Supplementary Materials

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

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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). ¹H-NMR and ¹³C-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, benzoyleuneurea, 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. Cs₂CO₃, KH₂PO₄, 1-bromo-4-chlorobutane and 4-N,N-dimethylaminopyridine were purchased from Wako. LiOH·H₂O, K₂CO₃, 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. Ru₃CO₁₂ was purchased from Strem Chemicals. Tetrahydrofuran was dehydrated and stabilizer free, and it was purchased from Kanto Chemical. Pyrrole, disopropylamine and 1,2-dichloroethane were distilled, and 2,6-diaminopyridine were purified by column chromatography (SiO₂, MeOH/CH₂Cl₂=1/9). Other reagents and solvents were used without purification.

2. Synthesis of Substrate 7

1,14-tetradecanediol
The product was synthesised by reported literature⁴¹ 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 Et₂O (30 ml × 3). The combined organic layers were washed with saturated NaHCO₃ aqueous (60 ml), 1 M Na₂S₂O₃ aqueous (60 ml) and saturated NaCl aqueous (60 ml), and dried over Na₂SO₄. 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 literature⁴².

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

S2
To a slurry of Benzoylencurea (1.43 g, 8.82 mmol) and K$_2$CO$_3$ (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$_2$Cl$_2$ (50 ml × 3). The combined organic layers were dried over Na$_2$SO$_4$. Evaporation of the solvent and purification by column chromatography (SiO$_2$, AcOEt/CH$_2$Cl$_2$ = 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.$^3$

MPM-7
A slurry of 3-(4-methoxybenzyl)quinazolin-2,4-dione (0.32 g, 1.1 mmol), Cs$_2$CO$_3$ (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$_2$Cl$_2$ (10 ml × 3). The combined organic layers were washed with saturated NaCl aqueous (10 ml) and dried over Na$_2$SO$_4$. 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$_4$Na$_1$O$_6$ [M+Na]$^+$: 781.3941, Found: 781.3925

Substrate 7
To a solution of MPM-7 (0.26 g, 0.34 mmol) in CH₃CN (2.5 ml), CH₂Cl₂ (2.5 ml) and H₂O (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 H₂O and then extracted with CH₂Cl₂ (20 ml × 3). The combined organic layers were washed with saturated NaCl aqueous and dried over Na₂SO₄. Evaporation of the solvent and purification by column chromatography (SiO₂, AcOEt/hexane = 2/3) afforded a white solid of 7 (0.096 g, 53 %): IR (film) ν 1700, 1608 cm⁻¹; ¹H-NMR (500 MHz, CDCl₃) 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); ¹³C-NMR (125 MHz, CDCl₃) δ 162.0, 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 C₃₀H₃₈N₄Na₁O₄ [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 literature²⁴ procedure about similar product 1-bromo-8-chlorooctane. The compound data was consistent with that of reported literature²⁵.

1-bromo-8-chlorooctane
The product was synthesised by reported literature²⁴ 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 CH₂Cl₂ (10 ml × 3). The combined organic layers were washed with saturated NaHCO₃ aqueous (10 ml × 2) and saturated NaCl aqueous (10 ml), and dried over Na₂SO₄. Evaporation of the solvent and purification by column chromatography (SiO₂, CH₂Cl₂/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; ¹H-NMR (500 MHz, CDCl₃) 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); ¹³C-NMR (125 MHz, CDCl₃) δ 47.6, 45.1, 35.4, 32.6, 30.5, 29.0, 28.6, 26.7, 26.5, 26.0; MS (FAB) 253
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; ¹H-NMR (500 MHz, CDCl₃) 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); ¹³C-NMR (125 MHz, CDCl₃) 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 C₁₁H₂₁ClS₂ [M⁺]: 252.0773, Found: 252.0775.

2-(1-Chlorooctyl)-2-(1-chlorohexyl)-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; ¹H-NMR (500 MHz, CDCl₃) 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); ¹³C-NMR (125 MHz, CDCl₃) 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 C₁₁H₂₁ClS₂ [M⁺]: 252.0773, Found: 252.0775.

2-(1-Chlorooctyl)-2-(1-chloropentyl)-1,3-dithiane
This compound was prepared from 2-(1-chlorooctyl)-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; ¹H-NMR (500 MHz, CDCl₃) 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); ¹³C-NMR (125 MHz, CDCl₃) 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 C₁₁H₂₁ClS₂ [M⁺]: 252.0773, Found: 252.0775.

2-(1-Chloropeptyl)-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; ¹H-NMR (500 MHz, CDCl₃) 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); ¹³C-NMR (125 MHz, CDCl₃) 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 C₁₁H₂₁ClS₂ [M⁺]: 252.0773, Found: 252.0775.
A slurry of 3-(4-methoxybenzyl)quinazolin-2,4-dione (0.13 g, 0.46 mmol), Cs₂CO₃ (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 CH₂Cl₂ (10 ml × 3). The combined organic layers were washed with saturated NaCl aqueous (10 ml) and dried over Na₂SO₄. Evaporation of the solvent and purification by column chromatography (SiO₂, AcOEt/CH₂Cl₂ = 1/10) afforded a white solid of DM-8 (0.079 g, 46 %); IR (film) ν 1747, 1597, 1509 cm⁻¹; ¹H-NMR (500 MHz, CDCl₃) 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); ¹³C-NMR (125 MHz, CDCl₃) δ 161.6, 161.5, 158.9, 150.6, 139.6, 134.9, 130.5, 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 C₄₉H₅₉N₄O₆S₂ [M+H]⁺: 863.3876, Found: 863.3868.

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; ¹H-NMR (500 MHz, CDCl₃) 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); ¹³C-NMR (125 MHz, CDCl₃) 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, 129.0, 127.9, 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
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 CH₂Cl₂ (10 ml × 3). The combined organic layers were washed with saturated NaHCO₃ aqueous (10 ml × 2) and saturated NaCl aqueous (10 ml), and dried over Na₂SO₄. Evaporation of the solvent and purification by column chromatography (SiO₂, CH₂Cl₂/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 CH₂Cl₂ (10 ml × 3). The combined organic layers were washed with saturated NaHCO₃ aqueous (10 ml × 2) and saturated NaCl aqueous (10 ml), and dried over Na₂SO₄. Evaporation of the solvent and purification by column chromatography (SiO₂, CH₂Cl₂/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), Cs₂CO₃ (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 CH₂Cl₂ (10 ml × 3). The combined organic layers were washed with saturated NaCl aqueous (10 ml) and dried over Na₂SO₄. Evaporation of the solvent and purification by column chromatography (SiO₂, AcOEt/CH₂Cl₂ = 1/10) afforded a white solid of DM-10 (49 mg, 11 % (3 steps)); IR (KBr) ν 1703, 1658, 1609 cm⁻¹; ¹H-NMR (500 MHz, CDCl₃) 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), 5.12-5.07 (m, 4H), 3.75 (s, 6H), 2.81-2.79 (m, 4H), 1.95-1.72 (m, 10H), 1.42-1.25 (m, 14H); ¹³C-NMR (125 MHz, CDCl₃) 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,

**MPM-8**

To a solution of **DM-8** (79 mg, 92 µmol) in CH₃CN (0.7 ml), CH₂Cl₂ (0.7 ml) and H₂O (0.1 ml) was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (31 mg, 0.14 mmol) in CH₃CN (0.2 ml) under Ar. After being stirred overnight at room temperature, the solution was poured into saturated NaHCO₃ aqueous (10 ml) and then extracted with CH₂Cl₂ (10 ml × 3). The combined organic layers were washed with saturated NaCl aqueous (10 ml), and dried over Na₂SO₄. Evaporation of the solvent and purification by column chromatography (SiO₂, AcOEt/CH₂Cl₂ = 1/10) afforded a white solid of **MPM-8** (49 mg, 69 %); IR (film) ν 1703, 1657, 1610 cm⁻¹; ¹H-NMR (500 MHz, CDCl₃) 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); ¹³C-NMR (125 MHz, CDCl₃) 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 C₄₆H₅₃N₄O₇ [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, CDCl₃) 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); ¹³C-NMR (125 MHz, CDCl₃) δ 211.0, 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 C₄₆H₅₃N₄O₇ [M+H]⁺: 773.3914, Found: 773.3908.
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, 42.4, 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 Calc'd for C_{46}H_{53}N_{4}O_{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) v 1702, 1657, 1609 cm⁻¹; ¹H-NMR (500 MHz, CDCl₃) 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); ¹³C-NMR (125 MHz, CDCl₃) 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 Calc'd for C_{46}H_{52}N_{4}O_{7}Na [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) v 1701, 1608 cm⁻¹; ¹H-NMR (500MHz, CDCl₃) 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); ¹³C-NMR (125 MHz, CDCl₃) 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 Calc'd for C_{30}H_{37}N_{4}O_{5} [M+H]+: 533.2764, Found: 533.2770.
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); \(^1\)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\(_4\)O\(_5\) [M+H]\(^+\): 533.2764, Found: 533.2749.

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); \(^1\)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\(_4\)O\(_5\)Na [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\(^{56}\) procedure.
5,15-Bis(4-methoxycarbonylphenyl)-10,20-bis(pentafluorophenyl)porphyrin (2)
The product was synthesised according to the reported literature 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·H2O (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 (10 ml). The organic phase was washed with 0.1 M HCl aqueous (15 ml) and saturated NaCl aqueous (10 ml). The organic layer was dried over Na2SO4 and evaporated. The residue was suspended in CHCl3 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 Na2SO4. 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, ¹H-NMR (500 MHz, CDCl₃) 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 C₆₆H₄₆F₁₈N₁₀O₄Na [M+Na]⁺:1255.3442, Found: 1255.3440; UV-vis (CH₂Cl₂) λ_max (ε) 416 nm (4.54 x 10⁴), 511 nm (2.73 x 10⁴);

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(CO)₃Cl₂ (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 Al₂O₃. The eluates from the column was evaporated, and purified by column chromatography (SiO₂, CH₂Cl₂/MeOH = 200/1) and recrystallised from CH₂Cl₂/hexane to afford a red solid of 3 (0.10 g, 69 %); IR (KBr) ν 1955, 1723, 1279 cm⁻¹; ¹H-NMR (500 MHz, CDCl₃) 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),
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-H₂O (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 Na₂SO₄ and evaporated. The residue was purified by column chromatography (SiO₂, 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; ¹H-NMR (500 MHz, DMSO-d₆) 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 10⁴), 526 nm (1.58 x 10⁴); Anal. Calcd for C₅₀H₃₀F₁₀N₄O₇.₅Ru (4 • 0.5n-hexane • 2.5H₂O): 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-valerlamidopyridyl))-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 Na₂SO₄. Evaporation of the solvent and purification by column chromatography (SiO₂, AcOEt/hexane = 1/9-1/1) afforded a red solid of 6a (33 mg, 39%); IR (KBr) ν 1950, 1678 cm⁻¹; ¹H-NMR (500 MHz, acetone-δ₆) 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 C₆₀H₄₅F₁₀N₁₀O₆Ru [M+H]⁺ 1361.2458, Found 1361.2448; UV-Vis (CH₂Cl₂) λ_max (ε) 411 nm (1.83 x 10⁵), 528 nm (1.81x 10⁴), 587 nm (4.28 x 10³). Anal. Calcd for C₆₀H₄₈F₁₀N₁₀O₇Ru (6a • 2H₂O): 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 Na2SO4. Evaporation of the solvent and purification by column chromatography (SiO2, AcOEt/hexane = 1/9-1/1) afforded a red solid of 6b (12 mg, 55 %); IR (KBr) ν 1946, 1609 cm⁻¹; ¹H-NMR (500 MHz, DMSO-d₆, 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 C₅₀H₂₃FN₁₀O₆S₄Ru [M+H]⁺:1177.2437, Found: 1177.2442. UV-Vis (CH₂Cl₂) λ_max (ε) 408 nm (1.65 x 10⁵), 527 nm (1.42x 10⁴).

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

A solution of 6a (5.4 mg, 3.9 µmol) in CH₃CN 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 CH₂Cl₂/hexane afforded a red solid of 1a (3.8 mg, 68%); ¹H-NMR (500 MHz, CD₃CN) 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 C₇₀H₅₁F₁₀N₁₂O₄Ru [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 CH₃CN 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 CH₂Cl₂/hexane afforded a red solid of 1b (2.4 mg, 57%); ¹H-NMR (500 MHz, CD₃CN) 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 C₆₂H₅₀F₁₀N₁₂O₄Ru [M+H]⁺:1230.2941, Found: 1230.2961.

S13
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$_3$CN)
\textsuperscript{1}H-NMR of 1b (CD\textsubscript{3}CN)

6. NOESY Spectrum of the 1:1 Complex of the Porphyrin 1a' with Substrate 7 in CDCl\textsubscript{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](image)

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

![Image of NMR spectra at different temperatures](image)
Figure S3. $^1$H NMR spectra of complex between 1$a'$ (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 1$a'$; Red circle indicates a proton of the benzene ring of 7).

9. ESI-Mass Spectra of 1$a'$-7 Complex

Figure S4. ESI mass spectrum of 1:1 mixture of 1$a'$ 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.

<table>
<thead>
<tr>
<th>Porphyrin : substrate (molar ratio)</th>
<th>2.0 mM porphyrin 1$a'$</th>
<th>0.5 mM substrate 7</th>
<th>CDCl$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20:1</td>
<td>0.50 ml (1.0 mM)</td>
<td>0.10 ml (0.05 mM)</td>
<td>0.40 ml</td>
</tr>
<tr>
<td>16:1</td>
<td>0.40 ml (0.8 mM)</td>
<td>0.10 ml (0.05 mM)</td>
<td>0.50 ml</td>
</tr>
<tr>
<td>10:1</td>
<td>0.25 ml (0.5 mM)</td>
<td>0.10 ml (0.05 mM)</td>
<td>0.65 ml</td>
</tr>
</tbody>
</table>
The binding constants were measured by using equation (1) where $\Delta =$ 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’, $\Delta c =$ 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.

$$\frac{1}{\Delta} = \frac{1}{K \Delta c [P]} + \frac{1}{\Delta c} \quad (1)$$

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

![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.]

**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 SiO₂, and eluates from the column with more CH₂Cl₂ : 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 KH₂PO₄ 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.
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 KH₂PO₄ aqueous : MeOH = 35 : 65
Flow rate: 1.0 ml/min
UV detection: 315 nm
Injection volume: 50 µl

[calibration curve]
8: y = 3.55 × 10⁻⁸ x + 9.42 × 10⁻⁵
9: y = 2.63 × 10⁻⁸ x + 5.23 × 10⁻⁴
10: y = 3.65 × 10⁻⁸ x + 1.03 × 10⁻³
(x: peak area, y: concentration)

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

14. ᵃH 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 CDCl₃ 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 (methylene) 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 \( 1b \)

![Graph showing the 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 \( \mu \)mol) and 2,6-dichloropyridine \( N \)-oxide (3.3 \( \mu \)mol) in CICD\(_2\)CD\(_2\)Cl (0.45 ml) was degassed for 2 min with Ar in an NMR tube. Catalyst \( 1a \) or \( 1b \) (0.010 \( \mu \)mol) in CICD\(_2\)CD\(_2\)Cl (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)

References