Supplementary Materials

Nitrous Oxide Reduction-Coupled Alkene-Alkene Coupling Catalysed by Metalloporphyrin

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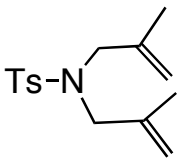
General: NMR spectra were recorded on a JEOL-JNM-LA500 (500 MHz for ^{1}H, 125 MHz for ^{13}C), or a Varian VNMRS 500 (500 MHz for ^{1}H, 125 MHz for ^{13}C) spectrometer. Chemical shifts are reported in δ ppm relative to tetramethylsilane (δ = 0.00) or $CHCl_3$ (δ = 7.26) for ^{1}H-NMR unless otherwise 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.

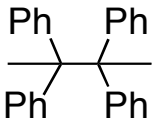
Reagents and solvents were of commercial grade, and were used without purification unless otherwise noted. Analytical TLC was performed using 0.025 mm Merck Kiesegel TLC plates (60 F_{254}). Bands were visualized by exposure to UV light (254 nm), or to 10 % aqueous phosphomolybdic acid or 8% *p*-anisaldehyde 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 Silysia BW 300 (300 mesh).



1e

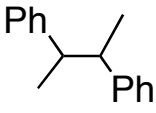
Synthesis of 1e: To a solution of *p*-toluenesulfonamide (1.72 g, 10.0 mmol) in DMF (15 mL) were added Cs_2CO_3 (6.52 g, 20.0 mmol) and 3-chloro-2-methyl-1-propane (2.94 mL, 30 mmol). The reaction mixture was stirred at 50 °C for 1 h and filtered. Hexane was added to the filtrate and the organic layer was washed with H_2O. The organic layer was dried over Na_2SO_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, $CDCl_3$) IR (KBr) ν 2973, 2912, 1339, 1161 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (125 MHz, $CDCl_3$) 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 $C_{15}H_{21}NO_2S$: 279.1293, found:272.1295.



2b

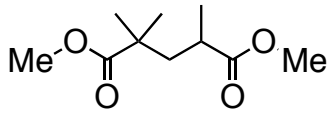
Synthesis of 2b: To a solution of **1b** (300 μl, 1.71 mmol) and Fe(TPP)Cl (12.1 mg, 17.1 μmol) in MeOH-toluene (1:1, 6 mL) were added Me_4NOH (10% in MeOH, 186 μl, 171 μmol) and $NaBH_4$ (130 mg, 3.44 mmol). Nitrous oxide was admitted via a balloon and the reaction mixture was stirred for 14 h at room 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 Na_2SO_4, and concentrated *in vacuo*. The crude mixture was purified by silica-gel column chromatography (CH_2Cl_2/ 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, $CDCl_3$) δ 2.04 (s, 6H), 6.96-7.05 (m, 8H), 7.07-7.16 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) 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]



2c

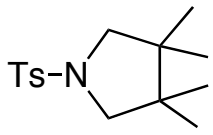
Synthesis of 2c: To a solution of **1c** (300 μl, 2.61 mmol) and Fe(TPP)Cl (18.4 mg, 26.1 μmol) in MeOH-toluene (1:1, 6 mL) were added Me_4NOH (10% in MeOH, 283 μl, 261 μmol) and $NaBH_4$ (197 mg, 5.21 mmol). Nitrous oxide was admitted via a balloon and the reaction mixture was stirred for 14 h at room 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 Na_2SO_4, and concentrated *in vacuo*. The crude mixture was purified by silica-gel column chromatography (CH_2Cl_2/ 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, $CDCl_3$) 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.



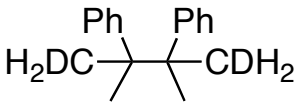
2d

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_2SO_4, and concentrated *in vacuo*. The crude mixture was purified by silica-gel column chromatography (CH_2Cl_2/ hexane=3/97) to afford **2d** (85.7 mg, 34%) as a brown oil: IR (KBr) ν 2924, 2602, 1732, 1036 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 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), 3.650 (s, 3H), 3.653 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 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]



2e

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_2SO_4, and concentrated *in vacuo*. The crude mixture was purified by silica-gel column chromatography (CH_2Cl_2/ hexane=3/1) to afford **2e** (50.9 mg, 18%) as a white solid: IR (KBr) ν 2967, 1340, 1160 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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 $C_{15}H_{23}NO_2S$: 281.1449, found:281.1451.



2a'

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 $NaBD_4$ (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 Na_2SO_4, and concentrated *in vacuo*. The crude mixture was purified by silica-gel column chromatography (CH_2Cl_2/ hexane=1/49) to afford **2a'** (71.1 mg, 77%) as a white solid: IR (KBr) ν 2974, 768, 702 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 1.29 (brs, 4H), 1.31 (s, 6H), 7.05-7.07 (m, 4H), 7.12-7.20 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.87 (t, $J_{C\text{-}D}$= 19.2 Hz), 25.13, 43.53, 125.46, 126.61, 128.60, 146.79; EI-MS: *m/z* 120 ($PhMe(CDH_2)C^+$). Molecular ion peak of compound **2a'**, which is easily decomposed under EI and FAB-MS conditions, was not observed.[1]

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 $NaBH_4$ (175 mg, 4.63 mmol) under N_2O 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 $NaBH_4$ (175 mM) and Me_4NOH (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 N_2O and UV-Vis spectrum of the resulting solution was measured (Figure S1 (b)).

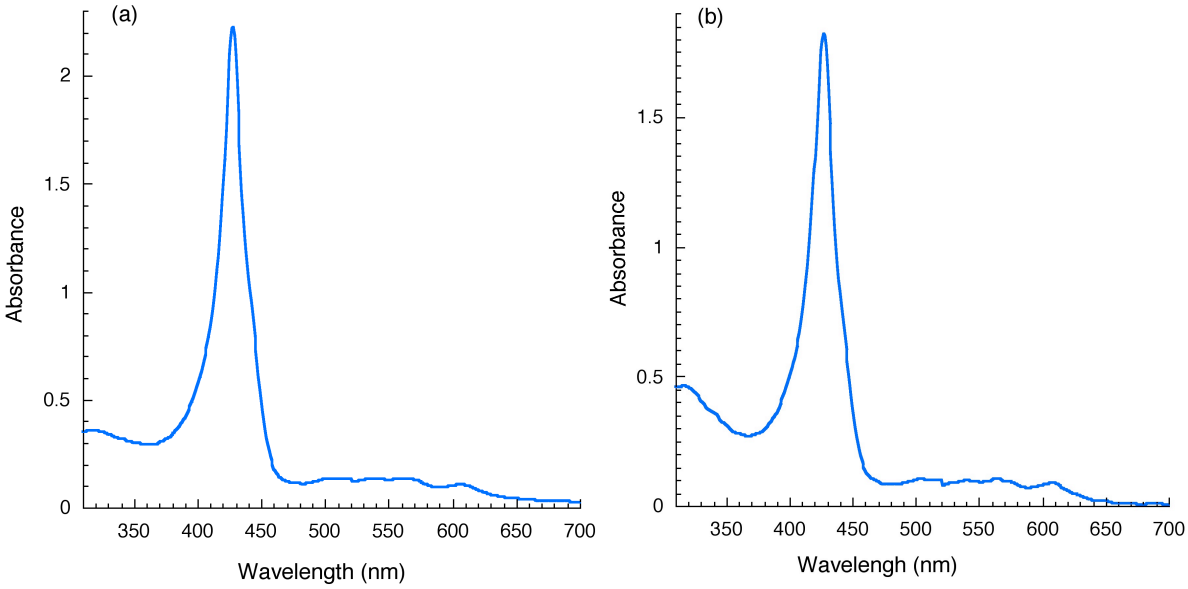


Figure S1. (a) UV-Vis Spectra of Fe(TPP) in MeOH-toluene (1:1) in the presence of $NaBH_4$ and Me_4NOH under Ar. (b) UV-Vis spectra of Fe(TPP) in MeOH-toluene (1:1) in the presence of $NaBH_4$ and Me_4NOH under Ar after the addition of **1e** and bubbling with N_2O.

EPR measurement: To a solution (800 μL) of $NaBH_4$ (200 μM) and Me_4NOH (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 N_2O. 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

1) Warrier, M.; K. Kaanumalle, L. S.; Ramamurthy, V. *Can. J. Chem.* **2003**, *81*, 620-631.