

1.1. General.

All the reactions dealing with air and moisture sensitive compounds were carried out in a dry reaction vessel under argon unless otherwise noted. All ^1H NMR spectra measured at 300 MHz and ^{13}C NMR spectra at 75.4 MHz using Varian GEMINI 2000, are reported in ppm (δ). J values are given in Hz. FT-IR spectra measured using Perkin Elmer Spectrum One, are reported (cm^{-1}). GC analyses were performed on Shimadzu GC-14B with capillary column (0.25 mm I.D. \times 25 m) coated with HR-1. Elemental analyses were performed on Yanaco CHN corder MT-6 or J-SCIENCE LAB MICRO CODER JM10 at the Center for Instrumental Analysis, Hokkaido University. ICP-MS measurements were performed on Agilent 7500 ICP-MS.

1.2. Solvents.

Anhydrous toluene and dichloromethane were purchased from Kanto Chemical Co. Octane and mesitylene were distilled from CaH_2 before use. All other solvents were distilled and dried over molecular sieves.

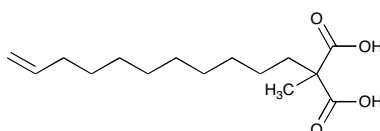
1.3. Materials.

Sulfuric acid (Super Special Grade), hydrogen peroxide (30% in water, S.S.G.), hydrofluoric acid (46% in water) and hydrochloric acid (20% in water, S.S.G.) were purchased from Wako Pure Chemical Industries, Ltd. Special grade ammonium fluoride solution (40% in water, for semiconductor industries) was purchased from Morita Chemicals Ltd. Water was purified using a Milli-Q system (Millipore). Palladium acetate was purchased from Wako Chemical Co. without further purification. Unless otherwise noted, materials were purchased from Junsei Chemical Co., Kanto Chemical Co., and other commercial suppliers. Single side polished Si(111) single crystal wafer (thickness = 625 ± 25 μm , resistivity = 10-40 $\Omega\cdot\text{cm}$, p-type) and double side polished Si(111) single crystal wafer (thickness = 420 ± 10 μm , resistivity = 279-321 $\Omega\cdot\text{cm}$, n-type) were donated by Shin-Etsu Semiconductor.

2. Preparation of BOX

The bisoxazoline with vinyl-terminated alkyl substituent was prepared according to the reported method¹ for the similar compounds.

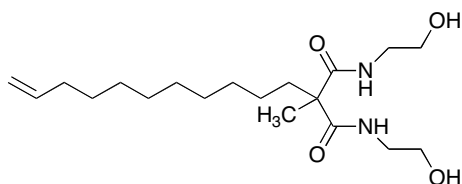
2.1. Methyl(10-undecenyl) Malonic Acid.



Diethyl methylmalonate (67 g, 380 mmol, 1.0 eq) was added dropwise with stirring to a suspension of NaH (17 g of a 60 % dispersion in mineral oil, 420 mmol, 1.1 eq) in dry DMF (220 mL). The mixture was stirred at room temperature for 30 min and

11-bromo-1-undecene (89 g, 380 mmol) was added. After stirring at room temperature for 20 hours, the reaction was quenched by the addition of H₂O and neutralized with 1 N HCl. Then the mixture was extracted with diethyl ether. The extract was washed with H₂O, dried over Na₂SO₄, and concentrated in vacuo. A solution of the crude alkylated product in 25 % ethanolic KOH (300 mL) was heated to reflux for 1 h. The EtOH was removed under reduced pressure, and the residue was dissolved in H₂O and cautiously acidified with conc. HCl to pH 7 while cooling the mixture at 0 °C. The solution was extracted with CH₂Cl₂ to remove the unreacted ester. The acidification was continued to pH 1, and precipitated dicarboxylic acid was extracted with CH₂Cl₂. The extract was dried over MgSO₄ and concentrated in vacuo. The crude product was purified by recrystallization from hexane/CHCl₃ to afford the title compound (71 g, 69%) as a white prisms (Found: C, 66.63; H, 9.65. Calc. for C₁₅H₂₆O₄: C, 66.64; H, 9.69%); $\nu_{\max}/\text{cm}^{-1}$ 3080w, 2968w, 2920s, 2851m, 2648br, 1718s, 1703s, 1643w, 1470m, 1453m, 1302m, 1285m, 1276m, 1258m, 1233m, 991m, 922s, 905s, 764w and 693w; δ_{H} (300 MHz; CDCl₃; Me₄Si) 5.81 (1H, ddt, *J* 17.1, 10.2 and 6.6, CH=CH₂), 5.03-4.92 (2H, m, CH=CH₂), 2.05 (2H, m), 1.91-1.86 (2H, m) and 1.48 (3H, s, CH₃).

2.2. N,N'-Bis(2-hydroxyethyl)-2-methyl(10-undecenyl)-1,3-propanediamide.

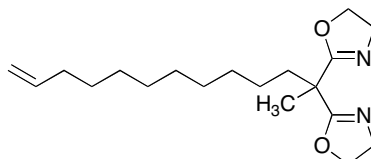


A mixture of the malonic acid (5.0 g, 18 mmol) and SOCl₂ (6.8 mL, 90 mmol, 5.0 eq) was heated to reflux for 3 h. The excess SOCl₂ was evaporated to afford the crude dichloride quantitatively as a yellow oil.

The crude dichloride in CH₂Cl₂ (35 mL) was added dropwise to an ice-cold solution of ethanolamine (2.3 mL, 38 mmol, 2.1 eq) in CH₂Cl₂ (35 mL) over 30 min. A white precipitate formed immediately. After complete addition of the dichloride, triethylamine (6.5 mL, 44 mmol, 2.5 eq) was added quickly. The mixture was allowed to warm to room temperature and was stirred for 23 h. The mixture was poured into saturated aqueous NaHCO₃ solution. The organic layer was separated and the aqueous phase was extracted with CHCl₃. The combined organic layers were successively washed with 1 N HCl, saturated NaHCO₃, and brine, dried with MgSO₄ and concentrated under reduced pressure. The crude diamide was purified by silica gel chromatography (250 g, CHCl₃/MeOH, 9/1) and recrystallization from EtOAc/hexane to afford the title compound (3.6 g, 56%) as white crystals; $\nu_{\max}/\text{cm}^{-1}$ 3334br, 3076w, 2976w, 2925s, 2854s, 1640brs, 1524brs, 1466m, 1437m, 1262br, 1060s, 992w, 908s and 720w; δ_{H} (300 MHz; CDCl₃; Me₄Si) 7.07 (2H, brt), 5.80 (1H, ddt, *J* 17.1, 10.2 and 6.6, CH=CH₂), 5.02-4.92 (2H, m, CH=CH₂), 3.70 (4H, t, *J* 4.8), 3.41 (4H, brq), 2.10-2.03 (2H, m), 1.88-1.80 (2H, m), 1.43 (3H, s, CH₃) and 1.38-1.18 (14H, m); δ_{C} (75.4 MHz; CDCl₃; Me₄Si) 174.5, 139.3,

114.2, 61.4, 53.6, 42.4, 38.1, 33.7, 29.8, 29.4, 29.3, 29.3, 29.0, 28.8, 24.5 and 18.6.

2.3. 2,2'-(1-Methyl-11-Dodecenylidene)Bis(4,5-Dihydrooxazole) (**BOX**).



The diamide (5.0 g, 14 mmol) was suspended in toluene (65 mL) at 65 °C. SOCl₂ (4.0 mL, 56 mmol, 4.0 eq) was added quickly, and the resulting mixture was stirred for 30 min. Then, the mixture was cooled to 0 °C, quenched with saturated aqueous NaHCO₃ solution and was extracted with CHCl₃. The organic extracts were combined, dried with Na₂SO₄ and concentrated under reduced pressure. The crude amide was heated to reflux in 5% methanolic NaOH solution (31 mL) for 1.5 h, during which time NaCl precipitated from the reaction mixture. The mixture was cooled to room temperature and concentrated under reduced pressure, the residue was partitioned between CH₂Cl₂ and H₂O, and the aqueous phase was extracted with CH₂Cl₂. The organic layers were combined, dried with MgSO₄, and concentrated under reduced pressure to afford the crude bisoxazoline. The crude product was purified by bulb-to-bulb distillation (140-150 °C, 8 Pa) to afford the title compound (**BOX**) (4.0 g, 90%) as a colorless oil (Found: C, 70.97; H, 9.90; N, 8.58. Calc. for C₁₉H₃₂N₂O₂: C, 71.21; H, 10.06; N, 8.74%); $\nu_{\max}/\text{cm}^{-1}$ 3076w, 2926m, 2855m, 1654s, 1481w, 1462m, 1378m, 1351m, 1228br, 1194m, 1139br, 1087m, 981s, 954s, 913s and 723w; δ_{H} (300 MHz; CDCl₃; Me₄Si) 5.81 (1H, ddt, *J* 17.1, 10.2, and 6.6, CH=CH₂), 5.02-4.91 (2H, m, CH=CH₂), 4.29 (4H, t, *J* 9.3), 3.89 (4H, t, *J* 9.3), 2.08-1.98 (2H, m), 1.94-1.89 (2H, m), 1.49 (3H, s, CH₃) and 1.40-1.20 (14H, m); δ_{C} (75.4 MHz; CDCl₃; Me₄Si) 169.6 (2C), 139.4, 114.1, 67.8 (2C), 54.3 (2C), 42.3, 36.4, 33.7, 29.7, 29.4, 29.3, 29.3, 29.0, 28.8, 24.0 and 21.2.

3. Preparation of ATR-IR Prism.

The double side polished silicon wafer was cut into 20 × 10 mm² pieces. The two opposite edges (20 mm) of the prisms were polished with 45° bevels, using mechanical polishing with SiC polishing papers (Maruto, No.100, 220, 400, 1000 and 2000). ATR prisms were then obtained by polishing the silicon samples using alumina paste (Maruto, 1– 0.3 μm). The internal reflection number within this ATR prism was estimated to be 24.

4.1. Preparation of Hydrogen-terminated Si(111) Surface (Si-H).

Sequential immersion of Si(111) surface was performed in freshly prepared sulfuric acid and hydrogen peroxide (2:1 by volume) at 60 °C for 30 min, in 0.5% HF aqueous solution at room temperature for 5 min and in freshly prepared RCA mixture (H₂O/20% aq. HCl/H₂O₂, 2:2:1 by volume) at 75-85 °C for 20 min. The oxidized surface thus obtained was then immersed in 40% deaerated aqueous NH₄F solution for 7 min under Ar.

4.2. Preparation of Si-BOX.

A solution of distilled **BOX** in mesitylene (0.33 M) was deaerated by the freeze-dry method more than three times. A hydrogen-terminated Si(111) surface (**Si-H**) was heated in the solution at 160 °C under argon atmosphere for 22 h. After being cooled to room temperature, the surface was removed from the solution and rinsed with diethyl ether, hexane and dichloromethane.

4.3. Preparation of Si-BOX-Pd.

A chip of **Si-BOX** surface was immersed in a solution of Pd(OAc)₂ in CH₂Cl₂ (0.1 M) at room temperature for 1 h. The surface was then removed from the solution and rinsed with dichloromethane.

5.1. ATR-IR spectroscopy.

ATR-IR spectra were measured using a Spectrum One spectrometer equipped with HgCdTe (MCT) detector cooled with liquid nitrogen. Nitrogen gas is continuously provided to the FTIR chamber in which containing a molecular sieve 13x.

The infrared beam was guided inside a silicon crystal and the absorption within the evanescent field was measured. The Fourier transformation of the measured intensities resulted in an absorption spectrum. All the spectra were measured with respect to a spectrum of an oxidized Si(111) surface. All the spectra were recorded by integrating 256 interferograms with a resolution of 2 cm⁻¹.

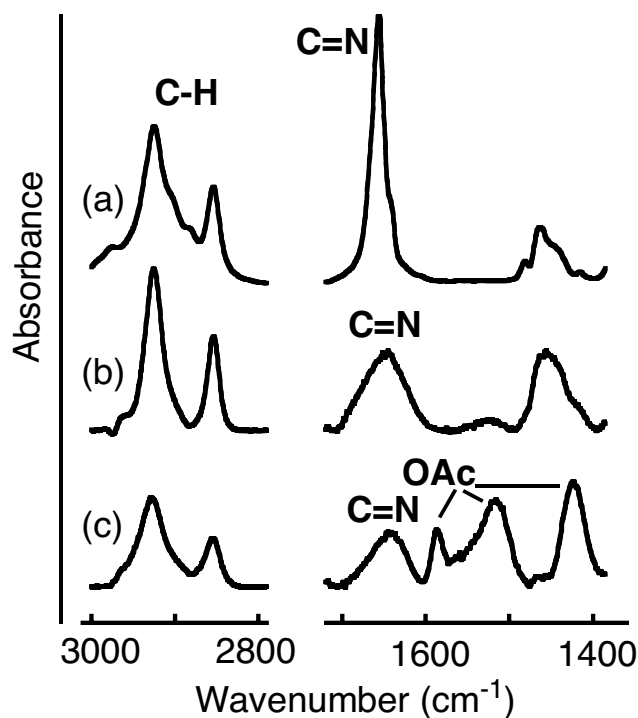


Fig. S-1 (a) IR spectrum of **BOX**; ATR-IR spectra of (b) **Si-BOX** and (c) **Si-BOX-Pd**.

5.2. X-Ray Photoelectron spectroscopy (XPS).

The XPS measurements were performed on Rigaku XPS-7000 Spectrometer using an Mg K α target (1253.6 eV) with an X-ray excitation of 25 W (for wide band) or 300 W (for narrow band) with a take-off angle of 40°. Binding energies were corrected by Si_{2p} peak at 99.15 eV.

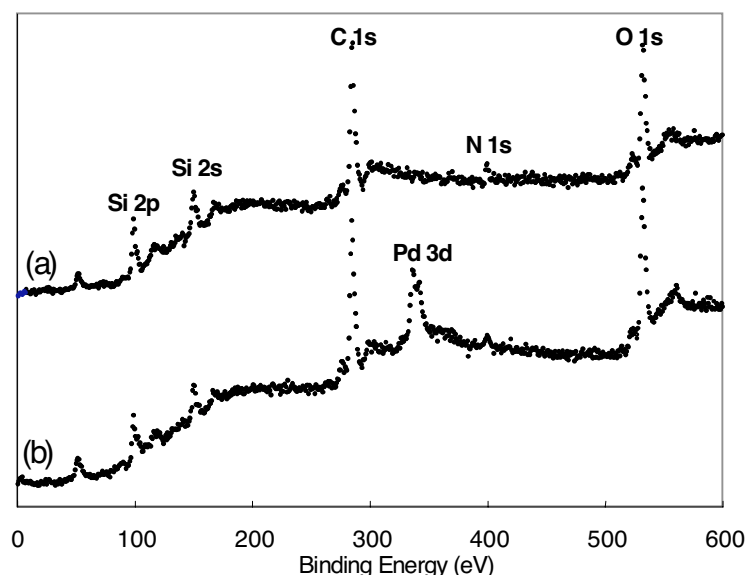


Fig. S-2 XP spectra of (a) **Si-BOX** and (b) **Si-BOX-Pd** (take-off angle = 40 degree).

Narrow band Pd 3d region XP spectrum of **Si-BOX-Pd** shown in Fig. S-3 (a) (the same spectrum with Fig. 1 (a)) indicates that the Pd species on **Si-BOX-Pd** exists as Pd(II). Another spectrum of the same surface after the prolonged acquisition time (1 day) is shown in Fig. S-3 (b), indicating that the peak at 338 eV in spectrum (a) shifted to the peak at 336 eV, probably due to the X-ray irradiation effect.

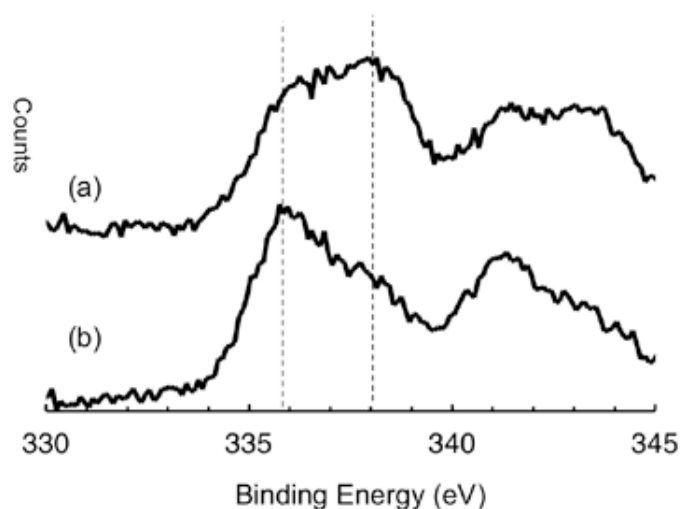


Fig. S-3 (a) Narrow band XP spectrum of **Si-BOX-Pd** as prepared in Pd 3d region. (b) The spectrum of the same surface after X-ray irradiation for 1 day.

The molar ratio of Pd/N of **Si-BOX-Pd** was calculated to be 0.66 as average of the values obtained in narrow band measurements of Pd 3d and N 1s regions on the several samples prepared independently.

The XPS spectra of **Si-BOX-Pd** after catalytic reactions are shown in Fig. S-4 (Fig. S-4 (a) is the same spectrum with Fig. 1 (b)). There was no obvious change depending on the X-ray irradiation time. The Pd species after the first run was found to be those of Pd(0). After the first catalytic reaction, the estimated molar ratio of Pd/N changed to 0.55. If the formation of Pd clusters was assumed, judging from the extent of the change in the peak intensities and the attenuation length of the photoelectron in Pd, the size of the clusters can be estimated as less than 1.5 nm.

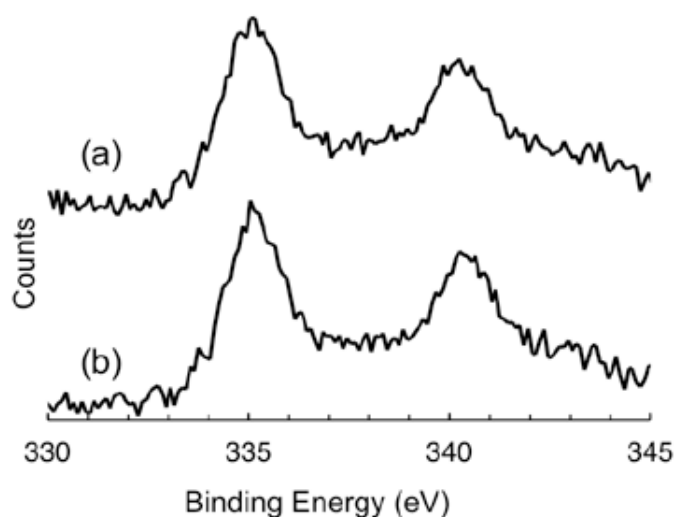


Fig. S-4 (a) Narrow band XP spectrum of **Si-BOX-Pd** after a catalytic reaction in Pd 3d region. (b) The spectrum of the same surface after X-ray irradiation for 1 day.

6.1. Aerobic Oxidation of Benzyl Alcohol Catalyzed by **Si-BOX-Pd** (Typical Procedure).

Into a round bottom flask were placed the oxygen saturated octane (5 mL), benzyl alcohol (52 μ L, 0.50 mmol) and mesitylene (40 μ L, 0.29 mmol, as an internal standard for GC analysis). After stirring at room temperature for a few minutes under O₂ atmosphere, 0.50 mL of the resulting solution (0.050 mmol of alcohol) was transferred into a screw cap test tube (Maruemu Corp., NN-13, ϕ 11 mm \times 100 mm) and **Si-BOX-Pd** (5 mm \times 5 mm \times 0.6 mm) was placed as shown in Fig. S-5. The test tube was purged with O₂ gas (8.0 mL, 0.34 mmol) and the reaction mixture was heated in an oil bath at 110 $^{\circ}$ C without stirring for 20 h. The products were analyzed by GC.

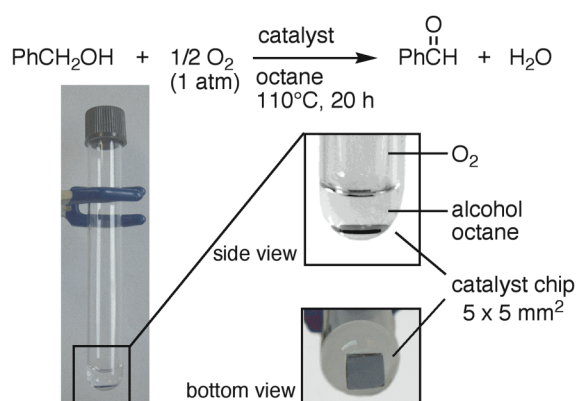


Fig. S-5 Aerobic Oxidation of Benzyl Alcohol Catalyzed by **Si-BOX-Pd**

6.2. Control Experiments in Pd-Catalyzed Aerobic Oxidation of Benzyl Alcohol.

Under the conditions described in 6.1 except for the absence of any catalyst, the conversion of benzyl alcohol was 1% (Table 1, entry 11). The catalyst for the reaction with Pd(OAc)₂ (entry 7) was introduced by evaporating a CH₂Cl₂ solution of Pd(OAc)₂ (10 μL, 2.5 mM, 25 nmol). The catalyst for the reaction with Pd(OAc)₂/**BOX** (entry 8) was introduced by evaporating a mixture of CH₂Cl₂ solutions of Pd(OAc)₂ (10 μL, 2.5 mM, 25 nmol) and **BOX** (5 μL, 5.0 mM, 25 nmol). Neither **Si-BOX** (entry 9) nor Si(111) surface alone showed the catalytic effect. The bare Si(111) surface pretreated in a solution of Pd(OAc)₂ in CH₂Cl₂ (0.1 M) at room temperature for 1 h and followed by washing with dichloromethane exhibited no catalytic activity (entry 10).

6.3. Scale-up Experiments in Aerobic Oxidation of Benzyl Alcohol Catalyzed by **Si-BOX-Pd**.

The reaction was carried out using **Si-BOX-Pd** with dimensions of 20 × 20 × 0.6 mm³ in 7.0 mL of octane in a reaction vessel as shown in Fig. S-6.

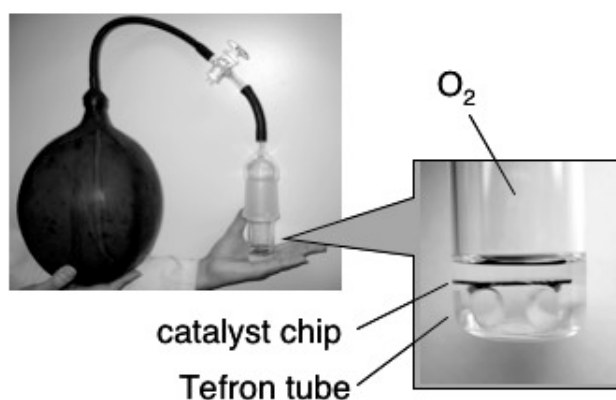


Fig. S-6 The reaction vessel for aerobic oxidation with a larger catalyst chip.

6.4. Aerobic Oxidation of Other Benzylic Alcohols.

Aerobic oxidation reactions of *p*-methylbenzyl alcohol (Table 3, entry 1) and 1-phenylethanol (entry 5) with **Si-BOX-Pd** were conducted in the same manner as described in 6.1, whereas oxidation of *p*-methoxybenzyl alcohol (13.8 mg, 0.10 mmol), *p*-chlorobenzyl alcohol (7.1 mg, 0.050 mmol) and 1-octanol (6.5 mg, 0.050 mmol) were conducted with larger catalyst chips (25 mm × 20 mm × 0.6 mm) in 2.0 mL of octane placed in a reaction vessel as shown in Fig. S-7.

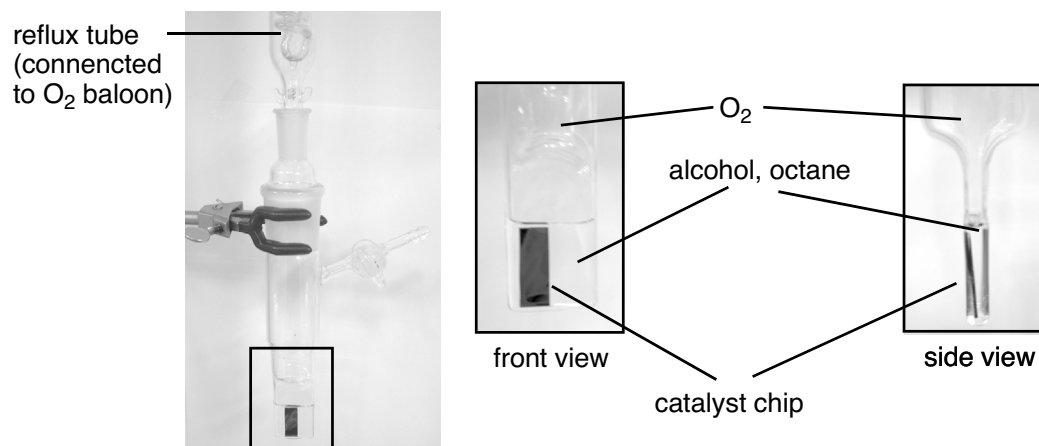


Fig. S-7 The reaction vessel for aerobic oxidation with a larger catalyst chip.

7. References.

S. E. Denmark, N. Nakajima, O. J.-C. Nicaise, A.-M. Faucher and J. P. Edwards, *J. Org. Chem.* 1995, **60**, 4884.