Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Materials

Methylene Chain Ruler for Evaluating the Regioselectivity of a Substrate-Recognising Oxidation Catalyst

Shota Teramae, Akane Kito, Tomoteru Shingaki, Yu Hamaguchi, Yuuki Yano, Takamori Nakayama, Yuko Kobayashi, Nobuki Kato, Naoki Umezawa, Yosuke Hisamatsu, Tetsuo Nagano, Tsunehiko Higuchi*

1. General and Materials

General : Flash column chromatography was performed on silica gel (Fuji Silysia Chemical Ltd., BW-300) or aluminum oxide 90 (Merck KGaA) using forced flow. A 400 W, high-pressure mercury lamp (Riko Kagaku Sangyo Co.) was employed as light source for reaction. Infrared (IR) spectra were recorded on a JASCO FT/IR-680 Fourier-transform infrared spectrophotometer (JASCO Corporation, Tokyo, Japan). UV-Vis spectra were recorded on a JASCO V-550 (JASCO Corporation, Tokyo, Japan). ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a JEOL ECZ-500 (JEOL Ltd., Tokyo, Japan) or a Varian VNMRS 500 (Varian Inc.). EI-MS and FAB-MS was done with a JEOL JMS-SX 102A (JEOL Ltd., Tokyo, Japan). ESI-MS was done with a JEOL JMS-T100LP4G (JEOL Ltd., Tokyo, Japan). HPLC were performed using a Shimadzu SPD-M10AVP variable-wavelength UV detector (Shimadzu Corporation, Kyoto, Japan). Inertsil ODS-3 (4.6 x 250 mm, GL Science Inc., Tokyo, Japan) columns were employed for analytical separation of oxidation products. GC-MS analysis was performed by using Agilent 6890N-5975 GC/MS system (Injector: 7683B).

Materials: Tetradecanedioic acid, benzoyleneurea, 4-methoxybenzyl chloride, 1,3-dithiane, 1,7-heptanediol, 1-bromo-6-chlorohexane, 1-bromo-5-chlorohexane, 1,9-dichlorononane, pyrrole, pentafluorobenzaldehyde, methyl terephthalaldehyde, 2-chloro-1-methylpyridinium iodide, valeryl chloride and 2,6-dichloropyridine *N*-oxide were purchased from TCI. 1-Bromo-8-octanol and 2,6-diaminopyridine were purchased from Sigma-Aldrich. Cs_2CO_3, KH_2PO_4, 1-bromo-4-chlorobutane and 4-*N,N*-dimethylaminopyridine were purchased from Wako. $LiOH·H_2O$, K_2CO_3, 1,2-dichloroethane and di-ammonium cerium(IV) nitrate were purchased from Nacalai Tesque. *n*-Butyllithium in hexane was purchased from Kanto Chemical, and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone was purchased from Chem-Impax International. Ru_3CO_{12} was purchased from Strem Chemicals. Tetrahydrofuran was dehydrated and stabilizer free, and it was purchased from Kanto Chemical. Pyrrole, diisopropylamine and 1,2-dichloroethane were distilled, and 2,6-diaminopyridine were purified by column chromatography (SiO_2, $MeOH/CH_2Cl_2$=1/9). Other reagents and solvents were used without purification.

2. Synthesis of Substrate **7**

1,14-tetradecanediol

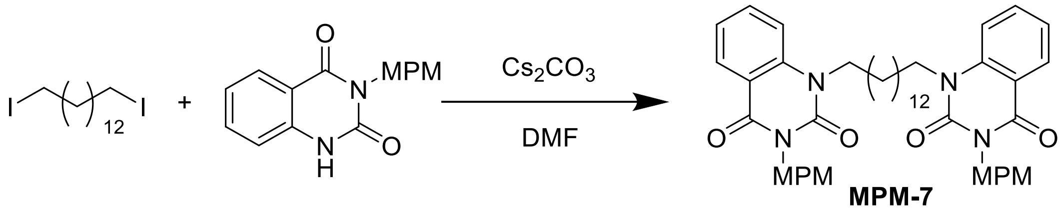
The product was synthesised by reported literature[S1] procedure from tetradecanedioic acid.

1,14-diiodotetradecane

A mixture of 1,14-tetradecanediol (1.15 g, 5.00 mmol) and hydroiodic acid aqueous (2.9 ml) was stirred and refluxed for 6 h. After cooling, the mixture was diluted with water (20 ml) and the product was extracted with Et_2O (30 ml × 3). The combined organic layers were washed with saturated $NaHCO_3$ aqueous (60 ml), 1 M $Na_2S_2O_3$ aqueous (60 ml) and saturated NaCl aqueous (60 ml), and dried over Na_2SO_4. Evaporation of the solvent afforded a white solid of 1,14-diiodotetradecane (1.94 g, 86%). The compound data was consistent with that of reported literature[S2].

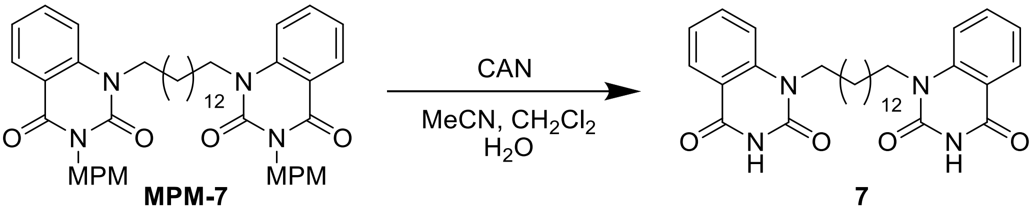
3-(4-methoxybenzyl)quinazolin-2,4-dione

To a slurry of Benzoyleneurea (1.43 g, 8.82 mmol) and K_2CO_3 (1.10 g, 7.97 mmol) in DMF (80 ml) was added 4-methoxybenzyl chloride (1.09 ml, 7.46 mmol), and the reaction mixture was stirred overnight. The solvent was removed by evaporation, and the mixture was suspended in water (30 ml) and then extracted with CH_2Cl_2 (50 ml × 3). The combined organic layers ware dried over Na_2SO_4. Evaporation of the solvent and purification by column chromatography (SiO_2, AcOEt/CH_2Cl_2 = 1/9) afforded a white solid of 3-(4-methoxybenzyl)quinazoline-2,4-dione (0.55 g, 25%). The compound data was consistent with that of reported literature.[S3]



MPM-7

A slurry of 3-(4-methoxybenzyl)quinazolin-2,4-dione (0.32 g, 1.1 mmol), Cs_2CO_3 (0.65 g, 2.0 mmol) and 1,14-diiodotetradecane (0.23 g, 0.50 mmol) in DMF (10 ml) was stirred overnight. The solvent was removed by evaporation, and the mixture was suspended in water and then extracted with CH_2Cl_2 (10 ml × 3). The combined organic layers were washed with saturated NaCl aqueous (10 ml) and dried over Na_2SO_4. Evaporation of the solvent and purification by column chromatography (SiO_2, AcOEt/hexane = 2/3) afforded a white solid of **MPM-7** (0.35 g, 92 %); IR (KBr) ν 1701, 1659, 1609 cm^{-1}, ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.23 (d, J = 7.8 Hz, 2H), 7.64 (t, J = 7.8 Hz, 2H), 7.49 (d, J = 7.8 Hz, 4H), 7.22 (t, J = 7.8 Hz, 2H), 7.15 (d, J = 7.8 Hz, 2H), 6.82 (d, J = 7.8 Hz, 4H), 5.21 (s, 4H), 4.09 (t, J = 7.8 Hz, 4H), 3.76 (s, 6H), 1.71 (m, 4H), 1.42-1.24 (m, 20H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 161.9, 159.1, 150.9, 139.9, 135.1, 130.8, 129.5, 129.4, 122.8, 115.9, 113.8, 113.6, 55.4, 44.5, 44.0, 29.73, 29.71, 29.68, 29.5, 27.5, 27.0; ESI-HRMS Calcd for $C_{46}H_{54}N_4Na_1O_6$ $[M+Na]^+$: 781.3941, Found: 781.3925



Substrate 7

To a solution of **MPM-7** (0.26 g, 0.34 mmol) in CH_3CN (2.5 ml), CH_2Cl_2 (2.5 ml) and H_2O (0.4 ml) was added di-ammonium cerium(IV) nitrate (1.7 g, 3.1 mmol) and the reaction mixture was stirred overnight. The reaction mixture was poured into H_2O and then extracted with CH_2Cl_2 (20 ml × 3). The combined organic layers were washed with saturated NaCl aqueous and dried over Na_2SO_4. Evaporation of the solvent and purification by column chromatography (SiO_2, AcOEt/hexane = 2/3) afforded a white solid of **7** (0.096 g, 53 %): IR (film) ν 1700, 1608 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.54 (s, 2H), 8.21 (d, J = 7.8 Hz, 2H), 7.69 (t, J = 8.0 Hz, 2H), 7.27-7.24 (m, 2H), 7.20 (d, J = 8.5 Hz, 2H), 4.09 (t, J = 7.7 Hz, 4H), 1.75-1.68 (m, 4H), 1.42-1.26 (m, 20H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ162.0, 150.3, 141.1, 135.6, 129.1, 123.1, 116.3, 114.2, 43.1, 29.63, 29.56, 29.5, 29.3, 27.4, 26.8; ESI-HRMS Calcd for $C_{30}H_{38}N_4Na_1O_4$ $[M+Na]^+$: 541.2791, Found: 541.2770

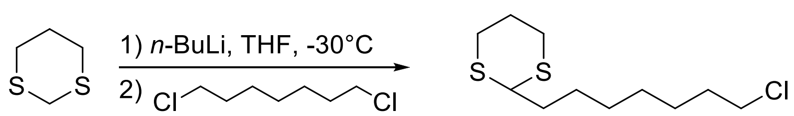
3. Synthesis of Oxidation Products **8, 9, 10** *via* the Route using Dithiane

1,7-dichloroheptane

The product was synthesized from 1,7-heptanediol by reported literature[S4] procedure about similar product 1-bromo-8-chlorooctane. The compound data was consistent with that of reported literature[S5].

1-bromo-8-chlorooctane

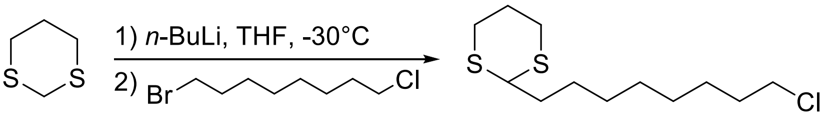
The product was synthesised by reported literature[S4] procedure from 8-bromo-1-octanol.



2-(1-Chloroheptyl)-1,3-dithiane

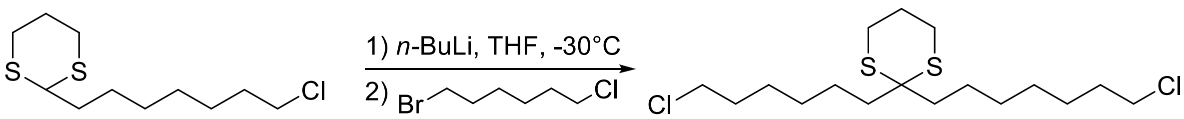
To a solution of 1,3-dithiane (0.60 g, 5.0 mmol) in THF (10 ml) was added 1.6 M *n*-butyllithium hexane solution (3.5 ml, 5.6 mmol) with stirring at –30 ˚C under Ar. After stirring for 1.5 h at –30 ˚C, 1,7-dichloroheptane (1.0 g, 6.0 mmol) was added, and warmed to 0 ˚C. A solution was stirred for 3 h, poured into water and then extracted with CH_2Cl_2 (10 ml × 3). The combined organic layers were washed with saturated $NaHCO_3$ aqueous (10 ml × 2) and saturated NaCl aqueous (10 ml), and dried over Na_2SO_4. Evaporation of the solvent and purification by column chromatography (SiO_2, CH_2Cl_2/hexane = 1/10-1/5) afforded a colorless oil of 2-(1-Chloroheptyl)-1,3-dithiane (0.32 g, 26 %) ; IR (neat) ν 2999, 1868, 1421 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.05 (t, J = 6.8 Hz, 1H), 3.53 (t, J = 7.0 Hz, 2H), 2.92-2.80 (m, 4H), 2.16-2.09 (m, 1H), 1.91-1.72 (m, 5H), 1.55-1.29 (m, 8H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 47.6, 45.1, 35.4, 32.6, 30.5, 29.0, 28.6, 26.7, 26.5, 26.0; MS (FAB) 253

$[M+H]^+$, 255 [M+3]; EI-HRMS Calcd for $C_{11}H_{21}$ Cl S_2 $[M]^+$: 252.0773, Found: 252.0775.



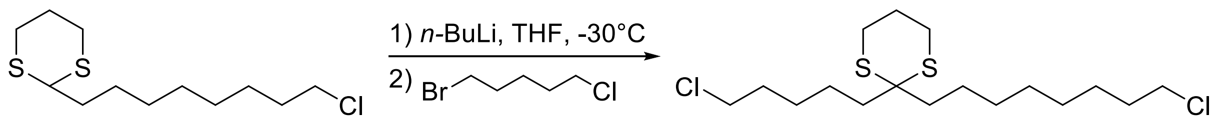
2-(1-Chlorooctyl)-1,3-dithiane

This compound was prepared from 1,3-dithiane (0.60 g, 5.0 mmol) and 1-bromo-8-chlorooctane (1.8 g, 6.4 mmol) in a manner similar to that described for 2-(1-chloroheptyl)-1,3-dithiane: yield 61 % (0.82 g); IR (neat) ν 2969, 2869 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.05 (t, J = 6.8 Hz, 1H), 3.53 (t, J = 6.8 Hz, 2H), 2.92-2.80 (m, 4H), 2.16-2.09 (m, 1H), 1.91-1.72 (m, 5H), 1.55-1.29 (m, 10H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 47.6, 45.1, 35.4, 32.6, 30.5, 29.1, 29.1, 28.7, 26.8, 26.5, 26.0; MS (FAB) 267 $[M+H]^+$, 269 [M+3]; EI-HRMS Calcd for $C_{12}H_{23}$ Cl S_2 $[M]^+$: 266.0930, Found: 266.0940.



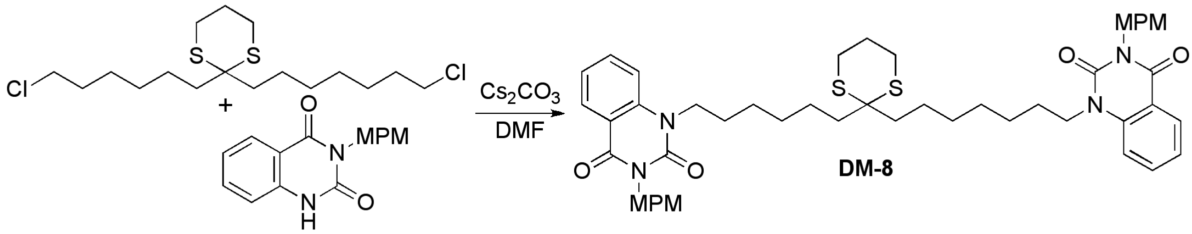
2-(1-Chloroheptyl)-2-(1-chlorohexyl)-1,3-dithiane

This compound was prepared from 2-(1-chloroheptyl)-1,3-dithiane (0.27 g, 1.1 mmol) and 1-bromo-6-chlorohexane (0.43 g, 2.2 mmol) in a manner similar to that described for 2-(1-chloroheptyl)-1,3-dithiane: yield 36 % (0.14 g); IR (neat) ν 2996, 2838, 1461 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.52 (t, J = 6.6 Hz, 4H), 2.78 (t, J = 5.8 Hz, 4H), 1.96-1.90 (m, 2H), 1.86-1.72 (m, 8H), 1.49-1.27 (m, 14H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 53.2, 45.1, 45.1, 38.2, 38.1, 32.6, 32.5, 29.6, 29.0, 28.7, 26.8, 26.7, 26.0, 25.5, 24.0, 23.9; MS (FAB) 371 $[M+H]^+$, 373 [M+3], 375[M+5]; EI-HRMS Calcd for $C_{17}H_{32}Cl_2S_2$ $[M]^+$: 370.1323, Found: 370.1317.



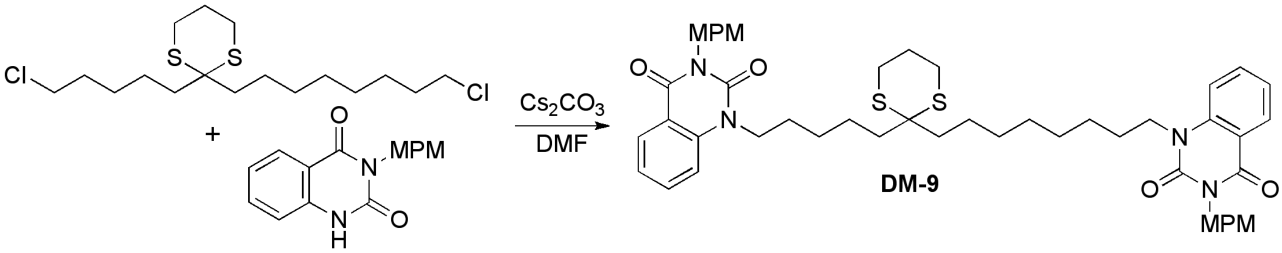
2-(1-Chlorooctyl)-2-(1-chloropentyl)-1,3-dithiane

This compound was prepared from 2-(1-chlorooctyl)-1,3-dithiane (0.11 g, 0.41 mmol) and 1-bromo-5-chloropentane (0.16 g, 0.85 mmol) in a manner similar to that described for 2-(1-chloroheptyl)-1,3-dithiane: yield 24 % (37 mg); IR (neat) ν 2953, 2016, 1462 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.52 (t, J = 6.6 Hz, 2H), 3.50 (t, J = 6.6 Hz, 2H), 2.78 (t, J = 5.8 Hz, 4H), 1.95-1.90 (m, 2H), 1.87-1.71 (m, 8H), 1.49-1.22 (m, 14H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 53.2, 45.1, 45.0, 38.3, 38.0, 32.6, 32.4, 29,6, 29.3, 28.8, 27.0, 26.8, 26.0, 25.5, 24.0, 23.5; MS (FAB) 371 $[M+H]^+$, 373 [M+3], 375 [M+5]; EI-HRMS Calcd for $C_{17}H_{32}Cl_2S_2$ $[M]^+$: 370.1323, Found: 370.1330.



DM-8

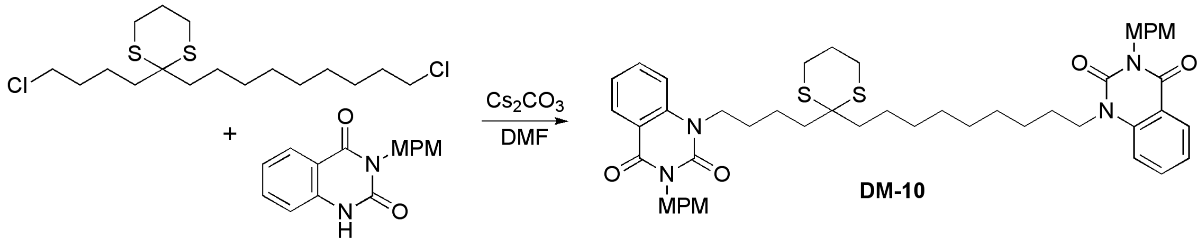
A slurry of 3-(4-methoxybenzyl)quinazolin-2,4-dione (0.13 g, 0.46 mmol), Cs_2CO_3 (0.26 g, 0.80 mmol) and 2-(1-chloroheptyl)-2-(1-chlorohexyl)-1,3-dithiane (0.075 g, 0.20 mmol) in DMF (2 ml) was stirred overnight. The solvent was removed by evaporation, and the reaction mixture was suspended in water and then extracted with CH_2Cl_2 (10 ml × 3). The combined organic layers were washed with saturated NaCl aqueous (10 ml) and dried over Na_2SO_4. Evaporation of the solvent and purification by column chromatography (SiO_2, AcOEt/CH_2Cl_2 = 1/10) afforded a white solid of **DM-8** (0.079 g, 46 %); IR (film) ν 1747, 1597, 1509 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.25-8.22 (m, 2H), 7.67-7.62 (m, 2H), 7.49 (d, J = 8.6 Hz, 4H), 7.25-7.20 (m, 2H), 7.17-7.14 (m, 2H), 6.83 (d, J = 8.6 Hz, 4H), 5.21 (s, 4H), 4.11-4.07 (m, 4H), 3.76 (s, 6H), 2.80 (t, J = 5.6 Hz, 4H), 1.97-1.70 (m, 10H), 1.48-1.32 (m, 14 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 161.6, 161.5, 158.9, 150.6, 139.6, 134.9, 130.5, 129.2, 129.2, 129.0, 122.5, 115.6, 113.6, 113.4, 55.1, 53.1, 44.2, 43.6, 43.6, 38.1, 38.0, 29.6, 29.4, 29.1, 27.1, 26.6, 26.5, 25.9, 25.4, 23.9, 23.9; MS (FAB) 863 $[M+H]^+$; FAB-HRMS Calcd for $C_{49}H_{59}N_4O_6S_2$ $[M+H]^+$: 863.3876, Found: 863.3868.



DM-9

This compound was prepared from 2-(1-chlorooctyl)-2-(1-chloropentyl)-1,3-dithiane (37 mg, 0.10 mmol) in a manner similar to that described for **DM-8**: yield 75 % (65 mg); IR (film) ν 2854, 1601, 1510, 1482 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.24-8.22 (m, 2H), 7.65-7.62 (m, 2H), 7.48 (d, J = 8.6 Hz, 4H), 7.23-7.20 (m, 2H), 7.16-7.13 (m, 2H), 6.82 (d, J = 8.6 Hz, 4H), 5.20 (s, 4H), 4.12-4.06 (m, 4H), 3.76 (s, 6H), 2.81-2.79 (m, 4H), 1.94-1.70 (m, 10 H), 1.49-1.32 (m, 14 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 161.7, 161.7, 159.0, 151.3, 150.8, 150.7, 139.9, 139.7, 135.0, 135.0, 130.6, 129.3, 129.2, 129.2, 128.9, 127.9, 122.7, 122.7, 115.8, 114.3, 113.7, 113.5, 55.2, 55.2, 53.2, 46.7, 44.3, 43.8, 43.7, 38.3, 38.1, 29.7, 29.4, 29.3, 27.3, 27.2, 27.0, 26.8, 26.0, 25.5, 24.0, 23.9; MS (FAB) 863

$[M+H]^+$; FAB-HRMS Calcd for $C_{49}H_{59}N_4O_6S_2$ $[M+H]^+$: 863.3876, Found: 863.3871.

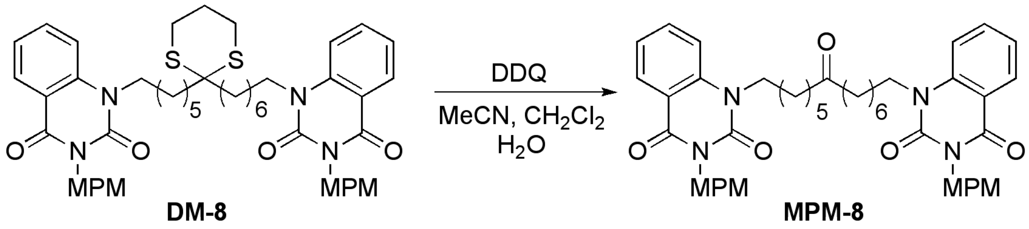


DM-10

To a solution of 1,3-dithiane (0.60 g, 5.0 mmol) in THF (10 ml) was added 1.6 M *n*-butyllithium hexane solution (3.5 ml, 5.6 mmol) with stirring at –30 ˚C under Ar. After stirring for 1.5 h at –30 ˚C, 1,9-dichlorononane (1.2 g, 6.1 mmol) was added, and warmed to 0 ˚C. A solution was stirred for 3 h, poured into water and then extracted with CH_2Cl_2 (10 ml × 3). The combined organic layers were washed with saturated $NaHCO_3$ aqueous (10 ml × 2) and saturated NaCl aqueous (10 ml), and dried over Na_2SO_4. Evaporation of the solvent and purification by column chromatography (SiO_2, CH_2Cl_2/hexane = 1/10-1/5) afforded a colorless oil of crude 2-(1-Chlorononyl)-1,3-dithiane (0.80 mg), which was used without further purification.

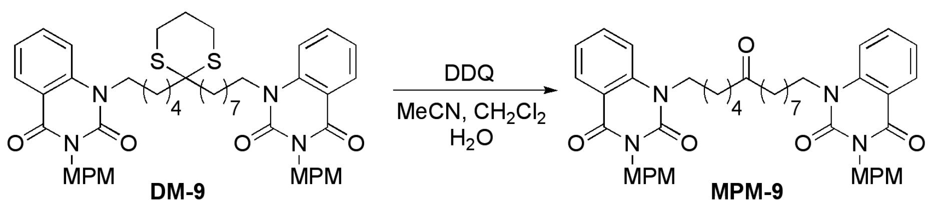
To a solution of crude 2-(1-chlorononyl)-1,3-dithiane (0.40 g, 1.4 mmol) in THF (2 ml) was added 1.6 M *n*-butyllithium hexane solution (1.1 ml, 1.7 mmol) with stirring at –30 ˚C under Ar. After stirring for 1.5 h at –30 ˚C, 1-bromo-4-chlorobutane (0.49 g, 2.9 mmol) was added, and warmed to 0 ˚C. A solution was stirred for 3 h, poured into water and then extracted with CH_2Cl_2 (10 ml × 3). The combined organic layers were washed with saturated $NaHCO_3$ aqueous (10 ml × 2) and saturated NaCl aqueous (10 ml), and dried over Na_2SO_4. Evaporation of the solvent and purification by column chromatography (SiO_2, CH_2Cl_2/hexane = 1/10-1/5) afforded a crude product 2-(1-chlorononyl)-2-(1-chlorobutyl)-1,3-dithiane (0.41 mg), which was used without further purification.

A slurry of 3-(4-methoxybenzyl)quinazolin-2,4-dione (0.13 mg, 0.46 mmol), Cs_2CO_3 (260 mg, 0.80 mmol) and crude 2-(1-chlorononyl)-2-(1-chlorobutyl)-1,3-dithiane (0.078 g, 0.20 mmol) in DMF (2 ml) was stirred overnight. The solvent was removed by evaporation, and the reaction mixture was suspended in water and then extracted with CH_2Cl_2 (10 ml × 3). The combined organic layers were washed with saturated NaCl aqueous (10 ml) and dried over Na_2SO_4. Evaporation of the solvent and purification by column chromatography (SiO_2, AcOEt/CH_2Cl_2 = 1/10) afforded a white solid of **DM-10** (49 mg, 11 % (3 steps)); IR (KBr) ν 1703, 1658, 1609 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.23 (d, J = 8.2 Hz, 2H), 7.66-7.62 (m, 2H), 7.48 (dd, J = 8.7 Hz, 2.4 Hz, 4H), 7.25-7.18 (m, 2H), 7.15 (d, J = 8.2 Hz, 2H), 6.82 (d, J = 8.7 Hz, 4H), 5.20 (s, 4H), 4.12-4.07 (m, 4H), 3.75 (s, 6H), 2.81-2.79 (m, 4H), 1.95-1.72 (m, 10H), 1.42-1.25 (m, 14H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 161.78, 161.74, 159.03, 159.02, 150.79, 150.77, 139.78, 139.67, 135.09, 135.02, 130.65, 130.62, 129.38, 129.31, 129.31, 129.24, 122.80, 122.70, 115.82, 115.81, 113.74, 113.71, 113.53, 113.43, 55.23, 53.15, 44.39, 44.36, 43.86, 43.71, 38.45, 37.92, 29.79, 29.70, 29.55, 29.41, 29.30, 27.39, 27.31, 26.84, 26.05, 25.44, 24.12, 21.65; ESI-HRMS Calcd for $C_{49}H_{58}N_4O_6S_2Na$ $[M+Na]^+$:885.3695, Found: 885.3712



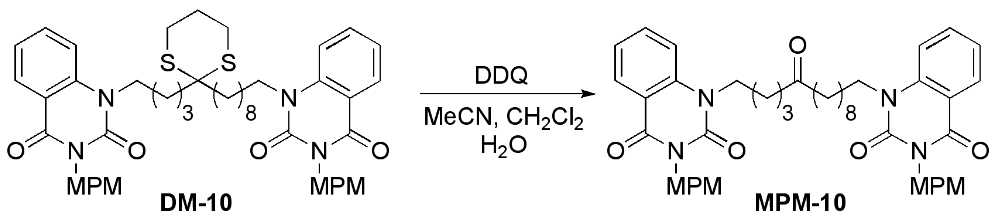
MPM-8

To a solution of **DM-8** (79 mg, 92 μmol) in CH_3CN (0.7 ml), CH_2Cl_2 (0.7 ml) and H_2O (0.1 ml) was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (31 mg, 0.14 mmol) in CH_3CN (0.2 ml) under Ar. After being stirred overnight at room temperature, the solution was poured into saturated $NaHCO_3$ aqueous (10 ml) and then extracted with CH_2Cl_2 (10 ml × 3). The combined organic layers were washed with saturated NaCl aqueous (10 ml), and dried over Na_2SO_4. Evaporation of the solvent and purification by column chromatography (SiO_2, AcOEt/CH_2Cl_2 = 1/10) afforded a white solid of **MPM-8** (49 mg, 69 %); IR (film) ν 1703, 1657, 1610 cm^{-1}; ^1H-NMR (500 MHz, $CDCl_3$) δ 8.22 (dd, J = 7.9 Hz, 1.5 Hz, 2H), 7.63 (td, J = 7.9 Hz, 1.5 Hz, 2H), 7.48 (d, J = 8.6 Hz, 4H), 7.21 (t, J = 7.5 Hz, 2H), 7.14 (dd, J = 8.5 Hz, 3.5 Hz, 2H), 6.82 (d, J = 8.6 Hz, 4H), 5.20 (s, 4H), 4.10-4.06 (m, 4H), 3.76 (s, 6H), 2.40-2.36 (m, 4H), 1.74-1.67 (m, 4H), 1.61-1.53 (m, 4H), 1.44-1.25 (m, 10H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 211.1, 161.7, 159.0, 150.8, 150.8, 139.7, 135.1, 135.0, 130.6, 129.3, 129.2, 127.9, 122.7, 122.7, 115.8, 114.3, 113.7, 113.5, 55.2, 44.3, 43.8, 43.7, 42.7, 42.5, 29.1, 29.1, 28.9, 28.9, 27.2, 27.1, 26.8, 26.6, 23.7, 23.6; MS (FAB) 773 $[M+H]^+$; FAB-HRMS Calcd for $C_{46}H_{53}N_4O_7$ $[M+H]^+$: 773.3914, Found: 773.3908.



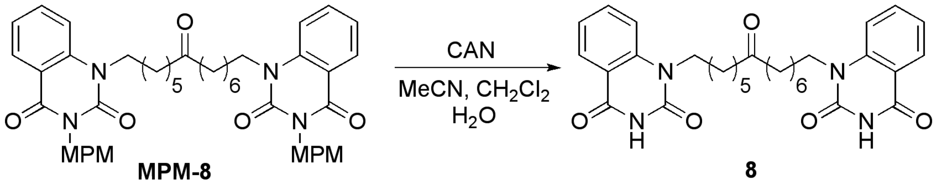
MPM-9

This compound was prepared from **DM-9** (27 mg, 31 μmol) in a manner similar to that described for **MPM-9**: yield 56 % (13 mg); IR (film) ν 1703, 1658, 1609 cm^{-1}; ^1H-NMR (500 MHz, $CDCl_3$) δ 8.25-8.23 (m, 2H), 7.67-7.63 (m, 2H), 7.50-7.48 (m, 4H), 7.23 (t, J = 7.3 Hz, 2H), 7.15 (d, J = 8.1 Hz, 2H), 6.83 (d, J = 8.8 Hz, 4H), 5.21 (s, 4H), 4.11-4.07 (m, 4H), 3.76 (s, 6H), 2.43-2.36 (m, 4H), 1.76-1.54 (m, 8H), 1.44-1.25 (m, 10H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 211.0, 161.7, 159.0, 150.8, 139.6, 135.0, 129.3, 129.3, 129.2, 128.9, 127.9, 122.7, 122.7, 115.8, 114.3, 113.7, 113.5, 113.4, 55.2, 55.2, 44.3, 43.8, 43.6, 42.8, 42.4, 29.3, 29.1, 27.2, 27.1, 26.7, 26.6, 26.4, 23.7, 23.3; MS (FAB) 773 [M+H]$^+$; FAB-HRMS Calcd for $C_{46}H_{53}N_4O_7$ [M+H]$^+$: 773.3914, Found: 773.3901.



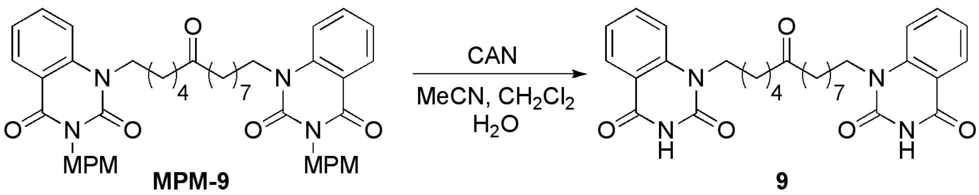
MPM-10

This compound was prepared from **DM-10** (49 mg, 56 μmol) in a manner similar to that described for **MPM-8**: yield 90 % (39 mg); IR (KBr) ν 1702, 1657, 1609 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.23 (dt, *J*=7.7, 1.7 Hz, 2H), 7.65-7.62 (m, 2H), 7.49-7.46 (m, 4H), 7.22 (t, J = 7.7 Hz, 2H), 7.16-7.13 (m, 2H), 6.82 (d, J = 8.7 Hz, 4H), 5.20 (s, 4H), 4.09-4.06 (m, 4H), 3.76 (s, 6H), 2.48 (t, J = 6.3 Hz, 2H), 2.37 (t, J = 6.3 Hz, 2H), 1.70-1.54 (m, 8H), 1.39-1.27 (m, 10H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 210.7, 161.8, 161.7 159.03, 159.02, 150.82, 150.79, 139.8, 139.7, 135.1, 135.0, 130.65, 130.62, 129.4, 129.31, 129.27, 129.25, 122.8, 122.7, 115.81, 115.78, 113.72, 113.71, 113.51, 113.47, 55.2, 44.37, 44.36, 43.8, 43.5, 42.9, 41.9, 29.4, 29.29, 29.25, 29.2, 27.3, 26.80, 26.76, 23.8, 20.7; ESI-HRMS Calcd for $C_{46}H_{52}N_4O_7Na$ [M+Na]$^+$:795.3734, Found: 795.3709



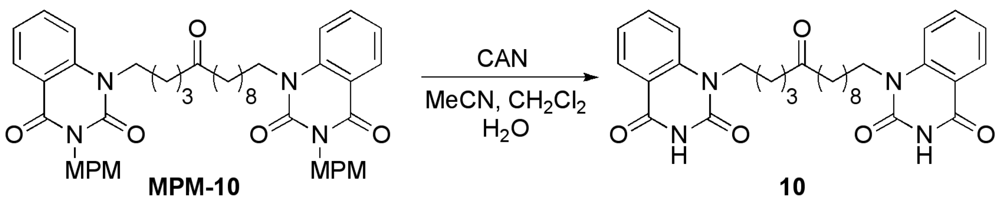
8

This compound was prepared from **MPM-8** (8.0 mg, 10 μmol) in a manner similar to that described for **7**: yield 38 % (2.0 mg); IR (film) ν 1701, 1608 cm^{-1}; ^{1}H-NMR (500MHz, $CDCl_3$) δ 9.09 (s, 1H), 9.08 (s, 1H), 8.22 (dd, J = 7.8 Hz, 1.4 Hz, 2H), 7.69 (td, J = 7.8 Hz, 1.4 Hz, 2H), 7.27-7.24 (m, 2H), 7.20 (dd, J = 8.5 Hz, 3.3 Hz, 2H), 4.11-4.08 (m, 4H), 2.42-2.38 (m, 4H), 1.75-1.69 (m, 4H), 1.61-1.54 (m, 4H), 1.45-1.25 (m, 10H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 211.5, 162.02, 162.01, 150.4, 141.10, 141.09, 135.68, 135.66, 129.1, 123.14, 123.12, 116.3, 114.2, 42.9, 42.8, 42.7, 29.1, 29.0, 28.8, 27.2, 27.1, 26.50, 26.48, 23.8, 23.7; MS (FAB) 533 [M+H]$^+$; FAB-HRMS Calcd for $C_{30}H_{37}N_4O_5$ [M+H]$^+$: 533.2764, Found: 533.2770.



9

This compound was prepared from **MPM-9** (76 mg, 98 μmol) in a manner similar to that described for **7**: yield 33 % (17 mg); IR (KBr) ν 1707, 1674, 1607 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.93 (s, 1H), 8.22 (d, J = 7.6 Hz, 2H), 7.69 (t, J = 7.4 Hz, 2H), 7.28-7.25 (m, 2H), 7.20 (dd, J = 8.3 Hz, 2.6 Hz, 2H), 4.10 (t, J = 7.3 Hz, 4H), 2.46-2.39 (m, 4H), 1.76-1.55 (m, 8H), 1.43-1.25 (m, 10H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 211.4, 162.1, 150.4, 141.12, 141.06, 135.7, 135.6, 129.11, 129.07, 123.2, 123.1, 116.3, 114.2, 114.1, 42.98, 42.95, 42.8, 42.4, 29.2, 29.1, 29.0, 27.22, 27.17, 26.6, 26.3, 23.9, 23.4; MS (FAB) 533 $[M+H]^+$; FAB-HRMS Calcd for $C_{30}H_{37}N_4O_5$ $[M+H]^+$: 533.2764, Found: 533.2749.



10

This compound was prepared from **MPM-10** (28 mg, 37 μmol) in a manner similar to that described for **7**: yield 49 % (9.8 mg); IR (KBr) ν 1701, 1607 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 9.20 (s, 1H), 9.17 (s, 1H), 8.22 (d, J = 7.7 Hz, 2H), 7.69 (t, J = 7.7 Hz, 2H), 7.27-7.24 (m, 2H), 7.22-7.19 (m, 2H), 4.12-4.08 (m, 4H), 2.53 (t, J = 7.0 Hz, 2H), 2.41 (t, J = 7.0 Hz, 2H), 1.72-1.56 (m, 8H), 1.42-1.29 (m, 10H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 211.1, 162.1, 162.0, 150.4, 150.3, 141.1, 141.0, 135.7, 135.6, 129.12, 129.08, 123.2, 123.1, 116.3, 116.2, 114.2, 114.1, 43.0, 42.9, 42.5, 42.0, 29.24, 29.19, 29.1, 27.2, 26.8, 26.6, 23.9, 20.7; ESI-HRMS Calcd for $C_{30}H_{36}N_4O_5Na$ $[M+Na]^+$:555.2583, Found: 555.2571

4. Synthesis of Porphyrins

***N*-(6-aminopyridin-2-yl)pentanamide**

The product was synthesised according to the reported literature[S6] procedure.

5,15-Bis(4-methoxycarbonylphenyl)-10,20-bis(pentafluorophenyl)porphyrin (2)

The product was synthesised according to the reported literature[S7] procedure.

5,15-bis(*N*-(2-(6-valerylamidoopyridyl))4-aminocarbonylphenyl)-10,20-bis(pentafluorophenyl)porphyrin (1a')

To a solution of **2** (40.9 mg, 44.9 μmol) in THF (3.0 ml) was added water (3.0 ml) and $LiOH{\cdot}H_2O$ (210 mg, 5.0 mmol) and then stirred at room temperature for 50 h. The solution was diluted with AcOEt (10 ml) and washed with 2 M HCl aqueous solution (10 ml × 2), water (10 ml) and saturated NaCl aqueous (10ml). The organic layer was dried over Na_2SO_4 and evaporated. The residue was suspended in $CHCl_3$ and filtration to afford a crude product of 5,15-bis(4-carboxyphenyl)-10,20-bis(pentafluorophenyl)porphyrin (24.5 mg), which was used without further purification.

To a solution of the crude product (24.5 mg) in THF (3 ml) and 1,2-dichloroethane (0.4 ml), molecular sieves 4A (300 mg) was added. The solution was stirred at room temperature under Ar for 1 h, and then 2-chloro-1-methylpyridinium iodide (42.5 mg, 166 μmol) and triethylamine (23.1 μl, 166 μmol) were added. After being stirred at room temperature for 1 h, *N*-(6-aminopyridin-2-yl)pentanamide (53.5 mg, 277 μmol) and 4-*N,N*-dimethylaminopyridine (3.4 mg, 27.7 μmol) was added, and the solution was stirred at 50 °C overnight. The solvent was evaporated, and the residue was dissolved in AcOEt (15 ml). The organic phase was washed with 0.1 M HCl aqueous (15 ml × 2) and saturated NaCl aqueous (15 ml), and dried over Na_2SO_4. Evaporation of the solvent and purification by silica-gel column chromatography (AcOEt/hexane = 2/8-4/6) and alumina column chromatography (AcOEt/hexane = 2/8-4/6) afforded a purple solid of **1a'** (11.0 mg, 19.9 %); IR (KBr) ν 3424, 3315, 1685, 1448 cm^{-1}, ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.89-8.84 (m, 8H), 8.59 (s, 2H), 8.32-8.27 (m, 8H), 8.23 (d, J = 7.9 Hz, 2H), 8.05 (d, J = 8.2 Hz, 2H), 7.87 (t, J = 8.1 Hz, 2H), 7.68 (s, 2H), 2.44 (t, J = 7.6 Hz, 4H), 1.79-1.73 (m, 4H), 1.47-1.43 (m, 4H), 0.98 (t, J = 7.4 Hz, 6H), -2.85 (s, 2H); ESI-HRMS Calcd for $C_{66}H_{46}F_{10}N_{10}O_4Na$ $[M+Na]^+$:1255.3442, Found: 1255.3440; UV-vis (CH_2Cl_2) λ_{max} (ε) 416 nm (4.54 x 10^5), 511 nm (2.73 x 10^4);

Carbonyl[5,15-bis(4-methoxycarbonylphenyl)-10,20-bis(pentafluorophenyl) porphyrinato]ruthenium(II) (3)

A solution of **2** (0.25 g, 0.27 mmol) and $Ru_3(CO)_{12}$ (0.13 g, 0.14 mmol) in 1,2,4-trichlorobenzene (6 ml) was refluxed under Ar for 2.5 h. After cooling, the reaction mixture was passed through Al_2O_3. The eluates from the column was evaporated, and purified by column chromatography (SiO_2, CH_2Cl_2/MeOH = 200/1) and recrystallised from CH_2Cl_2/hexane to afford a red solid of **3** (0.10 g, 69 %); IR (KBr) ν 1955, 1723, 1279 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.73 (d, J = 4.9 Hz, 4H), 8.65 (d, J = 4.9 Hz, 4H), 8.43 (t, J = 8.9 Hz, 4H), 8.30 (d, J = 8.7 Hz, 2H), 8.25 (d, J = 8.7 Hz, 2H), 4.10 (s, 6H); MS (FAB) 1038 $[M]^+$, 1010 [M-CO]; UV-vis (CH_2Cl_2) λ_{max} (ε) 407 nm (1.84 x 10^5), 526 nm (1.54 x 10^4); Anal. Calcd for $C_{49}H_{26}F_{10}N_4O_7Ru$ (**3** • $2H_2O$): C, 54.81; H, 2.44; N, 5.22. Found: C, 54.73; H, 2.57; N, 5.30.

Carbonyl[5,15-bis(4-carboxyphenyl)-10,20-bis(pentafluorophenyl)porphyrinato] ruthenium(II) (4)

To a solution of **3** (91.3 mg, 87.8 μmol) in THF (8.0 ml) was added water (8.0 ml) and $LiOH{\cdot}H_2O$ (673 mg, 16.0 mmol) and then stirred at room temperature for 50 h. The solution was diluted with AcOEt (40 ml) and washed with 2 M HCl aqueous solution (40 ml × 2), water (40 ml) and saturated NaCl aqueous (40 ml). The organic layer was dried over Na_2SO_4 and evaporated. The residue was purified by column chromatography (SiO_2, AcOEt/hexane/AcOH = 1/19/2 → 3/7/1) to afford a red solid of **4** (81.0 mg, 91.3%); IR (KBr) ν 3437, 1957, 1698, 1489, 1271 cm^{-1}; ^{1}H-NMR (500 MHz, DMSO-d_6) δ 8.90-8.88 (m, 4H), 8.65-8.63 (m, 4H), 8.36-8.31 (m, 6H), 8.25-8.22 (m, 2H); MS (ESI) 1009 $[M-H]^-$; UV-vis (MeOH) λ_{max} (ε) 405 nm (2.34 x 10^5), 526 nm (1.58 x 10^4); Anal. Calcd for $C_{50}H_{30}F_{10}N_4O_{7.5}Ru$ (**4** •0.5*n*-hexane •$2.5H_2O$): C, 54.70; H, 2.75; N, 5.10. Found: C, 54.63; H, 2.95; N, 5.15.

Carbonyl[5,15-bis(*N*-(2-(6-valerylamidopyridyl))4-aminocarbonylphenyl)-10,20-bis(pentafluorophenyl)porphyrinato] ruthenium(II) (6a)

To a solution of **4** (60 mg, 60 μmol) in THF (7 ml) and 1,2-dichloroethane (1 ml), molecular sieves 4A (750 mg) was added. The solution was stirred at room temperature under Ar for 1 h, and then 2-chloro-1-methylpyridinium iodide (92 mg, 360 μmol) and triethylamine (50 μl, 360 μmol) were added. After being stirred at room temperature for 1 h, *N*-(6-aminopyridin-2-yl)pentanamide (116 mg, 600 μmol) and 4-*N,N*-dimethylaminopyridine (7.3 mg, 60 μmol) were added, and the solution was stirred at 50 °C overnight. The solvent was evaporated, and the residue was dissolved in AcOEt (15 ml). The organic phase was washed with 0.1 M HCl aqueous (15 ml × 2) and saturated NaCl aqueous (15 ml), and dried over Na_2SO_4. Evaporation of the solvent and purification by column chromatography (SiO_2, AcOEt/hexane = 1/9-1/1) afforded a red solid of **6a** (33 mg, 39 %); IR (KBr) ν 1950, 1678 cm^{-1}; ^{1}H-NMR (500 MHz, acetone-d_6) δ 9.72 (s, 2H), 9.24 (s, 2H), 8.95 (brs, 4H), 8.77 (brs, 4H), 8.49-8.43 (m, 6H), 8.29 (brs, 2H), 8.18 (d, J = 8.1 Hz, 2H), 8.05 (d, J = 8.1 Hz, 2H), 7.90 (t, J = 8.1 Hz, 2H), 2.52 (t, J = 7.4 Hz, 4H), 1.73-1.67 (m, 4H), 1.44-1.40 (m, 4H), 0.95 (t, J = 7.4 Hz, 6H); ESI-HRMS Calcd. for $C_{67}H_{45}F_{10}N_{10}O_5Ru$ $[M+H]^+$ 1361.2458, Found 1361.2448; UV-Vis (CH_2Cl_2) λ_{max} (ε) 411 nm (1.83 x 10^5), 528 nm (1.81x 10^4), 587 nm (4.28 x 10^3). Anal. Calcd for $C_{67}H_{48}F_{10}N_{10}O_7Ru$ (**6a** •$2H_2O$): C, 57.64; H, 3.47; N, 10.03. Found: C, 57.56; H, 3.75; N, 9.93.

Carbonyl[5,15-bis(4-(*N,N*-diisopropylaminocarbonylphenyl))-10,20-bis(pentafluorophenyl)porphyrinato] ruthenium(II) (6b)

To a solution of **4** (19 mg, 19 μmol) in THF (4 ml) and 1,2-dichloroethane (0.5 ml), molecular sieves 4A (180 mg) was added. The solution was stirred at room temperature under Ar for 1 h, and then 2-chloro-1-methylpyridinium iodide (29 mg, 110 μmol) and triethylamine (15 μl, 110 μmol) were added. After being stirred at room temperature for 1 h, diisopropylamine (52 μl, 370 μmol) and 4-*N,N*-dimethylaminopyridine (2.3 mg, 19 μmol) were added, and the solution was stirred at 50 °C overnight. The solvent was evaporated, and the residue was dissolved in AcOEt (15 ml). The organic phase was washed with 0.1 M HCl aqueous (15 ml × 2) and saturated NaCl aqueous (15 ml), and dried over Na_2SO_4. Evaporation of the solvent and purification by column chromatography (SiO_2, AcOEt/hexane = 1/9-1/1) afforded a red solid of **6b** (12 mg, 55 %); IR (KBr) ν 1946, 1609 cm^{-1}; ^{1}H-NMR (500 MHz, DMSO-d_6, 60 °C) δ 8.87 (d, J = 4.9 Hz, 4H), 8.67 (d, J = 4.9 Hz, 4H), 8.26 (d, J = 6.7 Hz, 2H), 8.15 (d, J = 6.7 Hz, 2H), 7.70 (d, J = 6.7 Hz, 4H), 3.97 (brs, 4H), 1.47 (brs, 24H); ESI-HRMS Calcd for $C_{59}H_{45}F_{10}N_6O_3Ru$ $[M+H]^+$:1177.2437, Found: 1177.2442. UV-Vis (CH_2Cl_2) λ_{max} (ε) 408 nm (1.65 x 10^5), 527 nm (1.42x 10^4).

***trans*-Diacetonitrile[5,15-bis(*N*-(2-(6-valerylamidopyridyl))4-aminocarbonylphenyl)-10,20-bis(pentafluorophenyl)porphyrinato] ruthenium(II) (1a)**

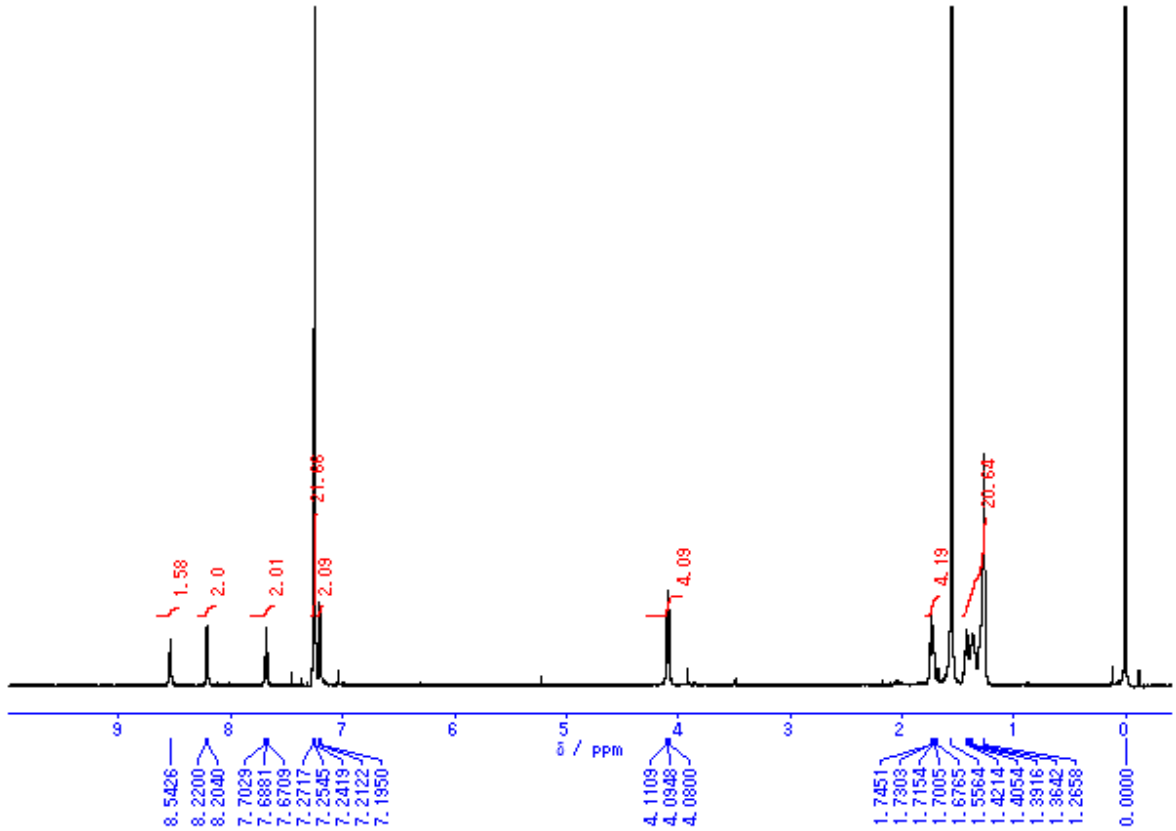
A solution of **6a** (5.4 mg, 3.9 μmol) in CH_3CN was irradiated with ultraviolet by using high-pressure mercury lamp (400 W) for 4 h under Ar. Evaporation of the solvent and purification by reprecipitation form CH_2Cl_2/hexane afforded a red solid of **1a** (3.8 mg, 68%): ^{1}H-NMR (500 MHz, CD_3CN) δ 9.12 (s, 2H), 8.50 (s, 2H), 8.40-8.38 (m, 8H), 8.31-8.27 (m, 8H), 8.12 (d, J = 7.9 Hz, 2H), 7.96 (d, J = 8.2 Hz, 2H), 7.86 (t, J = 8.1 Hz, 2H), 2.44 (t, J = 7.4 Hz, 4H), 1.69-1.66 (m, 4H), 1.43-1.38 (m, 4H), 0.96 (t, J = 7.4 Hz, 6H), -0.091 (s, 6H) ; ESI-HRMS Calcd for $C_{70}H_{51}F_{10}N_{12}O_4Ru$ $[M+H]^+$:1415.3040, Found: 1415.3010.

***trans*-Diacetonitrile[5,15-bis(4-(*N,N*-diisopropylaminocarbonylphenyl))-10,20-bis(pentafluorophenyl)porphyrinato] ruthenium(II) (1b)**

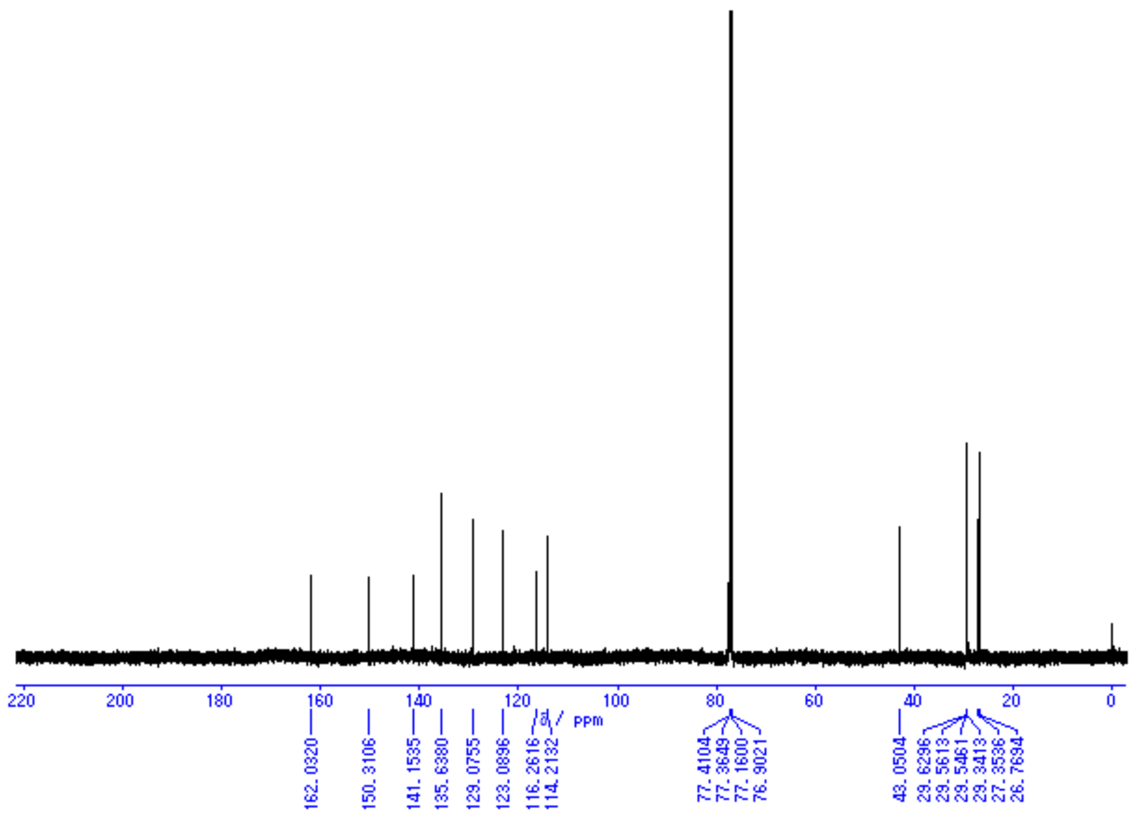
A solution of **6b** (4.0 mg, 3.4 μmol) in CH_3CN was irradiated with ultraviolet by using high-pressure mercury lamp (400 W) for 4 h under Ar. Evaporation of the solvent and purification by re-precipitation form CH_2Cl_2/hexane afforded a red solid of **1b** (2.4 mg, 57%):^{1}H-NMR (500 MHz, CD_3CN) δ 8.41 (d, J = 4.9 Hz, 4H), 8.38 (d, J = 4.9 Hz, 4H), 8.18 (d, J = 7.9 Hz, 4H), 7.64 (d, J = 7.9 Hz, 4H), 4.25 (brs, 2H), 3.72 (brs, 2H), 1.60 (brs, 12H), 1.35 (brs, 12H), -0.11 (s, 6H) ; ESI-HRMS Calcd for $C_{62}H_{50}F_{10}N_6O_2Ru$ $[M]^+$:1230.2941, Found: 1230.2961

5. NMR Spectra

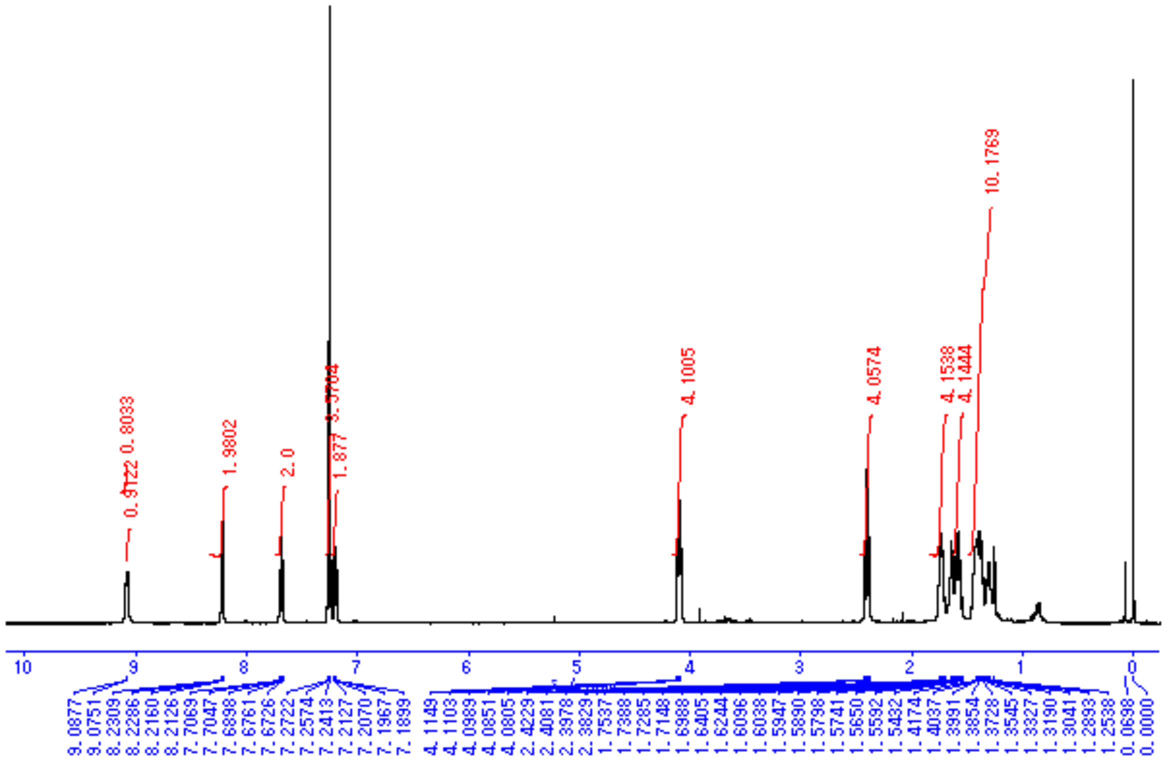
^{1}H-NMR of **7** ($CDCl_3$)



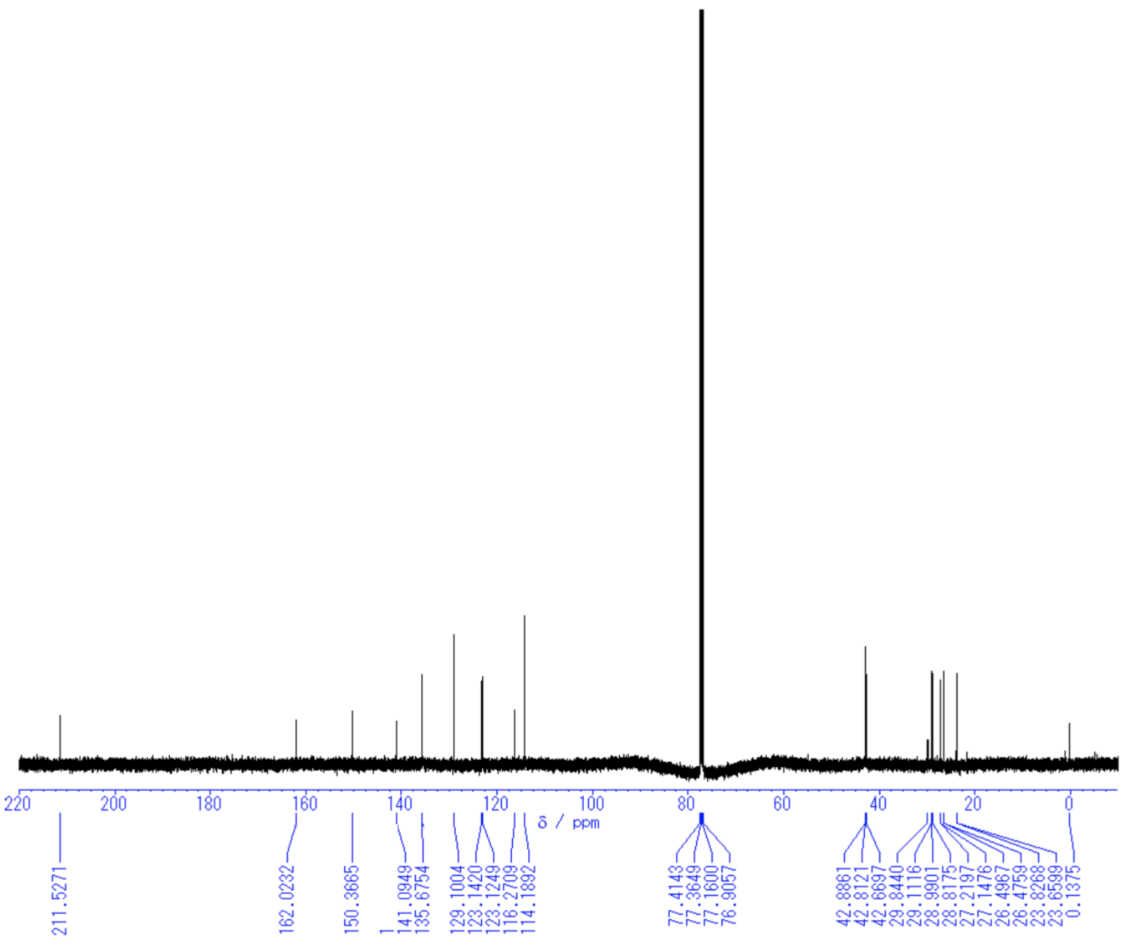
^{13}C-NMR of **7** ($CDCl_3$)



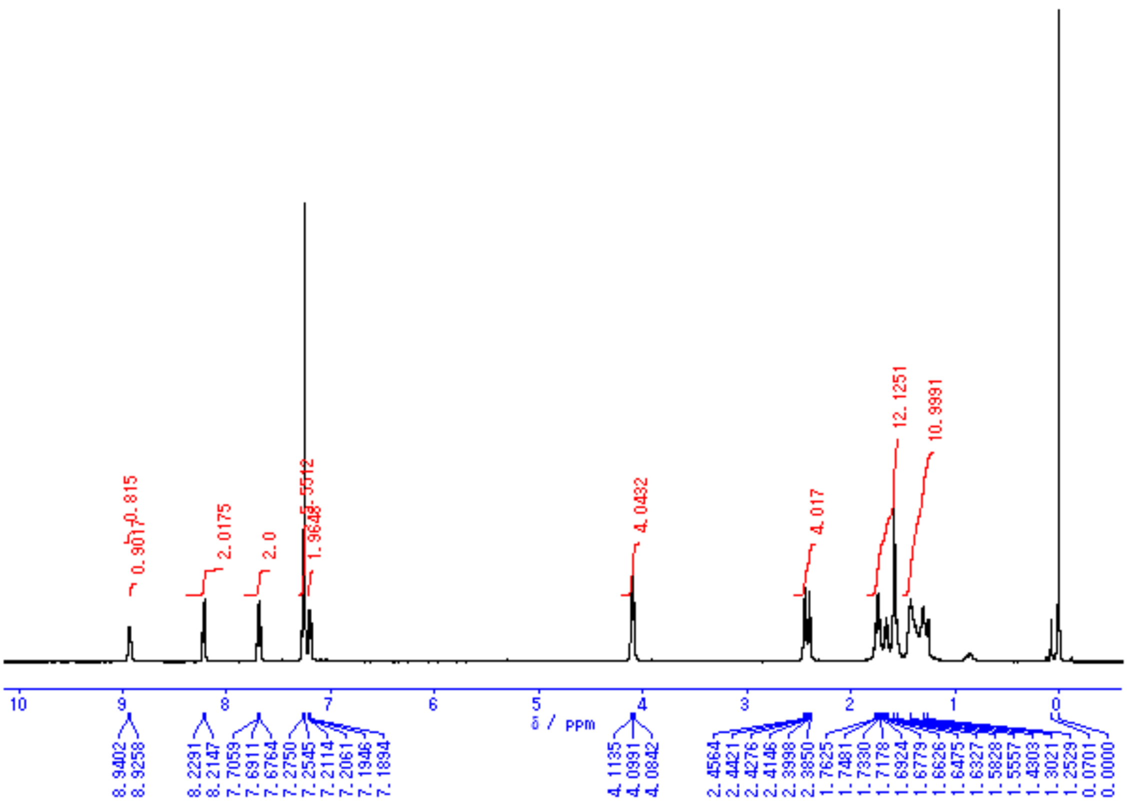
[1]H-NMR of **8** ($CDCl_3$)



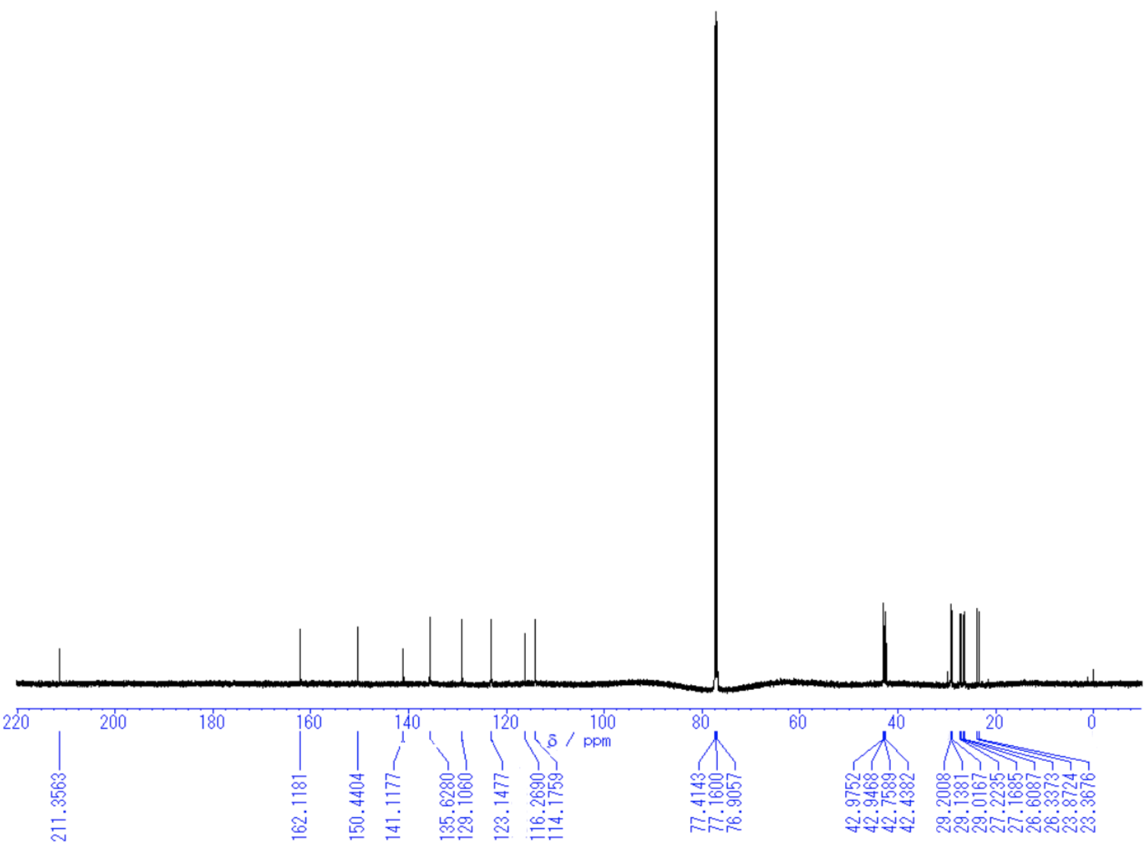
[13]C-NMR of **8** ($CDCl_3$)



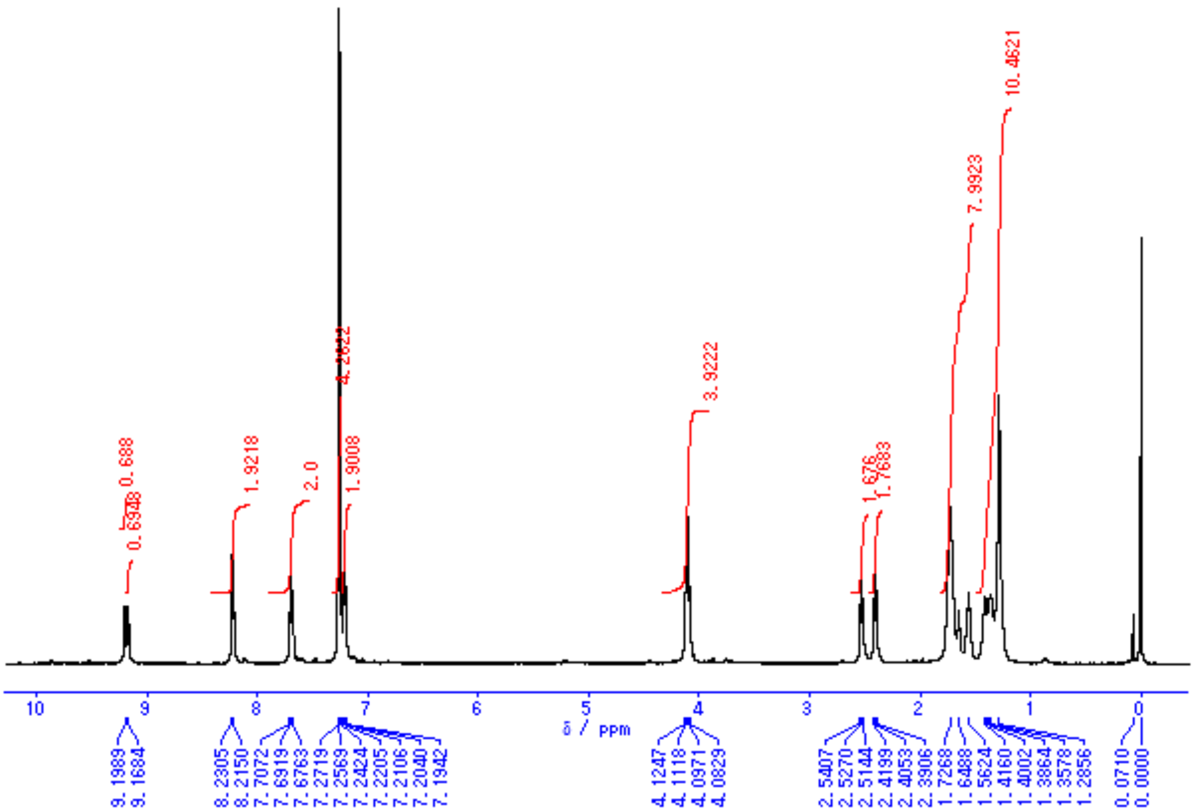
[1]H-NMR of **9** ($CDCl_3$)



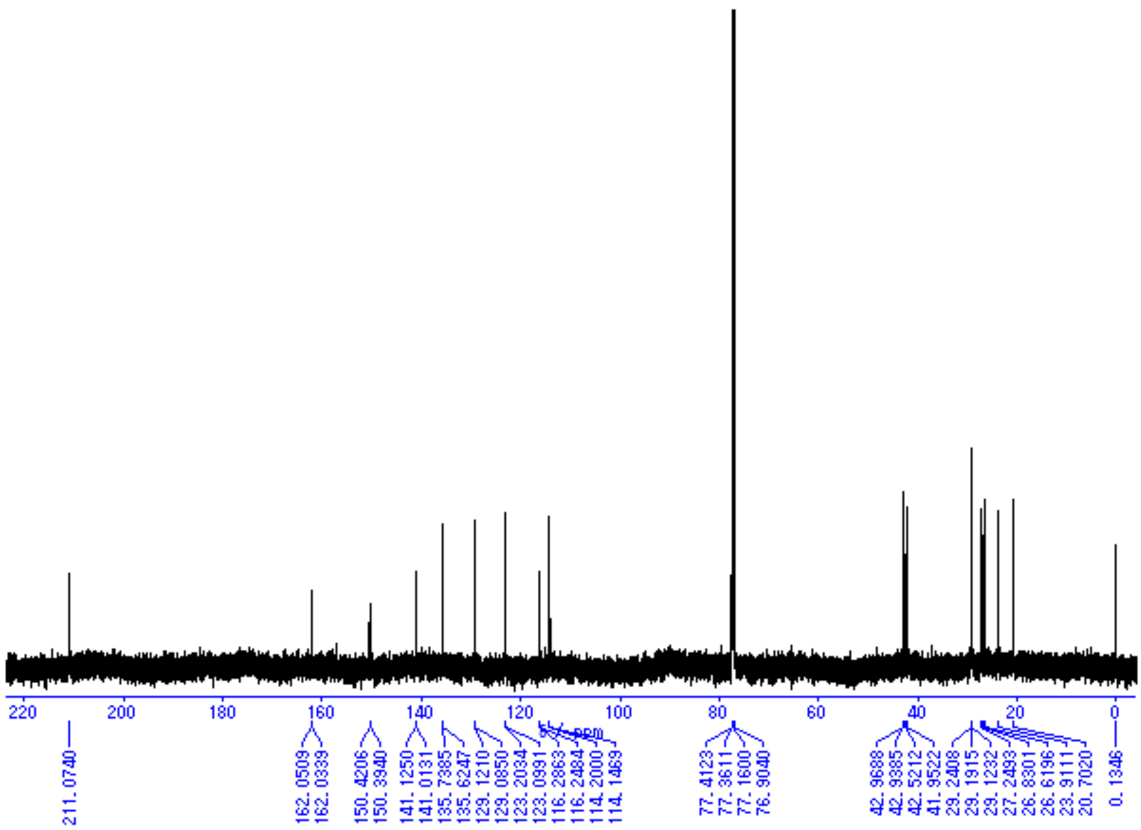
[13]C-NMR of **9** ($CDCl_3$)



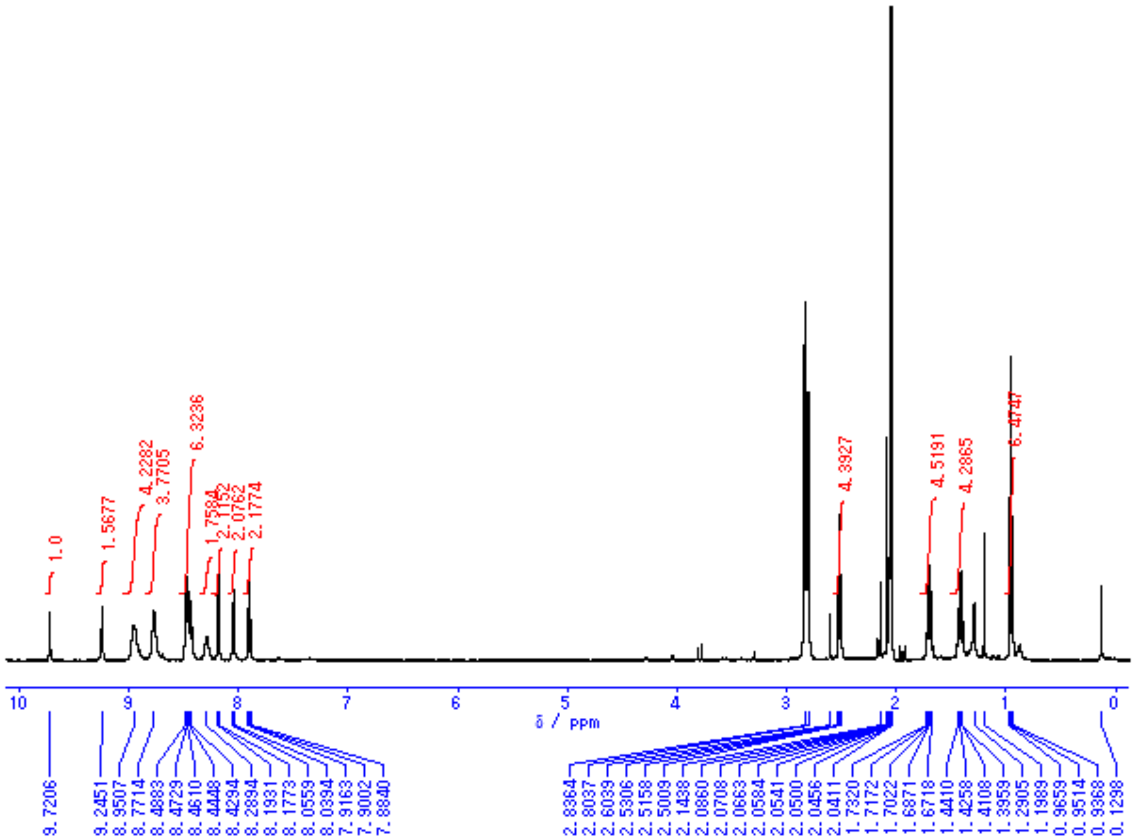
^{1}H-NMR of **10** ($CDCl_3$)



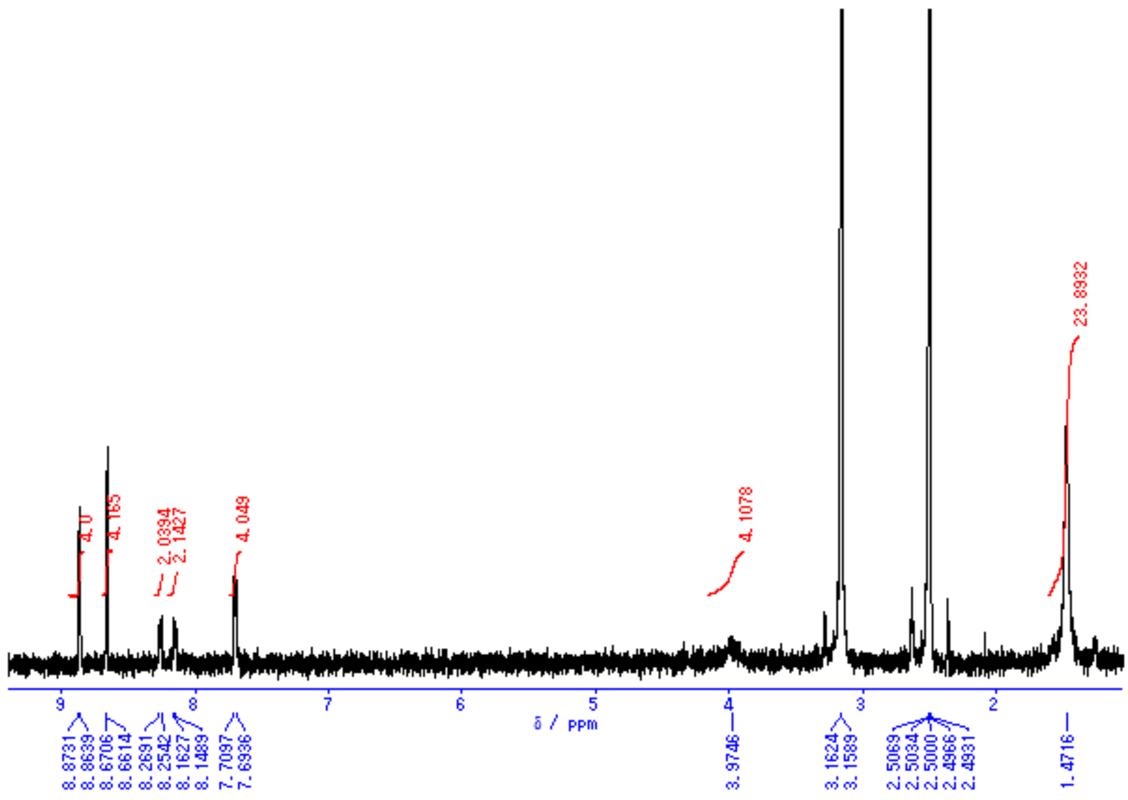
^{13}C-NMR of **10** ($CDCl_3$)



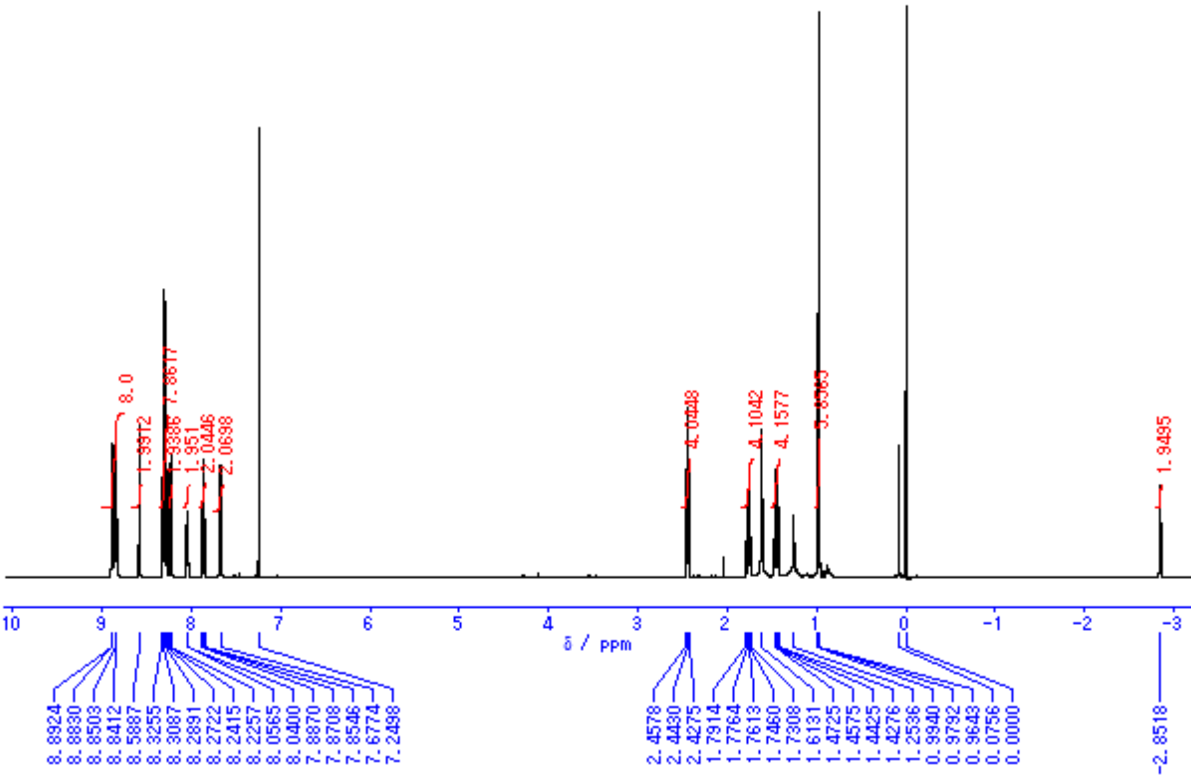
[1]H-NMR of **6a** (acetone-d_6)



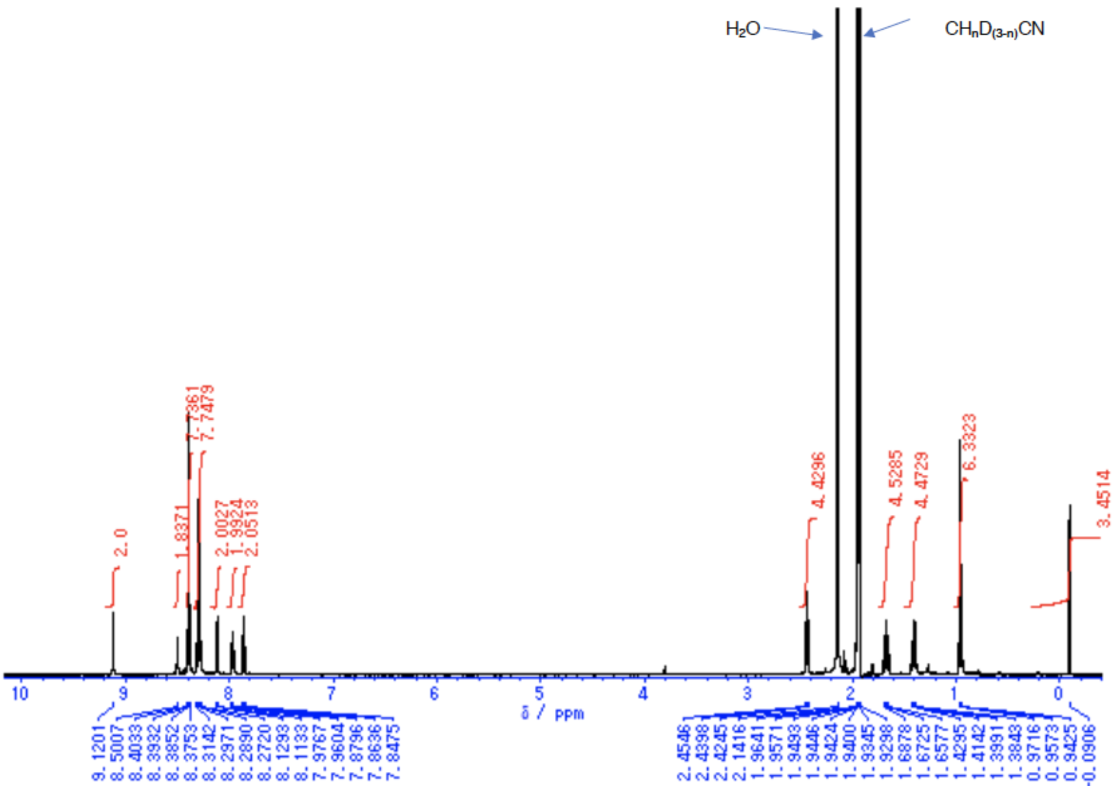
[1]H-NMR of **6b** (DMSO-d_6)



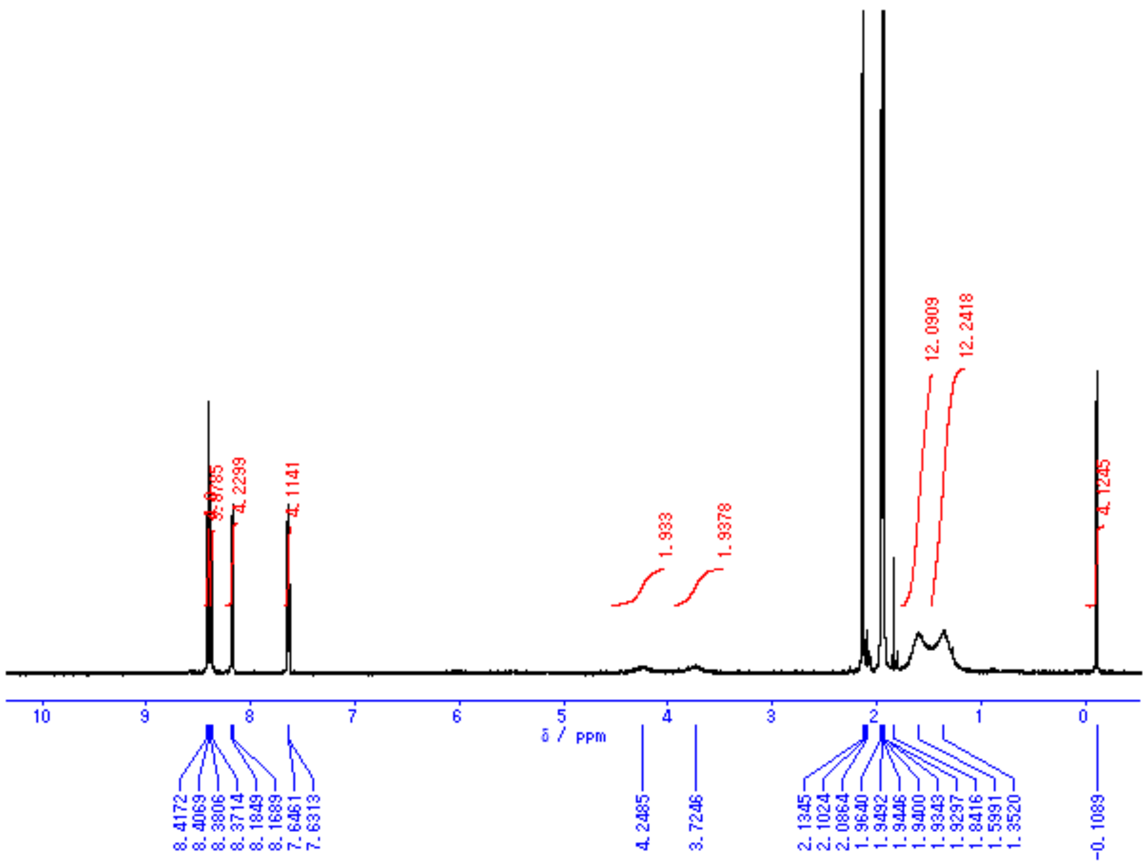
^{1}H-NMR of **1a'** ($CDCl_3$)



^{1}H-NMR of **1a** (CD_3CN)



[1]H-NMR of **1b** (CD_3CN)



6. NOESY Spectrum of the 1:1 Complex of the Porphyrin **1a'** with Substrate **7** in $CDCl_3$

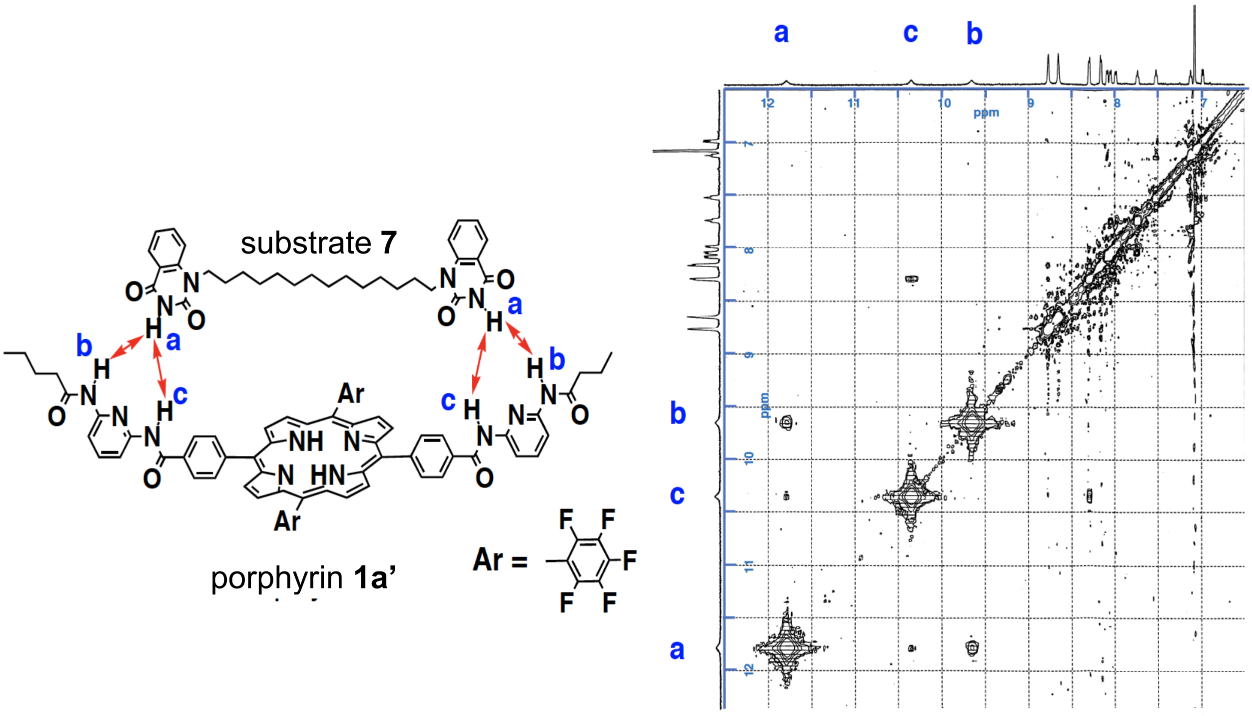


Figure S1

7. [1]H NMR Spectra of Substrate **7** in the Presence of **1a’** (1.0 equiv.) (below) and in the Absence of **1a’** (above) in $CDCl_3$ at 50˚C.

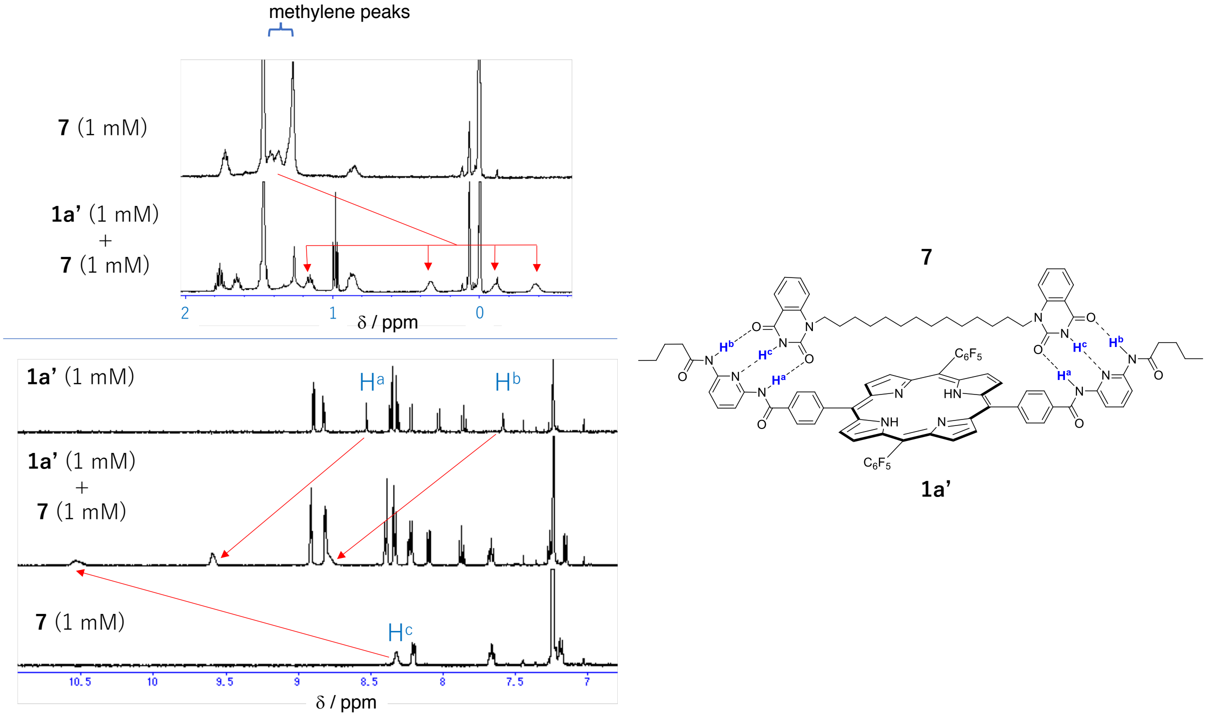


Figure S2. [1]H NMR spectra of substrate **7** in the presence of **1a’** (1.0 equiv.) (below) and in the absence of **1a’** (above) in $CDCl_3$ at 50˚C.

8. [1]H NMR Spectra of the Complex between **1a’** and **7** at Low Temperature

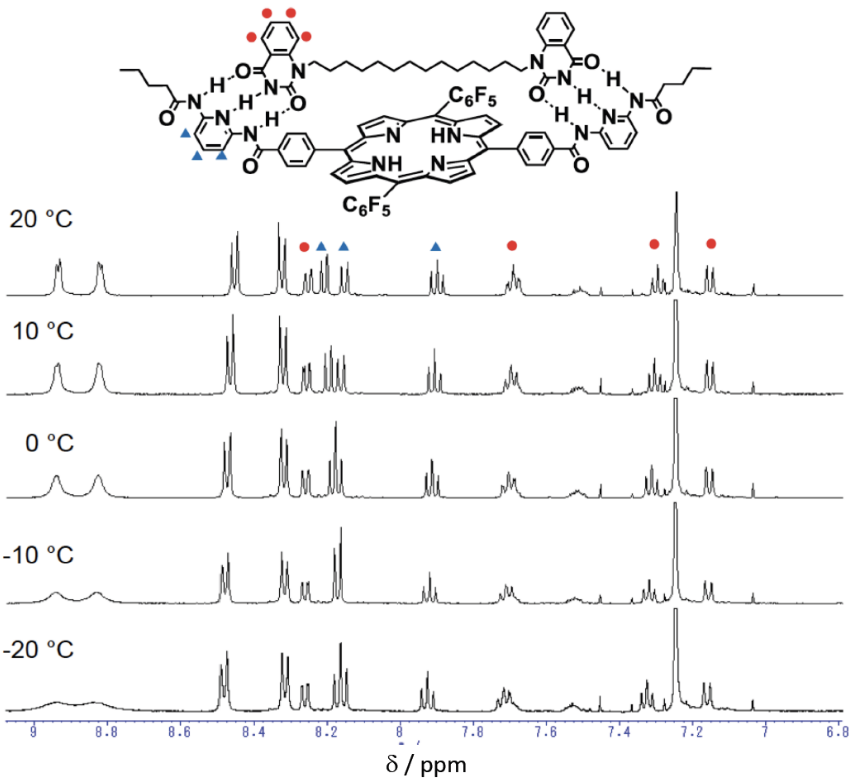


Figure S3. ^{1}H NMR spectra of complex between **1a’** (1.0 mM) and **7** (1.0 mM) at various temperature including low temperature. Each assigned signal is marked (Blue triangle indicates a proton of the pyridine ring of **1a’**; Red circle indicates a proton of the benzene ring of **7**).

9. ESI-Mass Spectra of **1a’-7** Complex

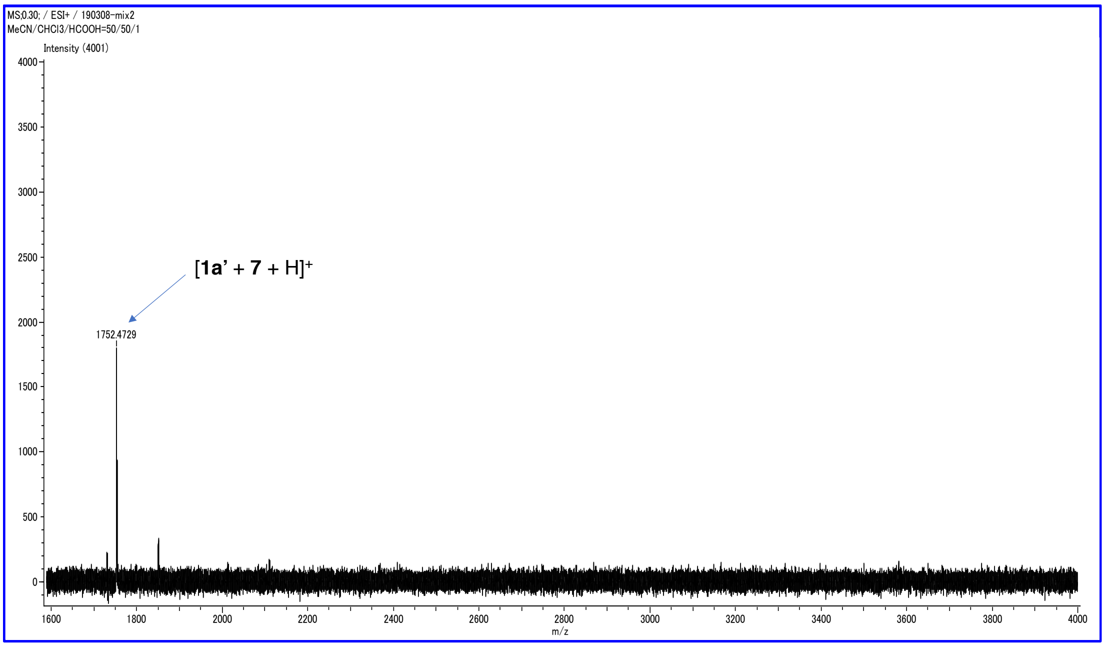


Figure S4. ESI mass spectrum of 1:1 mixture of **1a’** and **7** (0.5 mM) in MeCN-$CHCl_3$-formic acid (50:50:1).

10. Binding Studies of Porphyrin with Substrate by ^{1}H NMR

The ^{1}H NMR binding studies were carried out in $CDCl_3$ at 25˚C. NMR spectrum of the substrates at known concentration in $CDCl_3$ was recorded to obtain chemical shifts of unbound substrates. Then, mixture solutions were prepared as follows: Upfield shifts of the signals for alkane CH_2 protons were monitored at different concentrations of porphyrin.

Porphyrin : substrate (molar ratio)	2.0 mM porphyrin **1a’**	0.5 mM substrate **7**	$CDCl_3$
20:1	0.50 ml (1.0 mM)	0.10 ml (0.05 mM)	0.40 ml
16:1	0.40 ml (0.8 mM	0.10 ml (0.05 mM)	0.50 ml
10:1	0.25 ml (0.5 mM)	0.10 ml (0.05 mM)	0.65 ml

The binding constants were measured by using equation (1) where Δ = chemical-shift change induced by porphyrin **1a'** at concentration [P], [P] = formal porphyrin **1a'** concentration, K = equilibrium constant for the formation of 1 : 1 complex between substrate and porphyrin **1a'**, Δc = chemical-shift difference between the substrate resonance in the unbound state and the state in which it is totally in the form of a 1 : 1 complex.

$$1/\Delta = 1/K\bullet\Delta c\bullet[P] + 1/\Delta c \qquad (1)$$

11. Conformer Optimisation of **1a** (*trans*-dioxo form) – Substrate **7** Complex by Calculation

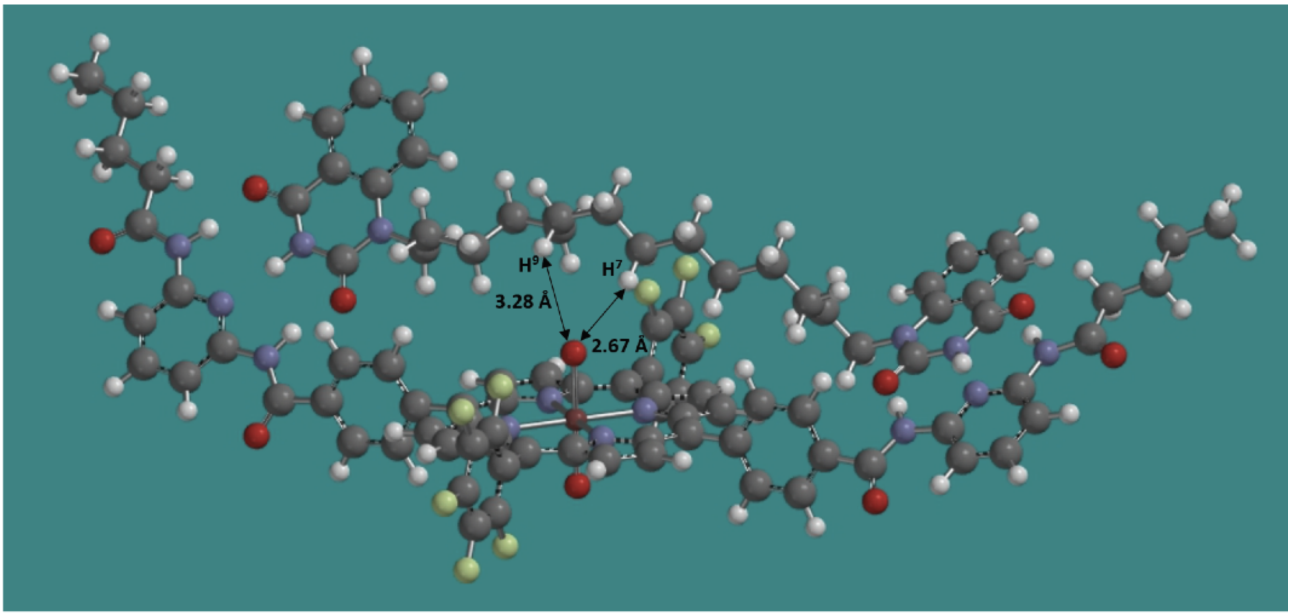
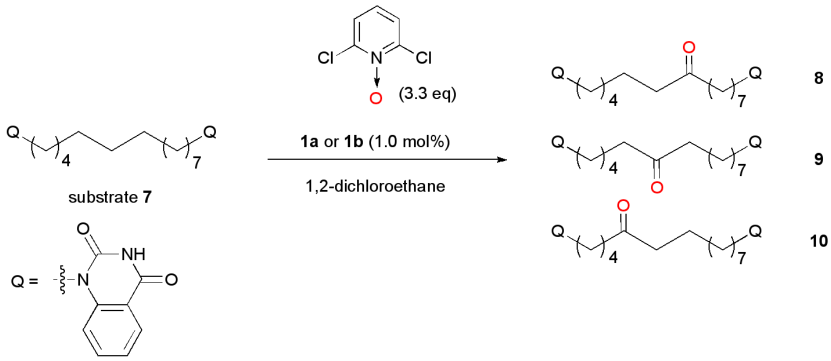


Figure S5. Optimised conformer of **1a** (*trans*-dioxo form) – Substrate **7** complex obtained by equilibrium conformer analysis (MMFF, SPARTAN'18). The shown conformer had the lowest energy among possible 7569 conformers.

12. Oxidation of Substrate **7** with 2,6-dichloropyridine *N*-oxide / Ru porphyrin system and the HPLC Analysis Method

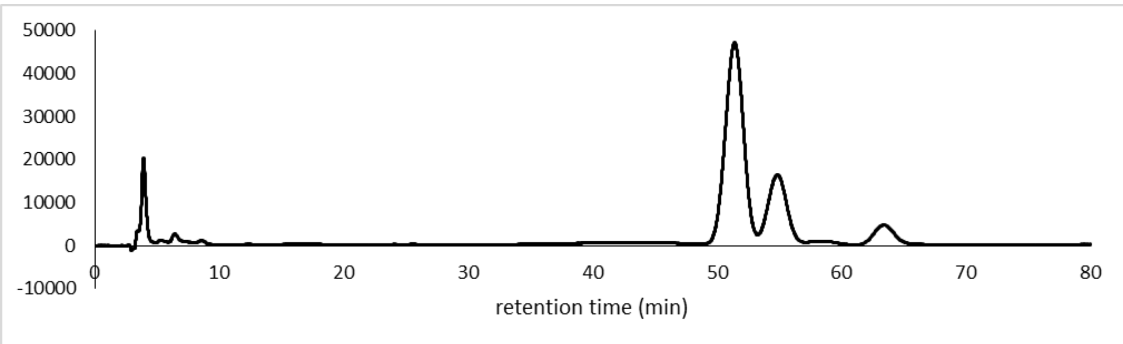


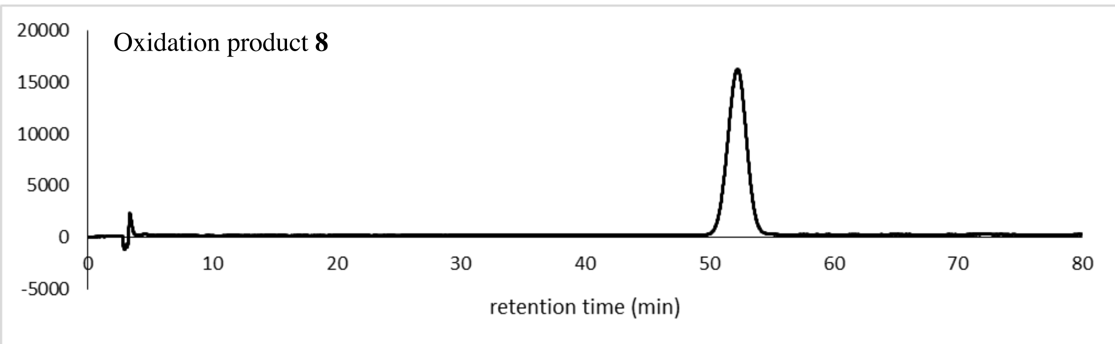
A typical procedure for oxidation of substrate **7** (Table 1) is as follows: A solution of substrate (3.0 μmol), 2,6-dichloropyridine *N*-oxide (10 μmol), and catalyst **1a** (0.03 μmol) in 1,2-dichloroethane (1.5 ml) was stirred at 50 ˚C under Ar for 24 h. A solution passed through SiO_2, and eluates from the column with more CH_2Cl_2 : AcOEt = 1 : 1 solution was evaporated. The residue was dissolved in MeOH (4 ml), and analysed by HPLC.

13. Quantification of Oxidation Products by using HPLC

Regioisomers of the oxidation products **8** (7-oxo, 6-oxo, 5-oxo) were successfully separated by HPLC (ODS-18 Reversed-phase system; eluent 20 mM KH_2PO_4 aqueous : MeOH = 35 : 65 (flow-rate 1.0 ml/min, UV detection: 315 nm)) (Figure S2). Each yield of the products in Table 1 was determined by using the HPLC analysis.

Reaction mixture





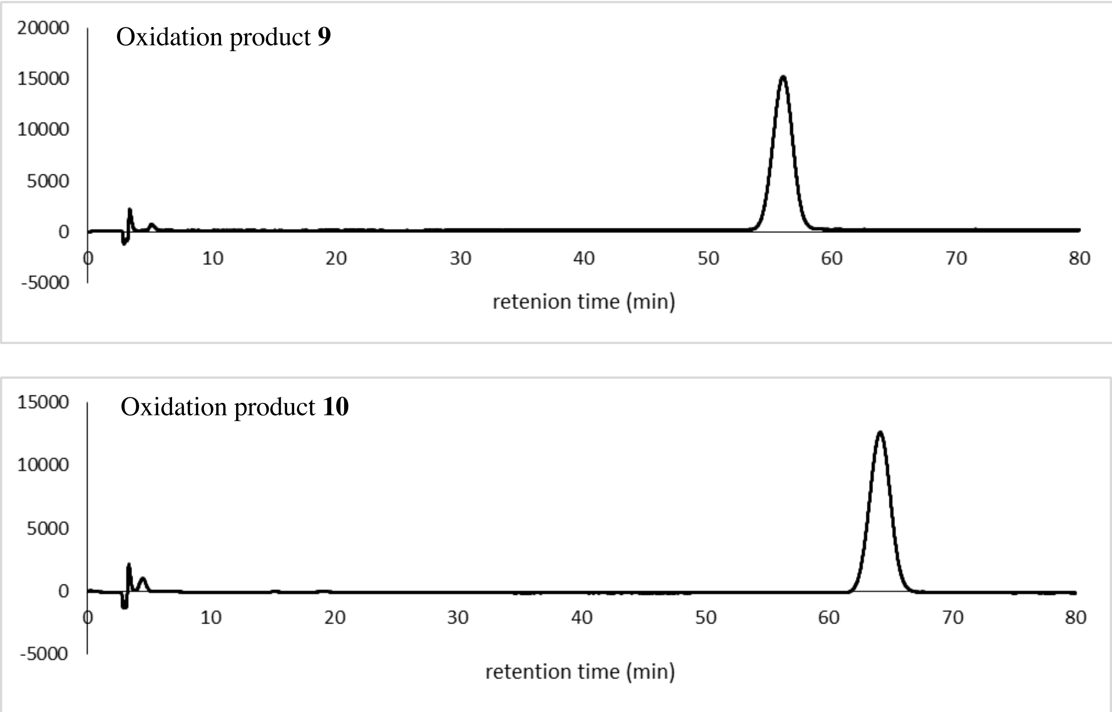


Figure S6

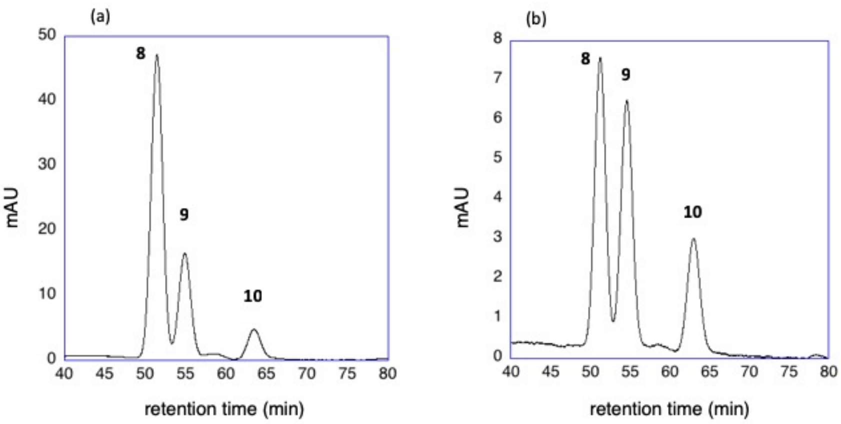


Figure S7. HPLC Profiles of oxidation products. (a) HPLC Profile of the reaction mixture obtained by the reaction (Entry 1 in Table 1, catalyst: **1a**). (b) HPLC Profile of the reaction mixture obtained by the reaction (Entry 5 in Table 1, catalyst: **1b**).

Calibration curve of **8**, **9** and **10**

Solutions of **8** (0.25 mg/ml, 0.125 mg/ml and 0.0625 mg/ml), **9** or **10** (0.05 mg/ml, 0.025 mg/ml and 0.0125 mg/ml) in MeOH were prepared. The solutions were analyzed by HPLC, and each of the peak area was determined. The calibration curve was obtained by plotting the concentration versus the peak area.

[Conditions of HPLC]

Column: Inertsil ODS-3 (5μm, 4.6 × 250 mm)

Eluent: 20 mM KH_2PO_4 aqueous : MeOH = 35 : 65

Flow rate: 1.0 ml/min

UV detection: 315 nm

Injection volume: 50 μl

[calibration curve]

8: $y = 3.55 \times 10^{-8} x + 9.42 \times 10^{-5}$

9: $y = 2.63 \times 10^{-8} x + 5.23 \times 10^{-4}$

10: $y = 3.65 \times 10^{-8} x + 1.03 \times 10^{-3}$

(x: peak area, y: concentration)

We quantified the products **8**, **9**, **10** by using the above obtained equations.

14. ^{1}H NMR Chart of Products in the Oxidation of *n*-Tetradecane Catalyzed by **1a**

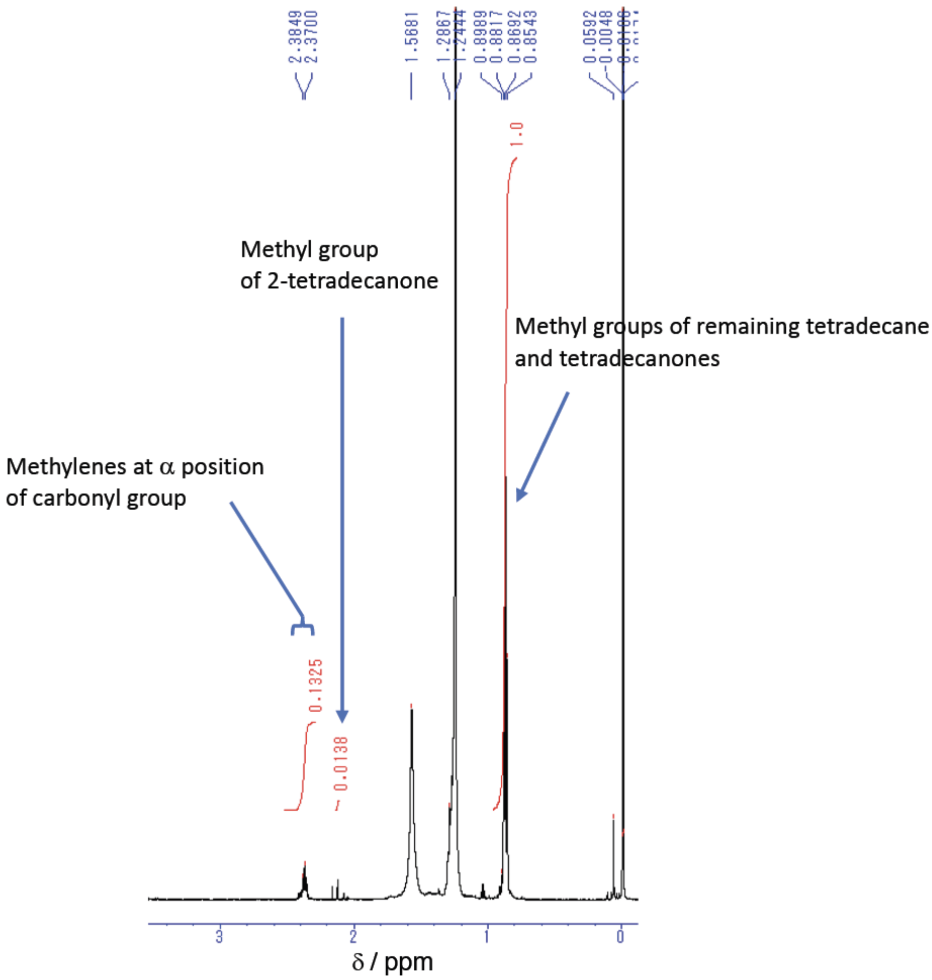


Figure S8. ^{1}H NMR Chart of products in the oxidation of n-tetradecane with 2,6-dichloropyridine *N*-oxide catalyzed by **1a**

Procedure: A solution of *n*-tetradecane (0.78 µl, 3.0 µmol), 2,6-dichloropyridine *N*-oxide (1.7 mg, 10 µmol), and catalyst **1a** (40 µg, 0.030 µmol) in 1,2-dichloroethane (1.5 ml) was stirred at 50 ˚C under Ar for 24 h. After removal of the solvent, the residue was dissolved in $CDCl_3$ and its ^{1}H NMR spectrum was observed. The yield of tetradecanones was 20%. The peaks used for the yield calculation were as follows:

Remaining tetradecane + tetradecanones other than 2-tetradecanone: δ 0.78-0.95 as methyl groups

total methylene and methyl protons at α position of carbonyls: δ 2.34-2.43 (methylenes) and δ 2.13 (methyl of 2-tetradecanone)

15. GC-MS Analysis of Products in the Oxidation of *n*-Tetradecane Catalyzed by **1a**

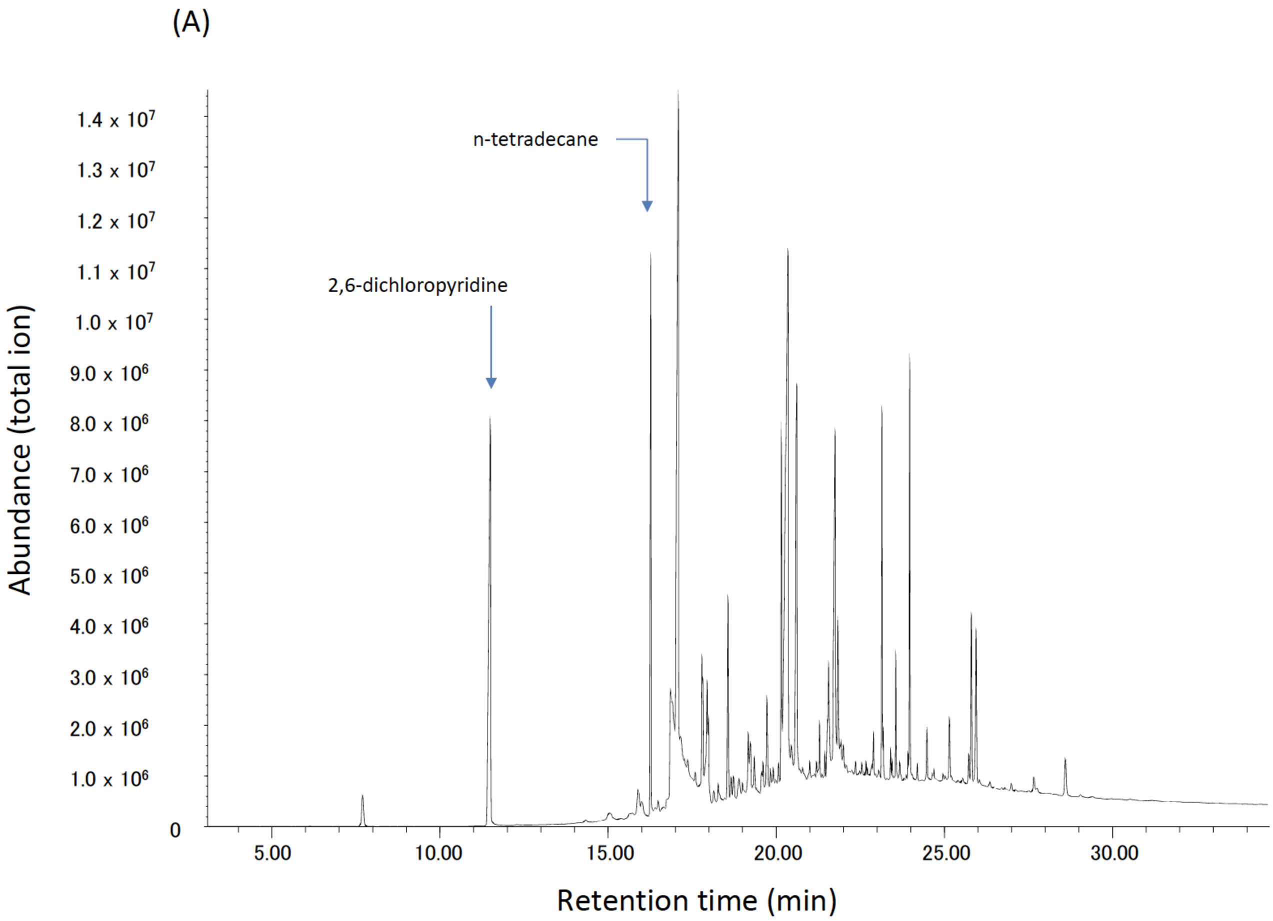


Figure S9A. Total ion chromatogram of the reaction mixture in the oxidation of *n*-tetradecane catalyzed by **1a**. The used column: HP-5 (19091J-413), 30 m × 0.320 mm, 0.25 Micron. Conditions; 60 °C 10 min keeping, then 15 °C/min to 280 °C rising, and then 10 min keeping at 280 °C).

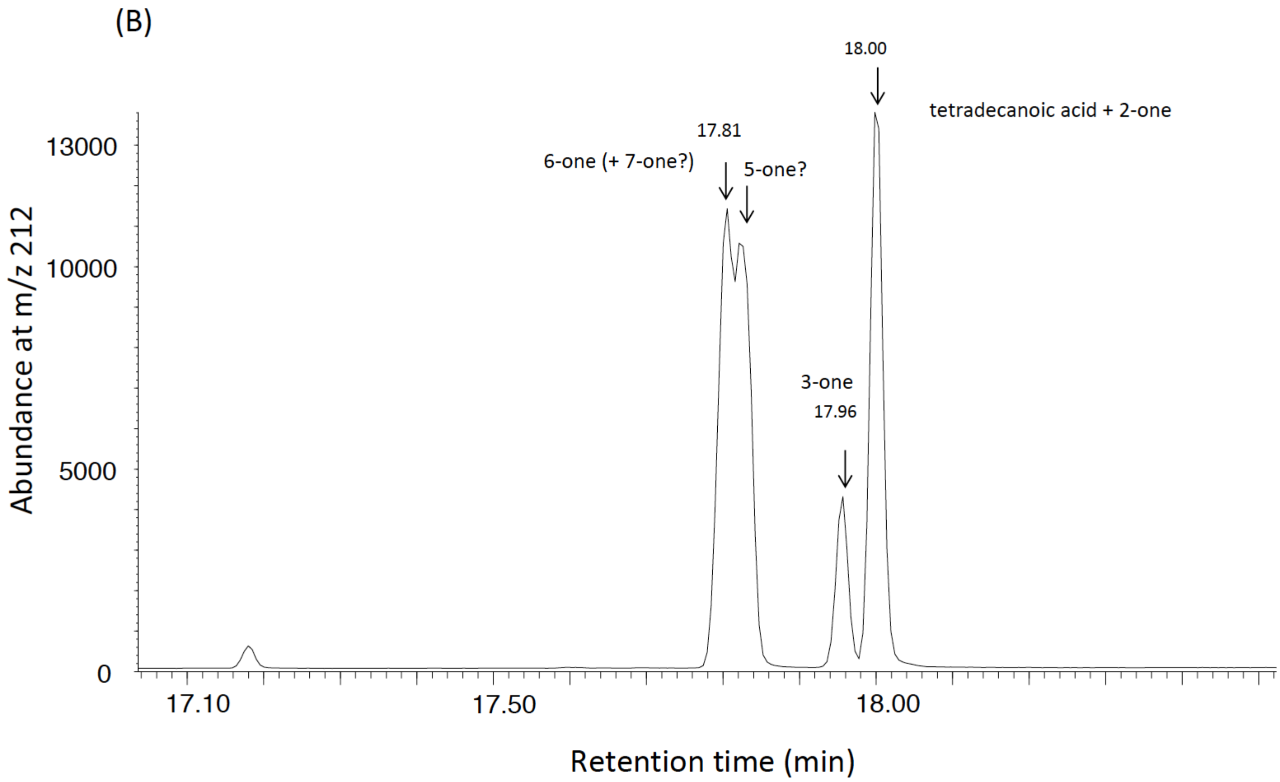


Figure S9B. Single ion monitor (m/z 212) of the reaction mixture in the oxidation of *n*-tetradecane catalyzed by **1a**. Each product was deduced from its known mass spectral pattern. The used column and conditions are same as described in Figure S9A. There was no known mass spectral data in the case of 5-tetradecanone (5-one).

16. Time Course of the Catalytic Oxidation of **7** by **1a** or **1b**

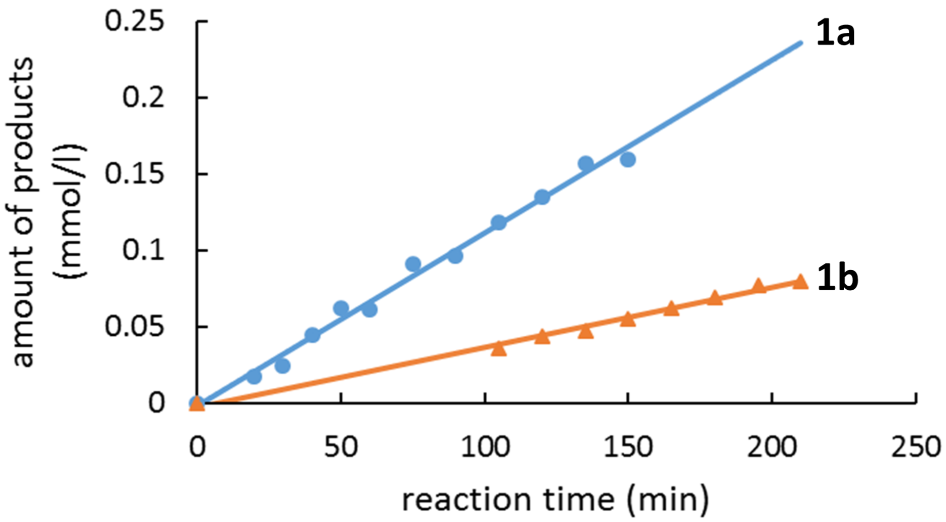


Figure S10

A typical procedure for Figure S8 (Figure 3 in main text) as follows: A solution of substrate **7** (1.0 μmol) and 2,6-dichloropyridine *N*-oxide (3.3 μmol) in $ClCD_2CD_2Cl$ (0.45 ml) was degassed for 2 min with Ar in an NMR tube. Catalyst **1a** or **1b** (0.010 μmol) in $ClCD_2CD_2Cl$ (0.05 ml) was added, and the mixture was kept at 40 ˚C. NMR spectra of reaction mixture were repeatedly recorded to determine the yield of products. The peaks used for the yield calculation were as follows:

Remaining substrate **7** + products (mixture of **7**, **8**, **9** and **10**): δ 4.15-4.08 (m, 4H)

Products (mixture of **8**, **9**, **10**): δ 2.53-2.38 (m, 4H)

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