Supplementary Materials

Nitrous Oxide Reduction-Coupled Alkene-Alkene Coupling Catalysed by Metalloporphyrin
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General: NMR spectra were recorded on a JEOL-JNM-LA500 (500 MHz for $^1$H, 125 MHz for $^{13}$C), or a Varian VNMRS 500 (500 MHz for $^1$H, 125 MHz for $^{13}$C) spectrometer. Chemical shifts are reported in δ ppm relative to tetramethylsilane (δ = 0.00) or CHCl$_3$ (δ = 7.26) for $^1$H-NMR unless otherwise noted. Multiplicity is expressed as s = singlet, d = doublet, t = triplet, m = multiplet, br = broad, etc. Chloroform-d (δ = 77.0 for $^{13}$C) was used as an internal standard for $^{13}$C-NMR. Mass spectra were determined on a JEOL JMS-LCmate spectrometer or a JEOL JMS-AX505 spectrometer. IR spectra were obtained using a FT/IR-680 plus Fourier-transform infrared spectrometer. UV–visible light (UV-vis) absorption spectra were measured with a JASCO STR-458 spectrophotometer. EPR spectra were taken on a JEOL JES-RE2X spectrometer.

Reagents and solvents were of commercial grade, and were used without purification unless otherwise noted. Analytical TLC was performed using 0.025 mm Merck Kiesegel TLC plates (60 F$_{254}$). Bands were visualized by exposure to UV light (254 nm), or to 10 % aqueous phosphomolybdic acid or 8% $p$-anisaldehyde solution in ethanol containing 6% sulfonic acid and 1% acetic acid, followed by heating on a hot plate. Flash column chromatography was performed using Fuji Silysis BW 300 (300 mesh).

![Synthesis of 1e](image)

Synthesis of 1e: To a solution of p-toluenesulfonylamine (1.72 g, 10.0 mmol) in DMF (15 mL) were added Cs$_2$CO$_3$ (6.52 g, 20.0 mmol) and 3-chloro-2-methyl-1-propane (2.94 mL, 30 mmol). The reaction mixture was stirred at 50 °C for 1 h and filtered. Hexane was added to the filtrate and the organic layer was washed with H$_2$O. The organic layer was dried over Na$_2$SO$_4$, and concentrated in vacuo to afford 1e (1.93 g, 69%) as a colorless oil. According to NMR, the product was pure and was used in the
reductive coupling reaction without purification. 1e: IR (KBr) ν cm⁻¹; ¹H NMR (500 MHz, CDCl₃) IR (KBr) ν 2973, 2912, 1339, 1161 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.60 (s, 6H), 2.41 (s, 3H), 3.69 (s, 4H), 4.77 (brs, 2H), 4.85 (brs, 2H), 7.27 (d, J=8.4 Hz, 2H), 7.70 (d, J=8.4 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 19.94, 21.44, 53.06, 114.44, 127.20, 129.44, 137.41, 140.05, 143.02; FAB-MS: m/z 279 (M+H⁺); HRMS (EI): m/z calcd. for C₁₅H₂₁NO₂S: 279.1293, found: 272.1295.

Ph Ph
Ph Ph 2b

Synthesis of 2b: To a solution of 1b (300 µl, 1.71 mmol) and Fe(TPP)Cl (12.1 mg, 17.1 µmol) in MeOH-toluene (1:1, 6 mL) were added Me₄NOH (10% in MeOH, 186 µl, 171 µmol) and NaBH₄ (130 mg, 3.44 mmol). Nitrous oxide was admitted via a balloon and the reaction mixture was stirred for 14 h at room temperature and the solvent was removed in vacuo. The residue was treated with water and extracted with hexane. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The crude mixture was purified by silica-gel column chromatography (CH₂Cl₂/ hexane=1/49) to afford 2b (288 mg, 93%) as a white solid: IR (KBr) ν 3023, 1494, 1441 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.04 (s, 6H), 6.96-7.05 (m, 8H), 7.07-7.16 (m, 12H); ¹³C NMR (125 MHz, CDCl₃) δ 27.88, 55.10, 125.46, 126.26, 131.90, 148.53. Molecular ion peak of compound 2b, which is easily decomposed under EI and FAB-MS conditions, was not observed.¹

Ph Ph
Ph Ph 2c

Synthesis of 2c: To a solution of 1c (300 µl, 2.61 mmol) and Fe(TPP)Cl (18.4 mg, 26.1 µmol) in MeOH-toluene (1:1, 6 mL) were added Me₄NOH (10% in MeOH, 283 µl, 261 µmol) and NaBH₄ (197 mg, 5.21 mmol). Nitrous oxide was admitted via a balloon and the reaction mixture was stirred for 14 h at room temperature and the solvent was removed in vacuo. The residue was treated with water and extracted with hexane. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The crude mixture was purified by silica-gel column chromatography (CH₂Cl₂/ hexane=1/49) to afford 2c (85.0 mg, 31%, 1:1 diastereomer mixture) as a white solid: IR (KBr) ν 2981, 1442, 1380, 732, 702 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.03 (dd, 3H, J = 4.5, 2.1 Hz), 1.28 (dd, 3H, J = 4.9, 1.9 Hz), 2.80 (dt, 1H, J = 6.6, 4.2
Hz), 2.94 (dt, 1H, $J = 6.7, 4.9$ Hz), 7.00-7.23 (m, 10H); EI-MS: $m/z$ 210 (M$^+$); HRMS (EI): $m/z$ calcd. for C$_{16}$H$_{18}$: 210.1410, found: 210.1409.

**Synthesis of 2d:** To a solution of 1d (266 µl, 2.50 mmol) and Fe(TPFPP)Cl (13.3 mg, 12.5 µmol) in MeOH-toluene (1:1, 6 mL) were added NaOMe (13.5 mg, 250 µmol) and NaBH$_4$ (94.5 mg, 2.50 mmol). Nitrous oxide was admitted via a balloon and the reaction mixture was stirred for 14 h at room temperature and the solvent was removed in vacuo. The residue was treated with water and extracted with hexane. The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, and concentrated in vacuo. The crude mixture was purified by silica-gel column chromatography (CH$_2$Cl$_2$/hexane=3/97) to afford 2d (85.7 mg, 34%) as a brown oil: IR (KBr) $\nu$ 2924, 2602, 1732, 1036 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.14 (d, $J = 7.2$ Hz, 3H), 1.15 (s, 3H), 1.19 (s, 3H), 1.62 (dd, $J = 14.2, 4.0$ Hz), 2.09 (dd, $J = 14.2, 8.8$ Hz), 2.45-2.52 (m 1H), 3.65 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 19.27, 24.70, 25.83, 36.39, 41.86, 43.92, 51.61, 51.72, 177.28, 177.88. Molecular ion peak of compound 2d, which is easily decomposed under EI and FAB-MS conditions, was not observed.$^1$

**Synthesis of 2e:** To a solution of 1e (283 mg, 1.01 mmol) and Fe(TPFPP)Cl (10.8 mg, 10.1 µmol) in MeOH-trifluoromethylbenzene (20:1, 21 mL) were added KOH (14.4 mg, 257 µmol) and NaBH$_4$ (76 mg, 2.00 mmol). Nitrous oxide was admitted via a balloon and the reaction mixture was stirred for 20 h at room temperature and the solvent was removed in vacuo. The residue was treated with water and extracted with hexane. The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, and concentrated in vacuo. The crude mixture was purified by silica-gel column chromatography (CH$_2$Cl$_2$/hexane=3/1) to afford 2e (50.9 mg, 18%) as a white solid: IR (KBr) $\nu$ 2967, 1340, 1160 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 0.74 (s, 12H), 2.42 (s, 3H), 3.13 (s, 4H), 7.30 (d, $J = 8.1$ Hz, 2H), 7.71 (d, $J = 8.1$ Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 21.49, 21.87, 42.43, 59.81, 127.25, 129.47, 134.34, 143.11; EI-MS: $m/z$ 281 (M$^+$); HRMS (EI): $m/z$ calcd. for C$_{15}$H$_{23}$NO$_2$S: 281.1449, found:281.1451.
Synthesis of 2a*: To a solution of 1d (100 µl, 770 µmol) and Fe(TPP)Cl (5.4 mg, 7.67 µmol) in MeOH-toluene (1:1, 2 mL) were added KOH (4.3 mg, 76.6 µmol) and NaBD₄ (64.5 mg, 1.54 mmol). Nitrous oxide was admitted via a balloon and the reaction mixture was stirred for 14 h at room temperature and the solvent was removed in vacuo. The residue was treated with water and extracted with hexane. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The crude mixture was purified by silica-gel column chromatography (CH₂Cl₂/hexane=1/49) to afford 2a* (71.1 mg, 77%) as a white solid: IR (KBr) ν 2974, 768, 702 cm⁻¹; ¹H-NMR (CDCl₃, 500 MHz): δ 1.29 (brs, 4H), 1.31 (s, 6H), 7.05-7.07 (m, 4H), 7.12-7.20 (m, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 24.87 (t, J_C,D = 19.2 Hz), 25.13, 43.53, 125.46, 126.61, 128.60, 146.79; EI-MS: m/z 120 (PhMe(CDH₂)C⁺). Molecular ion peak of compound 2a*, which is easily decomposed under EI and FAB-MS conditions, was not observed.

FT-IR measurement: To a solution of 1a (300 µl, 2.31 mmol) in MeOH-toluene (1:1, 6 ml) were added KOH (13.0 mg, 230 µmol) and NaBH₄ (175 mg, 4.63 mmol) under N₂O in a septum-capped sealed vessel. After stirring for 3 h, 2 mL of gas over the reacting solution was taken with a gas tight syringe and injected into a sealed cell filled with Ar, and FT-IR spectra of gas layer was measured (Figure 1 (a)). After the measurement, Fe(TPP)Cl (16.3 mg, 23.2 µmol, 1 mol%) in 2 mL of MeOH-toluene (1:1) was further added into the reaction vessel, the reaction mixture was stirred at room temperature. After stirring for 2 h, 2 mL of gas over the reacting solution was taken and injected into a cell filled with Ar, and FT-IR spectra of the gas layer was measured (Figure 1 (b)).

UV-Vis measurement: To a solution (2.0 mL) of NaBH₄ (175 mM) and Me₄NOH (37 mM) in MeOH-toluene (1:1) was added a solution of Fe(TPP)Cl (75 µM, 500 µl) in MeOH-toluene (1:1) under an argon atmosphere. The resulted solution (2.5 mL) was transferred to a quartz cell and UV-Vis spectrum was measured (Figure S1 (a)). Subsequently, the substrate 1a (32.5 µL, 250 µmol) was added to the quartz cell and UV-Vis spectrum was measured again (Figure 2 (a)). Finally, the solution was bubbled with N₂O and UV-Vis spectrum of the resulting solution was measured (Figure S1 (b)).
Figure S1. (a) UV-Vis Spectra of Fe(TPP) in MeOH-toluene (1:1) in the presence of NaBH₄ and Me₄NOH under Ar. (b) UV-Vis spectra of Fe(TPP) in MeOH-toluene (1:1) in the presence of NaBH₄ and Me₄NOH under Ar after the addition of 1e and bubbling with N₂O.

EPR measurement: To a solution (800 µL) of NaBH₄ (200 µM) and Me₄NOH (23 mM) in MeOH-toluene (1:1) was added a solution of Fe(TPP)Cl (9.9 mM, 100 µL) in MeOH-toluene (1:1) under an argon atmosphere. The resulted solution (900 µL) was transferred to an EPR tube and frozen in liquid nitrogen (77 K). EPR spectrum was then measured. The reaction mixture was warmed to room temperature and a solution of 1a (0.90 M, 100 µL) in MeOH-toluene (1:1) was added and mixed well. After freezing in liquid nitrogen, EPR spectrum was measured. The reaction mixture was warmed to room temperature once again, and the solution was bubbled with N₂O. After freezing in liquid nitrogen, EPR spectrum of the resulting mixture was measured. The measurement conditions were as follows; microwave power, 10 mW; frequency, 9.145 GHz; field, 336.5 mT; sweep width, 40 mT; sweep time, 1 min; modulation width, 0.63 mT; gain, 500; and time constant; 0.03 s.

Reference