Electronic Supplementary Information for

Vinylogy in Nitronates: Utilization of α-Aryl Conjugated Nitroolefins as a Nucleophile for Highly Stereoselective Aza-Henry Reaction

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General Information: Infrared spectra were recorded on a SHIMADZU IRAffinity-1 spectrometer. ¹H NMR spectra were recorded on a JEOL JNM-ECS400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane (0.00 ppm) resonance as the internal standard. Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), and coupling constants (Hz). ¹³C NMR spectra were recorded on a JEOL JNM-ECS400 (101 MHz) spectrometer or JEOL JNM-ECA600 (151 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance (CDCl₃: 77.16 ppm). The high resolution mass spectra were conducted on Thermo Fisher Scientific Exactive (ESI). Analytical thin layer chromatography (TLC) was performed on silica gel 60 (spherical, 40-50 µm; Kanto Chemical Co., Inc.). Enantiomeric excesses were determined by HPLC analysis using chiral columns [ϕ 4.6 mm x 250 mm, DAICEL CHIRALPAK IA (IA), CHIRALPAK IC (IC), CHIRALPAK ID-3 (ID-3), CHIRALPAK IF-3 (IF-3), CHIRALPAK AD-3 (AD-3), CHIRALPAK AZ-3 (AZ-3), CHIRALPAK AD-H (AD-H), and CHIRALCEL OD-3 (OD-3) with hexane (H), 2-propanol (IPA), and ethanol (EtOH) as eluent].

Diethyl ether (Et₂O) was supplied from Kanto Chemical Co., Inc. as "Dehydrated" and further purified by passing through neutral alumina under nitrogen atmosphere. Betaines¹, nitro olefins², and *N*-Boc imines³ were prepared by following the literature procedure. Powdered 4Å molecular sieves (MS 4A) was supplied by NACALAI TESQUE, INC. Other simple chemicals were purchased and used as such.

 ^{(1) (}a) D. Uraguchi, K. Koshimoto, T. Ooi, *Chem. Commun.* 2010, 46, 300. (b) D. Uraguchi, K. Oyaizu, T. Ooi, *Chem. Eur. J.* 2012, 18, 8306.

⁽²⁾ F. Asaro, G. Pitacco, E. Valentin, *Tetrahedron* 1987, **43**, 3279.

⁽³⁾ A. G. Wenzel, E. N. Jacobsen, J. Am. Chem. Soc. 2002, 124, 12964.

Experimental Section:

Characterization of Nitroolefins:

2a: The synthesis was performed by following the literature procedure.² Yellow oil; ¹H NMR (400 MHz, CDCl₃) *E* isomer δ 7.53–7.43 (4H, m), 7.31–7.24 (2H, m), 1.83 (3H, d, *J* = 7.3 Hz); *Z* isomer δ 7.42–7.37 (3H, m), 7.36–7.31 (2H, m), 6.15 (1H, q, *J* = 7.3 Hz), 2.00 (3H, d, *J* = 7.3 Hz); ¹³C NMR (151 MHz, CDCl₃) *E* isomer δ 152.3, 134.0, 130.5, 129.7, 128.7, 126.5, 14.5; *Z* isomer δ 129.6₄, 129.5₅, 129.0, 123.7, 14.1, two carbon atoms were not found probably due to overlapping; IR (film) 3057, 1667, 1514, 1443, 1327, 1184, 1074, 930 cm⁻¹; HRMS (ESI) Calcd for C₉H₉N₁O₂Na⁺ ([M+Na]⁺) 186.0525. Found 186.0527.

2b: The synthesis was performed by following the literature procedure.² Yellow oil; ¹H NMR (400 MHz, CDCl₃) *E* isomer δ 7.44 (1H, q, *J* = 7.3 Hz), 7.26 (2H, d, *J* = 8.2 Hz), 7.16 (2H, d, *J* = 8.2 Hz), 2.41 (3H, s), 1.82 (3H, d, *J* = 7.3 Hz); *Z* isomer δ 7.30–7.18 (4H, m), 6.09 (1H, q, *J* = 7.3 Hz), 2.37 (3H, s), 1.98 (3H, d, *J* = 7.3 Hz); ¹³C NMR (151 MHz, CDCl₃) *E* isomer δ 152.3, 139.8, 133.6, 130.4, 129.4, 126.6, 21.6, 14.5; *Z* isomer δ 129.6, 129.0, 126.4, 122.7, 21.4, 14.1, two carbon atoms were not found

probably due to overlapping; IR (film) 2914, 1667, 1514, 1377, 1327, 1180, 1113, 1038, 930 cm⁻¹; HRMS (ESI) Calcd for $C_{10}H_{11}N_1O_2Na^+$ ([M+Na]⁺) 200.0682. Found 200.0682.



2c: The synthesis was performed by following the literature procedure.² Yellow oil; ¹H NMR (400 MHz, CDCl₃) *E* isomer δ 7.50 (1H, q, *J* = 7.8 Hz), 7.30–7.23 (2H, m), 7.15 (2H, t, *J* = 8.7 Hz), 1.83 (3H, d, *J* = 7.8 Hz); ¹³C NMR (151 MHz, CDCl₃) *E* isomer δ 163.4 (d, *J*_{F-C} = 250.1 Hz), 151.3, 134.5, 132.6 (d, *J*_{F-C} = 8.6 Hz), 125.5 (d, *J*_{F-C} = 3.0 Hz), 115.9 (d, *J*_{F-C} = 21.6 Hz), 14.6; IR (film) 2922, 1667, 1633, 1504, 1327, 1225, 1159, 1098, 932 cm⁻¹; HRMS (ESI) Calcd for C₉H₈N₁O₂F₁Na⁺ ([M+Na]⁺) 204.0431.

Found 204.0433.

Me 2d: The synthesis was performed by following the literature procedure.² Yellow oil; ¹H NMR (400 MHz, CDCl₃) *E* isomer δ 7.47 (1H, q, *J* = 7.3 Hz), 7.37 (1H, t, *J* = 8.2 Hz), 7.02–6.97 (1H, m), 6.88– 6.83 (1H, m), 6.82–6.79 (1H, m), 3.83 (3H, s), 1.83 (3H, d, *J* = 7.3 Hz); *Z* isomer δ 7.30 (1H, t, *J* = 8.2 Hz), 6.96–6.91 (2H, m), 6.88–6.84 (1H, m), 6.14 (1H, q, *J* = 7.3 Hz), 3.81 (3H, s), 1.99 (3H, d, *J* = 7.3 Hz); ¹³C NMR (151 MHz, CDCl₃) *E* isomer δ 159.7, 152.1, 134.1, 130.7, 129.8, 122.8, 116.1, 115.3, 55.5, 14.5; *Z* isomer δ 159.9, 133.0, 130.0, 123.7, 118.9, 112.1, 14.1, three carbon atoms were not found probably due to overlapping; IR (film) 2959, 2833, 1667, 1580, 1514, 1331, 1240, 1159, 1036, 951 cm⁻¹; HRMS (ESI) Calcd for C₁₀H₁₁N₁O₃Na⁺ ([M+Na]⁺) 216.0631. Found 216.0633.

Et Ph NO_2 2e: The synthesis was performed by following the literature procedure.² Yellow oil; ¹H NMR (400 MHz, CDCl₃) *E* isomer δ 7.47–7.43 (3H, m), 7.38 (1H, t, *J* = 7.8 Hz), 7.30–7.25 (2H, m), 2.15 (2H, quintet, *J* = 7.8 Hz), 1.09 (3H, t, *J* = 7.8 Hz); ¹³C NMR (101 MHz, CDCl₃) *E* isomer δ 151.1, 139.9, 130.5, 129.8, 129.7, 128.7, 22.2, 13.2; IR (film) 2972, 1667, 1547, 1518, 1356, 1331, 1184, 1070, 959 cm⁻¹; HRMS (ESI) Calcd for C₁₀H₁₁N₁O₂Na⁺ ([M+Na]⁺) 200.0682. Found 200.0684.

2f: The synthesis was performed by following the literature procedure.² Yellow oil; ¹H NMR (400 MHz, CDCl₃) *E* isomer δ 7.48–7.42 (3H, m), 7.39 (1H, t, *J* = 7.8 Hz), 7.29–7.23 (2H, m), 2.12 (2H, q, *J*

= 7.8 Hz), 1.48 (2H, quintet, J = 7.8 Hz), 1.35–1.15 (10H, m), 0.87 (3H, t, J = 7.8 Hz); ¹³C NMR (101 MHz, CDCl₃) E isomer δ 151.4, 139.0, 130.5, 129.9, 129.7, 128.6, 31.9, 29.3, 29.2, 28.7, 28.6, 22.8, 14.2, one carbon atom was not found probably due to overlapping; IR (film) 2916, 2855, 1661, 1518, 1360, 1329, 1177, 1028, 964 cm⁻¹; HRMS (ESI) Calcd for C₁₆H₂₃N₁O₂Na⁺ ([M+Na]⁺) 284.1621. Found 284.1620.



Representative Procedure for Catalytic Asymmetric Aza-Henry Reaction: A magnetic stirrer bar and MS 4A (100.0 mg) were placed in an oven-dried test tube under argon (Ar) atmosphere. The MS 4A was dried with a heat gun under reduced pressure for 5 min and the test tube was refilled with Ar. Chiral ammonium betaine 1f (3.83 mg, 0.0050 mmol) and Et₂O (0.30 mL) were added to the test tube successively under Ar at 25 °C. After the mixture was cooled to 0 °C, nitroolefin 2a (17.9 mg, 0.11 mmol) and benzaldehyde-derived N-Boc imine 3a (20.5 mg, 0.10 mmol) were introduced to the tube sequentially. The reaction mixture was stirred for 24 h and then, poured into ice-cooled 1 N hydrochloric acid. The aqueous phase was extracted with ethyl acetate (EA) twice. The combined organic phases were washed with brine, dried over Na₂SO₄, and filtered. All volatiles were removed by evaporation to afford the crude residue, which was analyzed by ¹H NMR (400 MHz) to determine the diastereometric ratio (anti/syn = >20:1). Purification of the residue by column chromatography on silica gel (H/CHCl₃ = 1:2 as eluent) gave 4a as a mixture of diastereomers (33.2 mg, 0.090 mmol, 90%), whose enantiomeric excesses were determined by HPLC analysis (96% ee for *anti* isomer). 4a: White solid; HPLC: IA, H/IPA = 98:2, flow rate = 0.3 mL/min, λ = 210 nm, 22.0 min (1*S*, 2*S*), 23.2 min (1*R*, 2*R*), 25.5 min (minor diastereomer), 27.6 min (minor diastereomer). Absolute and relative configurations were assigned by the derivatization to 7 (see below). ¹H NMR (400 MHz, CDCl₃) anti isomer δ 7.60–7.39 (3H, m), 7.39–7.30 (3H, m), 7.30–7.18 (4H, m), 6.44 (1H, d, J = 9.6 Hz), 6.15 (1H, dd, J = 17.4, 11.0 Hz), 5.64 (1H, d, J = 9.6 Hz), 5.37 (1H, d, J = 11.0 Hz), 4.64 (1H, d, J = 17.4 Hz), 1.34 (9H, s); ¹³C NMR (101 MHz, CDCl₃) anti isomer δ 155.1, 136.7, 136.0, 135.0, 129.0, 128.8, 128.7, 127.4, 121.4, 101.9, 80.2, 59.3, 28.4, two carbon atoms were not found probably due to overlapping; IR (film) 3447, 2976, 1713, 1547, 1479, 1366, 1312, 1294, 1159, 1057, 945 cm⁻¹; HRMS (ESI) Calcd for $C_{21}H_{24}N_2O_4Na^+$ ([M+Na]⁺) 391.1628. Found 391.1626.



4b: Yellow oil; HPLC: AD-3, H/IPA = 98:2, flow rate = 0.3 mL/min, λ = 210 nm, 27.1 min (minor enantiomer of major diastereomer), 29.5 min (major enantiomer of major diastereomer), 32.2 min (minor diastereomer), 37.2 min (minor diastereomer). Absolute

and relative configurations were assigned on the analogy of **4a**. ¹H NMR (400 MHz, CDCl₃) *anti* isomer δ 7.44–7.37 (3H, m), 7.24–7.19 (2H, m), 7.16 (2H, d, J = 9.4 Hz), 7.13 (2H, d, J = 9.2 Hz), 6.40 (1H, d, J = 9.6 Hz), 6.17 (1H, dd, J = 17.4, 11.0 Hz), 5.60 (1H, d, J = 9.6 Hz), 5.36 (1H, d, J = 11.0 Hz), 4.63 (1H, d, J = 17.4 Hz), 2.34 (3H, s), 1.33 (9H, s); ¹³C NMR (101 MHz, CDCl₃) *anti* isomer δ 155.1, 138.5, 136.1, 135.1, 133.6, 129.5, 129.0, 128.7,

128.5, 127.4, 121.3, 102.0, 80.1, 59.0, 28.4, 21.3; IR (film) 3449, 2974, 1713, 1547, 1483, 1366, 1310, 1290, 1165, 941 cm⁻¹; HRMS (ESI) Calcd for $C_{22}H_{26}N_2O_4Na^+$ ([M+Na]⁺) 405.1785. Found 405.1786.

Boc∖_NH **4c:** Yellow oil; HPLC: ID-3, H/IPA = 97:3, flow rate = 0.2 mL/min, λ = 210 nm, 30.1 min (minor enantiomer of major diastereomer), 32.2 min (major enantiomer of major Ph NO₂ diastereomer), 39.6 min (minor diastereomer), 51.2 min (minor diastereomer). Absolute and relative configurations were assigned on the analogy of 4a. ¹H NMR (400 MHz, CDCl₃) anti isomer δ 7.45–7.39 (3H, m), 7.26–7.16 (4H, m), 7.05 (2H, dd, J_{H-H} = 7.6 Hz, J_{F-H} = 7.6 Hz), 6.39 (1H, brd, J = 9.8 Hz), 6.14 (1H, dd, J= 17.4, 11.0 Hz), 5.62 (1H, d, J = 9.8 Hz), 5.40 (1H, d, J = 11.0 Hz), 4.67 (1H, d, J = 17.4 Hz), 1.34 (9H, s); ¹³C NMR (101 MHz, CDCl₃) anti isomer δ 162.8 (d, J_{F-C} = 251.6 Hz), 155.1, 135.7, 134.8, 132.5, 130.4 (d, J_{F-C} = 8.7 Hz), 129.1, 128.8, 127.3, 121.7, 115.8 (d, *J*_{F-C} = 22.3 Hz), 101.8, 80.4, 58.7, 28.4; IR (film) 3449, 2980, 1711, 1605, 1547, 1479, 1366, 1294, 1225, 1161, 849 cm⁻¹; HRMS (ESI) Calcd for $C_{21}H_{23}N_2O_4F_1Na^+$ ([M+Na]⁺) 409.1534. Found 409.1535.



(major enantiomer of major diastereomer), 36.0 min (minor enantiomer of major diastereomer), 41.4 min (minor diastereomer), 43.8 min (minor diastereomer). Absolute and relative configurations were assigned on the analogy of **4a**. ¹H NMR (400 MHz, CDCl₃) *anti* isomer δ 7.45–7.39 (3H, m), 7.33 (2H, d, J = 8.7 Hz), 7.24–7.15 (4H, m), 6.38 (1H, d, J = 9.4 Hz), 6.14 (1H, dd, J = 17.4, 11.0 Hz), 5.61 (1H, d, J = 9.4 Hz), 5.40 (1H, d, J = 11.0 Hz), 4.67 (1H, d, J = 17.4 Hz), 1.34 (9H, s); ¹³C NMR (101 MHz, CDCl₃) anti isomer δ 155.0, 135.6, 135.3, 134.7, 130.0, 129.2, 129.0, 128.8, 127.3, 121.8, 101.7, 80.5, 58.7, 28.4, one carbon atom was not found probably due to overlapping; IR (film) 3451, 2980, 1713, 1549, 1483, 1344, 1163, 1092, 1015, 947, 849 cm⁻¹; HRMS (ESI) Calcd for $C_{21}H_{23}^{35}Cl_1N_2O_4Na^+$ ([M+Na]⁺) 425.1239. Found 425.1239.



4e: White solid; HPLC: IA, H/IPA = 98:2, flow rate = 0.5 mL/min, λ = 221 nm, 12.1 min (major enantiomer of major diastereomer), 15.4 min (minor diastereomer), 16.4 min (minor diastereomer), 17.9 min (minor enantiomer of major diastereomer). Absolute and relative

4d: Yellow oil; HPLC: AZ-3, H/EtOH = 98:2, flow rate = 0.2 mL/min, λ = 224 nm, 31.0 min

configurations were assigned on the analogy of 4a. ¹H NMR (400 MHz, CDCl₃) anti isomer δ 7.62 (2H, d, J = 8.2Hz), 7.46–7.41 (3H, m), 7.39 (2H, d, J = 8.2 Hz), 7.24–7.17 (2H, m), 6.43 (1H, d, J = 9.6 Hz), 6.13 (1H, dd, J = 17.4, 10.8 Hz), 5.70 (1H, d, *J* = 9.6 Hz), 5.43 (1H, d, *J* = 10.8 Hz), 4.71 (1H, d, *J* = 17.4 Hz), 1.35 (9H, s); ¹³C NMR (101 MHz, CDCl₃) anti isomer δ 155.1, 140.8, 135.4, 134.5, 130.9 (q, J_{F-C} = 33.2 Hz), 129.3, 129.2, 128.9, 127.3, 125.8 (q, $J_{F-C} = 3.9$ Hz), 124.0 (q, $J_{F-C} = 276.1$ Hz), 122.1, 101.5, 80.6, 59.0, 28.4; IR (film) 3464, 2976, 1711, 1620, 1551, 1479, 1323, 1163, 1125, 1069, 947, 853 cm⁻¹; HRMS (ESI) Calcd for $C_{22}H_{23}N_2O_4F_3Na^+$ ([M+Na]⁺) 459.1502. Found 459.1501.



4f: White solid; HPLC: IA, H/IPA/EtOH = 96:2:2, flow rate = 0.2 mL/min, λ = 214 nm, 25.7 min (major enantiomer of major diastereomer), 28.2 min (minor enantiomer of major diastereomer), 29.3 min (minor diastereomer), 31.0 min (minor diastereomer). Absolute and

relative configurations were assigned on the analogy of **4a**. ¹H NMR (400 MHz, CDCl₃) anti isomer δ 7.47 (1H, dt, J = 7.3, 1.6 Hz), 7.45–7.35 (4H, m), 7.23 (1H, t, J = 7.8 Hz), 7.22–7.15 (3H, m), 6.38 (1H, d, J = 9.6 Hz), 6.16 (1H, dd, J = 17.4, 10.8 Hz), 5.60 (1H, d, J = 9.6 Hz), 5.43 (1H, d, J = 10.8 Hz), 4.69 (1H, d, J = 17.4 Hz), 1.35 (9H, s); ¹³C NMR (101 MHz, CDCl₃) *anti* isomer δ 155.0, 139.0, 135.5, 134.7, 131.9₃, 131.8₈, 130.4, 129.2, 128.8, 127.3, 122.8, 122.0, 101.6, 80.5, 58.8, 28.4, one carbon atom was not found probably due to overlapping; IR (film) 3453, 2976, 1713, 1547, 1470, 1410, 1339, 1288, 1161, 1059, 947, 839 cm⁻¹; HRMS (ESI) Calcd for C₂₁H₂₃N₂O₄⁷⁹Br₁Na⁺ ([M+Na]⁺) 469.0733. Found 469.0735.

Boc NH Ph NO₂ + General Structure 4g: Yellow oil; HPLC: IA, H/IPA = 98:2, flow rate = 0.5 mL/min, λ = 210 nm, 15.6 min (major enantiomer of major diastereomer), 17.4 min (minor enantiomer of major diastereomer), 18.9 min (minor diastereomer), 35.0 min (minor diastereomer). Absolute and relative configurations were assigned on the analogy of 4a. ¹H NMR (400 MHz, CDCl₃) *anti* isomer δ 7.47– 7.37 (3H, m), 7.26 (1H, t, *J* = 8.0 Hz), 7.24–7.17 (2H, m), 6.89–6.82 (2H, m), 6.79 (1H, s), 6.40 (1H, d, *J* = 10.1 Hz), 6.20 (1H, dd, *J* = 17.4, 11.0 Hz), 5.61 (1H, d, *J* = 10.1 Hz), 5.37 (1H, d, *J* = 11.0 Hz), 4.64 (1H, d, *J* = 17.4 Hz), 3.79 (3H, s), 1.34 (9H, s); ¹³C NMR (101 MHz, CDCl₃) *anti* isomer δ 159.7, 155.1, 138.1, 136.0, 135.0, 129.8, 129.0, 128.7, 127.4, 121.4, 120.9, 114.7, 113.9, 101.8, 80.2, 59.2, 55.4, 28.4; IR (film) 3431, 2976, 1711, 1601, 1547, 1479, 1342, 1256, 1157, 1038, 947, 862 cm⁻¹; HRMS (ESI) Calcd for C₂₂H₂₆N₂O₅Na⁺ ([M+Na]⁺) 421.1734. Found 421.1729.



4h: Yellow oil; HPLC: ID-3, H/EtOH = 95:5, flow rate = 0.1 mL/min, λ = 210 nm, 46.6 min (minor enantiomer of major diastereomer), 50.4 min (major enantiomer of major diastereomer),

^{Ph' NO₂} 53.6 min (minor diastereomer), 56.2 min (minor diastereomer). Absolute and relative configurations were assigned on the analogy of **4a**. ¹H NMR (400 MHz, CDCl₃) *anti* isomer δ 7.47–7.38 (3H, m), 7.38–7.29 (1H, m), 7.29–7.19 (3H, m), 7.16 (1H, t, *J* = 7.1 Hz), 7.09 (1H, t, *J*_{H-H} = 7.1 Hz, *J*_{F-H} = 11.4 Hz), 6.43 (1H, d, *J* = 9.6 Hz), 6.10 (1H, d, *J* = 9.6 Hz), 6.06 (1H, ddd, *J* = 17.2, 10.7, 3.0 Hz), 5.40 (1H, d, *J* = 10.7 Hz), 4.64 (1H, d, *J* = 17.2 Hz), 1.34 (9H, s); ¹³C NMR (101 MHz, CDCl₃) *anti* isomer δ 160.2 (d, *J*_{F-C} = 251.6 Hz), 155.0, 134.7 (d, *J*_{F-C} = 5.8 Hz), 130.5 (d, *J*_{F-C} = 8.7 Hz), 129.1, 128.8, 128.7, 127.5, 125.1, 124.5 (d, *J*_{F-C} = 12.6 Hz), 122.4, 115.8 (d, *J*_{F-C} = 23.2 Hz), 102.1, 80.4, 51.9, 28.4, one carbon atom was not found probably due to overlapping; IR (film) 3449, 2932, 1713, 1549, 1481, 1344, 1298, 1229, 1157, 1057, 839 cm⁻¹; HRMS (ESI) Calcd for C₂₁H₂₃N₂O₄F₁Na⁺ ([M+Na]⁺) 409.1534. Found 409.1535.



4i: Yellow oil; HPLC: OD-3, H/IPA = 98:2, flow rate = 0.3 mL/min, λ = 210 nm, 18.9 min (major enantiomer of major diastereomer), 35.2 min (minor enantiomer of major diastereomer), minor diastereomers were not assigned. Absolute and relative configurations were assigned

on the analogy of **4a**. ¹H NMR (400 MHz, CDCl₃) *anti* isomer δ 8.20 (1H, d, J = 8.5 Hz), 7.87 (2H, t, J = 8.5 Hz), 7.57–7.40 (7H, m), 7.38–7.35 (2H, m), 6.72 (1H, d, J = 9.6 Hz), 6.69 (1H, d, J = 9.6 Hz), 5.79 (1H, dd, J = 17.4, 10.8 Hz), 5.22 (1H, d, J = 10.8 Hz), 4.58 (1H, d, J = 17.4 Hz), 1.32 (9H, s); ¹³C NMR (101 MHz, CDCl₃) *anti* isomer δ 155.2, 136.2, 135.0, 133.8, 133.7, 131.7, 129.5, 129.1₂, 129.0₇, 128.8, 127.6, 126.8, 126.0, 125.9, 125.4, 123.7, 122.0, 103.1, 80.0, 52.4, 28.4; IR (film) 2926, 1713, 1549, 1487, 1368, 1325, 1165, 1067 cm⁻¹; HRMS (ESI) Calcd for C₂₅H₂₆N₂O₄Na⁺ ([M+Na]⁺) 441.1785. Found 441.1783.



4j: Yellow oil; HPLC: AD-3, H/EtOH = 98:2, flow rate = 0.5 mL/min, λ = 210 nm, 12.7 min (major enantiomer of major diastereomer), 13.9 min (minor diastereomer), 15.7 min (minor

diastereomer), 17.7 min (minor enantiomer of major diastereomer). Absolute and relative configurations were assigned on the analogy of **4a**. ¹H NMR (400 MHz, CDCl₃) *anti* isomer δ 7.45–7.31 (5H, m), 7.24–7.15 (2H, m), 6.40–6.26 (3H, m), 6.06 (1H, d, J = 10.5 Hz), 5.84 (1H, d, J = 10.5 Hz), 5.46 (1H, d, J = 10.5 Hz), 4.87 (1H, d, J = 17.4 Hz), 1.34 (9H, s); ¹³C NMR (101 MHz, CDCl₃) *anti* isomer δ 155.0, 150.3, 142.7, 134.9, 134.5, 129.0, 128.7, 127.1, 122.0, 110.7, 109.5, 101.1, 80.4, 53.6, 28.3; IR (film) 3431, 2976, 1713, 1551, 1485, 1366, 1329, 1231, 1155, 1013, 949, 870 cm⁻¹; HRMS (ESI) Calcd for C₁₉H₂₂N₂O₅Na⁺ ([M+Na]⁺) 381.1421. Found 381.1420.



4k: White solid; HPLC: IA, H/IPA = 95:5, flow rate = 0.5 mL/min, λ = 210 nm, 10.3 min (major enantiomer of major diastereomer), 10.9 min (minor enantiomer of major diastereomer), 11.6 min (minor diastereomer), 12.7 min (minor diastereomer). Absolute and relative configurations were assigned on the analogy of **4a**. ¹H NMR (400 MHz, CDCl₃) *anti* isomer δ 7.38–7.29 (3H, m), 7.27–7.22 (2H, m), 7.21 (2H, d, *J* = 8.2 Hz), 7.10 (2H, d, *J* = 8.2 Hz), 6.43 (1H, d, *J* = 9.9 Hz), 6.14

(1H, dd, J = 17.3, 10.9 Hz), 5.60 (1H, d, J = 9.9 Hz), 5.36 (1H, d, J = 10.9 Hz), 4.66 (1H, d, J = 17.3 Hz), 2.38 (3H, s), 1.35 (9H, s); ¹³C NMR (101 MHz, CDCl₃) *anti* isomer δ 155.1, 139.0, 136.8, 136.2, 132.1, 129.4, 128.8, 128.7, 127.3, 121.3, 101.7, 80.2, 59.2, 28.4, 21.2, one carbon atom was not found probably due to overlapping; IR (film) 3447, 2970, 1713, 1547, 1483, 1366, 1310, 1292, 1169, 1057, 843 cm⁻¹; HRMS (ESI) Calcd for C₂₂H₂₆N₂O₄Na⁺ ([M+Na]⁺) 405.1785. Found 405.1787.



41: White solid; HPLC: IC, H/IPA = 97:3, flow rate = 0.5 mL/min, λ = 210 nm, 10.5 min (major enantiomer of major diastereomer), 13.0 min (minor diastereomer), 14.0 min (minor diastereomer), 18.7 min (minor enantiomer of major diastereomer). Absolute and relative configurations were assigned on the analogy of **4a**. ¹H NMR (400 MHz, CDCl₃) *anti* isomer δ 7.39–7.31 (3H, m), 7.26–7.18 (4H, m), 7.10 (2H, t, J_{H-H} = 8.7 Hz, J_{F-H} = 8.7 Hz), 6.38 (1H, d, J = 9.8 Hz), 6.16 (1H, dd,

J = 17.2, 11.0 Hz), 5.60 (1H, d, J = 9.8 Hz), 5.39 (1H, d, J = 11.0 Hz), 4.65 (1H, d, J = 17.2 Hz), 1.35 (9H, s); ¹³C NMR (101 MHz, CDCl₃) *anti* isomer δ 162.8 (d, $J_{F-C} = 253.5 \text{ Hz}$), 155.1, 136.4, 136.0, 130.9 (d, $J_{F-C} = 2.9 \text{ Hz}$), 129.5 (d, $J_{F-C} = 8.7 \text{ Hz}$), 128.9, 128.8, 128.6, 128.5, 121.5, 115.7 (d, $J_{F-C} = 22.3 \text{ Hz}$), 101.4, 80.4, 59.3, 28.4; IR (film) 3453, 2978, 1709, 1605, 1549, 1514, 1485, 1312, 1236, 1169, 1055, 943, 837 cm⁻¹; HRMS (ESI) Calcd for C₂₁H₂₃N₂O₄F₁Na⁺ ([M+Na]⁺) 409.1534. Found 409.1535.



4m: White solid; HPLC: IF-3, H/IPA/EtOH = 94:2:4, flow rate = 0.5 mL/min, λ = 210 nm, 11.0 min (minor enantiomer of major diastereomer), 12.1 min (major enantiomer of major diastereomer), 13.2 min (minor diastereomer), 13.8 min (minor diastereomer). Absolute and relative configurations were assigned on the analogy of **4a**. ¹H NMR (400 MHz, CDCl₃) *anti*

isomer δ 7.38–7.29 (4H, m), 7.27–7.22 (2H, m), 6.94 (1H, dd, J = 8.2, 2.3 Hz), 6.83–6.74 (2H, m), 6.44 (1H, d, J = 9.6 Hz), 6.13 (1H, dd, J = 17.3, 10.9 Hz), 5.62 (1H, d, J = 9.6 Hz), 5.38 (1H, d, J = 10.9 Hz), 4.73 (1H, d, J = 17.3 Hz), 3.81 (3H, s), 1.34 (9H, s); ¹³C NMR (101 MHz, CDCl₃) *anti* isomer δ 159.8, 155.1, 136.7, 136.3, 135.8, 129.7, 128.8, 128.7, 121.4, 119.6, 114.8, 113.1, 101.8, 80.2, 59.2, 55.5, 28.4, one carbon atom was not found probably due to overlapping; IR (film) 3443, 2978, 1703, 1601, 1547, 1487, 1352, 1288, 1227, 1167, 1030, 949 cm⁻¹; HRMS (ESI) Calcd for C₂₂H₂₆N₂O₅Na⁺ ([M+Na]⁺) 421.1734. Found 421.1733.

Boc NH Me Ph NO₂ An: White solid; HPLC: AZ-3, H/IPA = 98:2, flow rate = 0.3 mL/min, λ = 210 nm, 21.5 min (minor enantiomer of major diastereomer), 25.3 min (major enantiomer of major diastereomer), 29.4 min (minor diastereomer), 31.6 min (minor diastereomer). Absolute and relative configurations were assigned on the analogy of 4a. ¹H NMR (400 MHz, CDCl₃) *anti* isomer δ 7.44–7.30 (6H, m), 7.28–7.16 (4H, m), 6.42 (1H, d, J = 9.6 Hz), 5.78 (1H, dd, J = 15.8, 3.2 Hz), 5.61 (1H, d, J = 9.6 Hz), 5.03 (1H, sextet, J = 9.0 Hz), 1.67 (3H, d, J = 6.4 Hz), 1.33 (9H, s); ¹³C NMR (101 MHz, CDCl₃) *anti* isomer δ 155.1, 136.9, 135.9, 133.5, 129.4, 128.8, 128.7₄, 128.6₉, 128.6₀, 127.4, 101.9, 80.1, 59.5, 28.4, 18.3, one carbon atom was not found probably due to overlapping; IR (film) 3451, 2972, 1713, 1547, 1479, 1366, 1292, 1161, 1047, 970, 843

 cm^{-1} ; HRMS (ESI) Calcd for $C_{22}H_{26}N_2O_4Na^+$ ([M+Na]⁺) 405.1785. Found 405.1785.



40: HPLC analysis was performed after reduction of the nitro group to give the corresponding amine **S1**. Absolute and relative configurations were assigned on the analogy of **4a**. White solid; ¹H NMR (400 MHz, CDCl₃) *anti* isomer δ 7.44–7.37 (3H, m), 7.37–7.30 (3H, m), 7.28–

7.16 (4H, m), 6.43 (1H, d, J = 10.1 Hz), 5.75 (1H, d, J = 16.0 Hz), 5.61 (1H, d, J = 10.1 Hz), 5.02 (1H, dt, J = 16.0, 6.8 Hz), 1.98 (2H, q, J = 6.8 Hz), 1.34 (9H, s), 1.31–1.17 (10H, m), 0.87 (3H, t, J = 6.9 Hz); ¹³C NMR (101 MHz, CDCl₃) *anti* isomer δ 155.1, 138.6, 136.9, 135.9, 128.7, 128.6, 128.3, 127.4, 102.0, 80.1, 59.6, 32.5, 31.9, 29.1, 28.6, 28.4, 22.8, 14.2, four carbon atoms were not found probably due to overlapping; IR (film) 3453, 2922, 1713, 1547, 1483, 1425, 1391, 1256, 1161, 972 cm⁻¹; HRMS (ESI) Calcd for C₂₈H₃₈N₂O₄Na⁺ ([M+Na]⁺) 489.2724. Found 489.2725. **S1**: The synthesis was performed by following the procedure for amine **S2** (shown below). White solid; HPLC: 1A, H/IPA = 98:2, flow rate = 0.3 mL/min, $\lambda = 210$ nm, 35.6 min (minor enantiomer of major diastereomer), 42.2 min (minor diastereomer), 47.6 min (minor diastereomer), 56.7 min (major enantiomer of major diastereomer). ¹H NMR (400 MHz, CDCl₃) *anti* isomer δ 7.49 (2H, d, J = 7.8 Hz), 7.33 (2H, t, J = 7.8 Hz), 7.29–7.20 (4H, m), 7.18 (2H, br), 5.95 (1H, d, J = 15.6 Hz), 5.64 (1H, brd, J = 7.5 Hz), 5.27 (1H, dt, J = 15.6, 6.8 Hz), 5.03 (1H, d, J = 7.5 Hz), 1.95 (2H, q, J = 6.8 Hz), 1.36–1.07 (19H, m), 0.87 (3H, t, J = 6.8 Hz); ¹³C NMR (101 MHz, CDCl₃) *anti* isomer δ 155.4, 144.5, 139.1, 136.4, 129.6, 128.5, 128.3, 127.7, 127.3, 126.8, 126.2, 79.2, 62.2, 32.4, 31.9, 29.3, 29.2, 28.3, 22.8, 14.3, two carbon atoms were not found probably due to overlapping; IR (film) 3362, 2965, 2924, 1703, 1514, 1366, 1248, 1163, 1011 cm⁻¹; HRMS (ESI) Calcd for C₂₈H₄₁N₂O₂ ([M+H]⁺) 437.3163. Found 437.3157.

Derivatization of 4a:



Conversion of Nitroalkene 4a to Differentially Protected Diamine 5: 4a (36.8 mg, 0.10 mmol) was taken in HCl/EtOH/H₂O (666.7 μ L, 3.0 M, 2.0 mmol, EtOH/H₂O = 1:2) and Zn powder (130.8 mg, 2.0 mmol) was introduced to the solution portionwise. The mixture was stirred for 12 h at ambient temperature. The reaction mixture was diluted

with water and the aqueous phase was extracted with EA twice. The combined organic extracts were washed with brine and dried over Na₂SO₄. After concentration, the resulting residue was purified by column chromatography on silica gel (H/EA = 1:1 as eluent) to afford the corresponding amine **S2** in 90% yield (30.5 mg, 0.090 mmol). **S2:** White solid; ¹H NMR (400 MHz, CDCl₃) δ 7.50 (2H, d, *J* = 7.8 Hz), 7.34 (2H, t, *J* = 7.8 Hz), 7.30–7.22 (4H, m), 7.19 (2H, brd, *J* = 6.9 Hz), 6.42 (1H, dd, *J* = 17.4, 10.8 Hz), 5.66 (1H, brd, *J* = 6.9 Hz), 5.09 (1H, d, *J* = 6.9 Hz), 5.04 (1H, d, *J* = 10.8 Hz), 4.93 (1H, d, *J* = 17.4 Hz), 1.23 (9H, s); ¹³C NMR (101 MHz, CDCl₃) δ 155.4, 144.4, 143.7, 138.9, 128.4₄, 128.3₇, 127.8, 127.4, 127.0, 126.2, 113.4, 79.3, 62.9, 62.0, 28.3; IR (film) 3318, 2976, 1703, 1585, 1514, 1366, 1248, 1169, 995 cm⁻¹; HRMS (ESI) Calcd for C₂₁H₂₇N₂O₄⁺ ([M+H]⁺) 339.2067. Found 339.2065.

The amine **S2** (30.5 mg, 0.090 mmol) was dissolved into CH₂Cl₂ (0.90 mL) and ¹Pr₂EtN (39.6 µL, 0.23 mmol) and benzyl chloroformate (19.3 µL, 0.14 mmol) were added sequentially. The reaction mixture was stirred for 24 h and poured to water. The mixture was then extracted with CHCl₃ twice and the combined organic extracts were washed with brine. Organic extracts were dried over Na₂SO₄ and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (H/EA = 5/1 as eluent) to afford **5** in 56% yield (23.6 mg, 0.050 mmol). **5**: White solid; ¹H NMR (400 MHz, acetone) δ 7.48 (1H, d, *J* = 8.2 Hz), 7.42–7.38 (3H, m), 7.38–7.28 (5H, m), 7.28–7.21 (1H, m), 7.21–7.11 (5H, m), 6.67 (1H, s), 6.08 (1H, dd, *J* = 17.4, 10.5 Hz), 5.38 (1H, d, *J* = 8.7 Hz), 5.19–5.09 (3H, m), 5.03 (1H, d, *J* = 12.4 Hz), 4.84 (1H, d, *J* = 17.4 Hz), 1.30 (9H, s); ¹³C NMR (101 MHz, CDCl₃) δ 156.1, 155.4, 140.6, 137.8, 137.5, 136.6, 128.7, 128.5, 128.4₁, 128.3₆, 127.7, 127.6, 127.5, 126.7, 116.4, 80.1, 66.9, 66.5, 62.3, 28.5, one carbon atom was not found probably due to overlapping; IR (film) 3354, 2970, 1715, 1699, 1489, 1456, 1364, 1246, 1165 cm⁻¹; HRMS (ESI) Calcd for C₂₉H₃₂N₂O₄Na⁺ ([M+Na]⁺) 495.2254. Found 495.2248.



Ozonolysis of the Double Bond in 5: Ozone (O₃) gas was generated from pure oxygen by using OZM-300SW (Blowerman co. jp.) and was passed through a solution of **5** (23.6 mg, 0.050 mmol) in CH₂Cl₂ (0.50 mL) at -78 °C for 1 h. Consumption of **5** was monitored by TLC and then, the passing O₃ gas was exchanged with pure oxygen. After a while, dimethyl sulfide (36.7 µL) was added to the solution and the mixture was allowed to warm up to room temperature. All volatiles were removed by evaporation to afford the crude residue, which was purified by column chromatography on silica gel (H/EA = 5:1 as eluent) to give **6** (19.0 mg, 0.040 mmol, 80%). **6:** White solid; ¹H NMR (400 MHz, CDCl₃) δ 9.40 (1H, s), 7.48–7.31 (11H, m), 7.27–7.18 (3H, m), 7.09 (2H, d, *J* = 7.8 Hz), 6.14 (1H, s), 5.96 (1H, d, *J* = 9.6 Hz), 5.24 (1H, d, *J* = 12.6 Hz), 5.08 (1H, d, *J* = 12.6 Hz), 1.37 (9H, s); ¹³C NMR (101 MHz, CDCl₃) δ 190.8, 156.5, 156.2, 137.7, 136.2, 132.5, 129.5, 129.0, 128.9, 128.8, 128.5, 128.3, 128.2, 127.5, 127.1, 79.8, 74.4, 67.5, 56.7, 28.5; IR (film) 3372, 2978, 1711, 1697, 1506, 1456, 1365, 1248, 1165, 1067 cm⁻¹; HRMS (ESI) Calcd for C₂₈H₃₀N₂O₅Na⁺ ([M+Na]⁺) 497.2047. Found 497.2047.



Pinnick Oxidation of 6: To a solution of **6** (19.0 mg, 0.040 mmol) in ¹BuOH/H₂O (0.45/0.35 mL) were added NaClO₂ (10.9 mg, 0.12 mmol), NaH₂PO₄ (24.0 mg, 0.20 mmol), and 2-methyl-2-butene (42.5 μ L, 0.40 mmol) at room temperature with stirring. After being stirred for 1 h, the reaction mixture was diluted with brine and the aqueous phase was extracted with EA twice. Organic phases were dried over Na₂SO₄, filtered, and concentrated. The residual material was purified by column chromatography on silica gel (CHCl₃/MeOH = 5:1 as eluent) to give 7 (12.0 mg, 0.024 mmol, 61%), whose enantiomeric excess was determined by HPLC analysis after derivatizing to the corresponding methyl ester (97% ee).^{1a} **7:** White solid; ¹H NMR (400 MHz, CDCl₃) δ 7.69 (1H, br), 7.50 (2H, brd, *J* = 6.4 Hz), 7.42–7.20 (11H, m), 7.15 (2H, t, *J* = 7.3 Hz), 6.57 (1H, br), 6.31 (1H, br), 5.21 (1H, d, *J* = 12.4 Hz), 5.05 (1H, d, *J* = 12.4 Hz), 1.32 (9H, s); ¹³C NMR (101 MHz, CDCl₃) δ 171.2, 157.1, 156.6, 138.0, 136.4, 136.2, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 127.9, 127.3, 80.8, 67.3, 28.5, three carbon atoms were not found probably due to overlapping; IR (film) 3368, 2926, 1713, 1667, 1497, 1368, 1248, 1163, 1051, 885 cm⁻¹; HRMS (ESI) Calcd for C₂₈H₃₀N₂O₆Na⁺ ([M+Na]⁺) 513.1996. Found 513.2009. HPLC (methyl ester): AD-H, H/EtOH = 95:5, flow rate = 1.0 mL/min, λ = 210 nm, 7.4 min (1*S*, 2*S*), 8.6 min (1*R*, 2*R*), 27.2 min (minor diastereomer). Absolute and relative configurations were assigned by comparison with the literature data.^{1a}























S20

















