4 Hz, 6H), 8.2 (d, J = 8.2 Hz, 6H), 8.1 (d, J = 8.4 Hz, 2H), 7.8 (d, J = 8.3 Hz, 6H), 7.2 (d, J = 8.5 Hz, 2H), 5.1 (br s, 1H,OH), -2.8 (br s, 2H, pyrrole H).

^{13}C-NMR ($CDCl_3$, 150 MHz, δ vs. TMS): 155.5, 140.5, 140.57, 140.4, 135.7, 134.4, 134.4, 134.3, 127.1, 120.5, 119.0, 118.8, 118.6, and 113. 8.

HRMS (ESI): m/z calculated for $C_{44}H_{27}Cl_3N_4O$ ($[M+H]^+$) = 733.132321; found ($[M+H]^+$) = 733.13265 (0.45 ppm). MALDI-TOF, calculated for $C_{44}H_{27}Cl_3N_4O$ = 732.12, Found = 732.

FTIR: ν = 3578, 3307, 3066,2162, 1605, 1507, 1090, 793, 731, 704 cm^{-1}.

Compound 10: Compound **9** (570 mg, 0.78 mmol), potassium carbonate (228 mg, 1.56 mmol) and potassium iodide (50 mg, cat.) were dissolved in 125 mL acetone contained in a 250 mL flask. Allyl bromide (90 μL, 0.98mmol) was added to the mixture. The reaction was heated to reflux for eight hours. The crude mixture was purified with silica gel flash chromatography; elution with DCM and EtOAc, y = 95%.

^{1}H NMR ($CDCl_3$, 600 MHz, δ vs. TMS): 8.8 (d, J = 4.5 Hz, 2H), 8.7 (d, J = 7.9 Hz, 6H), 8.0 (d, J = 8.2 Hz, 6H), 7.9 (d, J = 8.5 Hz, 2H), 7.6 (d, J = 8.1 Hz, 6H), 7.2 (d, J = 8.5 Hz, 2H), 6.1 (m, 1H, C<u>H</u>=CH_2), 5.6 (dd, J = 17.3 Hz, J = 1.5 Hz, CH=C<u>H_2</u>), 5.3 (dd, J = 10.6 Hz, J = 1.3 Hz, CH=C<u>H_2</u>), 4.7 (dt, J = 5.3 Hz, J = 1.5 Hz, 2H, OCH_2), -2.9 (s, 2H, pyrrole H).

^{13}C-NMR ($CDCl_3$, 150 MHz, δ vs. TMS): 158.6, 146.1, 140.58, 140.4, 139.6, 135.7, 134.4, 133.3, 128.8, 127.03, 127.0, 120. 7, 119.0, 118.8, 118.6, 118.1, 113.1, 69.2 (O-CH).

HRMS (APCI): m/z calculated for $C_{47}H_{31}Cl_3N_4O$ ($[M+H]^+$) = 773.163621; found ($[M+H]^+$) = 773.165982 (3.05 ppm). MALDI-TOF, calculated for $C_{47}H_{32}Cl_3N_4O$=772.16, Found = 772.

FTIR: ν = 3314, 3065, 2920, 2162, 1602, 1505, 1089, 793, 728, 705 cm^{-1}.

Compound 7: Compound **10** (418 mg, 0.54 mmol) and cobalt acetate tetrahydrate (142 mg, 0.57 mmol) were dissolved in dry CH_3OH (150 mL) under a N_2 atmosphere. The mixture was stirred at 70 °C for 24 hours, cooled to 25 °C, and stirred in air for two hours. The mixture was concentrated to around 20 mL under reduced pressure. The crude mixture was purified with silica gel flash chromatography; elution with DCM and EtOAc, y = 73%.

^1H NMR ($CDCl_3$, 600 MHz, δ vs. TMS): 15.8 (br s, 8H), 12.8 (br s, 8H), 9.8 (br s, 6H), 9.4 (br s, 2H), 6.6 (br s, 1H), 6.0 (m, 3H), 5.2 (br s, 2H).

^{13}C NMR ($CDCl_3$, 150 MHz, δ vs. TMS): ^{13}C NMR of this sample failed due to the cobalt metal interference. A single crystal structure is provided to confirm the compound.

HRMS (APCI): m/z calculated for $C_{49}H_{32}Cl_3CoN_4O_3$ ($[M-OAc]^+$) = 829.073895; found ($[M-OAc]^+$) = 829.074221 (0.39 ppm).

MALDI-TOF, calculated for $C_{49}H_{32}Cl_3CoN_4O_3$ = 890.10, Found = 890.

FTIR: ν = 2962, 1728, 1603, 1488, 1348, 1259, 1089, 1014, 795, 721 cm^{-1}.

Single Crystal Structure Determination Experimental Description (Compound 7)

A red slab-like crystal with the size of 0.02 × 0.17 × 0.54 mm^3 was selected for geometry and intensity data collection with a Bruker SMART APEXII CCD area detector on a D8 goniometer at 100 K. The temperature during the data collection was controlled with an Oxford Cryosystems Series 700+ instrument. Preliminary lattice parameters and orientation matrices were obtained from three sets of frames. Data were collected using graphite-monochromated and 0.5 mm-MonoCap-collimated MoK_α radiation (λ = 0.71073 Å) with the ω scan method.[6] Data were processed with the INTEGRATE program of the APEX2 software[6] for reduction and cell refinement. Multi-scan absorption corrections were applied by using the SCALE program for the area detector. The structure was solved by the direct method and refined on F^2 (SHELX).[7] Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms on carbons were placed in idealized positions (C-H = 0.95-0.98 Å) and included as riding with U_{iso}(H) = 1.2 or 1.5 U_{eq}(non-H). Except one of chlorophenyl groups, the other two chlorophenyl groups, the alkene group, and the acetate ion are disordered. The disorder of the chlorophenyl groups could be modeled based on the electron density distributions; however, the position of the alkene group could not be determined. IR and NMR confirmed the existence of the alkene group; therefore, an idealized geometry for the group was built using the theoretical values for the further refinement. Constraints and restraints in geometry and displacement parameters were applied to these disordered groups in the structure refinement.

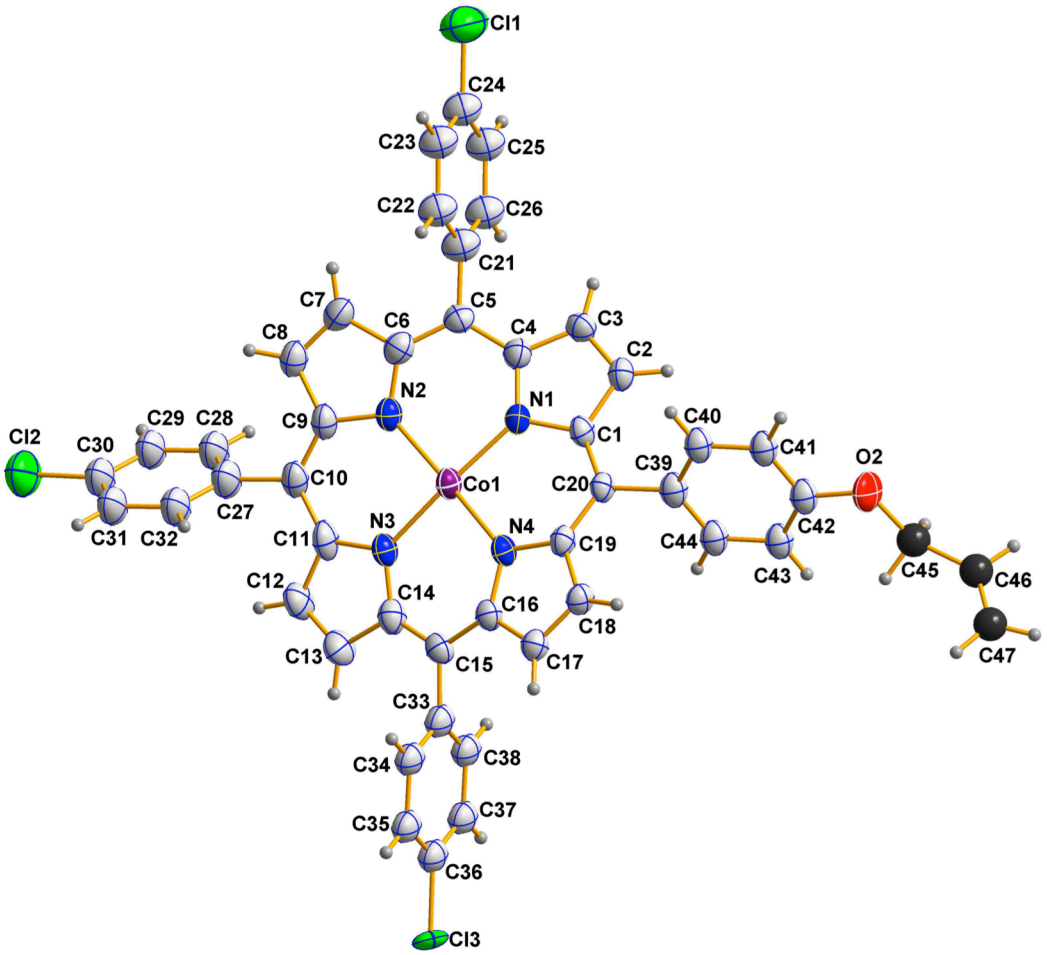
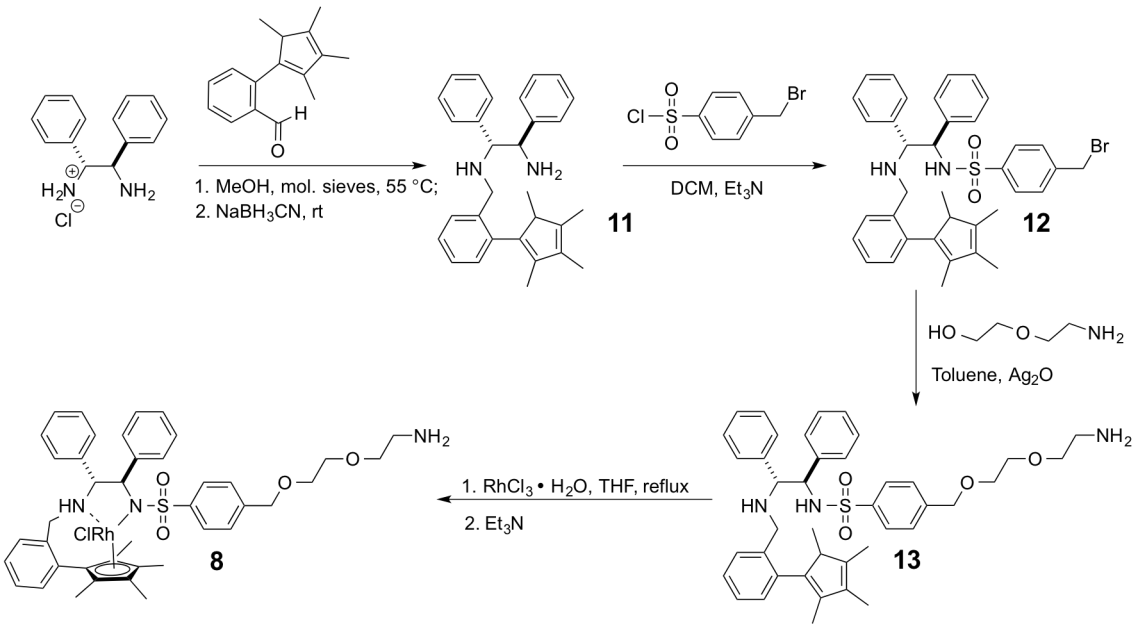


Figure S6. The molecular structure of one of the conformers. The disordered alkene group (highlighted as black balls) could be located from the electron density maps and was modeled using the theoretical geometry. Other disordered groups were omitted for clarity.

2.4 Amine-functionalized rhodium catalyst



Scheme S4. Synthesis of amine-functionalized Rh-TsDPEN catalyst.

Compound 11: In a Schlenk flask, the monohydrochloride of (1*R*,2*R*)-(+)-1,2-diphenylethylenediamine (DPEN; 10 mmol, 2.49 g) was dissolved in methanol (60 mL). 2-(2,3,4,5-Tetramethylcyclopentadienyl)-benzaldehyde[8] (10 mmol, 2.26 g) and molecular sieves (3 g) were added successively. The mixture was heated to 55 °C and stirred overnight. Triethylamine (15 mmol, 2.1 mL) was then added, and after stirring for 30 min at room temperature, sodium cyano borohydride (40 mmol, 1.5 g) was added in two portions, and the mixture was stirred for additional 20 hours. All solid components were filtered off. The filtrate was washed with water and brine, then dried over magnesium sulfate and concentrated under reduced pressure. The residue was purified via column chromatography (DCM:MeOH = 95:5), after which the product was obtained as a yellow foam in 37 % yield.

^{1}H NMR ($CDCl_3$, 600 MHz, δ vs. TMS): 7.35-6.78 (14H, m, ArH), 6.26-6.03 (1H, m, NHTs), 4.05-3.83 (1H, m, PhC<u>H</u>NH), 3.73-3.54 (H, m, PhC<u>H</u>NHCH_2), 3.51-3.18 (2H, m, CH_2), 2.51-2.05 (3H, m, NH and NH_2), 1.88-0.67 (14H, m);

^{13}C-NMR ($CDCl_3$, 150 MHz, δ vs. TMS): 143.3, 141.2, 141.1, 138.9, 138.4, 133.8 (8 C, C_{Ar}); 130.1, 130.0, 129.6, 129.3, 128.9, 128.4, 128.0, 127.9, 127.8, 127.0, 126.9, 126.8, 126.6, 126.5, 126.4, 126.3, 125.8 (14 C, $C_{Ar}H$); 69.0 (m, CH-NH); 61.6 (CH-NH); 51.4 (m, Cp*CH); 49.6 (d, CH_2); 14.1, 12.4, 11.7, 11.0 (4 C, Cp*-CH_3).

HRMS (ESI): m/z calculated for $C_{30}H_{35}N_2$ ($[M+H]^+$) = 423.279476; found = 423.280476 (+2.36 ppm).

FTIR: ν = 3263, 2244, 1601, 1491, 1072, 907, 760, 728, 697 cm^{-1}.

Compound 12: Compound **11** (4.96 mmol, 2.1 g) and 4-bromomethylbenzenesulfonyl chloride (5.46 mmol, 1.42 g) were dissolved in dichloromethane (15 mL), and triethylamine was added (6.5 mL, 0.915 mL). The mixture was stirred at room temperature for 16 hours. It was then washed with water and brine. The collected organic phase was dried over magnesium sulfate and concentrated under reduced pressure. Column purification (DCM:MeOH = 99:1 - 95:5) and concentration *in vacuo* yielded the product, a light yellow foam (y = 25 %).

^{1}H NMR ($CDCl_3$, 600 MHz, δ vs. TMS): 7.35-6.78 (18H, m, ArH), 6.26-6.03 (1H, m, NHTs), 4.51-4.23 (2H, m, CH_2Br), 3.73-3.04 (5H, m, PhC<u>H</u>NHCH_2 and CpH), 1.88-0.67 (16H, m);

^{13}C-NMR ($CDCl_3$, 150 MHz, δ vs. TMS): 141.3, 141.2, 140.4, 140.1, 138.7, 138.1, 134.0, 133.5 (10 C, overlapping signals, C_{Ar}); 130.4, 130.3, 129.9, 129.1, 128.6, 128.4,

128.3, 128.1, 127.7, 127.6, 127.5, 127.4, 127.1, 126.9, 126.7 (18 C, $C_{Ar}H$); 67.1 (m, CH-NH); 63.0 (CH-NH); 61.7 (CH_2); 51.6 (m, CpCH); 49.3 (m, CH_2); 45.0 (CH_2-Br) 14.2, 12.5, 11.8, 11.1 (4 C, Cp-CH_3).

HRMS (ESI): m/z calculated for $C_{37}H_{40}BrN_2O_2S$ ($[M+H]^+$) = 655.198839; found = 655.196883 (-2.99 ppm).

FTIR: ν = 3265, 2253, 1601, 1494, 1329, 1157, 1266, 1091, 908, 761, 729, 697 cm^{-1}.

Compound 13: A flask was charged with 2-(2-aminoethoxy)ethanol (1.74 mmol, 0.175 mL) and silver oxide (2.1 mmol, 485 mg) under inert and anhydrous conditions and dissolved/suspended in toluene. A solution of compound **12** (2.1 mmol, 1.37 g) in toluene (6 mL) was slowly added, and the mixture was stirred for 20 hours at room temperature. Excess silver oxide was then filtered-off using a frit with celite which was washed with MeOH. The filtrate was concentrated under reduced pressure and the residue further purified via column chromatography (DCM:MeOH:TEA / 95:4:1). The product was obtained after concentration under reduced pressure as light yellow foam in 32 % yield.

^{1}H NMR ($CDCl_3$, 600 MHz, δ vs. TMS): 7.48-7.33 (2H, m, CH), 7.27-6.80 (16H, m, CH), 6.35-6.10 (1H, br s, NHTs), 4.41-4.23 (1H, m, PhC<u>H</u>NHTs), 3.76-3.11 (8H, m, CH_2), 2.73-2.43 (2H), 2.00-0.47 (16H, m).

^{13}C-NMR ($CDCl_3$, 150 MHz, δ vs. TMS): 143.7, 141.1, 140.3, 139.1, 138.9, 138.2, 133.8, 133.4 (10 C, C_{Ar}); 130.3, 130.2, 129.9, 129.8, 129.0, 128.3, 128.2, 127.8, 127.7, 127.5, 127.4, 127.1, 127.0, 126.7, 126.6 (18 C, $C_{Ar}H$); 72.1 (CH_2); 69.5 (CH_2); 67.2 (m, CH-NH); 62.9 (m, CH-NH); 61.7 (CH_2); 58.1 (CH_2); 52.7 (CH_2); 51.6 (m, CpCH); 48.8 (m, CH_2); 14.3, 14.1, 11.7, 10.9 (4 C, Cp-CH_3).

HRMS (ESI): m/z calculated for $C_{41}H_{50}N_3O_4S$ ($[M+H]^+$) = 680.35615; found = 680.347083 (-6.71 ppm).

FTIR: ν = 3535, 3263, 2247, 1600, 1493, 1328, 1155, 1090, 909, 760, 729, 699 cm^{-1}.

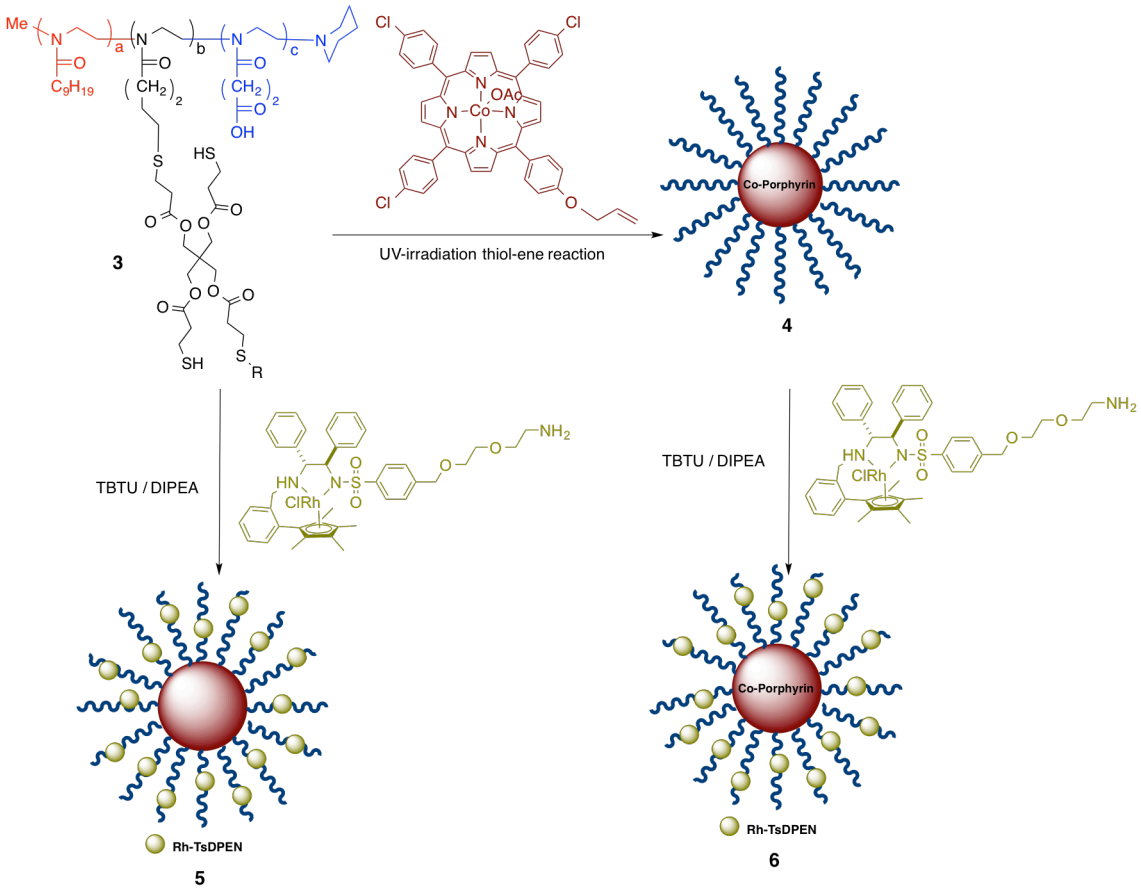
Compound 8: A flask was charged with compound **13** (0.47 mmol, 320 mg) and rhodium trichloride hydrate (0.56 mmol, 118 mg) under inert and anhydrous conditions and dissolved in tetrahydrofuran (16 mL). The solution was heated and stirred under reflux for 20 h. Triethylamine (1.89 mmol, 0.26 mL) was then added and the mixture was continued to stir for three hours. The reaction mixture was concentrated under reduced pressure and the residue purified via column chromatography (DCM:MeOH / 9:1). Concentration *in vacuo* yielded the product as a red solid (53 %).

^{1}H NMR ($CDCl_3$, 600 MHz, δ vs. TMS): 7.27-6.80 (16H, m, CH), 6.58-6.43 (2H, m, CH), 6.35-6.10 (1H, br s, NHTs), 4.91-5.13 (1H, m, PhC<u>H</u>NHTs), 3.76-3.11 (8H, m, CH_2), 2.73-2.43 (2H), 2.00-0.47 (16H, m).

^{13}C-NMR ($CDCl_3$, 150 MHz, δ vs. TMS): 144.3, 138.7, 138.4, 135.6, 135.3 (5 C, C_{Ar}); 133.4-126.2 (18 C, $C_{Ar}H$); 106.3, 99.3, 97.2, 88.1, 80.9 (5 C, C-CH_3); 75.8 (CH-N_{tosyl}); 72.2, 72.1 (2C, CH_2-O); 69.6 (CH-NH); 69.5, 61.8 (2C, CH_2-O); 58.3/58.1 (CH_2-NH); 52.1 (CH_2-NH_2); 11.0, 10.6, 10.2, 8,2 (4 C, Cp-CH_3).

HRMS (APCI): m/z calculated for $C_{41}H_{47}N_3O_4SRh$ ($[M-Cl]^+$) = 780.233683; found = 780.230336 (-4.29 ppm).

FTIR: ν = 3727, 3472, 3208, 2242, 1600, 1493, 1330, 1158, 1128 1085, 909, 760, 729, 699 cm^{-1}.



Scheme S5. Core-shell micelle supported catalytic systems.

2.5 Micelle supported catalysts

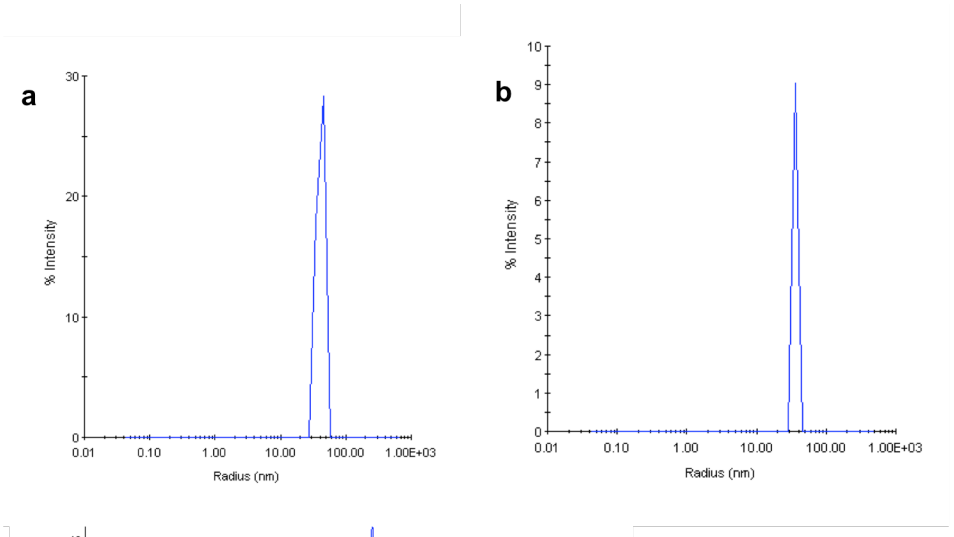
Micelle supported Co-porphyrin (nanoreactor 4): The purified cross-linked micelles were dissolved in a water and methanol 1:1 mixture (1 mg/mL). Alkene functionalized Co-porphyrin (compound **7**, 2 eq) was added to the micelle solution based on the thiol groups. The mixture was degassed via three cycles of freeze-pump-thaw. The thiol-ene reaction was initiated by DMPA (0.1 eq) and irradiated with UV light (15W UVP Black Ray UV Bench Lamp XX-15L) while stirring for 24 hours at 4 °C. The reaction mixture was purified by dialysis and dried by lyophilization. The cobalt content was determined

by ICP-MS was 2.6%, which corresponds to a degree of functionalization with three Co-catalyst per polymer chain.

Micelle supported Rh-TsDPEN (nanoreactor 5): Purified cross-linked micelle (carboxylic group 10 eq, 100 mg) was dissolved in DMF (1 mg/mL). Amine-functionalized Rh-TsDPEN (compound **8**, 1 eq, 20 mg), TBTU (1.2 eq, 10 mg) and DIPEA (3 eq, 50 ul) were added to the micelle solution. The mixture was stirred at room temperature for 24 hours, purified by dialysis, and dried by lyophilization. The rhodium content as determined by ICP-MS was 1.87% corresponding to a degree of functionalization of one Rh-catalyst per polymer chain.

Micelle supported Co-porphyrin and Rh-TsDPEN (nanoreactor 6): Micelle supported Co-porphyrin was dissolved in DMF at 5 mg/mL. Amine-functionalized Rh-TsDPEN was coupled to the carboxylic groups of the micelle support in a reaction similar to that described for nanoreactor **5**. The mixture was purified by dialysis and dried by lyophilization. The cobalt content and rhodium content as determined by ICP-MS was 0.72% and 0.75%, respectively.

Dynamic light scattering (DLS) of micelles and nanoreactor 6



DLS	Micelle	Solvent	Size (nm)
a	Polymer 2	water	40 ± 5
b	Micelle 3	MeOH	32 ± 3
c	Nanoreactor 6	water	36 ± 4

Figure S7. DLS profiles of a) polymer **2**, b) cross-linked micelles **3** and c) Nanoreactor **6**.

SEM characterization of nanoreactor 6

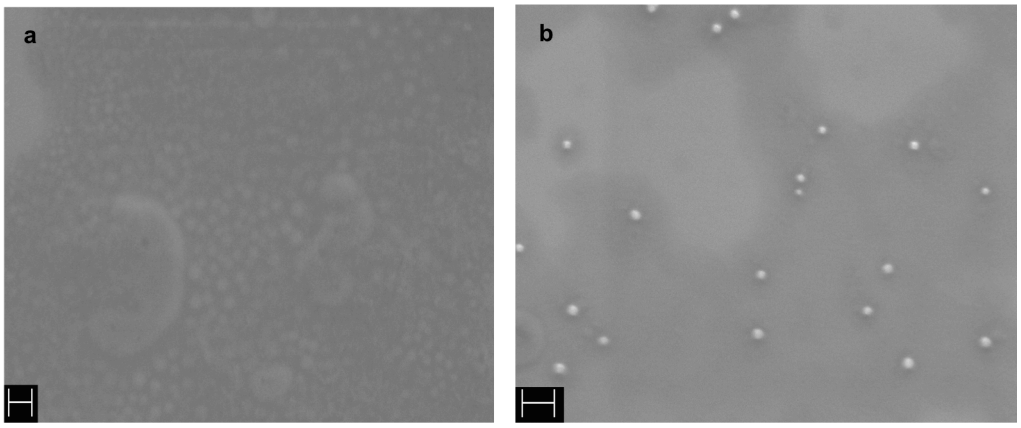


Figure S8. SEM of a) cross-linked micelle **3** and b) nanoreactor **6** (scale bar: 200 nm).

3. General procedures for the enantioselective tandem reaction

The tandem reaction of phenylacetylene catalyzed by nanoreactor **6** is described as an example: 1 mg **6** (containing 0.12 μmol Co(III)-porphyrin and 0.07 μmol Rh-TsDPEN) and 32.5 mg HCOONa (0.5 mmol) were weighed into a 3 mL vial. 1 mL DI water was added, and the mixture was stirred until **6** was completely dissolved. The reaction was immerged in an oil bath at 40 °C and then a catalytic amount of $HNTf_2$ and phenylacetylene (11 μL, 0.1 mmol) were added. Aliquots were taken at certain time intervals and subjected to GC analysis to monitor the conversion. The final product was extracted from the micelle solution with ethyl acetate and passed through a silica plug to fully remove the micelle catalyst before the filtrate was subjected to HPLC analysis using an OD-H column. Authentic samples were used to assign the peaks of substrates, intermediates and products.

Phenylacetylene (Table 3, entry 1)

Nanoreactor **6** micelle solution (1 mg/mL), reaction time: 36 hours. The final alcohol was obtained in 95% conversion (retention time of starting material phenylacetylene is 4.67 min and product phenylethyl alcohol is 9.12 min) and 97% *ee* (retention times of the two enantiomers are 9.01 min (major) and 11.04 min (minor) using i-PrOH/hexane (8/92) as the eluent at a flow rate of 0.6 mL/min).

^{1}H NMR ($CDCl_3$, 500 MHz, δ vs. TMS): 7.37-7.30 (4H, m), 7.27-7.22 (1H, m), 4.86 (1H, q, $J = 6.2$ *Hz*), 1.90 (1H, br s), 1.47 (3H, d, $J = 6.6$ *Hz*).

4-Nitrophenylacetylene (Table 3, entry 2)

Nanoreactor **6** micelle solution (1 mg/mL), reaction time: 36 hours. The final alcohol was obtained in 12% conversion (retention time of starting material 4-nitrophenyl acetylene is 11.41 min and alcohol product is 11.79 min) and *ee* was not determined due to the low conversion.

1-Hexyne (Table 3, entry 3)

Nanoreactor **6** micelle solution (1 mg/mL), reaction time: 36 hours. The final alcohol was obtained in 88% conversion (retention time of starting material 1-hexyne is 1.92 min and product 2-hexanol is 7.13 min). Phenyl carbamate from 2-hexanol: retention times of the two enantiomers are 9.78 min (major) and 16.78 min (minor) using i-PrOH/hexane (8/92) as the eluent at a flow rate of 0.6 mL/min. The final alcohol was obtained in 94% *ee*.

^{1}H NMR ($CDCl_3$, 400 MHz, δ vs. TMS): 7.42-7.40 (2H, m), 7.34-7.28 (2H, m), 7.09-7.05 (1H, m), 6.57 (1H, br s), 4.94-4.92 (1H, m), 1.72-1.51 (2H, m), 1.39-1.32 (4H, m), 1.30-1.24 (3H, d, $J = 6.2$ *Hz*), 0.95-0.91 (3H, t, $J = 7.1$ *Hz*).

Cyclohexyl acetylene (Table 3, entry 4)

Nanoreactor **6** micelle solution (1 mg/mL), reaction time: 36 hours. The final alcohol was obtained in 67% conversion (retention time of starting material cyclohexyl acetylene is 3.55 min and product 1-cyclohexylethanol is 6.73 min). Phenyl carbamate from 1-cyclohexylethanol: retention times of the two enantiomers are 12.54 min (major) and 17.22 min (minor) using i-PrOH/hexane (8/92) as the eluent at a flow rate of 0.6 mL/min. The final alcohol was obtained in 96% *ee.*

^{1}H NMR ($CDCl_3$, 400 MHz, δ vs. TMS): 7.42-7.40 (2H, m), 7.34-7.28 (2H, m), 7.09-7.05 (1H, m), 6.57 (1H, br s), 4.92-4.89 (1H, m), 1.54-1.28 (11H, m), 1.24-1.20 (3H, d, J = *6.2 Hz*)

Preparation of phenyl carbamates from alcohols for HPLC analysis[9]

Aliphatic alcohols were extracted from the micelle mixture using ethyl acetate. The solvent was removed under reduced pressure and the aliphatic alcohols were redissolved in pyridine. Phenyl isocyanate was added to the mixture, which was then stirred for 0.5 hours at room temperature. Pyridine was removed under reduced pressure. The residue was purified by column chromatography on silica gel.

4. Appendix

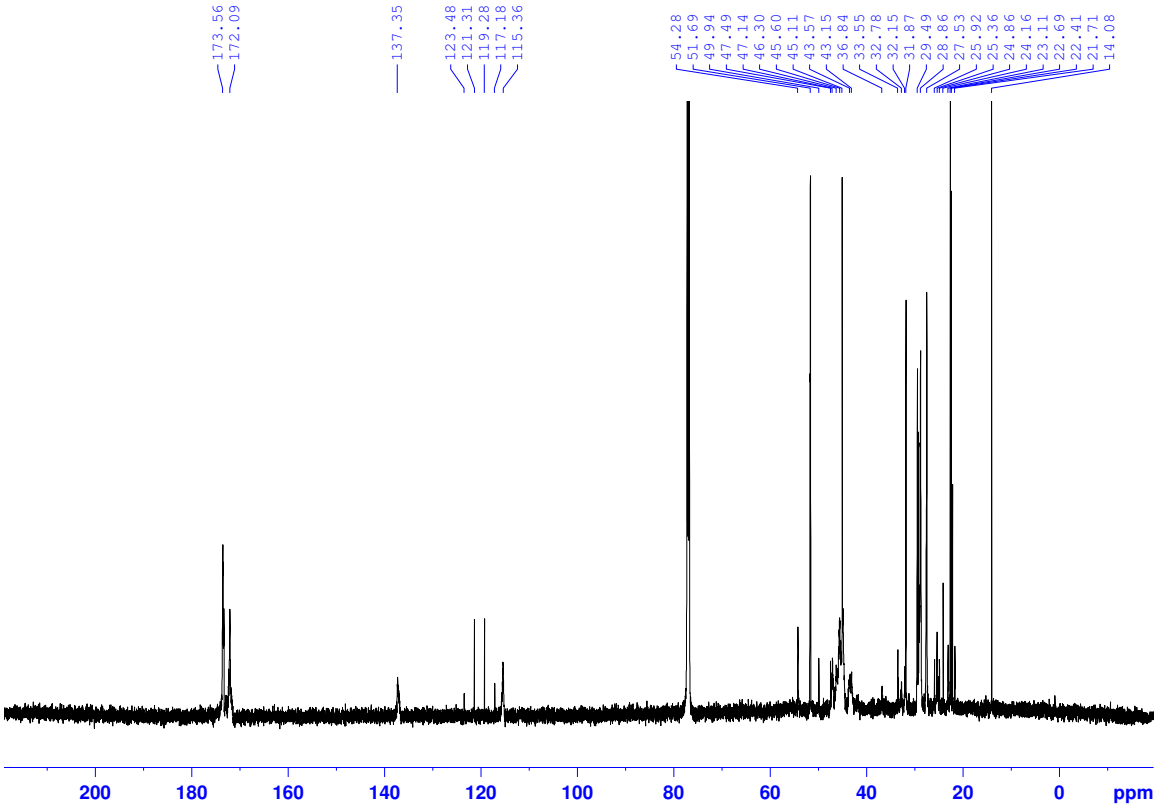


Figure S9. ^{13}C NMR spectrum of polymer **1**.

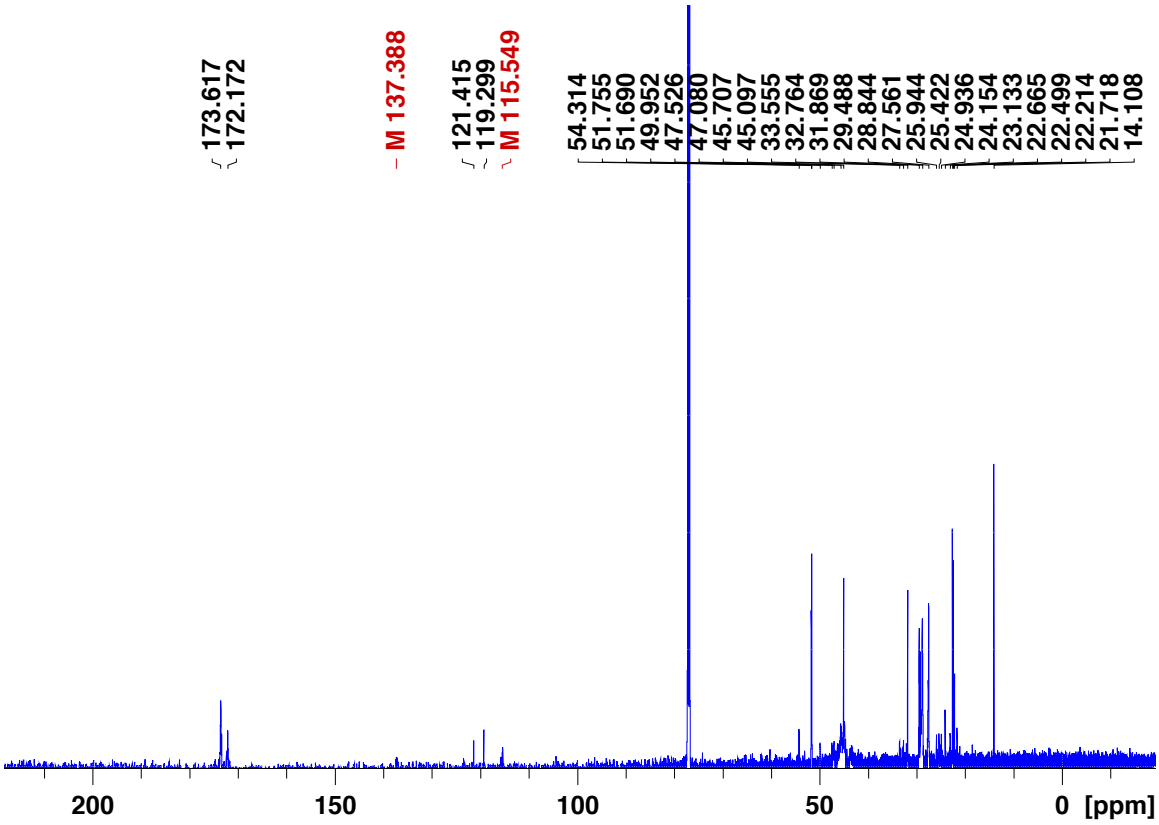


Figure S10. ^{13}C NMR spectrum of polymer **2**.

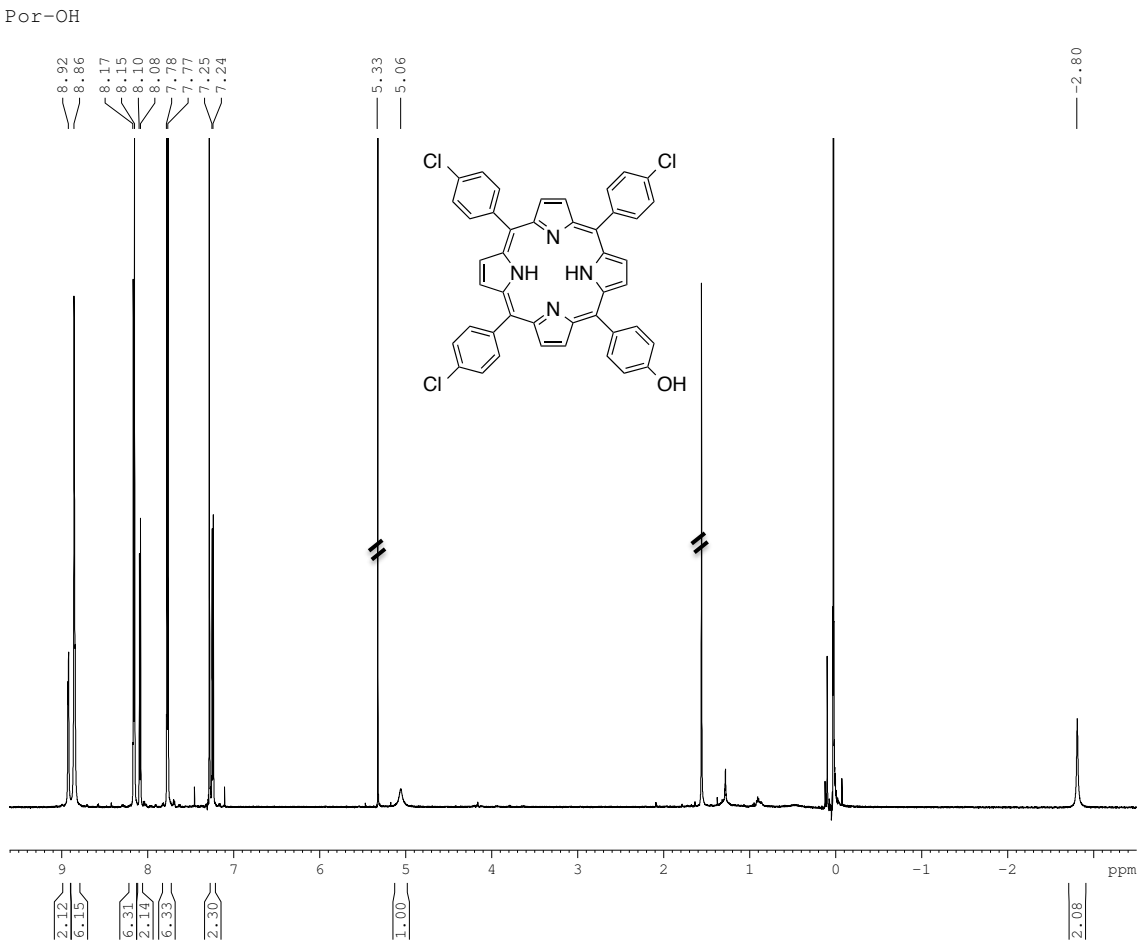


Figure S11. ^{1}H NMR spectrum of compound **9**.

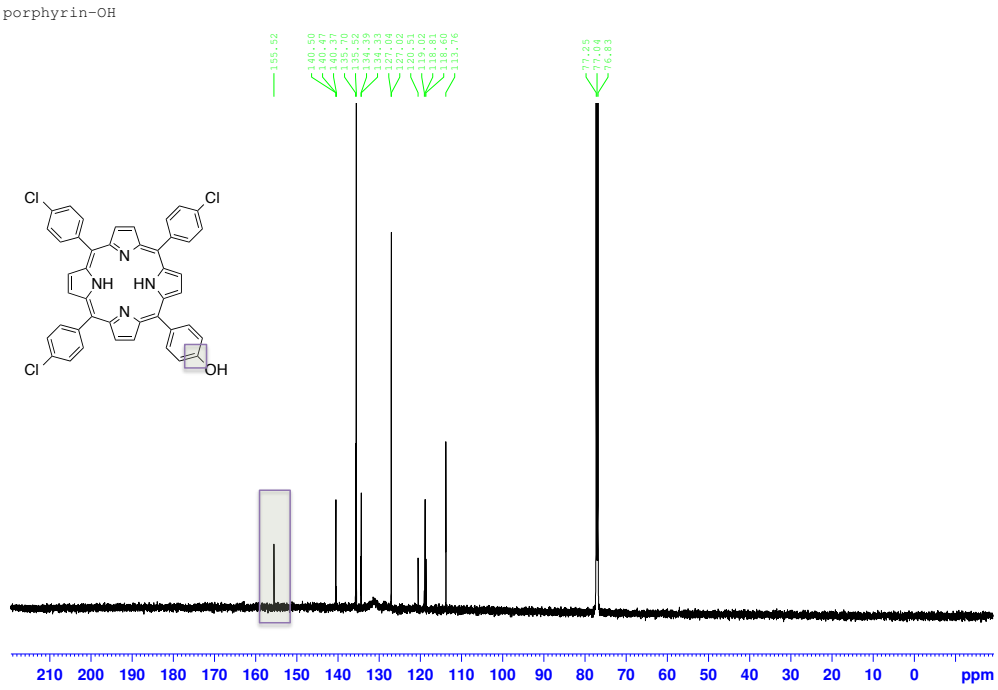


Figure S12. ^{13}C NMR spectrum of compound **9**.

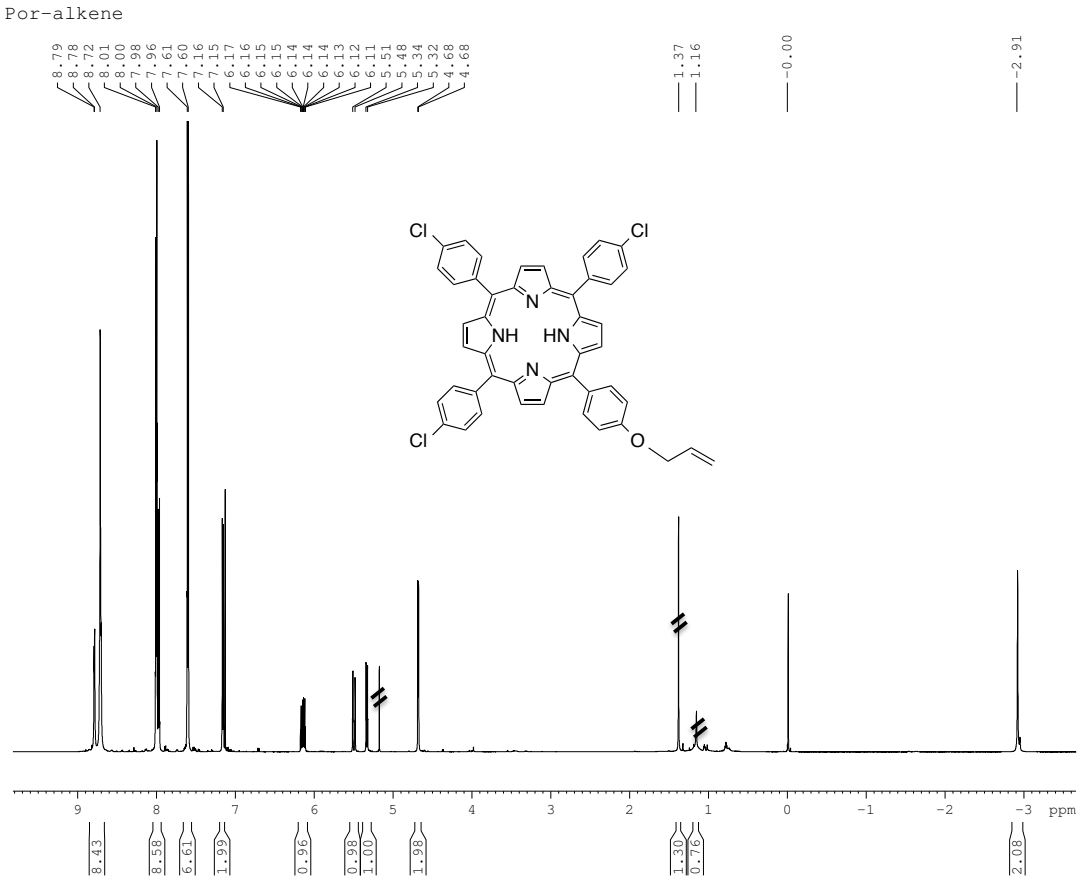


Figure S13. ^{1}H NMR spectrum of compound **10**.

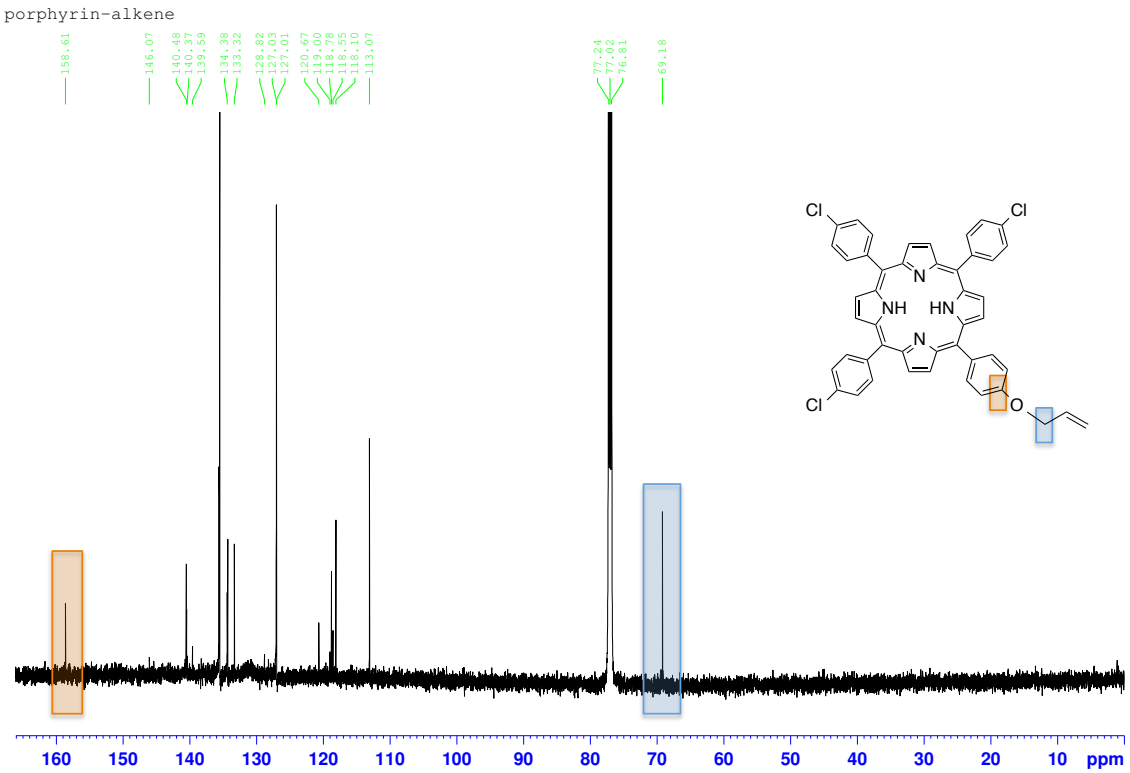


Figure S14. ^{13}C NMR spectrum of compound **10**.

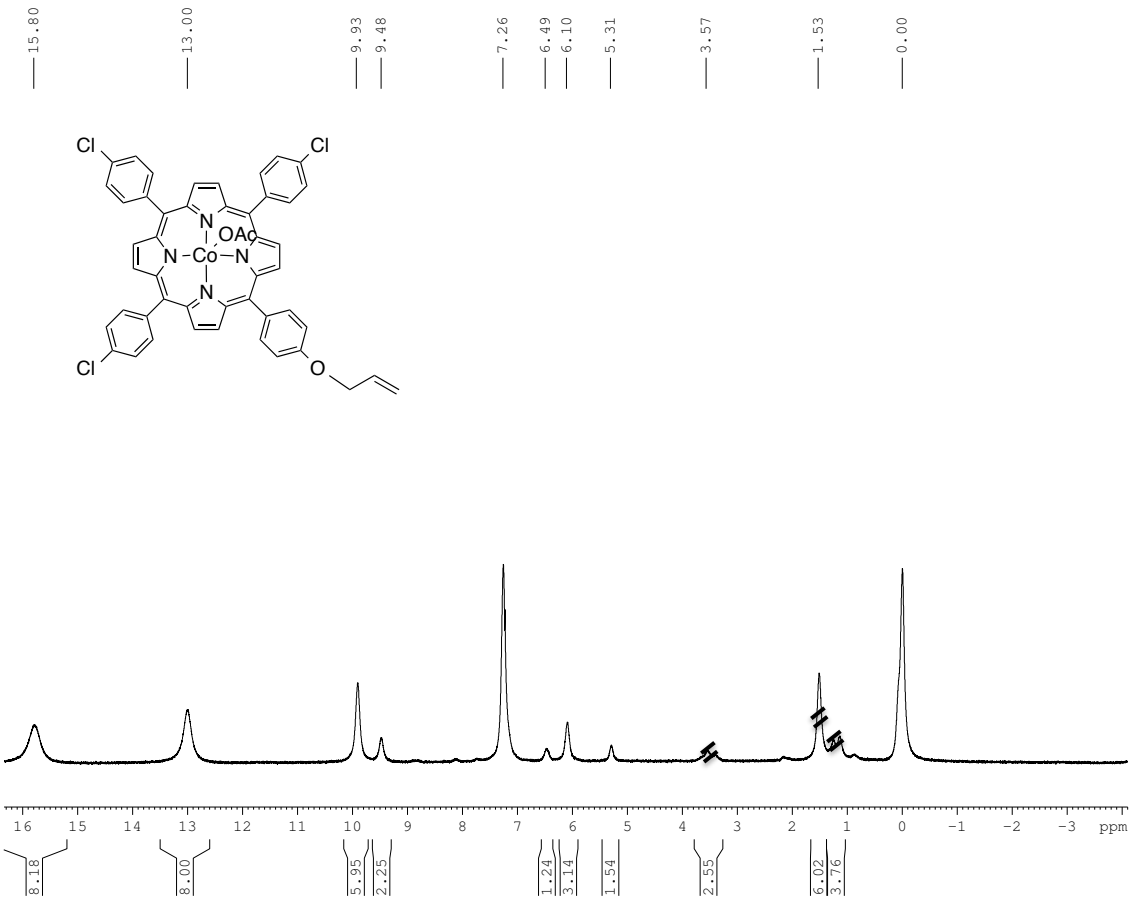


Figure S15. ^{1}H NMR spectrum of compound **7**.

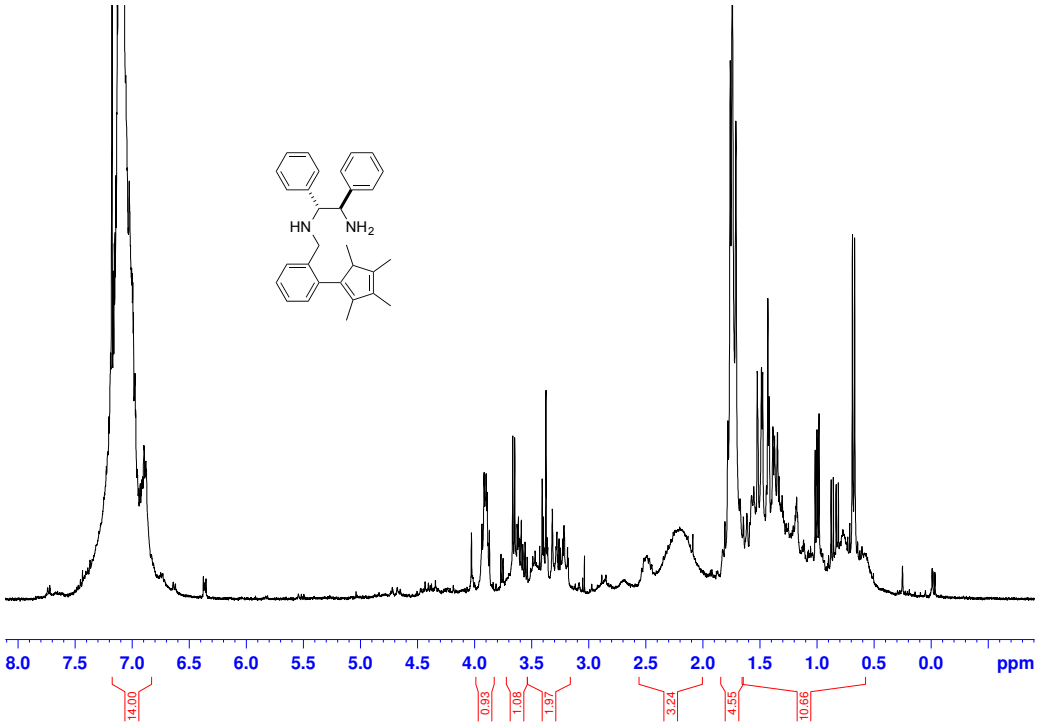


Figure S16. ^{1}H NMR spectrum of compound **11**.

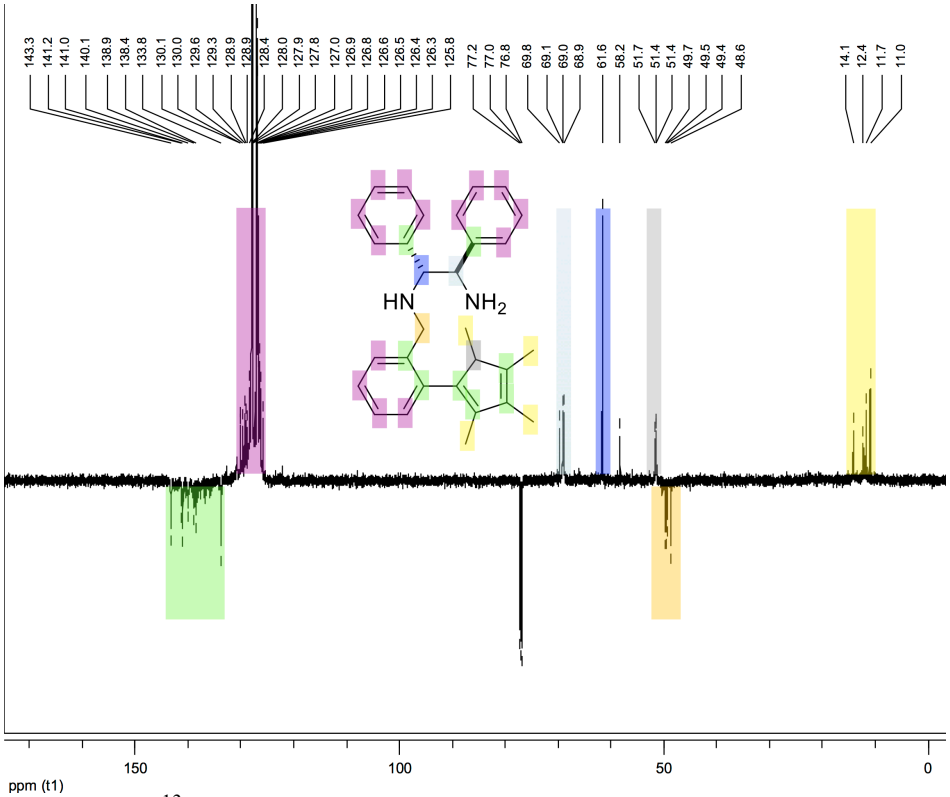


Figure S17. ^{13}C NMR spectrum of compound **11**.

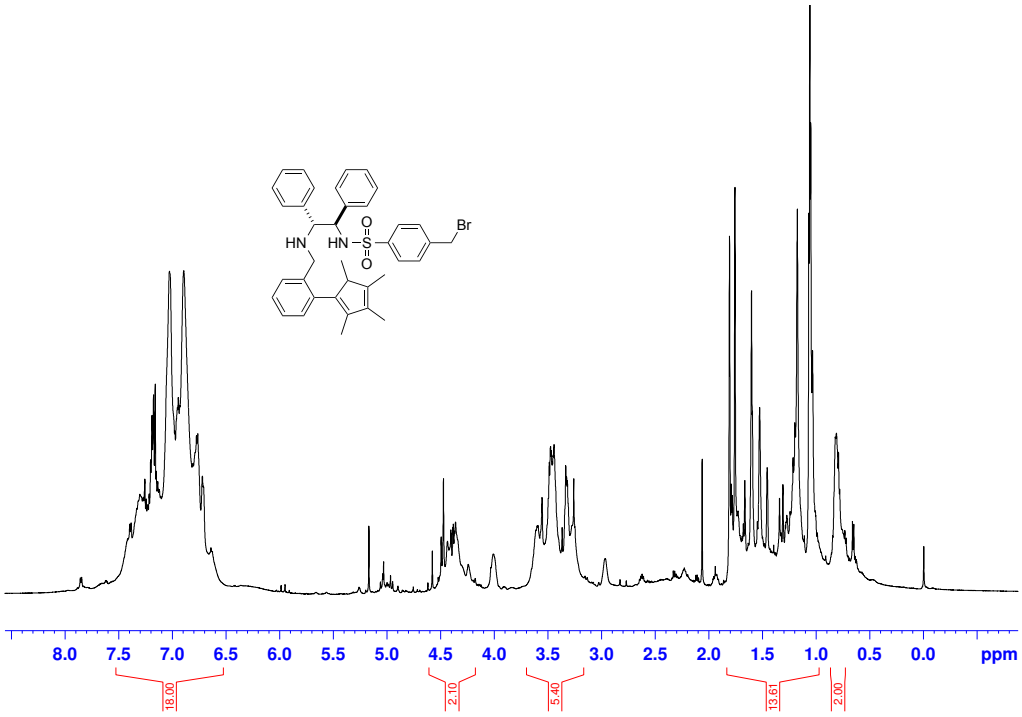


Figure S18. ^{1}H NMR spectrum of compound **12**.

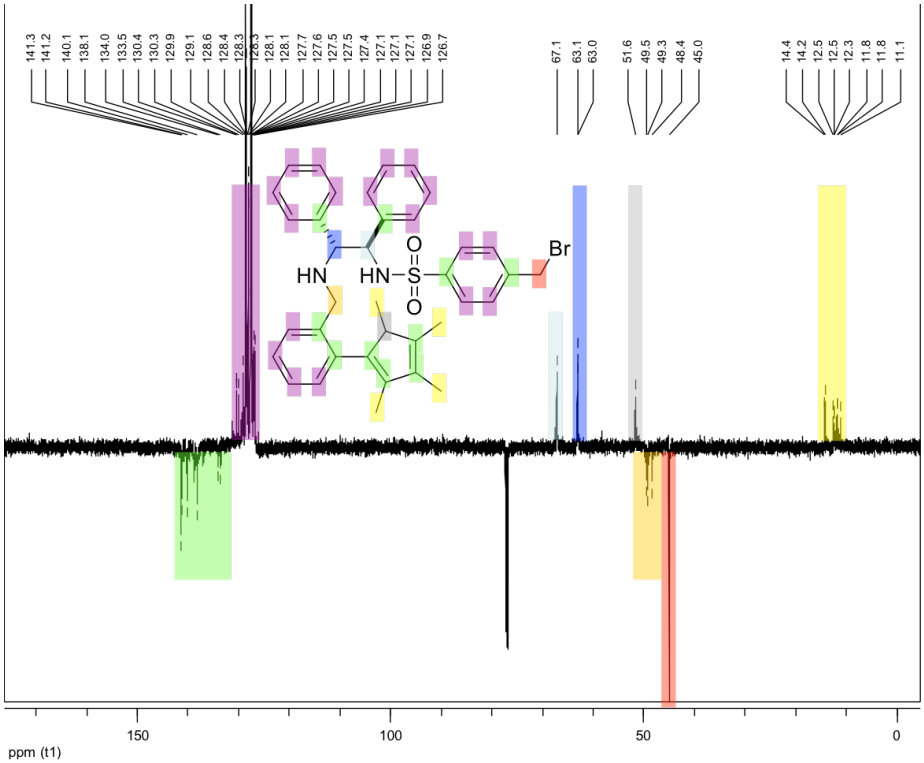


Figure S19. ^{13}C NMR spectrum of compound **12**.

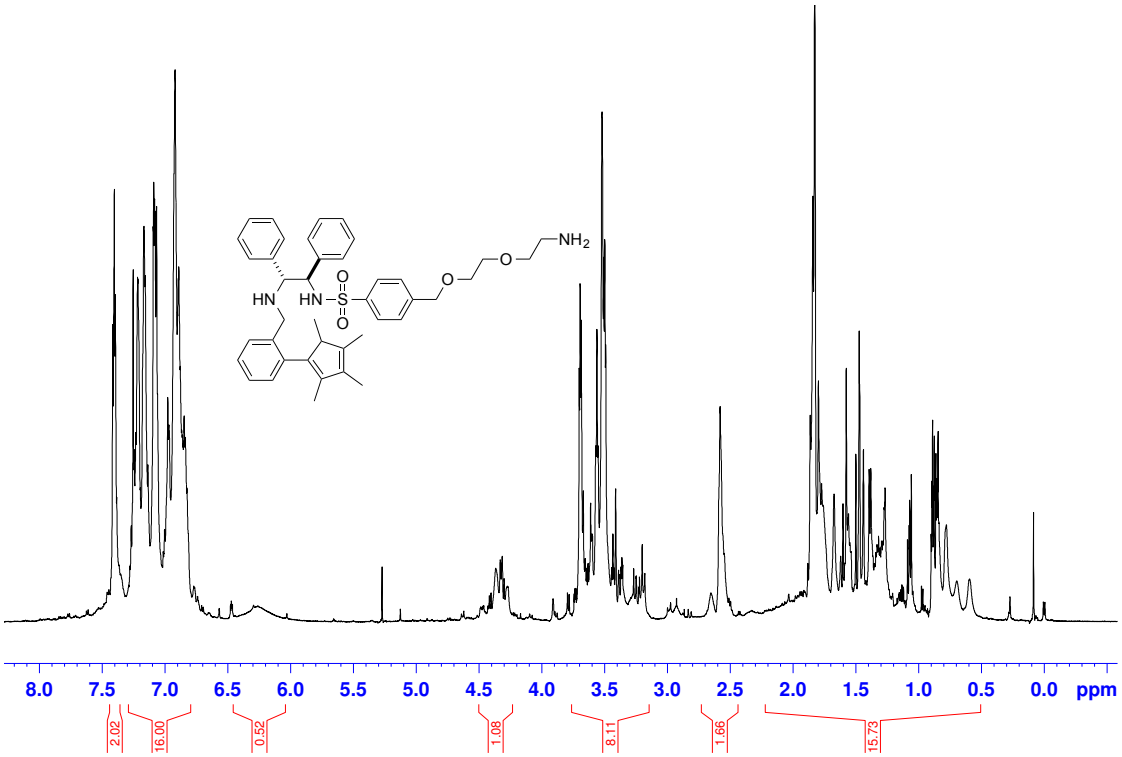


Figure S20. ^{1}H NMR spectrum of compound **13**.

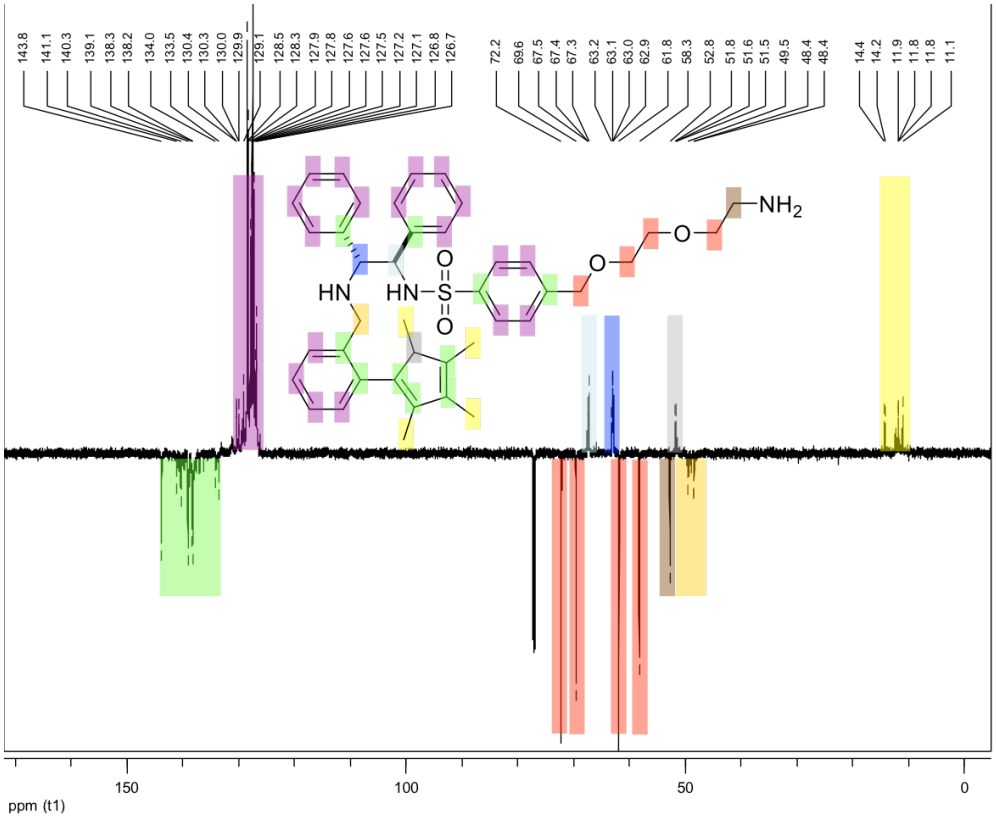


Figure S21. ^{13}C NMR spectrum of compound **13**.

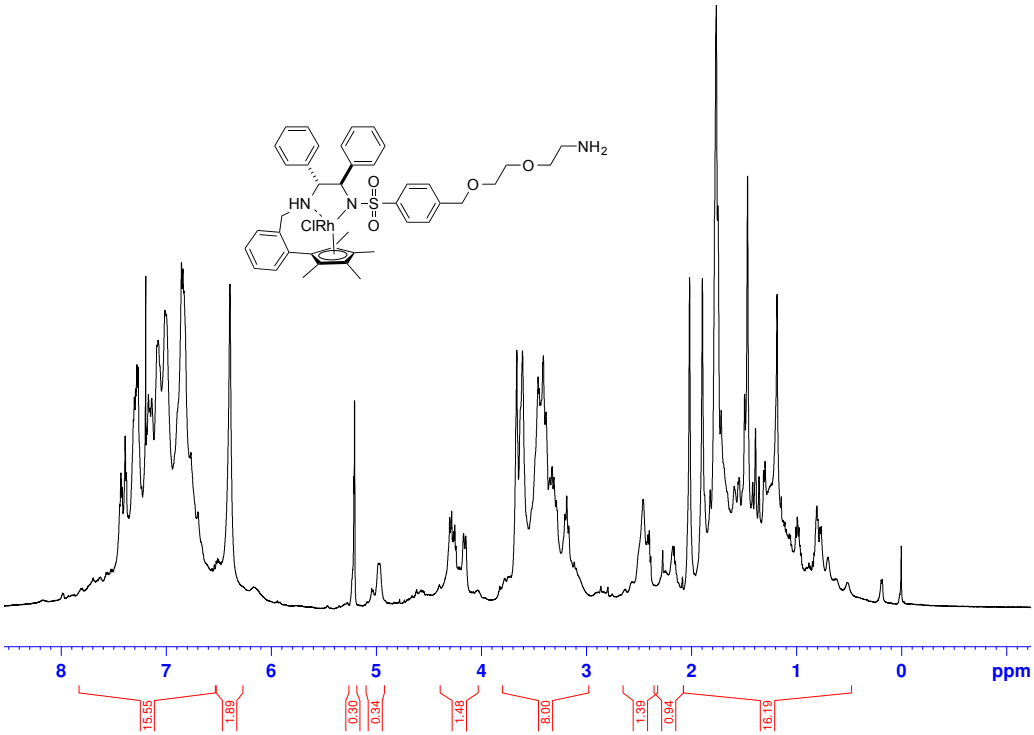


Figure S22. ^{1}H NMR spectrum of compound **8**.

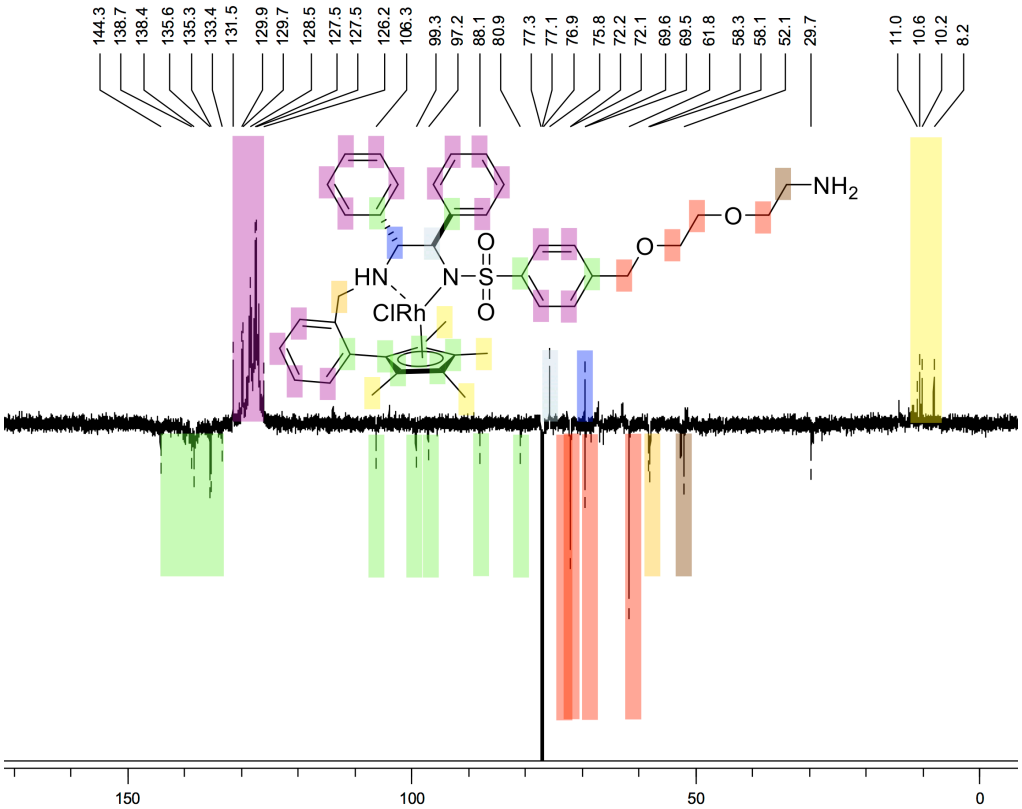


Figure S23. ^{13}C NMR spectrum of compound **8**.

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