Supplementary Material (ESI) for Chemical Communications

Anodic Aluminum Oxide Catalytic Membranes for Asymmetric Epoxidation

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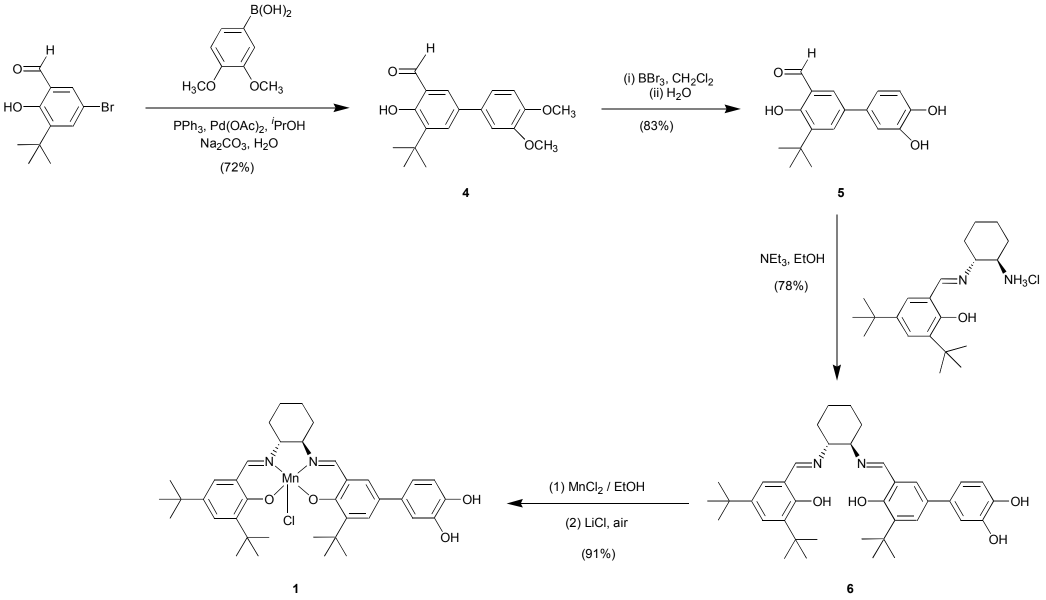
General. All reactions were carried out under dry nitrogen gas using standard Schlenk techniques or in an inert-atmosphere glove box, unless otherwise noted. Controlled addition of reagents was performed using a syrignge pump (KD Scientifics). Dichloromethane was distilled over calcium hydride, 2-propanol was degassed with a steady flow of nitrogen, and alsolute ethanol was degassed with a steady flow of nitrogen and stored over activated 4-Å molecular sieves. All solvents were kept under nitrogen in Strauss flasks prior to use. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used without further purification. Cyclohexyldiamine, 3,5-*tert*-butyl-2-hydroxybenzaldehyde, (3,4-dimethoxyphenyl)boronic acid, boron tribromide, triphenylphosphine, palladium diacetate, manganese chloride, lithium chloride, inductively coupled plasma (ICP) calibration standard solution of manganese (1000 µg/mL Mn), KBr powder for IR analysis, and all other reagents and solvents were purchased from the Aldrich Chemical Company and used without further purification, unless otherwise specified. 2-(tert-Butylsulfonyl)iodosylbenzene,[1] 2,2-dimethyl-2*H*-chromene,[2] 2,2-dimethyl-3,4-epoxychroman,[3] 5-bromo-3-tert-butyl-2-hydroxybenzaldehyde,[4] and (1*R*,2*R*)-cyclohexanediamino-*N*-(3,5-di-tert-butylsalicylidene)-*N'*-ammonium chloride[5] were synthesized according to the literature procedures.

^{1}H NMR and ^{13}C NMR spectra for all the synthesized compounds were recorded on either a Varian INOVA 500 NMR spectrometer (500 MHz for ^{1}H NMR, 125 MHz for ^{13}C NMR) or a Varian Mercury 400 NMR spectrometer (400 MHz for ^{1}H NMR, 75 MHz for ^{13}C NMR). Chemical shifts of ^{1}H NMR spectra are reported in ppm against residual solvent resonance as the internal standard ($CDCl_3$: 7.27 ppm, CD_2Cl_2: 5.32 ppm). ^{1}H NMR data are reported as follows: chemical shift (multiplicity (b = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), integration, assignment). Chemical shifts of ^{13}C NMR spectra are reported in ppm against the solvent resonance as the internal standard ($CDCl_3$: 77.23 ppm, CD_2Cl_2: 54.00 ppm). Gas Chromatography-Mass (EI) Spectrometry (GC-MS) analyses were performed on a Hewlett-Packard 6890 GC/MSD interfaced to a HP 5972 Mass Selective Detector Quadrupole Mass Spectrometer equipped with an FID detector and ChemStation software. Electrospray-ionization mass spectrometry (ESIMS) and Atmospheric-pressure chemical ionization mass spectrometry (APCIMS) were conducted on a Micromass Quattro II triple quadrupole HPLC/MS/MS mass spectrometer. Diffuse reflectance UV-Vis spectra were obtained on a Varian Cary 500 spectrophotometer. Fourier-Transform Infrared (FT-IR) Spectroscopy was performed on a Nicolet Nexus 870 FT-IR spectrometer. X-ray Photoelectron Spectroscopy (XPS) measurements were conducted on an Omicron Nanotechnology XPS instrument. ICP spectroscopy was conducted with a Thermo Jarrell Ash Atomscan Model 25 Sequential ICP spectrometer, equipped with vacuum optics covering the spectral range from 160 to 850 nm. Melting points were uncorrected and were determined on a Fisher-Johns melting point apparatus.

Product selectivity of 2,2-dimethyl-*2H*-chromene epoxidation (epoxide over ketone) was measured via NMR spectroscopy. Quantitative GC analyses were carried out on a Hewlett-Packard 6890A GC equipped with an FID detector and ChemStation software. The column used was a 30-m HP-5 (crosslinked 5% PhMe Siloxane) capillary column with 0.32-mm inner diameter and 0.25-µm film thickness (column head pressure = 9.3 psi, initial time = 0 min, initial temperature = 80 °C, final temperature = 250 °C, final time = 5 min, rate of 5 °C/min). Calibration curves were produced using analytically pure samples prepared and characterized by literature methods.[3] Product yields were determined by comparing the combined areas of the epoxide (retention time = 12.5 min) and the ketone peaks (retention time = 11.5 min) against that of the undecane internal standard (approximately 30% of epoxide products were isomerized to ketone under the GC condition as verified by injection of an authentic chromene epoxide samples). For determination of enantiomeric excess, a Supelco β–DEX 120 column was used on a Hewlett-Packard 6890 GC equipped with an FID detector and ChemStation software (column head pressure = 23 psi, initial time = 0 min, initial temperature = 140 °C, final temperature = 175 °C, final time = 20 min, rate of 1 °C/min). The retention time of the first isomer [(3*R*,4*R*), minor] was 17.5 min and that of the second isomer [(3*S*,4S), major] was 18.5 min.

Scheme S1. Synthesis of **1**.



3-*Tert*-butyl-2-hydroxy-5-(3,4-dimethoxyphenyl)benzaldehyde (4). Under a nitrogen atmosphere, 5-bromo-3-*tert*-butyl-2-hydroxybenzaldehyde (1.03 g, 4.01 mmol), 3,4-dimethoxyphenyl boronic acid (0.89 g, 4.20 mmol), and 2-propanol (7 mL) were added to a 50-mL round-bottom flask equipped with a magnetic stir bar. To this mixture were then added PPh_3 (0.0095 g, 36 μmol) and $Pd(OAc)_2$ (0.0027 g, 12 μmol) followed by Na_2CO_3 (aq) (4.8 mL of a 1.2-M solution). The flask was then attached to a water-cooled reflux condenser; the resulting suspension was heated at 110 °C under N_2. After 2 h, the suspension was allowed to cool to room temperature and H_2O (5 mL) was added. The mixture was then stirred for an additional 1 h and extracted with EtOAc (3 × 20 mL). The combined organic layers were then washed with 5% aqueous $NaHCO_3$ (2 × 10 mL) and saturated brine (20 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude yellow product was purified by silica gel chromatography (4 cm × 18 cm, hexane/EtOAc, 10:1). Yield = 0.91 g (72%) of **4** as a pale yellow solid (m.p. = 96-98 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 9.97 (s, 1H, C(O)*H*), 7.72 (d, $^2J_{HH}$ = 2 Hz, 1H, Ar*H*) 7.55 (d, $^2J_{HH}$ = 2 Hz, 1H, Ar*H*), 7.10 (d, $^2J_{HH}$ = 8 Hz, 1H, Ar*H*), 7.05 (s, 1H, Ar*H*), 6.96 (d, $^2J_{HH}$ = 8 Hz, 1H, Ar*H*), 3.98 (s, 3H, O*Me*), 3.94 (s, 3H, O*Me*), 1.48 (s, 9H, C*Me*$_3$). ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ 197.9 (*C*(O)H), 160.2 (Ar), 149.6 (Ar), 139.0 (Ar), 133.5 (Ar), 133.2 (Ar), 132.6 (Ar), 129.9 (Ar), 120.9 (Ar), 119.3 (Ar), 111.8 (Ar), 110.0 (Ar), 108.0 (Ar), 56.3 (O*Me)*, 56.2 (O*Me)*, 35.2 (*C*Me$_3$), 29.5 (C*Me$_3$*). IR (KBr): ν 2958, 1652, 1520, 1439, 1398, 1335, 1243, 1215, 1142, 1027, 770, 733. GC-MS(EI): m/z (%): 314 (100) [M^+], 299 (50), 281 (35), 207 (85), 115 (25).

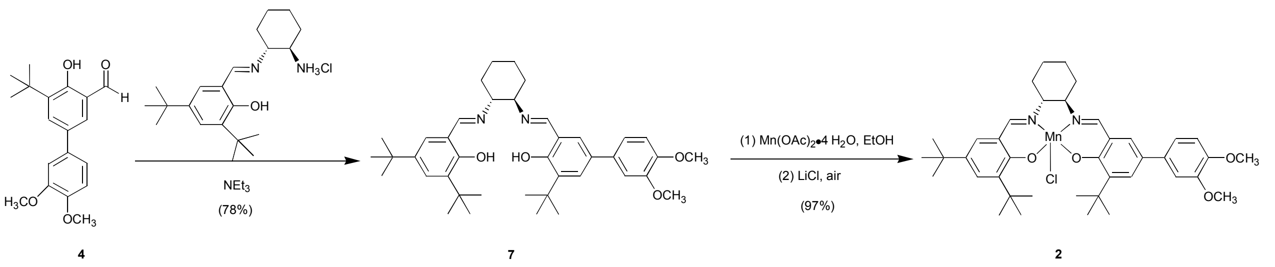
3-*Tert*-butyl-2-hydroxy-5-(3,4-dihydroxyphenyl)benzaldehyde (5). Under a nitrogen atmosphere, compound **4** (1.74 g, 5.57 mmol) was dissolved in CH_2Cl_2 (30 mL) in a 100-mL Schlenk flask equipped with a magnetic stir bar and a rubber septum. This solution was cooled to -40 °C in a dry ice/isopropanol bath. Boron tribromide solution (1.0 M in CH_2Cl_2, 13.9 mL, 13.9 mmol) was added slowly over 10 minutes via a gas-tight syringe, after which the bath was removed. The reaction was stirred for 2 h at room temperature and then ice-cold H_2O (20 mL) was added. The resulting mixture was stirred for an additional 20 minutes before the addition of EtOAc (70 mL). The organic layer was separated, washed with brine (3 × 30 mL), and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was dried under vacuum giving a solid yellow product, which was then recrystallized with a minimal amount of EtOAc and CH_2Cl_2. Yield = 1.33 g (83%) of **5** as a yellow powder (m.p. = 226-229 °C). ^1H NMR (500 MHz, $CDCl_3$): δ 11.75 (s, 1H, O*H*), 9.95 (s, 1H, C(O)*H*), 7.69 (s, 1H, Ar*H*), 7.51 (s, 1H, Ar*H*), 7.02 (d, $^2J_{HH}$ = 8.5, 1H, Ar*H*), 6.96 (d, $^2J_{HH}$ = 8.5, 1H, Ar*H*), 5.21 (s, 1H, O*H*), 5.11 (s, 1H, O*H*), 1.45 (s, 9H, C*Me*$_3$). ^{13}C NMR (125 MHz, DMSO-*d*$_6$): δ 196.7 (*C*(O)H), 158.6 (Ar), 145.7 (Ar), 145.0 (Ar), 137.4 (Ar), 131.9 (Ar), 131.6 (Ar), 130.6 (Ar), 129.4 (Ar), 120.9 (Ar), 117.3 (Ar), 116.1 (Ar), 113.6 (Ar), 34.6 (*C*Me$_3$), 29.1 (C*Me$_3$)*. ESIMS: Exact mass calcd. for $[C_{17}H_{18}O_4 - H]^-$: 285.12. Found: 285.40.

(1*R*,2*R*)-Cyclohexanediamino-*N*-(3,5-di-*tert*-butylsalicylidene)-*N'*-(3-*tert*-butyl-5-(3,4-dihydroxyphenyl)salicylidene) (6). Under a nitrogen atmosphere, (1*R*,2*R*)-cyclohexanediamino-*N*-(3,5-di-*tert*-butylsalicylidene)-*N'*-ammonium chloride (0.601 g, 1.64 mmol) was dissolved in absolute EtOH (20 mL) in a 100-mL Schlenk flask equipped with a magnetic stir bar. To the solution, were added activated 4-Å molecular sieves (0.23 g), a solution of **5** (0.416 g, 1.45 mmol) in EtOH (15 mL), and Et_3N (0.227 mL, 1.64 mmol), consecutively. The resulting mixture was stirred at room temperature overnight, filtered over a Celite pad, and washed with CH_2Cl_2 (20 mL). The combined organics were evaporated under reduced pressure and the resulting crude product was dissolved in Et_2O (20 mL). Insoluble impurities were filtered off; the remaining solution was evaporated under reduced pressure to yield a yellow solid, which was recrystallized from toluene (40 mL) and dried under vacuum. Yield = 0.668 g (68%) of **6** as a yellow powder. ^1H NMR (500 MHz, CD_2Cl_2): δ 8.33 (s, 1H, N=C*H*), 8.30 (s, 1H, N=C*H*), 7.41 (s, 1H, Ar*H*), 7.29 (s, 1H, Ar*H*), 7.14 (s, 1H, Ar*H*), 6.99 (s, 2H, Ar*H*), 6.84 (s, 2H, Ar*H*), 3.34 (m, 2H, C*H*-N), 1.98 (m, 2H, C*H$_2$*), 1.85 (m, 2H, C*H$_2$*), 1.73 - 1.77 (m, 2H, C*H$_2$*), 1.40-1.53 (m, 2H, C*H$_2$*), 1.42 (s, 9H, C*Me$_3$*), 1.38 (s, 9H, C*Me$_3$*), 1.20 (s, 9H, C*Me$_3$*). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 166.6 (N=CH), 166.3 (N=*C*H), 159.9 (Ar), 158.5 (Ar), 145.0 (Ar), 143.8 (Ar), 140.6

(Ar), 137.9 (Ar), 136.8 (Ar), 134.4 (Ar), 131.1 (Ar), 128.5 (Ar), 128.1 (Ar), 127.4 (Ar), 126.6 (Ar), 119.6 (Ar), 119.1 (Ar), 118.3 (Ar), 116.5 (Ar), 114.5 (Ar), 73.0 (*C*H-N), 72.8 (*C*H-N), 35.4 (*C*H$_2$), 34.5 (*C*H$_2$), 33.6 (*C*H$_2$), 31.7 (*C*H$_2$), 29.7 (C*Me$_3$*), 24.9 (*C*Me$_3$). ESIMS: Exact mass calcd. for $[C_{38}H_{50}N_2O_4 + H]^+$: 599.38. Found: 599.51.

(1*R*,2*R*)-Cyclohexanediamino-*N*-(3,5-di-*tert*-butylsalicylidene)-*N'*-(3-*tert*-butyl-5-(3,4-dihydroxyphenyl)salicylidene)manganese(III) chloride (1). To a 500-mL two-neck round bottom flask equipped with a 50-mL addition funnel and a water-cooled condenser was added **6** (1.163 g, 1.94 mmol) and degassed EtOH (200 mL) under a nitrogen atmosphere. A solution of anhydrous MnCl$_2$ (0.244 g, 1.94 mmol) dissolved in degassed ethanol solution (40 mL) was then added to the addition funnel under a nitrogen atmosphere. The solution of **6** was heated at 90^{o}C and the MnCl$_2$ solution was added slowly over a period of 2 h. The resulting mixture was refluxed overnight. LiCl (0.247 g, 5.82 mmol) was then added, and the solution was refluxed for additional 2 h in air. The reaction mixture was evaporated under reduced pressure to give a brown solid, which was then dissolved in CH$_2$Cl$_2$ (50 mL) and filtered through a Celite pad. The filtrate was then precipitated by addition of a diethylether/hexane (2/1, v/v) mixture (100 mL). The precipitates were filtered, washed with a diethylether/hexane (2/1, v/v) mixture (3 × 50 mL) and water (3 × 50 mL), and dried under vacuum overnight. Yield = 1.20 g (91%) of **1** as a dark brown solid. UV-Vis (EtOH): $\lambda_{\max}$ nm (log ε) 255 (4.65), 289 (4.49), 364 (4.02), 403 (4.00). IR (KBr): ν 3397 (br), 2952, 2867, 1611, 1536, 1432, 1458, 1390, 1341, 1311, 1253, 1201, 1172, 1030, 872, 847, 815, 781. EA: Calcd. for $C_{38}H_{48}ClMnN_2O_4{\bullet}3/2\ H_2O$: C, 63.90; H, 7.20; N, 3.92; Cl, 4.96. Found: C, 63.93; H, 7.06; N, 4.05; Cl, 5.31. ESIMS: Exact mass calcd. for $[C_{38}H_{48}ClMnN_2O_4 - H]^-$: 685.26. Found: 685.01.

Scheme S2. Synthesis of **2**.



(1*R*,2*R*)-cyclohexanediamino-*N*-(3,5-di-*tert*-butylsalicylidene)-*N'*-(3-*tert*-butyl-5-(3,4-dimethoxyphenyl)salicylidene) (7). Under a nitrogen atmosphere, (1*R*,2*R*)-cyclohexanediamino-*N*-(3,5-di-*tert*-butylsalicylidene)-*N'*-ammonium chloride (0.809 g, 2.20 mmol) was dissolved in absolute EtOH (25 mL) in a 100-mL Schlenk flask equipped with a magnetic stir bar. To the solution, were added activated 4-Å molecular sieves (0.3 g), a solution of **4** (0.692 g, 2.20 mmol) dissolved in absolute EtOH (20 mL), and Et$_3$N (0.623 mL, 4.40 mmol), consecutively. The resulting mixture was stirred at room temperature overnight, filtered over a Celite pad, and washed with CH$_2$Cl$_2$ (25 mL). The combined organics were evaporated under reduced pressure and the crude product was purified by silica gel chromatography (4 cm × 18 cm, hexane/EtOAc, 5:1 with 1% Et$_3$N). Yield = 0.88 g (64%) of **7** as a yellow powder. ^{1}H NMR (500 MHz,): δ 8.37 (s, 1H, N=C*H*), 8.32 (s, 1H, N=C*H*), 7.44 (s, 1H, Ar*H*), 7.31 (s, 1H, Ar*H*), 7.17 (s, 1H, Ar*H*), 6.98 (m, 3H, Ar*H*), 6.90 (d, $^2J_{HH}$ = 8 Hz, 1H, Ar*H*), 3.92 (s, 3H, O*CH$_3$*), 3.92 (s, 3H, O*CH$_3$*), 3.36 (m, 2H, C*H*-N), 1.99 (m, 2H, CH$_2$), 1.91 (m, 2H, CH$_2$), 1.77 (m, 2H, CH$_2$), 1.47 (s, 9H, C*Me$_3$*), 1.41 (s, 9H, C*Me$_3$*), 1.28 (m, 2H, CH$_2$), 1.23 (s, 9H, C*Me$_3$*). ^{13}C NMR (125 MHz, CD$_2$Cl$_2$): δ 166.2 (N=*C*H), 165.7 (N=*C*H), 160.0 (Ar), 158.2 (Ar), 149.3 (Ar), 148.2 (Ar), 140.2 (Ar), 137.7 (Ar), 136.6 (Ar), 134.6 (Ar), 131.0 (Ar), 128.4 (Ar), 128.1 (Ar), 127.1 (Ar), 126.2 (Ar), 119.1 (Ar), 118.9 (Ar), 118.0 (Ar), 111.6 (Ar), 110.4 (Ar), 72.7 (*C*H-N), 56.2 (O*Me*), 56.1 (O*Me*), 35.1 (*C*H$_2$), 35.1 (*C*H$_2$), 34.2 (*C*H$_2$), 33.4 (*C*H$_2$), 31.8 (C*Me$_3$*), 31.6 (C*Me$_3$*), 29.6 (C*Me$_3$*), 24.5(*C*Me$_3$), 22.9 (*C*Me$_3$). IR (KBr): ν 2932, 2859, 1629, 1604, 1519, 1465, 1436, 1262, 1243, 1215, 1142, 1028. APCIMS (CH$_2$Cl$_2$): Exact mass calcd. for $[C_{40}H_{54}N_2O_4 + H]^+$: 627.41. Found: 627.51.

(1*R*,2*R*)-Cyclohexanediamino-*N*-(3,5-di-*tert*-butylsalicylidene)-*N'*-(3-*tert*-butyl-5-(3,4-dimethoxyphenyl)salicylidene)manganese(III) chloride (2). In a 100-mL round bottom flask equipped with a water-cooled condenser and a magnetic stir bar, compound **7** (1.163 g, 1.86 mmol) and Mn(OAc)$_2$•4H$_2$O (0.910 g, 3.71 mmol) were combined with absolute EtOH (32 mL) and refluxed for 2 h. LiCl (0.236 g, 5.58 mmol) was then added and the resulting solution was refluxed for an additional hour before being cooled to room temperature. The crude reaction mixture was concentrated to ~ 10 mL under reduced pressure and placed in the freezer (-10 ^{o}C) for 2 h. The precipitates formed were filtered, washed with cold EtOH (3 × 30mL) and water (3 × 30 mL), and dried under vacuum overnight. Yield = 1.29 g (97%) of **2** as a dark brown powder. IR (KBr): ν 2943, 2862, 1611, 1539, 1519, 1465, 1433 1394, 1337, 1311, 1251, 1209, 1174, 1024, 847, 815, 780. EA: Calcd. for $C_{40}H_{52}ClMnN_2O_4$: C, 67.17; H, 7.33; N, 3.92; Cl, 4.96. Found: C, 67.01; H, 7.42; N, 3.65; Cl, 4.77. APCIMS(CH$_2$Cl$_2$): Exact mass calcd. for $[C_{40}H_{52}ClMnN_2O_4 - Cl]^+$: 679.33. Found: 679.54.

ICP spectrometric evaluation of catalyst loading. In a typical procedure, **1-AAO** was treated with a stirring mixture of hydrochloric and nitric acid (0.5 mL, 3/1 v/v) for 10 minutes (or until the AAO membrane was bleached). The mixture was then heated to dryness, dissolved in hot (100 ^{o}C) concentrated phosphoric acid (0.5 mL), and then diluted with distilled water to 10 mL. The acidic solution was then evaluated by inductively coupled plasma (ICP) spectroscopy for Mn content.[6] The Mn content was obtained in ppm based on a calibration curve obtained with a blank solution (5% phosphoric acid, aqueous) and a standard (5% phosphoric acid, doped with Mn calibration standard to make a 2-ppm Mn-containing solution). The loading of **1** on AAO was calculated to be 62 nmole per membrane (average of 5 **1-AAO** membranes). Since a membrane weighs approximately 15 mg (average of 5 membranes), the catalyst loading is 4.1 μmol g^{-1}. When the surface loading was considered, the catalyst (62 nmole, dimension of **1** = 4.4 Å × 12 Å (by Spartan modeling)) occupies about 38% of the total surface area of the AAO membrane (0.053 m^2 per membrane, as provided by the Whatman company).

General procedure for the asymmetric epoxidation catalyzed by 1-AAO under conventional batch reaction conditions. To a glass shell vial (15 mm × 45 mm) were added an anhydrous dichloromethane solution of 2,2-dimethyl-2*H*-chromene (0.2 mL of a 31.2 mM solution, 6.23×10^{-3} mmol) and undecane (1 µL) as an internal standard. A **1-AAO** membrane (prepared as described in the Notes and references section, containing 6.21×10^{-5} mmol of **1**) was placed in the vial along with a micro stir bar. The oxidant, 2-(*t*-butylsulfonyl)iodosylbenzene (4.25 mg, 1.25×10^{-2} mmol), was added to the solution slowly over 30 min in ~ 1-mg portions. The mixture was stirred for an additional 30 min after complete addition of the oxidant. The membrane was removed, washed with dichloromethane (3 × 2 mL), sonicated in dichloromethane (2 mL) for 1 min, and dried in air prior to being recycled. The remaining solution was passed through a plug of silica gel (60 mg) and washed with dichloromethane (4 mL) to remove the excess oxidants. The filtrate was analyzed by GC, chiral GC, and NMR spectroscopy for yield, enantioselectivity, and epoxide selectivity, respectively.

General procedure for the asymmetric epoxidation catalyzed by 1-AAO in a liquid phase forced-through-flow catalytic reactor system. In a stainless steel syringe filter holder (Fisher, 13-mm diameter) was placed an **1-AAO** membrane (prepared as described in the Notes and references section, containing 6.21×10^{-5} mmol of **1**). To a 5-mL vial were added 2,2-dimethyl-2*H*-chromene (102 mg, 6.38×10^{-1} mmol), undecane as the internal standard (20 µL), 2-(*t*-butylsulfonyl)iodosylbenzene (54.4 mg, 1.60×10^{-1} mmol), and anhydrous dichloromethane (2 mL). The solution was drawn into a 2.5-mL syringe which was then connected to the membrane holder. The assembly was attached to a syringe pump (KD Scientifics) and the reaction was started with injection of the substrate solution at a constant rate. The solution that exited from the outlet of the membrane holder was collected, passed through a plug of silica gel (100 mg), and washed with dichloromethane (10 mL) to remove the excess oxidants. The filtrate was analyzed by GC, chiral GC, and NMR spectroscopy for turnover numbers, enantioselectivity, and epoxide selectivity, respectively.

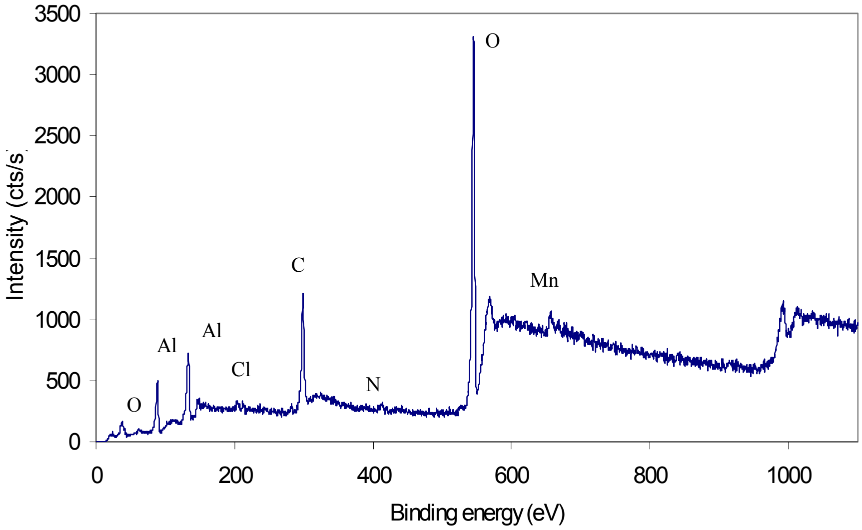


Figure S1. The X-ray photoelectron spectrum of **1-AAO**.

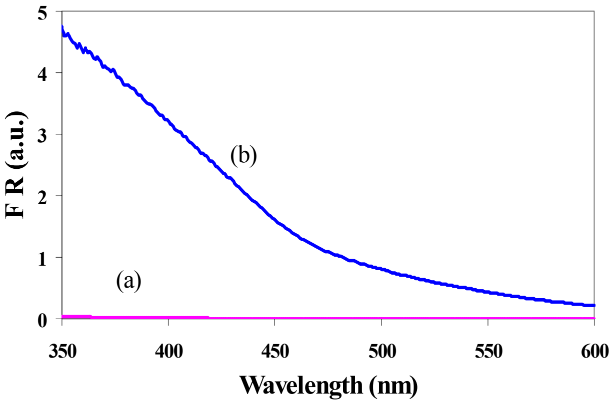


Figure S2. (a) The diffuse reflectance UV-Vis spectrum of a blank AAO. (b) The diffuse reflectance UV-Vis spectrum of **1-AAO**. a.u. = arbitray unit.

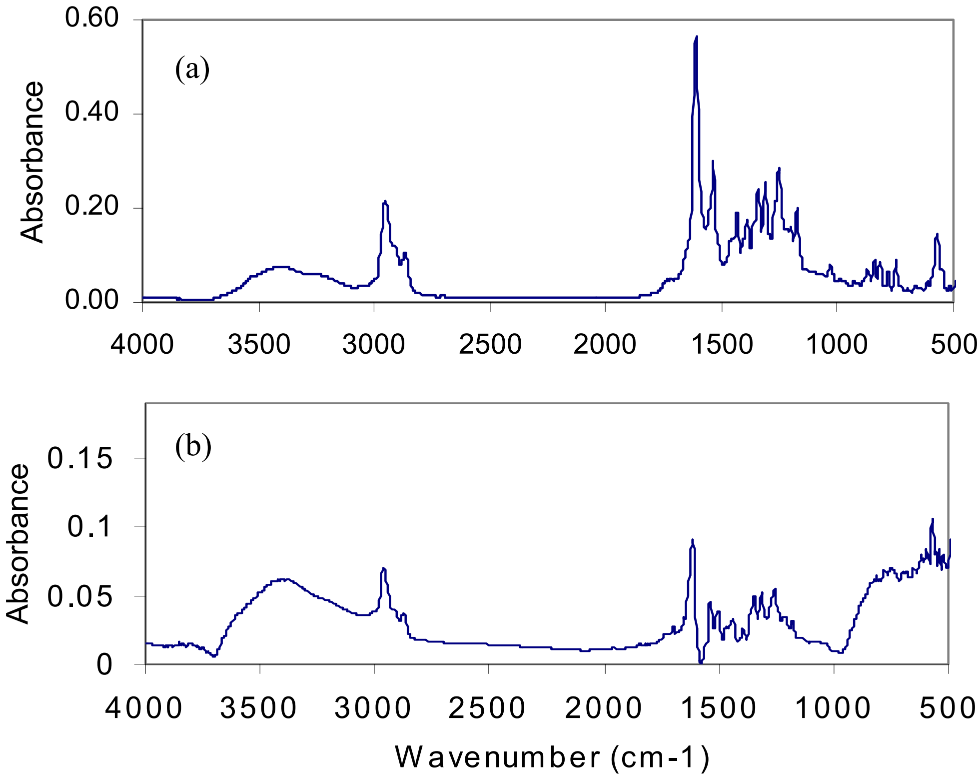


Figure S3. (a) The FT-IR spectrum of complex **1** (KBr pellet). (b) The FT-IR spectrum of **1-AAO** (KBr pellet).

References.

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