Supplementary Material (ESI) for Chemical Communications

Catalytic Aziridination of Electron-Deficient Olefins Using *N*-Chloro-*N*-sodiocarbamate and Application of the Novel Method to Asymmetric Synthesis

Supporting Information

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Experimental Procedures

General Methods.

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were obtained on a Jasco FT/IR-410 infrared spectrophotometer. ^{1}H and ^{13}C-NMR spectra were recorded on a JEOL FT-NMR JNM EX 270 spectrometer (1H-NMR, 270 MHz; ^{13}C-NMR, 68 MHz) using tetramethylsilane as an internal standard. Mass spectra were measured with a Shimadzu Model GCMS-QP5000 spectrometer. High-resolution mass spectral data were obtained on a JEOL DX-303 mass spectrometer. Elemental analyses were performed at the Analytical Center, Faculty of Engineering, Osaka University. Flash column chromatography (FCC) was performed using silica gel FL60D (Fuji Silysia Chemical Co.). Preparative gel permeation liquid chromatography (GPLC) was performed on a JAI (Japan Analytical Industry) LC-908 instrument with JAIGEL 1H-2H columns and chloroform as an eluent. Analytical thin layer chromatography was performed using EM reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light and spraying with an ethanolic phosphomolybdic acid solution followed by heating.

Preparation of acrylamides and catalysts.

Acrylamides bearing oxazolidinones[1] and 3,5-dimethylpyrazole[2] moieties were prepared according to the literature procedures. 3,5-Diisopropylpyrazole was acylated with acryloyl chloride and triethyl amine. Ammonium catalysts **4**-**6** are commercially available and **7**[3], **8**[4] and **9**[5] were prepared by the known procedures.

Synthesis of azirizines

A suspension of olefin (0.3 mmol), chloramine **2** (61 mg, 0.3 mmol) and ammonium catalyst was stirred in CH_3CN or CH_2Cl_2 (1 mL) for the durations indicated. The solution was then diluted with Et_2O (5 mL), filtered, and the solvent evaporated under reduced pressure. The residue was purified using silica-gel column chromatography (eluent: hexane/AcOEt) to give the corresponding aziridines

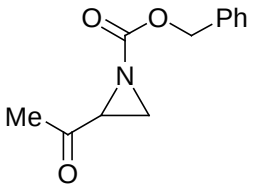
Removal of auxiliary

A solution of aziridine **3d** or **3g** (0.3 mmol) and DMAP (11 mg, 0.09 mmol) was stirred in MeOH (1 mL) for the durations indicated. The solvent then was evaporated under reduced pressure and the resulting residue was immediately purified using silica-gel column chromatography (eluent: hexane/AcOEt) to give aziridine **3b**.

3,5-Diisopropyl-1-(2-propenoyl)pyrazole (1g)

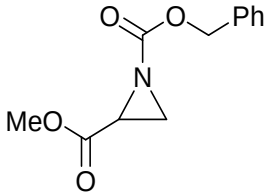
Colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.25 (d, 6H, *J* = 0.8 Hz), 1.28 (d, 6H, *J* = 1.1 Hz), 2.94 (m, 1H), 3.76 (m, 1H), 5.94 (dd, 1H, *J* = 1.9 Hz, 10.3 Hz), 6.60 (dd, 1H, *J* = 1.9 Hz, 17.5 Hz), 7.63 (dd, 1H, *J* = 10.3 Hz, 17.5 Hz)

2-Acetyl-1-benzyloxycarbonylaziridine (3a)



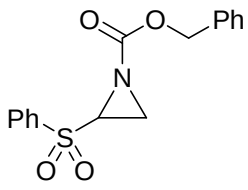
Colorless oil; R_f = 0.45 (hexane/EtOAc, 1:1, v/v, silica gel plate); IR (neat) 1730 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.19 (s, 3H), 2.47 (dd, 1H, *J* = 1.1 Hz, 3.2 Hz), 2.53 (dd, 1H, *J* = 1.1 Hz, 5.9 Hz), 3.19 (dd, 1H, 3.2 Hz, 5.9 Hz), 5.14 (d, 2H, *J* = 6.8 Hz), 7.36 (s, 5H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 27.1, 31.9, 40.8, 68.7, 128.4, 128.5, 135.1, 160.9, 202.9; MS (EI) *m*/*z* (relative intensity, %) 219 (M^+, 5); HRMS (CI, isobutane) calcd for $C_{12}H_{14}NO_3$ $(M + H)^+$ 220.0974, found 220.0971.

1-Benzyloxycarbonyl-2-methoxycarbonylaziridine (3b)



Spectroscopic data were in agreement with those for the previously reported material.[6] Colorless oil; R_f = 0.49 (hexane/EtOAc, 1:1, v/v, silica gel plate); HPLC (Daicel Chiralcel OD, hexane/2-propanol, 9:1, 0.2 mL/min, 254 nm, 30 °C) *t* = 56.8 and 66.0 min.; IR (neat) 1743, 1732 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.49 (dd, 1H, *J* = 1.2, 5.4 Hz), 2.60 (dd, 1H, *J* = 1.2, 3.2 Hz), 3.11 (dd, 1H, *J* = 3.2, 5.4 Hz), 3.71 (s, 3H), 5.17 (s, 2H), 7.36 (m, 5H); ^{13}C NMR (68MHz, $CDCl_3$) δ 31.4, 34.9, 52.7, 68.6, 128.3, 128.4, 135.2, 160.5, 168.4; MS (CI, isobutane) *m*/*z* (relative intensity, %) 236 (M^+ + H, 20), 192 (M^+ + H – CO_2, 100), 91 (CH_2Ph, 39); HRMS (CI, isobutane) calcd for $C_{12}H_{14}NO_4$ $(M + H)^+$ 236.0923, found 236.0917.

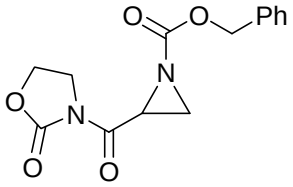
1-Benzyloxycarbonyl-2-phenylsulfonylaziridine (3c)



Colorless solid; mp 57-60 °C; R_f = 0.53 (hexane/EtOAc, 1:1, v/v, silica gel plate); IR (KBr) 3433, 1736, 1448, 1385, 1325, 1271, 1196, 1155, 1086 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.74 (dd, 2H, *J* = 0.3, 5.7 Hz), 2.96 (dd, 1H, *J* = 0.3 Hz, 3.0 Hz), 3.80 (dd, 1H, *J* = 3.0 Hz, 5.7 Hz), 4.98 (d, 2H, *J* = 7.8 Hz), 7.10 (m, 2H), 7.32 (m, 3H), 7.52 (dd, 2H, *J* = 7.0 Hz, 7.3 Hz), 7.65 (t, 1H, *J* = 7.3 Hz), 7.95 (d, 2H, *J* = 7.0 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 30.3, 50.9, 69.0, 128.0, 128.4, 128.5, 128.7, 129.1, 134.2, 137.0, 159.6; MS (CI) *m*/*z* (relative

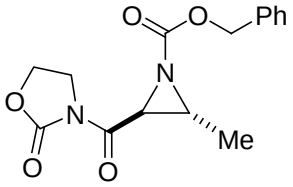
intensity, %) 318 (M^++H, 4), 274 (M^+ + H – CO_2, 100), 91 (CH_2Ph, 26); HRMS (CI, isobutane) calcd for $C_{16}H_{16}NO_4S$ $(M + H)^+$ 318.0800, found 318.0793.

3-[{(1'-Benzyloxycarbonyl)aziridin-2'-yl}carbonyl]-2-oxazolidinone (3d)



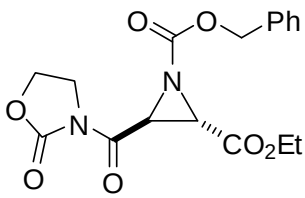
Colorless solid; mp 105 °C; R_f = 0.20 (hexane/EtOAc, 1:1, v/v, silica gel plate); HPLC (Daicel Chiralcel OB-H, hexane/2-propanol, 5:5, 0.6 mL/min, 254 nm, 35 °C) t = 56.0 and 75.8 min.; IR (KBr) 1765, 1736, 1707 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.60 (dd, 1H, J = 1.6, 5.6 Hz), 2.63 (dd, 1H, J = 1.6, 3.3 Hz), 3.94 (ddd, 1H, J = 6.9, 8.7, 11.0 Hz), 4.01 (ddd, 1H, J = 7.4, 8.9, 11.0 Hz), 4.41 (ddd, 1H, J = 7.4, 8.7, 8.8 Hz), 4.46 (ddd, 1H, J = 6.9, 8.8, 8.9 Hz), 4.53 (dd, 1H, J = 3.3, 5.6 Hz), 5.14 (s, 2H), 7.36 (m, 5H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 32.5, 33.9, 42.5, 62.5, 68.4, 128.1, 128.3, 135.1, 153.1, 160.5, 167.1; MS (CI, isobutane) m/z (relative intensity, %) 291 (M^+ + H, 100), 91 (CH_2Ph, 36); Anal. Calcd for $C_{14}H_{14}N_2O_5$: C, 57.93; H, 4.86; N, 9.65. Found: C, 57.70; H, 4.80; N, 9.57.

3-[{(1'-Benzyloxycarbonyl-*trans*-2'-methyl)aziridin-3'-yl}carbonyl]- 2-oxazolidinone (3e)



Colorless oil; R_f = 0.22 (hexane/EtOAc, 1:1, v/v, silica gel plate); IR (neat) 1697, 1726, 1778 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.39 (d, 3H, J = 5.4 Hz), 2.91 (m, 1H), 3.93 (m, 2H), 4.26 (d, 1H, , J = 2.7 Hz), 4.36 (m, 2H), 5.15 (s, 2H), 7.35 (s, 5H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 16.6, 40.7, 41.5, 42.5, 62.6, 68.3, 128.5, 135.7, 153.4, 160.3, 167.5; MS (CI, isobutane) m/z (relative intensity, %) 305 (M^+ + H, 100), 261 (M^+ + H – CO_2, 11), 91 (CH_2Ph, 30); HRMS (CI, isobutane) calcd for $C_{15}H_{17}N_2O_5$ $(M + H)^+$ 305.1137, found 305.1139.

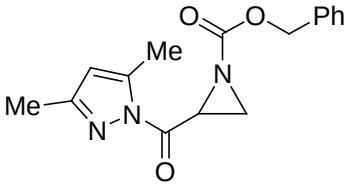
3-[{(1'-Benzyloxycarbonyl-*trans*-3'-etoxycarbonyl)aziridin-2'-yl}carbonyl]-2-oxazolidinone (3f)



Colorless oil; R_f = 0.18 (hexane/EtOAc, 1:1, v/v, silica gel plate); IR (neat) 1782, 1740 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.27 (t, 3H, J = 7.0 Hz), 3.41 (d, 1H, J = 2.4 Hz), 3.93 (ddd, 1H, J = 7.0, 8.8, 11.1 Hz), 4.01 (ddd, 1H, J = 7.3,

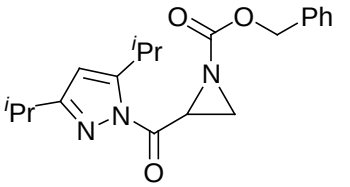
8.8, 10.8 Hz), 4.19 (ddd, 1H, *J* = 7.0, 10.8, 14.3 Hz), 4.23 (ddd, 1H, *J* = 7.3, 11.1, 14.3 Hz), 4.45 (m, 2H), 4.72 (d, 1H, *J* = 2.4 Hz), 5.13 (d, 2H, *J* = 4.1 Hz), 7.36 (m, 5H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.1, 39.8, 41.2, 42.6, 62.4, 62.7, 68.8, 128.4, 128.4, 134.9, 152.9, 158.3, 165.1, 165.8; MS (CI, isobutane) *m*/*z* (relative intensity, %) 363 (M^+ + H, 85), 319 (M^+ + H – CO_2, 100), 91 (CH_2Ph, 22); HRMS (CI, isobutane) calcd for $C_{12}H_{14}NO_4$ $(M + H)^+$ 363.1192, found 363.1187.

1-[{(1'-Benzyloxycarbonyl)aziridin-2'-yl}carbonyl]- 3,5-dimethyl-1*H*-pyrazole (3g)



Colorless oil; R_f = 0.45 (hexane/EtOAc, 7:3, v/v, silica gel plate); HPLC (Daicel Chiralcel OB-H, hexane/2-propanol, 9:1, 0.4 mL/min, 254 nm, 35 °C) *t* = 37.0 and 46.3 min.; IR (neat) 1732 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.26 (s, 3H), 2.49 (s, 3H), 2.63 (dd, 1H, *J* = 1.6, 5.4 Hz), 2.68 (dd, 1H, *J* = 1.6, 3.5 Hz), 4.61 (dd, 1H, *J* = 3.5, 5.4 Hz), 5.18 (d, 2H, *J* =1.9 Hz), 6.02 (s, 1H), 7.33 (m, 5H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.9, 14.3, 32.7, 34.8, 68.5, 111.8, 128.2, 128.4, 135.4, 144.5, 153.3, 161.0, 167.0; MS (CI, isobutane) *m*/*z* (relative intensity, %) 300 (M^+ + H, 100), 319 (M^+ + H – CO_2, 100), 91 (CH_2Ph, 20); HRMS (CI, isobutane) calcd for $C_{16}H_{17}N_3O_3$ $(M + H)^+$ 300.1348, found 300.1342.

1-[{(1'-Benzyloxycarbonyl)aziridin-2'-yl}carbonyl]- 3,5-diisopropyl-1*H*-pyrazole (3h)



Colorless oil; R_f = 0.64 (hexane/EtOAc, 7:3, v/v, silica gel plate); HPLC (Daicel Chiralpak IB, hexane/2-propanol, 95:5, 0.5 mL/min, 254 nm, 35 °C) *t* = 11.6 and 15.3 min.; IR (neat) 1736 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.23 (m, 12H), 2.63 (d, 1H, *J* = 5.4 Hz), 2.68 (d, 1H, *J* = 3.0 Hz), 2.93 (m, 1H), 3.60 (m, 1H), 4.68 (dd, 1H, *J* = 3.0, 5.4 Hz), 5.18 (d, 2H, *J* = 5.1 Hz), 6.12 (s, 1H), 7.34 (m, 5H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.8, 21.9, 22.2, 22.3, 26.9, 28.1, 32.7, 35.2, 68.4, 105.7, 128.2, 128.3, 135.3, 155.8, 161.0, 162.6, 166.9; MS (CI, isobutane) *m*/*z* (relative intensity, %) 356 (M^++H, 100), 91 (CH_2Ph, 11); HRMS (CI, isobutane) calcd for $C_{20}H_{25}N_3O_3$ $(M + H)^+$ 356.1974, found 356.1971.

References

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