Supporting Information

Catalytic Aerobic Production of Imines en Route to Mild, Green, and Concise Derivatization of Amines

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1. General Method

$^1$H NMR spectra were recorded on JEOL JNM-LA500, JEOL ECX500 (500 MHz for $^1$H NMR and 125.65 MHz for $^{13}$C NMR), and JEOL ECS400 (400 MHz for $^1$H NMR and 100 MHz for $^{13}$C NMR) spectrometer. Chemical shifts were reported downfield from TMS ($\delta = 0$ ppm) for $^1$H NMR. For $^{13}$C NMR, chemical shifts were reported in the scale relative to the solvent used as an internal reference. Infrared (IR) spectra were recorded on a JASCO FT/IR 410 Fourier transform infrared spectrophotometer. ESI-mass spectra were measured on a Waters ZQ4000 spectrometer (for LRMS), and a JEOL JMS-T100LC AccuTOF spectrometer (for HRMS). Electron spin resonance (ESR) spectra were recorded on a JES-FA200 X-band spectrometer operating at 9.45 GHz (Microwave Frequency) and 100 kHz (Modulation Frequency) at room temperature.

Column chromatographies were performed with silica gel Merck 60 (230-400 mesh ASTM) or basic activated alumina (Wako, 300 mesh). HPLC analysis was conducted by JASCO HPLC systems (pump: PU-2080; detector: UV-2075, measured at 254 nm; column: DAICEL CHIRALPAK OD-H; mobile phase: 2-propanol/hexane). UV/Vis spectra were recorded on SHIMADZU UV-1800. X-ray crystallographic analysis was performed on a Rigaku R-AXIS RAPID II imaging plate area detector with graphite-monochromated Cu-Kα radiation. All non-commercially available compounds were prepared and characterized as described in Section 4 of this SI. Other reagents were purchased from Aldrich, Tokyo Chemical Industry Co., Ltd. (TCI), Kanto Chemical Co., Inc., and Wako Pure Chemical Industries, Ltd. and used without further purification.

2. General Procedure for Catalytic Oxidation of Amines (Table 1 and 2, Scheme 5)

Gram THF (21.2 mL, 0.2 M), CuBr (30.3 mg, 211 µmol), $^1$Bu$_2$bipy (56.6 mg, 211 µmol), DMAP (77.3 mg, 633 µmol) and ketoABNO (32.5 mg, 211 µmol) were added in flamed-dry test tube containing activated MS13X (422 mg, 100 g/mol) under argon atmosphere. The resulting mixture was stirred for one hour at room temperature. Bis(4-bromobenzyl)amine 6a (1.5 g, 4.22 mmol) was added in the test tube and the inside atmosphere was replaced to oxygen (1 atm, balloon). After stirring for 26 hours at room temperature, the reaction mixture was directly loaded onto basic alumina charged in column cylinder, and purified by flash column chromatography rapidly (basic alumina; hexane/CH$_2$Cl$_2$= 3/1) to afford 7a in 62% isolated yield as a white solid.

Combined NMR yield of imines and hydrolyzed aldehydes were determined from $^1$H NMR of crude mixture by comparison of integration of characteristic peaks of them with that of mesitylene used as the internal standard. The sample of crude mixture was generally obtained after rapid filtration over short pad basic alumina and evaporation of the solvent.
3. Procedures for Catalytic Oxidative Transformation of Amines through C-C Bond-Formation

3-1. Stepwise Addition of Grignard Reagent (Scheme 3, eq. 1)

CuBr (1.5 mg, 10 µmol), 1Bu2bipy (2.7 mg, 10 µmol) and ketoABNO (1.5 mg, 10 µmol) were added into flamed-dry test tube containing THF (1.0 mL). After the mixture was stirred for one hour under argon atmosphere, then 6m (54.1 mg, 0.20 mmol) was added in the test tube and the inside atmosphere was replaced to oxygen (1 atm, balloon). After stirring for one hour at room temperature, the reaction mixture was directly loaded onto short pad basic alumina and eluted with Et2O. All volatiles were removed under reduced pressure and THF (1.0 mL) was added into the flask. The inside atmosphere was filled with argon gas. The solution was cooled to −78 °C and MeMgBr (3.0 M in Et2O, 90 µL, 0.3 mmol) was added dropwise. After the reaction mixture was stirred at −78 °C for one hour, the cooling bath was removed and the reaction was quenched by saturated aqueous NH4Cl. The resulting mixture was extracted with EtOAc (three times) and the combined organic layer was washed with brine, dried over Na2SO4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, CH2Cl2/acetone = 15/1) to afford 8 (34.1 mg, 0.12 mmol) as a white solid 60% yield.

3-2. General Procedure for Oxidative Friedel-Crafts (CDC) Reaction (Scheme 3, eq. 2)

CuBr (1.5 mg, 10 µmol), 1Bu2bipy (2.7 mg, 10 µmol) and ketoABNO (1.5 mg, 10 µmol) were added into flamed-dry test tube containing THF (0.4 mL). After the mixture was stirred about one hour under argon atmosphere, 6m (54.1 mg, 0.20 mmol), indole (35.1 mg, 0.30 mmol) and silica gel (100 mg, 500 g/mol) were added and the inside atmosphere was replaced to air (1 atm, balloon). After stirring for 20 hours at room temperature, the reaction mixture was directly loaded onto short pad basic alumina and eluted with EtOAc. All volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 3/2 to 1/1) to afford 9 (71.7 mg, 0.189 mmol) as a brown solid in 93% yield.

Reactions shown in Scheme 3, eq 3 and 4 were conducted following the same procedure.
3-3. Oxidative aza-Diels-Alder Reaction (Scheme 3, eq. 5)

CuBr (1.5 mg, 10 μmol), 1Bu2bipy (2.7 mg, 10 μmol) and ketoABNO (1.5 mg, 10 μmol) were added into flamed-dry test tube containing THF (0.4 mL). After the mixture was stirred for one hour under argon atmosphere, 6m (54.1 mg, 0.20 mmol), Danishefsky’s diene (116 μL, 0.60 mmol) and silica gel (100 mg, 500 g/mol) were added and the inside atmosphere was replaced to oxygen (1 atm, balloon). After stirring for 21 hours at room temperature, the mixture was directly loaded onto short pad basic alumina and eluted with EtOAc. All volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 1/3 to 100% EtOAc) to afford 12 (36 mg, 0.106 mmol) as yellow solid in 53% yield.

3-4. Oxidative Strecker Reaction (Scheme 3, eq. 6)

CuBr (3.0 mg, 20 μmol), 1Bu2bipy (5.4 mg, 20 μmol) and ketoABNO (3.1 mg, 20 μmol) were added into flamed-dry test tube containing THF (1 mL) and activated MS13X (20 mg, 100 g/mol). After the mixture was stirred for one hour under argon atmosphere, 6h (42 μL, 0.20 mmol), HCN in 1.0 M THF solution (300 μL, 0.30 mmol; HCN solution was prepared by premixing TMSCN (125 μL, 1.0 mmol) and tBuOH (95 μL, 1.0 mmol) in THF (1.0 mL)), and DMAP (7.2 mg, 60 μmol) were added and the inside atmosphere was replaced to oxygen (1 atm, balloon). After stirring for 25 hours at 50 °C, the reaction mixture was directly loaded onto short pad basic alumina and eluted with Et2O. All volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (silica gel, hexane/CH2Cl2 = 2/1) to afford 13 (44.1 mg, 0.180 mmol) as a white solid in 90% yield.

3-5. Catalytic Asymmetric Aerobic CDC Reaction between Glycine Ester and Nitroalkane (Scheme 4)

CuOTf 1/2tol (10.3 mg, 40 μmol), (−)-Ph-Box (13.4 mg, 40 μmol), ketoABNO (6.2 mg, 40 μmol), and THF (2 mL) were added into flamed-dry test tube containing activated MS3A (100 mg, 250 g/mol) under argon...
atmosphere. The resulting mixture was stirred for one hour, then 6p (84 mg, 0.40 mmol), 1-nitropropane (356 µL, 4.0 mmol) and Et₃N (2.8 µL, 20 µmol) were added and the inside atmosphere was replaced to oxygen (1 atm, balloon). After stirring for 52 hours at room temperature, the mixture was directly loaded onto short pad basic alumina and eluted with EtOAc. All volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 8/1) to afford 14 (92 mg, 0.31 mmol) as brown oil in 78% yield. Diastereomeric ratio (syn/anti = 19.6/1) and enantiomeric excess (92% ee for syn isomer, 64% ee for anti isomer) were determined by HPLC analysis.

4. Synthesis and Characterization of New Compounds

4-1. Synthesis of Components for Catalyst

t-Bu₂bipy¹ and ABNO (2)² were synthesized following the literature procedure and characterized by comparison with reported spectroscopic data, respectively. Other catalytic components were commercially available and used as purchased.

9-benzyl-9-azabicyclo[3.3.1]nonan-3-one (S1)

Benzylamine hydrochloride (37.7 g, 0.263 mol) and glutaraldehyde (25% in water, 88 mL, 0.219 mol) were added in a 500 mL flask containing water (100 mL) under air. The mixture was cooled to 0 °C, then acetonedicarboxylic acid (32.0 g, 0.219 mol) and 10% NaOAc aq (75 mL) were added. After the removal of ice bath, the mixture was stirred for 2 hours at room temperature then stirred for 12 hours at 50 °C. The mixture was cooled to room temperature and 10% HCl aq was added to adjust the pH to 2. The solution was washed with Et₂O for 3 times, and the pH was adjusted to 6 by careful addition of saturated NaHCO₃ aq. The mixture was extracted with CH₂Cl₂ several times. The combined organic layer was washed with brine and dried over Na₂SO₄. After concentration of filtered organic layer under reduced pressure, the residue was filtered over short pad silica gel using hexane/EtOAc (3/2) as the eluent. Concentration of filtrate afforded S1 as a brown solid in 82% yield (41.0 g, 0.178 mol). All analytical data of the product were in accordance with reported data.³

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9-azabicyclo[3.3.1]nonan-3-one N-oxyl (ketoABNO (5))

To a 500mL flask charged with S1 (22.9 g, 100 mmol) and Pd/C (10% Pd, 5 mol%, 5.32 g) was added degassed MeOH (500 mL) under argon atmosphere, and the flask was filled with pure hydrogen gas (1 atm, balloon). The reaction mixture was stirred at 50 °C for 24 hours then cooled to room temperature. The black suspension was filtered over Celite and washed with degassed MeOH thoroughly. All volatiles were removed under reduced pressure to afford pure deprotected amine.

To the mixture of the crude amine, Na₂WO₄·2H₂O (3.3 g, 10 mmol) and acetonitrile (200 mL) was added H₂O₂·urea (28.2 g, 300 mmol) at 0 °C. After stirring for 12 hours at room temperature, the mixture was filtered over short pad silica gel using hexane/EtOAc (1/2) as the eluent. All volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 2/1 to 1/2) to afford ketoABNO 5 as a crystalline yellow powder in 71% yield (10.9 g, 70.6 mmol). UV/Vis: λmax 263, 478 nm; IR (KBr): 2964, 1705, 1354 cm⁻¹; LRMS (ESI): m/z 177 [M+Na⁺]; HRMS (ESI): m/z calcld for C₉H₁₂NO₂Na [M+Na⁺] 177.0760, Found 177.0769. The 3D structure of 5 was revealed by X-ray crystallography. Single crystal of 5 was grown by slow evaporation of acetone solution at room temperature.

4-2. Synthesis of Substrates

Non-commercially available amines 6c, 6f, 6h and 6m-r were synthesized following original procedures described below. Danishefsky’s diene was prepared following the reported procedure⁴. Other substrates were commercially available and used as purchased.

N, N-bis(4-methoxybenzyl)-2-nitrobenzenesulfonamide (S2)

A mixture of NsNH₂ (4.04 g, 20 mmol), p-methoxybenzyl chloride (5.97 mL, 44 mmol), K₂CO₃ (11.0 g, 80 mmol), NaI (1.50 g, 10 mmol) and acetonitrile (100 mL) was heated at reflux. After stirring for 3 hours, the reaction mixture was cooled to room temperature and H₂O was added. The aqueous layer was extracted with EtOAc. The organic layer was washed with brine and dried over Na₂SO₄. After filtration, all volatiles were removed under reduced pressure and the residue was purified by flash chromatography (hexane/EtOAc = 4/1 to 1/2) to afford S2 (7.8 g, 32.2 mmol) as a yellow powder in 88% yield. ¹H NMR (CDCl₃): δ = 3.76 (s, 3H), 4.37 (s, 4H), 6.77 (m, 4H), 7.00 (m, 4H), 7.54-7.59 (m, 1H), 7.67 (d, J = 4.0 Hz, 2H), 7.90 (d, J = 7.9 Hz, 1H); ¹³C NMR (CDCl₃): δ = 159.3, 147.8, 134.4, 133.3, 131.7, 130.9, 129.8, 127.1, 124.2, 114.0, 55.2, 49.7.

IR (KBr): 2924, 1613, 1541, 1342 cm\(^{-1}\); LRMS (ESI): \(m/z\) 465 [M+Na]\(^+\); HRMS (ESI): \(m/z\) calcd for 
\(C_{22}H_{22}N_2O_6SNa\) [M+Na]\(^+\) 465.1091, Found 465.1083.

**bis(4-methoxybenzyl)amine (6c)**

To a mixture of S2 (2.21 g, 5.0 mmol), LiOH \(H_2O\) (839 mg, 20 mmol) and DMF (25 mL) was added thioglycolic acid (698 \(\mu L\), 10 mmol) at room temperature, and the mixture was stirred for 8 hours. The reaction mixture was diluted with EtOAc and washed with NaHCO\(_3\) aq. The organic layer was dried over Na\(_2\)SO\(_4\). After filtration, all volatiles were removed under reduced pressure. The residue was purified by flash column chromatography (basic alumina, hexane/EtOAc = 5/1 to 3/1) to afford 6c (934 mg, 3.63 mmol) as a yellow oil in 73% yield. All analytical data of the product were in accordance with reported data.\(^5\)

**N-benzyl-2-nitrobenzenesulfonamide (S3)**

To a solution of benzylamine (4.1 mL, 37.3 mmol) and \(CH_2Cl_2\) (125 mL) were added NsCl (4.3 g, 24.9 mmol) and pyridine (6.0 mL, 74.7 mmol) at room temperature, and the mixture was stirred for 14 hours. The reaction was quenched by 10\% HCl aq and the pH was adjusted to 1. The aqueous layer was extracted with \(CH_2Cl_2\). The organic layer was washed with brine and dried over Na\(_2\)SO\(_4\). After filtration, all volatiles were removed under reduced pressure to afford pure S3 (5.7 g, 19.5 mmol) as yellow solid in 78% yield. All analytical data of the product were in accordance with reported data.\(^6\)

**N-benzyl-2-nitro-N-(3-phenylpropyl)benzenesulfonamide (S4)**

To a solution of 3-phenyl-1-propanol (1.5 mL, 11.0 mmol), S3 (3.2 g, 11.0 mmol), PPh\(_3\) (3.7 g, 14.1 mmol) in toluene (110 mL) was slowly added diethyl azodicarboxylate (40\% in toluene, 6.4 mL, 14.1 mmol) at 0 \(^\circ\)C. The mixture was warmed to room temperature and stirred for 16 hours. The reaction mixture was filtered through Celite and washed with toluene. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (silica gel, hexane/\(CH_2Cl_2\) = 1/1) to afford S4 (4.43 g, 10.8 mmol) as a pale orange oil in 98\% yield. \(^1\)H NMR (CDCl\(_3\)): \(\delta = 7.86\) (dd, \(J = 8.0, 1.7\) Hz, 1H), 7.65-7.35 (m, 3H), 7.27-7.23 (m, 3H), 7.21-7.16 (m, 4H), 7.14-7.10 (m, 1H), 6.93 (d, \(J = 7.5\) Hz, 2H), 4.47 (s, 2H), 3.21 (2H), 2.39 (t, \(J = 7.5\) Hz, 2H), 1.70-1.63 (m, 2H); \(^1^3\)C NMR (CDCl\(_3\)): \(\delta = 147.9, 140.9, 135.7, 133.7, 5\)


131.6, 130.9, 128.7, 128.3, 128.2, 127.9, 126.0, 124.2, 51.3, 46.7, 32.6; IR (neat): 3435, 1637, 1543, 1162 cm$^{-1}$; LRMS (ESI): m/z 433 [M+Na]$^+$; HRMS (ESI): m/z calcd for C$_{22}$H$_{22}$N$_2$O$_4$SNa [M+Na]$^+$ 433.1192, Found 433.1184.

**N-benzyl-3-phenylpropan-1-amine (6f)**

To a solution of S4 (2.0 g, 4.87 mmol), LiOH·H$_2$O (818 mg, 19.5 mmol) in DMF (24 mL) was added thioglycolic acid (680 µL, 9.74 mmol) at room temperature, and the mixture was stirred for 11 hours. The mixture was diluted with Et$_2$O and washed with saturated NaHCO$_3$ aq. The aqueous layer was extracted with Et$_2$O. Combined organic layer was washed with water and brine, dried over Na$_2$SO$_4$. After filtration, all volatiles were removed under reduced pressure to afford pure 6f (956 mg, 4.24 mmol) as a yellow oil in 87% yield. All analytical data of the product were in accordance with reported data.$^7$

**N-(cyclohexylmethyl)-4-methoxyaniline (6h)**

Flame-dry MgSO$_4$ (20 g, 1.0 g/mmol), cyclohexanecarboxaldehyde (2.4 mL, 20 mmol) and p-anisidine (2.5 g, 20 mmol) in CH$_2$Cl$_2$ (20 mL) were added into flask and stirred at room temperature for two hours under argon atmosphere. The reaction mixture was filtered over Celite. All the volatiles were removed under reduced pressure then MeOH (20 mL) was added. The solution was cooled to 0 °C and NaBH$_4$ (1.13 g, 30 mmol) was added portionwise at 0 °C. After stirring for four hours at 0 °C, 10% HCl aq was added to the reaction mixture. After stirring for 30 min, pH was maintained to 7 by careful addition of solid NaHCO$_3$. Aqueous layer was extracted with EtOAc, combined organic layer was washed with brine and dried over Na$_2$SO$_4$. After filtration, all the volatiles were removed under reduced pressure to afford pure 6h (4.25 g, 19.4 mmol) as a brown oil in 97% yield. All analytical data of the product were in accordance with reported data.$^8$

**N-benzyl-2-bromoacetamide (S5)**

To the mixture of benzylamine (5.46 mL, 50 mmol) and triethylamine (8.36 mL, 60 mmol) in THF (100 mL), bromoacetyl bromide (4.80 mL, 55 mmol) in THF (250 mL) was added dropwise at 0 °C and stirred for four

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hours. The solvent was removed under reduced pressure. The residue was purified by short pad column chromatography (silica gel, hexane/EtOAc = 2/1) to afford S5 as white solid (11.6 g, 55 mmol) in quantitative yield. All analytical data of the product were in accordance with reported data.  

N-benzyl-2-(4-methoxyphenylamino)acetamide (6m)  

S5 (2.28 g, 10.0 mmol), potassium carbonate (2.07 g, 15.0 mmol) and p-anisidine (1.35 g, 11.0 mmol) were added into acetonitrile (50 mL) and the mixture was heated at reflux for 21 hours under argon atmosphere. After the mixture was cooled to room temperature, inorganic precipitates were filtered off and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 3/2 to 1/1) to afford 6m (1.5 g, 5.5 mmol) as a brown solid in 55% yield.  

1H NMR (CDCl3): δ = 7.23-7.17 (m, 3H), 7.16-7.13 (m, 2H), 7.08 (s, 1H), 6.73-6.69 (m, 2H), 6.51-6.48 (m, 2H), 4.40 (d, J = 6.3 Hz, 2H), 3.72 (s, 2H), 3.67 (s, 3H); 13C NMR (CDCl3) δ = 170.6, 153.2, 141.1, 138.1, 128.6, 127.6, 127.4, 114.9, 114.5, 55.7, 49.7, 43.1; IR (KBr): 3366, 3246, 2962, 1653 cm⁻¹; LRMS (ESI): m/z 293 [M+Na]⁺; HRMS (ESI): m/z calcd for C24H22N2O3Na [M+Na]⁺ 293.1266, found 293.1252.

benzyl 2-chloroacetate (S6)  

To a mixture of benzyl alcohol (26.2 mL, 252 mmol) and Et3N (22 mL, 158 mmol) in CH2Cl2 (1.3 L) was added chloroacetylchloride (10 mL, 126 mmol) dropwise at 0 °C and stirred for 30 min. H2O was added into the reaction mixture and the aqueous layer was extracted with CH2Cl2. Combined organic layer was washed with brine and dried over Na2SO4. After filtration, all the volatiles were removed under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/EtOAc = 3/2) to afford S6 as colorless oil (17 g, 110 mmol) in 87% yield. All analytical data of the product were in accordance with reported data.  

benzyl 2-(4-methoxyphenylamino)acetamide (6o)  

S6 (8.0 g, 43.3 mmol), sodium acetate (3.6 g, 43.3 mmol) and p-anisidine (5.3 g, 43.3 mmol) were added into MeCN (433 mL) and the mixture was stirred at 60 °C for 20 hours under argon atmosphere. The inorganic

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precipitate was filtered off and all the volatiles were removed under reduced pressure. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 4/1) to afford 6o (11.0 g, 40.5 mmol) as a brown solid in 94% yield. 1H NMR (CDCl3): δ = 7.40-7.34 (m, 5H), 6.83-6.78 (m, 2H), 6.61-6.57 (m, 2H), 5.21 (s, 2H), 4.06 (s, 1H), 3.93 (s, 2H), 3.75 (s, 3H); 13C NMR (CDCl3) δ = 171.3, 152.7, 141.2, 135.3, 128.6, 128.4, 128.3, 114.9, 114.4, 66.9, 55.7, 46.8; IR (KBr): 3389, 2955, 1729, 1517 cm-1; LRMS (ESI): m/z 294 [M+Na]+; HRMS (ESI): m/z calcd for C16H17NO3Na [M+Na]+ 294.1106; found 294.1102.

ethyl 2-(4-methoxyphenylamino)acetoamide (6p)

S7 (3.32 mL, 30 mmol) was added to the mixture of p-anisidine (5.54 g, 45 mmol) and potassium carbonate (6.22 g, 45 mmol) in MeCN (150 mL). The reaction mixture was heated at reflux and stirred for two hours under argon atmosphere. After filtration, all the volatiles were removed under reduced pressure. The residue was purified by flash column chromatography (silica gel, hexane/acetone = 6/1 to 5/1) to afford 6p (3.1 g, 14.7 mmol) in 49% yield. All analytical data of the product were in accordance with reported data.

2-nitro-N-phenylbenzenesulfonamide (S8)

To a solution of aniline (9.1 mL, 100 mmol) in CH2Cl2 (500 mL), NsCl (8.8 g, 50 mmol) and pyridine (12.1 mL, 150 mmol) were added at room temperature, and the mixture was stirred for 18 hours. The reaction was quenched by 10% HCl aq. and the pH was maintained to 1. The aqueous layer was extracted with CH2Cl2, and the combined organic layer was washed with brine and dried over Na2SO4. After filtration, all the volatiles were removed under reduced pressure to afford pure S8 (8.3 g, 29.8 mmol) as pale yellow solid in 67% yield. All analytical data of the product were in accordance with reported data.

2-nitro-N-phenyl-N-((2-phenylcyclopropyl)methyl)benzenesulfonamide (S10)

To a solution of S9 (667 mg, 4.50 mmol), S8 (1.25 g, 4.50 mmol) and PPh3 (1.50 g, 5.72 mmol) in toluene (45 mL), diethyl azodicarboxylate (40% toluene solution, 2.62 mL, 5.76 mmol) was slowly added at 0 °C. The mixture was warmed to room temperature and stirred for 16 hours. The reaction mixture was filtered over Celite and washed with toluene. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 3/1) to afford S10 (1.15 g, 2.79 mmol)

as a colorless oil in 62% yield. \(^1\)H NMR (CDCl\(_3\)): \(\delta = 7.68-7.64\) (m, 2H), 7.57-7.56 (m, 1H), 7.50-7.47 (m, 1H), 7.37-7.30 (m, 3H), 7.26-7.22 (m, 4H), 7.17-7.14 (m, 1H), 6.95-6.93 (m, 2H), 3.99 (dd, \(J = 14.0, 6.1\) Hz, 1H), 3.75 (dd, \(J = 14.0, 6.1\) Hz, 1H), 1.77-1.73 (m, 1H), 1.35-1.28 (m, 1H), 1.00-0.96 (m, 1H), 0.94-0.90 (m, 1H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta = 147.9, 141.9, 138.1, 133.4, 132.3, 131.9, 131.0, 130.0, 129.4, 128.5, 128.1, 125.7, 125.6, 123.8, 56.9, 22.7, 22.6, 14.2; \(\text{IR (neat)}: 3027, 2925, 1539, 1371\) cm\(^{-1}\); LRMS (ESI): \(m/z\) 431 [M+Na]\(^+\); HRMS (ESI): \(m/z\) calcd for C\(_{22}\)H\(_{20}\)N\(_2\)O\(_3\)Na [M+Na]\(^+\) 431.1036, found 431.1028.

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N\-((2\text{-phenylcyclopropyl})\text{methyl})\text{aniline (6q)}
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To a solution of S10 (816 mg, 2.0 mmol) and LiOH H\(_2\)O (335 mg, 8.0 mmol) in DMF (10 mL), thioglycolic acid (279 \(\mu\)L, 4.0 mmol) was added at room temperature. The mixture was stirred for 11 hours and diluted with Et\(_2\)O. Organic layer was washed with saturated NaHCO\(_3\) aq. The aqueous layer was extracted with Et\(_2\)O. Combined organic layer was washed with water and brine, and dried over Na\(_2\)SO\(_4\). After filtration, all the volatiles were removed under reduced pressure to afford pure 6q (308 mg, 1.38 mmol) as a yellow oil in 69% yield. \(^1\)H NMR (CDCl\(_3\)): \(\delta = 1.09-1.17\) (m, 2H), 1.58-1.64 (m, 1H), 1.99-2.02 (m, 1H), 3.30 (d, \(J = 10\) Hz, 2H), 3.92 (brs, 1H), 6.79 (dd, \(J = 8.6, 2.4\) Hz, 2H), 6.91 (t, \(J = 7.2\) Hz, 1H), 7.25 (d, \(J = 7.2\) Hz, 2H), 7.33-7.39 (m, 3H), 7.45 (t, \(J = 7.7\) Hz, 2H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta = 148.2, 142.5, 129.1, 128.2, 125.7, 125.5, 117.3, 112.7, 48.1, 22.7, 22.0, 14.6; \(\text{IR (neat)}: 3408, 3022, 2853, 1602, 1505\) cm\(^{-1}\); LRMS (ESI): \(m/z\) 246 [M+Na]\(^+\); HRMS (ESI): \(m/z\) calcd for C\(_{16}\)H\(_{13}\)N\(_3\)Na [M+Na]\(^+\) 246.1253, found 246.1267.

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\text{ tert-butyl 2-phenylcyclopropylcarbamate (S12)}
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To a solution of S11\(^{14}\) (5.76 g, 35.5 mmol) in acetonitrile, triethylamine (6.93 mL, 49.7 mmol) and ethyl chloroformate (4.75 mL, 49.7 mmol) were added at \(-10^\circ\text{C}\) (NaCl/ice bath) and the mixture was stirred for two hours. Na\(_2\)O\(_3\) (4.16 g, 64 mmol) in H\(_2\)O (130 mL, 0.5 M) was added into the mixture. After stirring for three hours, ice-cooled H\(_2\)O was poured into the mixture and organic compounds were extracted with toluene. Combined organic layer was dried over Na\(_2\)SO\(_4\). The mixture was filtered and concentrated under reduced pressure up to ca. 25 mL. The mixture was heated at \(90^\circ\text{C}\) and stirred for three hours. \(\text{BuOH}\) (2.37 mL, 25 mmol) was then added into the reaction mixture and stirred at \(90^\circ\text{C}\) for 36 hours. After the mixture was cooled to room temperature, all the volatiles were removed under reduced pressure. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 15/1, 10/1, 7/1) to afford S12 (6.19 g, 26.3 mmol) as a colorless solid in 74% yield. \(^1\)H NMR (CDCl\(_3\)): \(\delta = 7.24\) (t, \(J = 6.9\) Hz, 2H), 7.15 (t, \(J = 7.5\) Hz, 1H), 7.11 (d, \(J = 7.5\) Hz, 1H), 5.15 (s, 1H), 2.71 (s, 1H), 2.02-1.98 (m, 1H), 1.46 (s, 9H), 1.15-1.10 (m, 2H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta = 156.1, 140.6, 128.1, 126.1, 125.7, 79.2, 32.3, 28.2, 24.7, 16.1; \(\text{IR (KBr)}: 3368, 2984\),

1685 cm⁻¹; LRMS (ESI): m/z 256 [M+Na]⁺; HRMS (ESI): m/z calcd for C₁₄H₁₆NO₂Na [M+Na]⁺ 256.1308, found 256.1317.

**tert-butyl benzyl(2-phenylcyclopropyl)carbamate (S13)**

To a solution of S12 (700 mg, 3.0 mmol) in DMF (12 mL, 0.25 M), sodium hydride (60 wt% in mineral oil, 180 mg, 4.5 mmol) was added at 0 °C and the mixture was stirred at the same temperature for 30 minutes. Benzyl bromide (535 µL, 4.5 mmol) was added to the mixture at 0 °C and the resulting mixture was allowed to warm up to room temperature. After stirring for 11 hours, H₂O was added and aqueous layer was extracted with Et₂O. Combined organic layer was washed with water and brine, and dried over Na₂SO₄. After filtration, all the volatiles were removed under reduced pressure. The residue was purified by flash column chromatography (silica gel hexane/ether = 10/1 to 7/1) to afford pure S13 (920 mg, 2.82 mmol) as a colorless oil in 94% yield. ¹H NMR (CDCl₃): δ = 7.31 (m, 1H), 7.23 (m, 5H), 7.16 (m, 1H), 7.05 (d, J = 6.9 Hz, 2H), 4.62 (brd, J = 13.8 Hz, 1H), 4.39 (d, J = 16.1 Hz, 1H), 2.69 (t, J = 6.9 Hz, 1H), 2.18-2.14 (m, 1H), 1.45 (s, 9H), 1.33-1.26 (m, 1H), 1.18 (s, 1H); ¹³C NMR (CDCl₃): δ = 156.6, 140.8, 138.7, 128.4, 128.1, 127.4, 126.2, 125.9, 80.0, 50.9, 38.8, 28.5, 26.5, 17.4; IR (neat): 2977, 1695, 1604 cm⁻¹; LRMS (ESI): m/z 346 [M+Na]⁺; HRMS (ESI): m/z calcd for C₂₁H₂₅NO₂Na [M+Na]⁺ 346.1778, found 346.1780.

**N-benzyl-2-phenylcyclopropanamine (6r)**

S13 (812 mg, 2.5 mmol) was added into 4 N HCl/dioxane (5 mL) and the mixture was stirred at room temperature for one hour. 1N NaOH aq. was added into the mixture and the aqueous layer was extracted with EtOAc. Combined organic layer was washed with brine and dried over Na₂SO₄. After filtration, all the volatiles were removed under reduced pressure. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 2/1) to afford 6r (550 mg, 2.48 mmol) as colorless oil in 99% yield. ¹H NMR (CDCl₃): δ = 7.24-7.20 (m, 4H), 7.17-7.13 (m, 3H), 7.06-7.03 (m, 1H), 6.92-6.90 (m, 2H), 3.79 (dd, J = 16.1, 2.9 Hz, 2H), 2.31-2.28 (m, 1H), 1.87-1.83 (m, 2H), 1.04-1.00 (m, 1H), 0.90-0.87 (m, 1H); ¹³C NMR (CDCl₃): δ = 142.5, 140.5, 128.6, 128.4, 127.2, 126.1, 125.6, 53.8, 41.4, 25.5, 17.4; IR (neat): 3317, 3027, 1604, 1496 cm⁻¹; LRMS (ESI): m/z 246 [M+Na]⁺; HRMS (ESI): m/z calcd for C₁₆H₁₃NNa [M+Na]⁺ 246.1253, found 246.1244.
4-3. Characterization of Catalytic Oxidation Products

Spectral data of imine 7a\textsuperscript{15}, 7b\textsuperscript{16}, 7c\textsuperscript{16}, 7d\textsuperscript{16}, 7e\textsuperscript{17}, 7g\textsuperscript{16}, 7h\textsuperscript{18}, 7i\textsuperscript{16}, 7j\textsuperscript{19}, 7k\textsuperscript{16}, 7l\textsuperscript{20}, 7m\textsuperscript{21} (R, R)-14\textsuperscript{22} were reported. Other imines 7f and 7q were characterized by comparing the imines which were prepared by mixing the corresponding aldehydes and amines.

7f: \textsuperscript{1}H NMR (CDCl\textsubscript{3}): δ = 8.18 (s, 1H), 7.67-7.63 (m, 2H), 7.35-7.30 (m, 3H), 7.21-7.17 (m, 2H), 7.15-7.08 (m, 3H), 3.55 (t, J = 6.9 Hz, 2H), 2.63 (t, J = 8.0 Hz, 2H), 2.00-1.94 (m, 2H); LRMS (ESI): m/z 246 [M+Na]\textsuperscript{+}; HRMS (ESI): m/z calcld for C\textsubscript{16}H\textsubscript{17}NNa [M+Na]\textsuperscript{+} 246.1253, found 246.1262.

7q: NMR was recorded as a mixture of imine and hydrolyzed aldehyde because pure 7q was impossible to prepare. Underlined chemical shifts were for imine 7q. \textsuperscript{1}H NMR (CDCl\textsubscript{3}): δ = 9.23 (d, J = 4.6 Hz, 1H), 7.47 (d, J = 6.9 Hz, 1H), 7.24-7.02 (m, 10H+5H), 2.55-2.51 (m, 1H), 2.38-2.35 (m, 1H), 2.12-2.06 (m, 1H+1H), 1.65-1.62 (m, 1H), 1.53-1.49 (m, 1H), 1.45-1.37 (m, 1H+1H); LRMS (ESI): m/z calcld for C\textsubscript{17}H\textsubscript{30}N\textsubscript{2}O\textsubscript{2}Na [M+Na]\textsuperscript{+} 307.1422, found 307.1424.

8: \textsuperscript{1}H NMR (CDCl\textsubscript{3}): δ = 7.34-7.25 (m, 3H), 7.21 (d, J = 6.9 Hz, 2H), 6.84-6.81 (m, 2H), 6.62-6.58 (m, 2H), 4.55 (dd, J = 14.9, 6.0 Hz, 1H), 4.41 (dd, J = 14.9, 6.0 Hz, 1H), 3.81 (q, J = 6.9 Hz, 1H), 3.79 (s, 3H), 3.70 (s, 1H), 1.56 (d, J = 6.9 Hz, 3H); \textsuperscript{13}C NMR δ = 174.2, 153.2, 140.5, 138.2, 128.6, 127.5, 127.3, 114.9, 56.0, 55.7, 43.0, 19.8; IR (KBr): 3341, 3283, 1644, 1509, 1237 cm\textsuperscript{-1}; LRMS (ESI): m/z 307 [M+Na]\textsuperscript{+}; HRMS (ESI): m/z calcld for C\textsubscript{17}H\textsubscript{30}N\textsubscript{2}O\textsubscript{2}Na [M+Na]\textsuperscript{+} 307.1422, found 307.1424.

9: \textsuperscript{1}H NMR (CDCl\textsubscript{3}): δ = 3.77 (s, 3H), 4.44 (dd, J = 15, 5.8 Hz, 1H), 4.61 (dd, J = 15, 6.1 Hz, 1H), 5.04 (s, 1H), 6.64 (d, J = 8.9 Hz, 2H), 6.80 (d, J = 8.9 Hz, 2H), 7.06-7.10 (m, 2H), 7.20 (t, J = 7.4 Hz, 3H), 7.25-7.26 (m, 2H), 7.35 (d, J = 8.3 Hz, 1H), 7.55 (t, J = 6.1 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 8.50 (s, 1H); \textsuperscript{13}C NMR δ = 172.6, 153.1, 141.1, 137.9, 136.4, 128.5, 127.5, 127.3, 125.4, 123.5, 122.2, 119.8, 118.8, 115.0, 114.8, 112.6, 111.8; IR (KBr): 3365, 1653, 1509, 1237 cm\textsuperscript{-1}; LRMS (ESI): m/z 408 [M+Na]\textsuperscript{+}; HRMS (ESI): m/z calcld for C\textsubscript{23}H\textsubscript{23}N\textsubscript{2}O\textsubscript{2}Na [M+Na]\textsuperscript{+} 408.1688, found 408.1686

\textsuperscript{21} Zhao, L.; Liao, X.; Li, C.-J. Synlett 2009, 18, 2953.
10: $^1$H NMR (CDCl$_3$): $\delta$ = 9.10 (s, 1H), 7.42-7.35 (m, 3H), 7.27-7.25 (m, 2H), 6.91-6.88 (m, 2H), 6.86-6.84 (m, 1H), 6.76-6.73 (m, 2H), 6.34-6.30 (m, 2H), 4.99 (s, 1H), 4.60 (dd, $J$ = 14.9, 6.3 Hz, 1H), 4.51 (dd, $J$ = 14.9, 6.3 Hz, 1H) 3.86 (s, 3H); $^{13}$C NMR (CDCl$_3$): $\delta$ = 171.3, 153.6, 140.9, 137.9, 129.8, 129.6, 127.7, 127.6, 118.6, 115.6, 115.1, 109.0, 105.8, 58.5, 55.9, 43.7; IR (KBr): 3362, 1653, 1509, 1238; LRMS (ESI): m/z 358 [M+Na]$^+$; HRMS (ESI): m/z calcd for C$_{20}$H$_{21}$N$_2$O$_2$Na [M+Na]$^+$ 358.1531, found 358.1547.

11: $^1$H NMR (CDCl$_3$): $\delta$ = 8.04 (s, 1H), 7.72 (d, $J$ = 8.0 Hz, 1H), 7.30 (d, $J$ = 8.0 Hz, 1H), 7.21-7.11 (m, 5H), 7.10-7.05 (m, 2H), 6.67-6.64 (m, 2H), 6.55-6.52 (m, 2H), 5.33 (s, 1H), 5.16 (d, $J$ = 12.6 Hz, 1H), 5.02 (d, $J$ = 12.6 Hz, 1H), 4.41 (s, 1H), 3.65 (s, 3H); $^{13}$C NMR(CDCl$_3$): $\delta$ = 172.9, 152.8, 141.0, 136.7, 135.7, 128.7, 128.5, 128.4, 126.1, 123.2, 122.9, 120.4, 119.9, 115.1, 113.0, 111.5; IR (KBr): 1735, 1510 cm$^{-1}$; LRMS (ESI): m/z 409 [M+Na]$^+$; HRMS (ESI): m/z calcd for C$_{24}$H$_{25}$N$_2$O$_3$Na [M+Na]$^+$ 409.1528, found 409.1528.

12: $^1$H NMR (CDCl$_3$): $\delta$ = 7.25 (d, $J$ = 8.0 Hz, 1H), 7.16-7.09 (m, 3H), 6.99 (d, $J$ = 6.9 Hz, 2H), 6.91-6.87 (m, 2H), 6.76-6.73 (m, 2H), 6.48 (brt, $J$ = 5.8 Hz, 1H), 5.09 (d, $J$ = 8.0 Hz, 1H), 4.47 (t, $J$ = 5.8 Hz, 1H), 4.30 (d, $J$ = 5.8 Hz, 2H), 3.67 (s, 3H), 2.86 (d, $J$ = 5.8 Hz, 2H); $^{13}$C NMR (CDCl$_3$): $\delta$ = 189.5, 169.0, 157.2, 148.2, 137.6, 137.4, 128.7, 127.6, 127.5, 120.5, 115.0, 102.6, 62.5, 55.5, 43.7, 38.4; IR (KBr): 3310, 2953, 1657, 1250 cm$^{-1}$; MS (ESI): m/z 359 [M+Na]$^+$; HRMS (ESI): m/z calcd for C$_{24}$H$_{25}$N$_2$O$_3$Na [M+Na]$^+$ 359.1372, found 359.1363.

13: $^1$H NMR (CDCl$_3$): $\delta$ = 6.83 (m, 2H), 6.69 (m, 2H) 3.95 (d, $J$ = 6.3 Hz, 2H), 3.76 (s, 3H), 3.52 (s, 1H), 1.97 (t, $J$ = 10.9 Hz, 2H), 1.83 (dd, $J$ = 14.3, 2.9 Hz, 3H), 1.73 (d, $J$ = 12.1 Hz, 1H), 1.19-1.33 (m, 5H); $^{13}$C NMR (CDCl$_3$): $\delta$ = 153.6, 138.9, 118.9, 115.9, 114.7, 55.4, 53.0, 40.5, 29.4, 28.6, 25.7, 25.4, 25.3; IR (KBr): 3340, 2928, 2850, 1233 cm$^{-1}$; MS (ESI): m/z 267 [M+Na]$^+$; HRMS (ESI): m/z calcd for C$_{15}$H$_{20}$N$_2$O$_3$Na [M+Na]$^+$ 267.1468, found 267.1478.

**Procedure for removal of PMP group**

![Diagram of PMP removal reaction](https://example.com/pmp_diagram.png)

To a solution of iodobenzene diacetate (294.7 mg, 0.92 mmol) in MeOH (2.5 mL), 8 (65.4 mg, 0.23 mmol) in MeOH (450 μL) was added over 30 min at 0 °C. After stirring for one hour under the temperature, 1 N aqueous HCl (5 mL) was added under 0 °C and stirred for two hours. The aqueous layer was washed with CH$_2$Cl$_2$, and the organic layer was extracted with 0.1 N aqueous HCl (10 mL). Combined aqueous layer was neutralized with saturated aqueous NaHCO$_3$ and extracted with CH$_2$Cl$_2$. The combined organic layer was washed with brine and dried over Na$_2$SO$_4$. After filtration, all volatiles were removed under reduced pressure.

Acetic anhydride (65.2 μL, 0.69 mmol), DMAP (5.6 mg, 0.046 mmol) and CH$_2$Cl$_2$ (3.5 mL) were added to the residue. The reaction mixture was stirred under room temperature for 11 hours. The mixture was diluted with ethyl acetate. The organic layer was washed with brine and dried over Na$_2$SO$_4$. After filtration, all the volatiles were removed under reduced pressure. The obtained residue was purified by flash column
chromatography (Silica gel, CH$_2$Cl$_2$/MeOH = 20/1 containing 1% of Et$_3$N) to afford 8' (35.2 mg, 0.16 mmol) as a white solid in 65% yield. $^1$H NMR (CDCl$_3$): $\delta = 7.31$-7.15 (m, 5H), 7.00 (s, 1H), 6.51 (d, $J = 7.5$ Hz, 1H), 4.49-4.44 (m, 1H), 4.36-4.27 (m, 2H), 1.87 (s, 3H), 1.27 (d, $J = 6.9$ Hz, 3H); $^{13}$C NMR (CDCl$_3$): $\delta = 172.6$, 170.4, 138.1, 128.9, 127.8, 127.7, 49.0, 43.7, 23.3, 18.6; IR (neat): 3290, 1651, 1556 cm$^{-1}$; LRMS (ESI): m/z 243 [M+Na]$^+$; HRMS (ESI): m/z calcld for C$_{12}$H$_{16}$N$_2$O$_2$Na [M+Na]$^+$ 243.2569, Found 243.2565.
5. CV analysis

We conducted cyclic voltammetric measurements to gain insights into electrochemical behaviors of N-oxyl radicals used in this study. The cyclic voltammograms were measured on an als600a electrochemical analyzer with a conventional three-electrode configuration at room temperature. Solution of TEMPO, ketoABNO or ABNO in acetonitrile was used throughout the cyclic voltammetric measurements. Bu$_4$NClO$_4$ (0.1 M) was used as supporting electrolyte. The cyclic voltammograms were obtained at various potential sweep rate ($v$) independently given in Fig S1 (TEMPO), Fig S2 (ABNO) and Fig S3 (ketoABNO), respectively. These N-oxyl radicals showed cyclic voltammograms within $n = 1000$ mV•s$^{-1}$.

The $E^{\circ}$ values of the N-oxyl radicals, which were calculated by $(E_{pa}+E_{pc})/2$. ($E_{pa}$ and $E_{pc}$ denote anodic and cathodic peak potentials, respectively. See Figure 4 in main text).

Fig S1. Cyclic voltammograms of TEMPO (2.0 mM) at varying scan rates.

Fig S2. Cyclic voltammograms of ABNO (2.0 mM) at varying scan rates.
6. ESR analysis

ESR of as synthesized ketoABNO (5) was recorded in 0.005 M THF solution at room temperature (Table 3, entry 1).

To 0.1 M THF solution of 5 was added CuBr (5 : CuBr = 1 : 1 molar ratio) and stirred for one hour under air. Supernatant of the suspension was diluted with THF to make 0.005 M solution and ESR was recorded at room temperature (entry 2).

To 0.1 M THF solution of 5 was added CuBr and iPr-PyBox (5 : CuBr : iPr-PyBox = 1 : 1 : 1 molar ratio) and stirred for one hour under air. Supernatant of the suspension was diluted with THF to make 0.005 M solution and ESR was recorded at room temperature (entry 3).

Both in ESR measurements of entries 2 and 3, significant peaks derived from other possible ESR-active species (i.e., Cu(II) complex etc.) were not observed at all.
AcH\text{N} \text{Me} \text{NHBN}
**Asymmetric reaction**

```
CuOTf (1.2 eq)  
Bn-Ph-Box ketol (BIO)  
EtN (5 mol%) each  

M51A, THF (0.2 M)  
O2 (1 atm), rt, 52 h

(R, R)-14  
78% isolated yield  
syn: anti = 9:1  
ee: 99% ee (syn)  
64% ee (anti)
```

**Racemic reaction**

```
CuOTf (1.2 eq)  
Bu-Bipy ketol (BIO)  
EtN (10 mol%)  

CH2Cl2 (0.2 M)  
O2 (1 atm), rt, 48 h

rac-14  
81% isolated yield  
syn: anti = 2:8:1
```

* Determined by HPLC.  
  Conditions: Chiralpak OD-H column, flow rate: 0.9 mL/min  
  n-hexane/i-PrOH = 45:1, λ = 254 nm  
  tR (min) = 17.1 (anti minor), 21.6 (anti major)  
  25.9 (syn minor), 26.7 (syn major)