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Supporting Information

69451 Weinheim, Germany

Experimental Part

1,2,4-Oxadiazolidinones as Configurationally Stable Chiral Building Blocks

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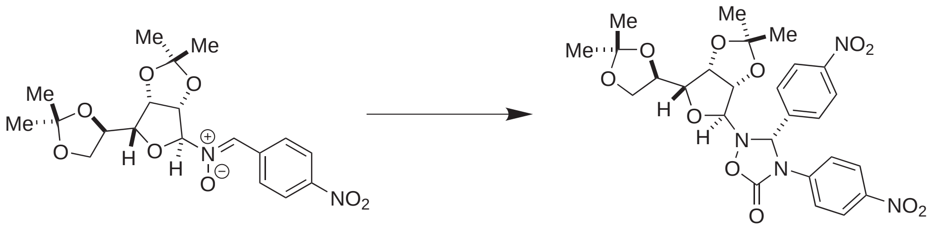
All non-aqueous reactions were carried out using oven-dried or flame-dried glassware under a positive pressure of dry nitrogen or argon unless otherwise noted. Acetonitrile, toluene, and CH_2Cl_2 were purified by distillation and dried by passage over activated alumina under an argon atmosphere (H_2O content < 30 ppm, Karl-Fischer titration).[i] Except as indicated otherwise, reactions were magnetically stirred and monitored by thin layer chromatography (TLC) using Merck Silica Gel 60 F254 plates and visualized by fluorescence quenching under UV light. In addition, TLC plates were stained using ceric ammonium molybdate or potassium permanganate stain. Chromatographic purification of products was performed on E. Merck Silica Gel 60 (230–400 mesh) using a forced flow of eluant at 0.3–0.5 bar pressure.[ii] Concentration under reduced pressure was performed by rotary evaporation at 40 ∘C at the appropriate pressure. Purified compounds were further dried under high vacuum (0.01–0.05 Torr). Yields refer to purified and spectroscopically pure compounds. Kugelrohr distillations were performed with a Buchi Glass Oven B-580. Melting points were measured on a Buchi 510 apparatus. All melting points were measured in open capillaries and are uncorrected. Optical rotations were measured on a Jasco DIP-1000 polarimeter operating at the sodium D line with a 100 mm path length cell. NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300 MHz and 75 MHz for 1H and 13C acquisitions, respectively, or on a Bruker DRX500 spectrometer operating at 500 MHz and 125 MHz for 1H and 13C acquisitions, respectively. Chemical shifts are reported in ppm with the solvent resonance as the internal standard. Data are reported as follows: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constants in Hz. IR spectra were recorded on a PerkinElmer Spectrum RXI FT-IR spectrophotometer. Absorptions are given in wavenumbers (cm^{-1}). Mass spectra were recorded by the MS service at ETH Zurich. EI-MS: VG-TRIBRID spectrometer; spectra were measured at 70 eV. FAB-MS: VG-ZAB2-SEQ spectrometer; spectra were determined in m-nitrobenzyl alcohol (3-NOBA) as matrix. MALDI-MS: IonSpec Ultima Fourier Transform Mass Spectrometer. Peaks are given in percent (m/z). Elemental analyses were performed at the Mikrolabor der ETH Zurich. Highperformance liquid chromatography was performed on aMerck Hitachi (Interface D-7000, UV-Detector L-7400, Pump L-7100, column: Sulentechnik 4 mm ID column packed with 5 m spherisorb SW silica gel). The detector wavelength was fixed at l = 254 nm. All chromatograms were taken at ambient temperature.

[i] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

[ii] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-2925.

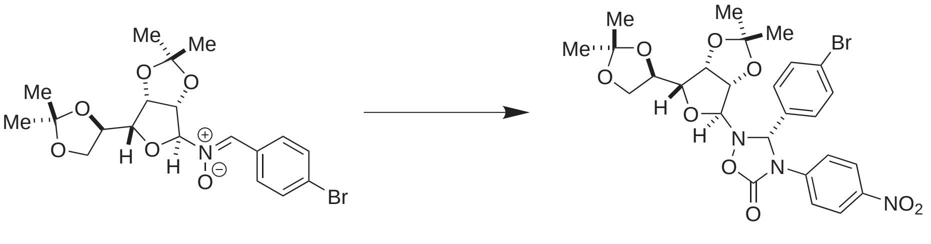
(*R*)-2-[(3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-Dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyltetrahydro-furo[3,4-*d*][1,3]dioxol-4-yl]-3,4- bis-(4-nitrophenyl)-[1,2,4]oxadiazolidin-5-one (I)



To nitrone **A** (1.00 g, 2.45 mmol, 1.00 equiv) in CH_2Cl_2 (1.6 ml) at 23 °C is added 4-nitrophenyl isocyanate (402 mg, 2.45 mmol, 1.00 equiv). The solution is stirred at 23 °C for 19 h and then concentrated *in vacuo* to afford a yellow solid. NMR analysis of the crude material indicated an 11:1 ratio of diastereomers. The solid is triturated with methanol for 3 h, filtered off, washed with hexane, and dried *in vacuo* to afford the target compound as a colorless solid (84% yield, > 99:1 dr). Recrystallization of this solid from isopropanol afforded bright yellow crystals suitable for X-ray analysis.

R*f* = 0.34 (2:1 hexane/EtOAc). Melting Point (isopropanol): mp 175 °C. Specific Rotation $[\alpha]_{33.8\ D}$ +63° (c 1.54, $CHCl_3$). NMR Spectroscopy: ^1H NMR (300 MHz, $CDCl_3$) δ: 8.31–8.28 (m, 2H), 8.22–8.19 (m, 2H), 7.62–7.56 (m, 2H), 7.48–7.45 (m, 2H), 6.34 (s, 1H), 4.93 (d, *J* = 5.9 Hz, 1H), 4.83 (dd, *J* = 5.9 Hz, 3.4 Hz, 1H), 4.83 (s, 1H), 4.50–4.47 (m, 1H), 4.18 (dd, *J* = 5.6 Hz, 3.4 Hz, 1H), 4.14–4.08 (m, 2H), 1.50 (s, 3H), 1.47 (s, 3H), 1.40 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 153.0, 148.8, 144.2, 141.4, 140.8, 127.3, 125.2, 124.9, 118.5, 113.3, 109.1, 97.4, 83.3, 83.0, 79.7, 76.9, 73.1, 66.0, 27.0, 25.9, 25.0, 24.4. IR Spectroscopy (thin film) 1777, 1597, 1524, 1342, 1219, 1084 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{26}H_{28}N_4O_{11}Na$, 595.1653. Found, 595.1654. Combustion Analysis: Anal. calcd for $C_{26}H_{28}N_4O_{11}$: C, 54.55; H, 4.93; N, 9.79. Found C, 54.57; H, 5.02; N, 9.72.

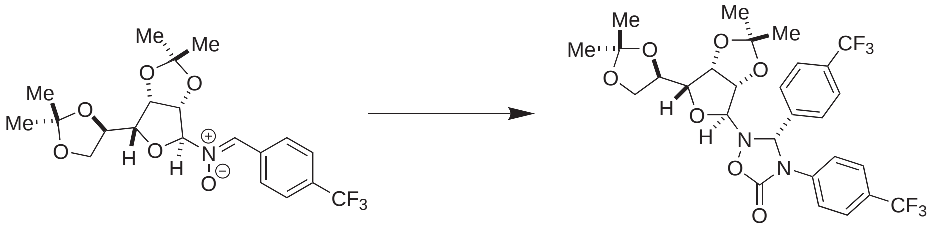
(*R*)-3-(4-Bromo-phenyl)-2-[(3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyl-tetrahydro-furo[3,4-*d*][1,3]dioxol-4-yl]-4-(4-nitro-phenyl)-[1,2,4]oxadiazolidin-5-one (II)



To nitrone **B** (1.59 g, 3.60 mmol, 1.00 equiv) in CH_2Cl_2 (7.2 ml) at 23 °C is added 4-nitrophenyl isocyanate (591 mg, 3.60 mmol, 1.00 equiv). The solution is stirred at 23 °C for 14 h and then concentrated *in vacuo* to afford a yellow solid. NMR analysis of the crude material indicated a 10:1 ratio of diastereomers. The solid is triturated with methanol for 3 h, filtered off, washed with hexane, and dried *in vacuo* to afford the target compound as a colorless solid (87% yield, > 99:1 dr).

R*f* = 0.44 (2:1 hexane/EtOAc). Melting Point (methanol): mp 167 °C. Specific Rotation $[\alpha]_{33.8\ D}$ +69° (c 1.42, $CHCl_3$). NMR Spectroscopy: ^1H NMR (300 MHz, $CDCl_3$) δ: 8.22–8.17 (m, 2H), 7.61–7.56 (m, 4H), 7.16–7.13 (m, 2H), 6.22 (s, 1H), 4.92 (d, *J* = 6.0 Hz, 1H), 4.82 (dd, *J* = 6.0 Hz, 3.4 Hz, 1H), 4.78 (s, 1H), 4.49–4.43 (m, 1H), 4.18–4.06 (m, 3H), 1.48 (s, 3H), 1.47 (s, 3H), 1.40 (s, 3H), 1.33 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 153.7, 144.4, 141.4, 134.1, 133.2, 128.0, 125.4, 124.7, 118.8, 113.5, 109.4, 97.5, 83.6, 83.2, 80.0, 77.6, 73.3, 66.4, 27.1, 26.0, 25.2, 24.6. IR Spectroscopy (thin film) 2988, 1774, 1597, 1521, 1503, 1382, 1340, 1219, 1084, 851, 771 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{26}H_{28}BrN_3O_9Na$, 628.0907. Found, 628.0894. Combustion Analysis: Anal. calcd for $C_{26}H_{28}BrN_3O_9$: C, 51.50; H, 4.65; N, 6.93. Found C, 51.42; H, 4.63; N, 7.17.

(*R*)-2-[(3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-Dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyltetrahydro-furo[3,4-*d*][1,3]dioxol-4-yl]-3,4- bis-(4-trifluoromethyl-phenyl)-[1,2,4]oxadiazolidin-5-one (III)



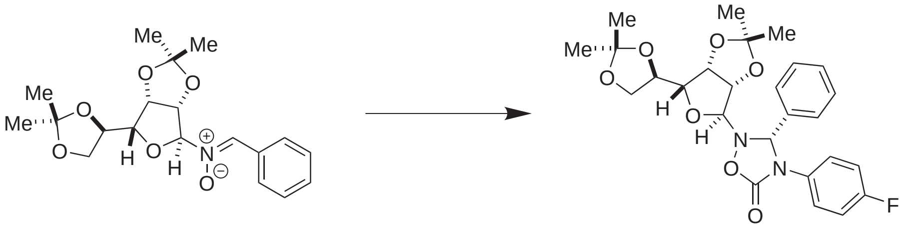
Procedure A: To nitrone **C** (431 mg, 1.00 mmol, 1.00 equiv) in CH_2Cl_2 (0.50 l) at 23 °C is added 4-trifluoromethylphenyl isocyanate (187 mg, 1.00 mmol, 1.00 equiv). The solution is stirred at 23 °C for 64 h and then concentrated *in acuo* to afford a colorless solid. NMR analysis of the crude material indicated 10:1 mixture of diastereomers. The solid is triturated with methanol for 3 h, filtered off, washed with hexane, and dried *in vacuo* to afford the target compound as a colorless solid (85% yield, > 99:1 dr).

Procedure B: To nitrone **C** (300 mg, 0.695 mmol, 1.00 equiv) in CH_2Cl_2 (0.35 ml) at 23 °C is added 4-trifluoromethylphenyl isocyanate (130 mg, 1.00 mmol, 1.00 equiv). The solution is heated at reflux, kept at this temperature for 10 h and then cooled and concentrated *in vacuo* to afford a colorless solid. NMR analysis of the crude material indicated a 9:1 ratio of diastereomers. The solid is triturated with methanol for 3 h, filtered off, washed with hexane, and dried *in vacuo* to afford the target compound as a colorless solid (81% yield, > 99:1 dr).

R*f* = 0.70 (2:1 hexane/EtOAc). Melting Point (methanol): mp 93 °C. Specific Rotation $[\alpha]_{28.8}$ $_D$ +11° (c 1.52, $CHCl_3$). NMR Spectroscopy: ^1H

NMR (300 MHz, $CDCl_3$) δ: 7.71 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 9.1 Hz, 2H), 7.53 (d, *J* = 9.1 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 6.28 (s, 1H), 4.95 (d, *J* = 6.0 Hz, 1H), 4.82 (dd, *J* = 6.0 Hz, 3.6 Hz, 1H), 4.81 (s, 1H), 4.50–4.44 (m, 1H), 4.20–4.08 (m, 3H), 1.48 (s, 3H), 1.48 (s, 3H), 1.40 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 139.4, 138.9, 132.4 (q, *J* = 33 Hz), 127.5 (q, *J* = 33 Hz), 126.9, 126.9, 123.9 (q, *J* = 272 Hz), 123.8 (q, *J* = 272 Hz), 119.0, 113.5, 109.4, 97.5, 83.6, 83.2, 80.0, 77.5, 73.3, 66.3, 27.1, 26.0, 25.2, 24.6. IR Spectroscopy (thin film) 2990, 1776, 1618, 1524, 1384, 1326, 1129, 1070, 841, 768 (cm^{-1}). Mass Spectrometry HRMS-MALDI (m/z): Calcd for $C_{28}H_{28}F_6N_2O_7Na$, 641.1699. Found, 641.1683. Combustion Analysis: Anal. calcd for $C_{28}H_{28}F_6N_2O_7$: C, 54.37; H, 4.56; N, 4.53. Found C, 54.31; H, 4.62; N, 4.48.

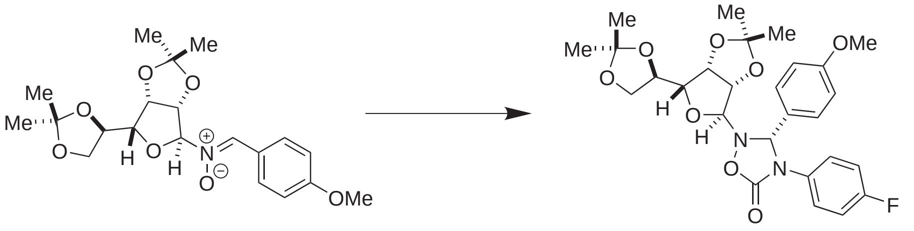
(*R*)-2-[(3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-Dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyl-tetrahydro-furo[3,4-*d*][1,3]dioxol-4-yl]-4-(4-fluoro-phenyl)-3-phenyl-[1,2,4]oxadiazolidin-5-one (IV)



To nitrone **D** (1.09 g, 3.00 mmol, 1.00 equiv) in CH_2Cl_2 (2.5 ml) at 23 °C is added 4-fluorophenyl isocyanate (411 mg, 3.00 mmol, 1.00 equiv). The solution is stirred at 23 °C for 38 h and concentrated *in vacuo* to afford an off-white solid. NMR analysis of the crude material indicated a 8:1 ratio of diastereomers. The solid is triturated with methanol for 3 h, filtered off, washed with hexane, and dried *in vacuo* to afford the target compound as a colorless solid (83% yield, >99:1 dr).

R*f* = 0.44 (2:1 hexane/EtOAc). Melting Point (methanol): mp 200 °C. Specific Rotation $[\alpha]_{28.8\ D}$ +10° (c 1.33, $CHCl_3$). NMR Spectroscopy: ^1H NMR (300 MHz, $CDCl_3$) δ: 7.46–7.25 (m, 7H), 7.04–6.96 (m, 2H), 6.10 (s, 1H), 4.97 (d, *J* = 6.2 Hz, 1H), 4.82 (d, *J* = 9.7 Hz, 1H), 4.82 (s, 1H), 4.46–4.40 (m, 1H), 4.14–4.09 (m, 2H), 4.00 (dd, *J* = 8.7 Hz, 4.7 Hz, 1H), 1.49 (s, 3H), 1.44 (s, 3H), 1.39 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 159.8 (d, *J* = 245 Hz), 135.6, 131.7, 129.8, 129.4, 126.3, 122.0 (d, *J* = 8 Hz), 116.1 (d, *J* = 23 Hz), 113.0, 109.2, 97.3, 83.5, 82.9, 79.8, 79.0, 73.0, 66.5, 26.9, 26.0, 25.2, 24.5. IR Spectroscopy (thin film) 2988, 1772, 1513, 1383, 1232, 1084, 840 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{26}H_{29}FN_2O_7Na$, 523.1857. Found, 523.1845. Combustion Analysis: Anal. calcd for $C_{26}H_{29}FN_2O_7$: C, 62.39; H, 5.84; N, 5.60. Found C, 62.38; H, 6.05; N, 5.66.

(*R*)-2-[(3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-Dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyltetrahydro-furo[3,4-*d*][1,3]dioxol-4-yl]-4-(4-fluoro-phenyl)-3-(4-methoxyphenyl)-[1,2,4]oxadiazolidin-5-one (V)



To nitrone **E** (216 mg, 0.550 mmol, 1.00 equiv) in CH_2Cl_2 (0.50 ml) at 23 °C is added 4-fluorophenyl isocyanate (75.4 mg, 0.550 mmol, 1.00 equiv). The solution is stirred at 23 °C for 5 h and then concentrated *in vacuo* to afford an off-white solid. NMR analysis of the crude material indicated a 12:1 ratio of diastereomers. The solid is triturated with methanol for 2 h, filtered off, washed with hexane, and dried *in vacuo* to afford the target compound as a colorless solid (81% yield, > 99:1 dr).

R*f* = 0.46 (2:1 hexane/EtOAc). Melting Point (methanol): mp 169 °C. Specific Rotation $[\alpha]_{28.7\ D}$ +18° (c 1.15, $CHCl_3$). NMR Spectroscopy: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.35–7.31 (m, 2H), 7.23–7.19 (m, 2H), 7.02–6.96 (m, 2H), 6.95–6.90 (m, 2H), 6.05 (s, 1H), 4.97 (d, *J* = 6.0 Hz, 1H), 4.83–4.79 (m, 2H), 4.45–4.39 (m, 1H), 4.14–4.06 (m, 2H), 4.00 (dd, *J* = 8.8 Hz, 4.7 Hz, 1H), 1.48 (s, 3H), 1.43 (s, 3H), 1.38 (s, 3H), 1.33 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 160.2 (d, *J* = 246 Hz), 160.9, 154.4, 132.0, 128.0, 127.8, 122.5 (d, *J* = 8 Hz), 116.4 (d, *J* = 23 Hz), 115.1, 113.2, 109.5, 97.5, 83.8, 83.1, 80.0, 79.0, 77.4, 73.2, 66.7, 55.6, 27.0, 26.1, 25.3, 24.6. IR Spectroscopy (thin film) 2988, 1770, 1513, 1372, 1253, 1083 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{27}H_{31}FN_2O_8Na$, 553.1962. Found, 553.1949. Combustion Analysis: Anal. calcd for $C_{27}H_{31}FN_2O_8$: C, 61.12; H, 5.89; N, 5.28. Found C, 60.93; H, 6.06; N, 5.18.

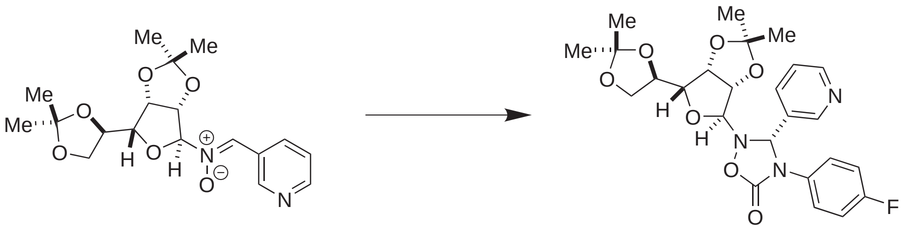
Methanesulfonic acid 4-[(*R*)-2-[(3a*S*,4*S*,6a*S*)-6-((*R*)-2,2-dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyl-tetrahydro-furo[3,4-*d*][1,3]dioxol-4-yl]-4-(4-fluoro-phenyl)-5-oxo-[1,2,4]oxadiazolidin-3-yl]-phenyl ester (VI)

Procedure A: To nitrone **F** (1.99 g, 4.35 mmol, 1.00 equiv) in CH_2Cl_2 (2.9 ml) at 23 °C is added 4-fluorophenyl isocyanate (626 mg, 4.57 mmol, 1.05 equiv). The solution is stirred at 23 °C for 48 h and then concentrated *in vacuo* to afford an off-white solid. NMR analysis of the crude material indicated a 8:1 ratio of diastereomers. The solid is triturated with methanol for 2 h, filtered off, washed with hexane, and dried *in vacuo* to afford the target compound as a colorless solid (84% yield, > 99:1 dr).

Procedure B: To nitrone **F** (1.99 g, 4.35 mmol, 1.00 equiv) in acetonitrile (2.9 ml) at 23 °C is added 4-fluorophenyl isocyanate (626 mg, 4.57 mmol, 1.05 equiv). The solution is stirred at 23 °C for 22 h and then concentrated *in vacuo* to afford an off-white solid. NMR analysis of the crude material indicated a 7:1 ratio of diastereomers. The solid is triturated with methanol for 2 h, filtered off, washed with hexane, and dried *in vacuo* to afford the target compound as a colorless solid (81% yield, > 99:1 dr).

R*f* = 0.67 (2:3 hexane/EtOAc). Melting Point (methanol): mp 191 °C. Specific Rotation $[\alpha]_{28.5\ D}$ +20° (c 1.70, $CHCl_3$). NMR Spectroscopy: ^1H NMR (300 MHz, $CDCl_3$) δ: 7.36–7.31 (m, 6H), 7.06–6.99 (m, 2H), 6.13 (s, 1H), 4.96 (d, *J* = 6.2 Hz, 1H), 4.84–4.80 (m, 2H), 4.47–4.41 (m, 1H), 4.13–4.10 (m, 2H), 4.01 (dd, *J* = 8.7 Hz, 4.7 Hz, 1H), 3.17 (s, 3H), 1.48 (s, 3H), 1.45 (s, 3H), 1.38 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 159.9 (d, *J* = 246 Hz), 153.7, 149.7, 134.9, 131.3, 128.1, 123.0, 121.9 (d, *J* = 9 Hz), 116.3 (d, *J* = 23 Hz), 113.0, 109.1, 97.3, 83.4, 82.8, 79.7, 78.1, 73.0, 66.2, 37.7, 26.9, 25.9, 25.1, 24.4. IR Spectroscopy (thin film) 2988, 2938, 1771, 1513, 1372, 1233, 1153, 1084, 971, 892, 756, 526 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{27}H_{31}FN_2O_{10}SNa$, 617.1581. Found, 617.1570. Combustion Analysis: Anal. calcd for $C_{27}H_{31}FN_2O_{10}S$: C, 54.54; H, 5.25; N, 4.71. Found C, 54.77; H, 5.34; N, 4.73.

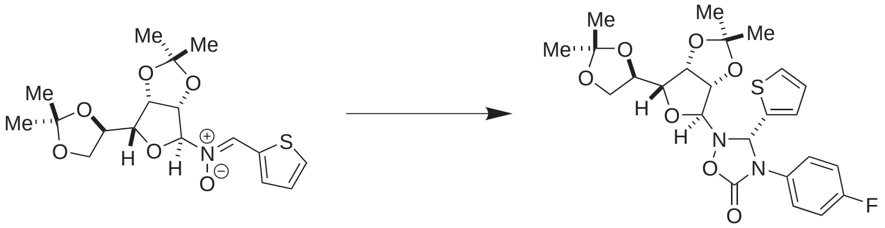
(*R*)-2-[(3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-Dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyltetrahydro-furo[3,4-*d*][1,3]dioxol-4-yl]-4-(4-fluoro-phenyl)-3-pyridin-3-yl-[1,2,4]oxadiazolidin-5-one (VII)



To nitrone **G** (1.92 g, 5.27 mmol, 1.00 equiv) in CH_2Cl_2 (2.6 ml) at 23 °C is added 4-fluorophenyl isocyanate (722 mg, 5.27 mmol, 1.00 equiv). The solution is stirred at 23 °C for 24 h and then concentrated *in vacuo* to afford an off-white solid. NMR analysis of the crude material indicated a 8:1 ratio of diastereomers. The solid is triturated with methanol for 2 h, filtered off, washed with hexane, and dried *in vacuo* to afford the target compound as a colorless solid (80% yield, > 99:1 dr).

R*f* = 0.39 (1:2 hexane/EtOAc). Melting Point (methanol): mp 205 °C. Specific Rotation $[\alpha]_{25.3}$ *D* +16° (c 1.67, $CHCl_3$). NMR Spectroscopy: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.65 (d, *J* = 3.7 Hz, 1H), 8.57 (d, *J* = 1.2 Hz, 1H), 7.65–7.62 (m, 1H), 7.37–7.30 (m, 3H), 7.05–6.99 (m, 2H), 6.15 (s, 1H), 4.97 (d, *J* = 5.9 Hz, 1H), 4.84–4.81 (m, 2H), 4.44–4.38 (m, 1H), 4.11–4.69 (m, 2H), 3.94 (dd, *J* = 8.4 Hz, 4.7 Hz, 1H), 1.48 (s, 3H), 1.43 (s, 3H), 1.36 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 160.1 (d, *J* = 247 Hz), 153.6, 150.9, 148.2, 134.0, 131.5, 131.1, 124.0, 122.4 (d, *J* = 9 Hz), 116.4 (d, *J* = 23 Hz), 113.0, 109.1, 97.5, 83.4, 83.1, 79.8, 77.3, 73.0, 66.2, 26.8, 25.9, 25.1, 24.4. IR Spectroscopy (thin film) 2989, 1775, 1513, 1373, 1232, 1085, 842 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{25}H_{28}FN_3O_7Na$, 524.1809. Found, 524.1798. Combustion Analysis: Anal. calcd for $C_{25}H_{28}FN_3O_7$: C, 59.87; H, 5.63; N, 8.38. Found C, 59.88; H, 5.74; N, 8.26.

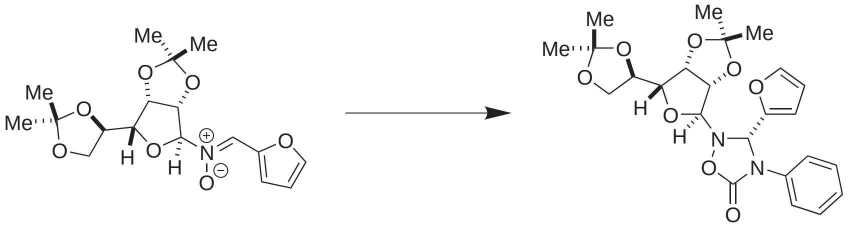
(*R*)-2-[(3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-Dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyltetrahydro-furo[3,4-*d*][1,3]dioxol-4-yl]-4-(4-fluoro-phenyl)-3-thiophen-2-yl-[1,2,4]oxadiazolidin-5-one (VIII)



To nitrone **H** (916 mg, 2.48 mmol, 1.00 equiv) in CH_2Cl_2 (1.5 ml) at 23 °C is added 4-fluorophenyl isocyanate (340 mg, 2.48 mmol, 1.00 equiv). The solution is heated at reflux for 39 h and then cooled and concentrated *in vacuo* to afford an off-white solid. NMR analysis of the crude material indicated a 8:1 ratio of diastereomers. The solid is triturated with methanol for 3 h, filtered off, washed with hexane, and dried *in vacuo* to afford the target compound as a colorless solid (79% yield, 95:5 dr).

R*f* = 0.40 (2:1 hexane/EtOAc). Melting Point (methanol): mp 188 °C. Specific Rotation $[\alpha]_{29.7\ D}$ +22° (c 1.31, $CHCl_3$). NMR Spectroscopy: ^1H NMR (300 MHz, $CDCl_3$) δ: 7.41–7.35 (m, 3H), 7.07–6.96 (m, 4H), 6.35 (s, 1H), 5.00 (d, *J* = 5.9 Hz, 1H), 4.89–4.56 (m, 1H), 4.82 (s, 1H), 4.45–4.39 (m, 1H), 4.15–4.10 (m, 2H), 3.95 (dd, *J* = 8.7 Hz, 4.4 Hz, 1H), 1.49 (s, 3H), 1.44 (s, 3H), 1.38 (s, 3H), 1.35 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 160.2 (d, *J* = 246 Hz), 153.4, 139.0, 139.0, 131.2, 127.4, 127.2, 126.7, 122.9 (d, *J* = 9 Hz), 116.2 (d, *J* = 24 Hz), 113.0, 109.3, 97.3, 83.5, 83.2, 79.8, 75.4, 72.8, 66.7, 26.9, 26.0, 25.2, 24.5. IR Spectroscopy (thin film) 2986, 1779, 1750, 1514, 1379, 1234, 1093, 1068, 846, 772 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{24}H_{27}FN_2O_7SH$, 507.1602. Found, 507.1592. Combustion Analysis: Anal. calcd for $C_{24}H_{27}FN_2O_7S$: C, 56.91; H, 5.37; N, 5.53. Found C, 56.97; H, 5.60; N, 5.50.

(*R*)-2-[(3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-Dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyl-tetrahydro-furo[3,4-*d*][1,3]dioxol-4-yl]-3-furan-2-yl-4-phenyl-[1,2,4]oxadiazolidin-5-one (IX)

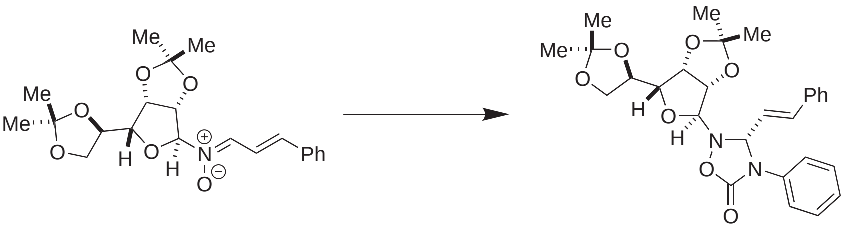


To nitrone **J** (1.31 g, 3.67 mmol, 1.00 equiv) in CH_2Cl_2 (3.7 ml) at 23 °C is added phenyl isocyanate (438 mg, 3.67 mmol, 1.00 equiv). The solution is stirred at 23 °C for 36 h and then concentrated *in vacuo* to afford an off-white solid. NMR analysis of the crude material indicated a 7:1 ratio of diastereomers. The solid is triturated with methanol for 2 h, filtered off, washed with hexane, and dried *in vacuo* to afford the target compound as a colorless solid (82% yield, > 93:7 dr).

R*f* = 0.40 (2:1 hexane/EtOAc). Melting Point (methanol): mp 166 °C. Specific Rotation $[\alpha]_{29.1\ D}$ +26° (c 1.30, $CHCl_3$). NMR Spectroscopy: ^1H NMR (300 MHz, $CDCl_3$) δ: 7.45–7.32 (m, 5H), 7.20–7.15 (m, 1H), 6.39–6.35 (m, 2H), 6.22 (s, 1H), 4.99 (d, *J* = 5.9 Hz, 1H), 4.86 (dd, *J* = 5.9 Hz, 3.7 Hz, 1H), 4.78 (s, 1H), 4.46–4.38 (m, 1H), 4.17–4.12 (m, 2H), 4.05 (dd, *J* = 8.7 Hz, 4.4 Hz, 1H), 1.48 (s, 3H), 1.45 (s, 3H), 1.39 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 153.5, 148.3, 143.8, 135.3, 129.2, 125.5, 120.0, 112.9, 110.6, 109.5, 109.2, 96.7, 83.5, 83.2, 79.8, 72.8, 72.3, 66.8, 26.8, 25.9, 25.1, 24.4. IR Spectroscopy (thin film) 2988, 1774, 1503, 1382, 1218, 1085, 772, 750 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{24}H_{28}N_2O_8H$, 473.1925. Found, 473.1930. Combustion Analysis: Anal. calcd for

$C_{24}H_{28}N_2O_8$: C, 61.01; H, 5.97; N, 5.93. Found C, 60.78; H, 6.16; N, 5.93.

(*R*)-2-[(3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-Dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyl-tetrahydro-furo[3,4-*d*][1,3]dioxol-4-yl]-4-phenyl-3-((*E*)-styryl)-[1,2,4]oxadiazolidin-5-one (X)

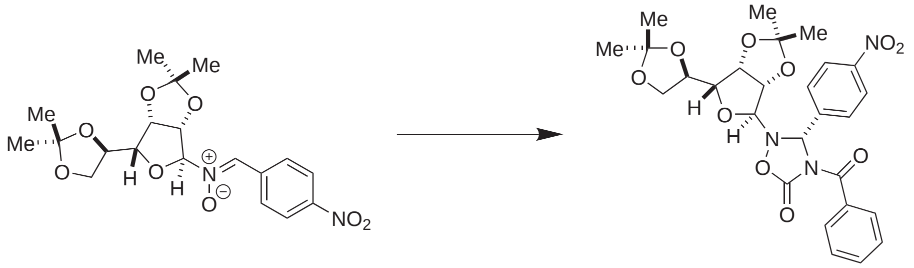


To nitrone **K** (683 mg, 1.75 mmol, 1.00 equiv) in CH_2Cl_2 (1.0 ml) at 23 °C is added phenyl isocyanate (209 mg, 1.75 mmol, 1.00 equiv). The solution is stirred at 23 °C for 31 h and then concentrated *in vacuo* to afford an off-white solid. NMR analysis of the crude material indicated a 10:1 ratio of diastereomers. The solid is triturated with methanol for 1 h, filtered off, washed with hexane, and dried *in vacuo* to afford the target compound as a colorless solid (76% yield, > 99:1 dr).

R*f* = 0.42 (2:1 hexane/EtOAc). Melting Point (methanol): mp 133 °C. Specific Rotation $[\alpha]_{29.6\,D}$ +54° (c 1.02, $CHCl_3$). NMR Spectroscopy: ^1H NMR (300 MHz, $CDCl_3$) δ: 7.51–7.17 (m, 10H), 6.71 (d, *J* = 16.2 Hz, 1H), 6.27 (dd, *J* = 15.9 Hz, 6.8 Hz, 1H), 5.82 (d, *J* = 6.5 Hz, 1H), 5.02 (d, *J* = 5.9 Hz, 1H), 4.86 (dd, *J* = 5.6 Hz, 3.7 Hz, 1H), 4.78 (s, 1H), 4.46–4.40 (m, 1H), 4.22–4.02 (m, 3H), 1.49 (s, 3H), 1.47 (s, 3H), 1.39 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 153.7, 135.6, 135.6, 134.7, 129.3, 128.8, 128.6, 127.0, 125.4, 122.6, 120.2, 112.9, 109.2, 69.7, 83.7, 83.2, 79.9, 77.5, 73.1, 66.6, 26.9, 26.0, 25.2, 24.5. IR Spectroscopy (thin film) 2989, 2936, 1771, 1501, 1383, 1217, 1084, 966, 772, 751 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z):

Calcd for $C_{28}H_{32}N_2O_7Na$, 531.2108. Found, 531.2107. Combustion Analysis: Anal. calcd for $C_{28}H_{32}N_2O_7$: C, 66.13; H, 6.34; N, 5.51. Found C, 65.90; H, 6.24; N, 5.49.

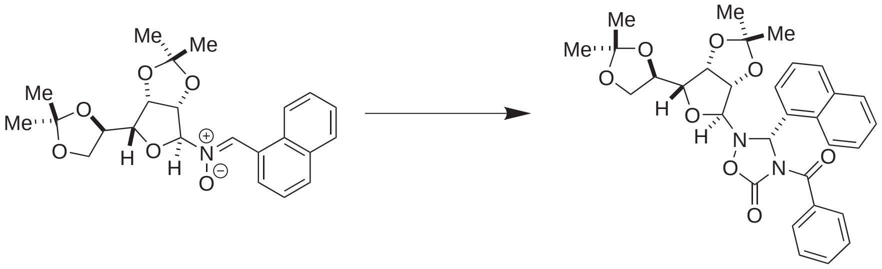
(*R*)-4-Benzoyl-2-[(3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyl-tetrahydro-furo[3,4-*d*][1,3]dioxol-4-yl]-3-(4-nitrophenyl)-[1,2,4]oxadiazolidin-5-one (XI)



To nitrone **A** (388 mg, 0.950 mmol, 1.00 equiv) in CH_2Cl_2 (1.0 ml) at 23 °C is added benzoyl isocyanate (140 mg, 0.950 mmol, 1.00 equiv). The solution is stirred at 23 °C for 40 h and then concentrated *in vacuo* to afford a yellow solid. NMR analysis of the crude material indicated a 5:1 ratio of diastereomers. The solid is triturated with methanol for 0.5 h, filtered off, washed with hexane, and dried *in vacuo* to afford the target compound as a colorless solid (71% yield, 96:4 dr).

R*f* = 0.52 (3:2 hexane/EtOAc). Melting Point (methanol): mp 136 °C. Specific Rotation $[\alpha]_{33.0\,D}$ +12° (c 1.23, $CHCl_3$). NMR Spectroscopy: ^1H NMR (300 MHz, $CDCl_3$) δ: 8.31–8.28 (m, 2H), 7.69–7.58 (m, 5H), 7.49–7.44 (m, 32), 6.50 (s, 1H), 4.96 (d, *J* = 5.9 Hz, 1H), 4.86–4.84 (m, 2H), 4.40–4.43 (m, 1H), 4.03 (dd, *J* = 8.7 Hz, 6.5 Hz, 1H), 3.95 (dd, *J* = 6.2 Hz, 3.4 Hz, 1H), 3.80 (dd, *J* = 8.7 Hz, 4.4 Hz, 1H), 1.50 (s, 3H), 1.40 (s, 3H), 1.35 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 167.7, 151.4, 148.5, 142.1, 133.5, 130.7, 129.3, 128.1, 127.9, 124.2, 113.3, 109.1, 97.9, 83.4, 83.2, 79.7, 76.8, 72.8, 66.1, 26.9, 25.9, 25.1, 24.4. IR Spectroscopy (thin film) 2988, 1801, 1696, 1527, 1349, 1294, 1212, 1069, 772 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{27}H_{29}N_3O_{10}Na$, 578.1751. Found, 578.1751. Combustion Analysis: Anal. calcd for $C_{27}H_{29}N_3O_{10}$: C, 58.38; H, 5.26; N, 7.56. Found C, 58.30; H, 5.29; N, 7.73.

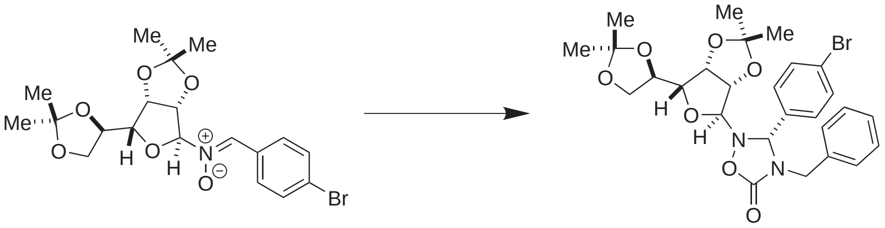
(*R*)-4-Benzoyl-2-[(3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyl-tetrahydro-furo[3,4-*d*][1,3]dioxol-4-yl]-3-naphthalen-2-yl-[1,2,4]oxadiazolidin-5-one (XII)



To nitrone **L** (974 mg, 2.36 mmol, 1.00 equiv) in CH_2Cl_2 (2.4 ml) at 23 °C is added benzoyl isocyanate (347 mg, 2.36 mmol, 1.00 equiv). The solution is stirred at 23 °C for 12 min and then concentrated *in vacuo* to afford an off-white solid. NMR analysis of the crude material indicated a >10:1 ratio of diastereomers. The solid is triturated with methanol for 1 h, filtered off, washed with hexane, and dried *in vacuo* to afford the target compound as a colorless solid (79% yield, > 99:1 dr).

R*f* = 0.58 (3:2 hexane/EtOAc). Melting Point (methanol): mp 168 °C. Specific Rotation $[\alpha]_{33.1}\ _D$ +41° (c 1.05, $CHCl_3$). NMR Spectroscopy: ^1H NMR (300 MHz, $CDCl_3$) δ: 8.27 (d, *J* = 8.5 Hz, 1H), 7.94–7.92 (m, 2H), 7.78–7.72 (m, 3H), 7.65–7.48 (m, 6H), 7.32 (s, 1H), 5.04 (bs, 1H), 4.97 (d, *J* = 6.0 Hz, 1H), 4.78 (dd, *J* = 5.8 Hz, 3.8 Hz, 1H), 4.50–4.39 (m, 2H), 4.11 (d, *J* = 5.8 Hz, 1H), 1.53 (s, 3H), 1.49 (s, 3H), 1.45 (s, 3H), 1.33 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 167.9, 153.4, 134.4, 133.5, 131.7, 131.7, 130.8, 129.6, 129.3, 128.5, 127.9, 126.6, 125.2, 123.2, 122.7, 113.4, 109.2, 98.4, 84.0, 83.6, 80.0, 75.3, 73.8, 65.9, 27.0, 26.1, 25.4, 24.4. IR Spectroscopy (thin film) 2988, 2936, 1801, 1697, 1381, 1294, 1210, 1079, 858, 759 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{31}H_{32}N_2O_8Na$, 583.2027. Found, 583.2045. Combustion Analysis: Anal. calcd for $C_{31}H_{32}N_2O_8$: C, 66.42; H, 5.75; N, 5.00. Found C, 66.34; H, 5.98; N, 4.98.

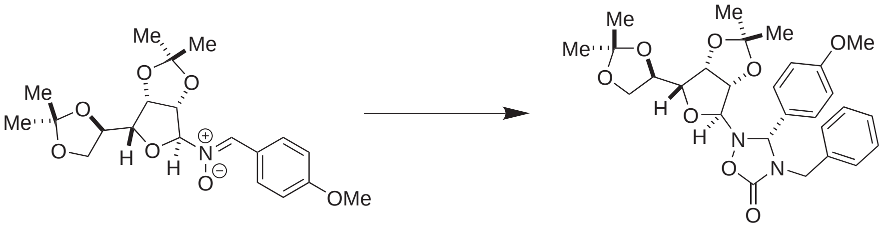
(*R*)-4-Benzyl-3-(4-bromo-phenyl)-2-[(3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyl-tetrahydro-furo[3,4-*d*][1,3]dioxol-4-yl]-[1,2,4]oxadiazolidin-5-one (XIII)



To nitrone **B** (1.35 g, 3.06 mmol, 1.00 equiv) in acetonitrile (3.0 ml) at 23 °C is added benzyl isocyanate (407 mg, 3.06 mmol, 1.00 equiv). The suspension is heated to reflux and kept at this temperature for 36 h. After cooling, the suspension is concentrated *in vacuo* to afford a yellow solid. NMR analysis of the crude material indicated a 7:1 ratio of diastereomers. The solid is triturated with methanol for 3 h, filtered off, washed with hexane, and dried *in vacuo* to afford the target compound as a colorless solid (74% yield, > 99:1 dr).

R*f* = 0.61 (2:1 hexane/EtOAc). Melting Point (methanol): mp 190 °C. Specific Rotation $[\alpha]_{28.6}\,_{D}$ +33° (c 1.19, $CHCl_3$). NMR Spectroscopy: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.57–7.53 (m, 2H), 7.37–7.31 (m, 3H), 7.15–7.08 (m, 4H), 5.21 (s, 1H), 4.91 (d, *J* = 5.9 Hz, 1H), 4.81 (d, *J* = 15.3 Hz, 1H), 4.73 (dd, *J* = 5.9 Hz, 3.4 Hz, 1H), 4.58 (s, 1H), 4.27–4.21 (m, 1H), 3.92 (dd, *J* = 8.7 Hz, 6.5 Hz, 1H), 3.68–3.64 (m, 2H), 3.55 (dd, J = 8.7 Hz, 5.0 Hz, 1H), 1.45 (s, 3H), 1.31 (s, 3H), 1.30 (s, 3H), 1.27 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 155.5, 134.3, 134.1, 132.3, 129.0, 128.9, 128.3, 128.2, 124.1, 112.7, 109.0, 98.1, 83.4, 82.5, 79.6, 77.9, 72.7, 66.3, 46.0, 26.6, 25.8, 25.6, 24.4. IR Spectroscopy (thin film) 2987, 1771, 1417, 1371, 1210, 1069, 847, 704 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{27}H_{31}BrN_2O_7Na$, 597.1213. Found, 597.1201. Combustion Analysis: Anal. calcd for $C_{27}H_{31}BrN_2O_7$: C, 56.35; H, 5.43; N, 4.87. Found C, 56.32; H, 5.52; N, 4.83.

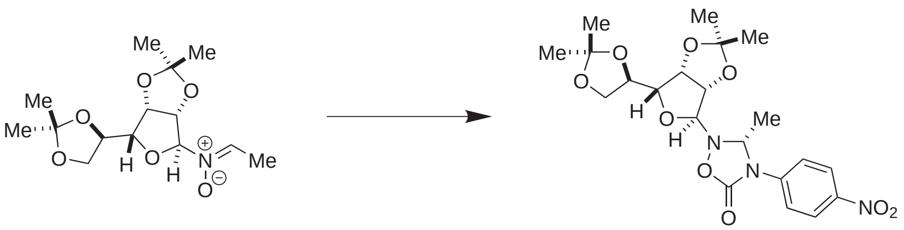
(*R*)-4-Benzyl-2-[(3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-[1,3]dioxolan-4-yl)- 2,2-dimethyl-tetrahydro-furo[3,4-*d*][1,3]dioxol-4-yl]-3-(4-methoxy-phenyl)-[1,2,4]oxadiazolidin-5-one (XIV)



To nitrone **E** (394 mg, 1.00 mmol, 1.00 equiv) in CH_2Cl_2 (1.0 ml) at 23 °C is added benzyl isocyanate (133 mg, 1.00 mmol, 1.00 equiv). The solution is heated to reflux and kept at this temperature for 40 h. After cooling, the suspension is concentrated *in vacuo* to afford an off-white solid. NMR analysis of the crude material indicated a 7:1 ratio of diastereomers. The solid is recrystallized from isopropanol and the crystals are dried *in vacuo* to afford the target compound as colorless crystals (76% yield, > 99:1 dr).

R*f* = 0.43 (2:1 hexane/EtOAc). Melting Point (methanol): mp 190 °C. Specific Rotation $[\alpha]_{28.7\ D}$ +20° (c 1.10, $CHCl_3$). NMR Spectroscopy: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.34–7.32 (m, 3H), 7.19–7.13 (m, 4H), 6.95–6.92 (m, 2H), 5.20 (s, 1H), 4.92 (d, J = 6.2 Hz, 1H), 4.81–4.72 (m, 2H), 4.59 (s, 1H), 4.26–4.20 (m, 1H), 3.91 (dd, *J* = 8.7 Hz, 6.5 Hz, 1H), 3.83 (s, 3H), 3.70–3.63 (m, 2H), 3.50 (dd, *J* = 8.4 Hz, 4.7 Hz, 1H), 1.45 (s, 3H), 1.31 (s, 3H), 1.30 (s, 3H), 1.26 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 160.1, 155.7, 134.5, 128.8, 128.7, 128.2, 127.0, 114.5, 112.7, 109.1, 98.1, 83.5, 82.5, 79.7, 78.3, 72.6, 66.5, 55.4, 45.8, 26.7, 25.9, 25.3, 24.4. IR Spectroscopy (thin film) 2987, 1769, 1612, 1515, 1372, 1252, 1081, 1008, 850, 704 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{28}H_{34}N_2O_8Na$, 549.2213. Found, 549.2201. Combustion Analysis: Anal. Calcd for $C_{28}H_{34}N_2O_8$: C, 63.87; H, 6.51; N, 5.32. Found C, 63.62; H, 6.58; N, 5.28.

(*R*)-2-[(3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-Dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyl-tetrahydro-furo[3,4-*d*][1,3]dioxol-4-yl]-3-methyl-4-(4-nitro-phenyl)-[1,2,4]oxadiazolidin-5-one (XV)



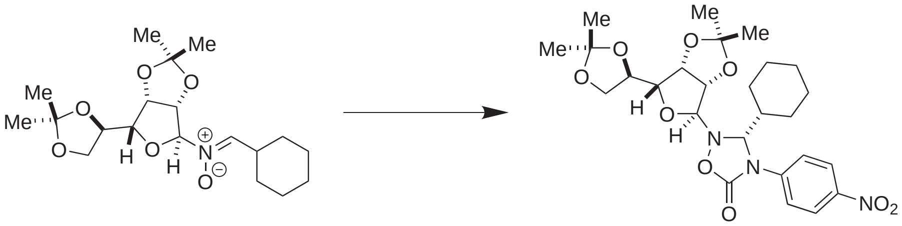
Procedure A: To nitrone **M** (982 mg, 3.26 mmol, 1.00 equiv) in CH_2Cl_2 (3.3 ml) at 23 °C is added 4-nitrophenyl isocyanate (535 mg, 3.26 mmol, 1.00 equiv).The solution is stirred at 23 °C for 0.1 h and then concentrated *in vacuo* to afford a yellow solid. NMR analysis of the crude material indicated a 4:1 ratio of diastereomers. The solid is triturated with methanol for 12 h, filtered off, washed with hexane, and dried *in vacuo* to afford the target compound as a colorless solid (69% yield, > 99:1 dr).

Procedure B: To nitrone **75** (982 mg, 3.26 mmol, 1.00 equiv) in acetonitrile (3.3 ml) at 23 °C is added 4-nitrophenyl isocyanate (535 mg, 3.26 mmol, 1.00 equiv). The solution is stirred at 23 °C for 0.1

h and then concentrated *in vacuo* to afford a yellow solid. NMR analysis of the crude material indicated a 4:1 ratio of diastereomers. The solid is triturated with methanol for 12 h, filtered off, washed with hexane, and dried *in vacuo* to afford the target compound as a colorless solid (69% yield, > 99:1 dr).

R*f* = 0.60 (1:1 hexane/EtOAc). Melting Point: mp 171 °C. Specific Rotation $[\alpha]_{25.6}$ *D* +4° (c 1.27, $CHCl_3$). NMR Spectroscopy: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.29–8.26 (m, 2H), 7.71–7.68 (m, 2H), 5.50 (q, *J* = 6.0 Hz, 1H), 4.96 (d, *J* = 6.0 Hz, 1H), 4.88 (dd, *J* = 5.8 Hz, 2.2 Hz, 1H), 4.62 (s, 1H), 4.45–4.39 (m, 1H), 4.17–4.11 (m, 2H), 4.01 (dd, *J* = 8.8 Hz, 4.4 Hz, 1H), 1.57 (d, *J* = 6.0 Hz, 3H), 1.46 (s, 3H), 1.45 (s, 3H), 1.38 (s, 3H), 1.35 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 153.3, 144.2, 141.6, 125.5, 118.5, 113.4, 109.5, 96.8, 83.7, 83.5, 80.1, 77.5, 73.2, 73.1, 66.8, 27.1, 26.1, 25.2, 24.6, 19.1. IR Spectroscopy (thin film) 2989, 2938, 1772, 1597, 1520, 1504, 1383, 1340, 1206, 1094, 1068, 854, 771 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{21}H_{27}N_3O_9Na$, 488.1645. Found, 488.1647. Combustion Analysis: Anal. calcd for $C_{21}H_{27}N_3O_9$: C, 54.19; H, 5.85; N, 9.03. Found C, 54.34; H, 5.88; N, 9.04.

(*R*)-3-Cyclohexyl-2-[(3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyl-tetrahydro-furo[3,4-*d*][1,3]dioxol-4-yl]-4-(4-nitro-phenyl)-[1,2,4]oxadiazolidin-5-one (XVI)

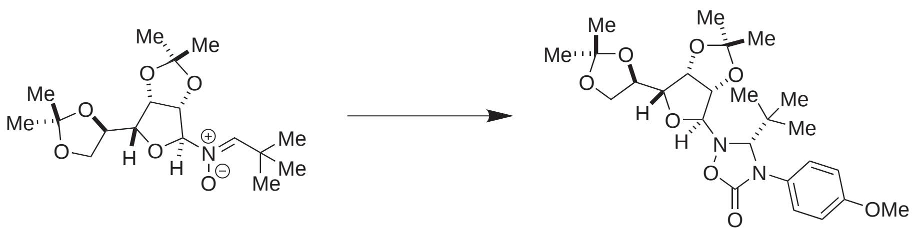


To nitrone **N** (1.26 g, 3.41 mmol, 1.00 equiv) in CH_2Cl_2 (3.4 ml) at 23 °C is added 4-nitrophenyl isocyanate (560 mg, 3.41 mmol, 1.00 equiv).

The solution is stirred at 23 °C for 0.1 h and then concentrated *in vacuo* to afford a yellow solid. NMR analysis of the crude material indicated a 5:1 ratio of diastereomers. The solid is triturated with methanol for 12 h, filtered off, washed with hexane, and dried *in vacuo* to afford the target compound as a colorless solid (84% yield, 95:5 dr).

R*f* = 0.59 (2:1 hexane/EtOAc). Melting Point: mp 199 °C. Specific Rotation $[\alpha]_{29.9\,D}$ +18° (c 1.10, $CHCl_3$). NMR Spectroscopy: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.29–8.26 (m, 2H), 7.74–7.71 (m, 2H), 5.24 (d, *J* = 3.4 Hz, 1H), 5.13 (d, *J* = 5.9 Hz, 1H), 4.92 (dd, *J* = 5.9 Hz, 3.4 Hz, 1H), 4.56 (s, 1H), 4.46–4.40 (m, 1H), 4.17–4.10 (m, 2H), 4.01 (dd, *J* = 8.7 Hz, 4.7 Hz, 1H), 1.80–1.09 (m, 11H), 1.46 (s, 3H), 1.46 (s, 3H), 1.39 (s, 3H), 1.35 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 153.4, 143.8, 141.6, 125.1, 118.9, 113.1, 109.3, 97.1, 83.3, 83.0, 79.9, 79.8, 72.9, 66.6, 40.1, 28.8, 27.0, 26.0, 25.6, 25.5, 25.2, 24.5. IR Spectroscopy (thin film) 2933, 1773, 1596, 1521, 1503, 1374, 1341, 1219, 1069, 913, 834, 750 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{26}H_{35}N_3O_9Na$, 534.2452. Found, 534.2448. Combustion Analysis: Anal. calcd for $C_{26}H_{35}N_3O_9$: C, 58.53; H, 6.61; N, 7.88. Found C, 58.32; H, 6.63; N, 8.04.

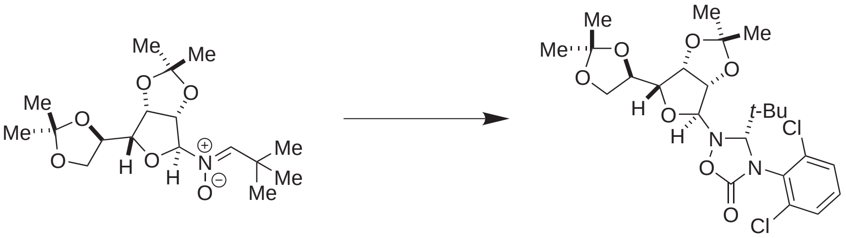
(*R*)-3-*tert*-Butyl-2-[(3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyl-tetrahydro-furo[3,4-*d*][1,3]dioxol-4-yl]-4-(4-methoxy-phenyl)-[1,2,4]oxadiazolidin-5-one (XVII)



To nitrone **O** (300 mg, 0.874 mmol, 1.00 equiv) in CH_2Cl_2 (1.0 ml) at 23 °C is added 4-methoxyphenyl isocyanate (130 mg, 0.874 mmol, 1.00 equiv). The solution is stirred at 23 °C for 2 h and then concentrated *in vacuo* to afford an off-white solid. NMR analysis of the crude material indicated a 6:1 ratio of diastereomers. The solid is triturated with methanol for 3 h, filtered off, washed with hexane, and dried *in vacuo* to afford the target compound as a colorless solid (70% yield, > 99:1 dr).

R*f* = 0.52 (2:1 hexane/EtOAc). Melting Point: mp 154 °C. Specific Rotation $[\alpha]_{32.7\,D}$ 0° (c 0.51, $CHCl_3$). NMR Spectroscopy: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.34–7.31 (m, 2H), 6.92–6.89 (m, 2H), 5.01 (d, *J* = 6.0 Hz, 1H), 4.91–4.86 (m, 2H), 4.59 (s, 1H), 4.47–4.41 (m, 1H), 4.16–4.10 (m, 2H), 4.02 (dd, *J* = 8.5 Hz, 4.4 Hz, 1H), 3.80 (s, 3H), 1.48 (s, 3H), 1.44 (s, 3H), 1.38 (s, 3H), 1.34 (s, 3H), 0.87 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 158.0, 155.5, 130.4, 125.0, 114.8, 113.1, 109.5, 97.7, 85.2, 83.5, 83.0, 80.0, 73.2, 66.8, 55.7, 38.0, 27.1, 26.1, 25.8, 25.4, 24.6. IR Spectroscopy (thin film) 2982, 2938, 1771, 1515, 1398, 1372, 1251, 1136, 1084, 758 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{25}H_{36}N_2O_8Na$, 515.2370. Found, 515.2357. Combustion Analysis: Anal. Calcd for $C_{25}H_{36}N_2O_8$: C, 60.96; H, 7.37; N, 5.69. Found C, 60.73; H, 7.38; N, 5.75.

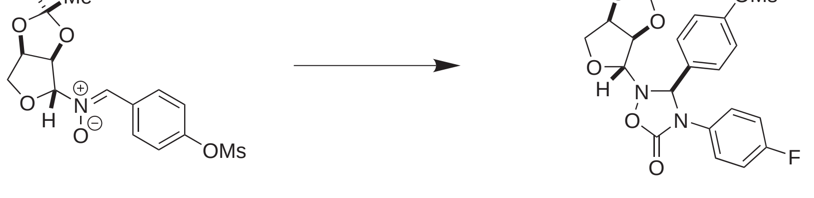
(*R*)-3-*tert*-Butyl-4-(2,6-dichloro-phenyl)-2-[(3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyl-tetrahydro-furo[3,4-*d*][1,3]dioxol-4-yl]-[1,2,4]oxadiazolidin-5-one (XVIII)



To nitrone **O** (267 mg, 0.778 mmol, 1.00 equiv) in CH_2Cl_2 (0.80 ml) at 23 °C is added 2,6-dichlorophenyl isocyanate (146 mg, 0.778 mmol, 1.00 equiv). The solution is stirred at 23 °C for 2 h and then concentrated *in vacuo* to afford a white solid. NMR analysis of the crude material indicated a 6:1 ratio of diastereomers. The solid is triturated with methanol for 1 h, filtered off, washed with hexane, and ried *in vacuo* to afford the target compound as a colorless solid (70% yield, > 99:1 dr).

R*f* = 0.53 (2:1 hexane/EtOAc). Melting Point (methanol): mp 164 °C. Specific Rotation $[\alpha]_{32.6 D}$ +23° (c 0.55, $CHCl_3$). NMR Spectroscopy: ^1H NMR (300 MHz, acetone-d_6) δ: 7.65–7.60 (m, 2H), 7.53–7.46 (m, 1H), 5.44 (s, 1H), 5.03–4.95 (m, 3H), 4.43–4.38 (m, 1H), 4.27 (dd, *J* = 6.2 Hz, 3.1 Hz, 1H), 4.11–4.01 (m, 2H), 1.44 (s, 3H), 1.37 (s, 3H), 1.35 (s, 3H), 1.31 (s, 3H), 0.97 (s, 9H). ^{13}C NMR (75 MHz, acetone-d_6) δ: 154.4, 136.4, 133.0, 132.1, 131.3, 131.1, 130.6, 129.0, 113.2, 109.2, 98.0, 84.9, 83.7, 83.5, 80.9, 73.9, 66.7, 38.2, 27.0, 26.4, 25.8, 25.1, 24.8. IR Spectroscopy (thin film) 2987, 2938, 1781, 1460, 1439, 1372, 1212, 1136, 1084, 1067, 757 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{24}H_{32}Cl_2N_2O_7Na$, 553.1484. Found, 553.1471. Combustion Analysis: Anal. calcd for $C_{24}H_{32}Cl_2N_2O_7$: C, 54.24; H, 6.07; N, 5.27. Found C, 53.98; H, 5.84; N, 5.48.

Methanesulfonic acid 4-[(*S*)-2-((3a*R*,4*R*,6a*R*)-2,2-dimethyl-tetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-4-(4-fluoro-phenyl)-5-oxo-[1,2,4]oxadiazolidin-3-yl]-phenyl ester (XIX)

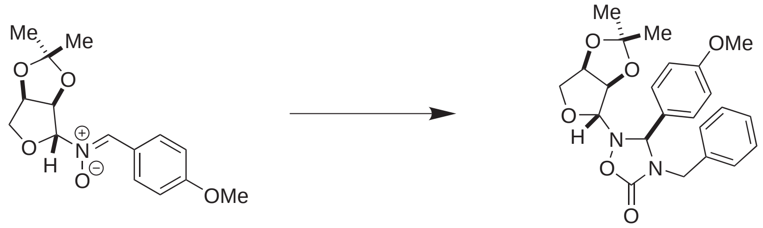


Procedure A: To nitrone **P** (855 mg, 2.39 mmol, 1.00 equiv) in CH_2Cl_2 (2.4 ml) at 23 °C is added 4-fluorophenyl isocyanate (328 mg, 2.39 mmol, 1.00 equiv). The solution is stirred at 23 °C for 42 h and then concentrated *in vacuo* to afford an off-white solid. NMR analysis of the crude material indicated a 12:1 ratio of diastereomers. The solid is triturated with methanol for 4 h, filtered off, washed with hexane, and dried *in vacuo* to afford the target compound as a colorless solid (84% yield, > 99:1 dr).

Procedure B: To nitrone **P** (1.32 g, 3.69 mmol, 1.00 equiv) in acetonitrile (3.7 ml) at 23 °C is added 4-fluorophenyl isocyanate (506 mg, 3.69 mmol, 1.00 equiv). The solution is stirred at 23 °C for 20 h and then concentrated *in vacuo* to afford an off-white solid. NMR analysis of the crude material indicated a 10:1 ratio of diastereomers. The solid is triturated with methanol for 3 h, filtered off, washed with hexane, and dried *in vacuo* to afford the target compound as a colorless solid (80% yield, > 99:1 dr).

R*f* = 0.66 (2:3 hexane/EtOAc). Melting Point (methanol): mp 220 °C. Specific Rotation $[\alpha]_{27.1}$ *D* −35° (c 0.80, $CHCl_3$). NMR Spectroscopy: ^1H NMR (300 MHz, $CDCl_3$) δ: 7.47–7.29 (m, 6H), 7.06–7.00 (m, 2H), 6.18 (s, 1H), 4.94 (d, *J* = 5.9 Hz, 1H), 4.87 (dd, *J* = 6.2 Hz, 3.7 Hz, 1H), 4.82 (s, 3H), 4.16 (d, *J* = 10.3 Hz, 1H), 3.96 (dd, *J* = 10.3 Hz, 3.4 Hz, 1H), 3.16 (s, 3H), 1.50 (s, 3H), 1.35 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 159.9 (d, *J* = 246 Hz), 153.9, 149.6, 135.1, 131.4, 128.2, 122.9, 121.9 (d, *J* = 9 Hz), 116.3 (d, *J* = 23 Hz), 112.7, 97.9, 83.4, 80.2, 77.8, 74.4, 37.8, 26.3, 24.7. IR Spectroscopy (thin film) 2939, 1769, 1513, 1372, 1220, 1153, 1084, 1058, 971, 871, 772 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{22}H_{23}FN_2O_8SNa$, 517.1057. Found, 517.1045. Combustion Analysis: Anal. calcd for $C_{22}H_{23}FN_2O_8S$: C, 53.44; H, 4.69; N, 5.67. Found C, 53.36; H, 4.72; N, 5.71.

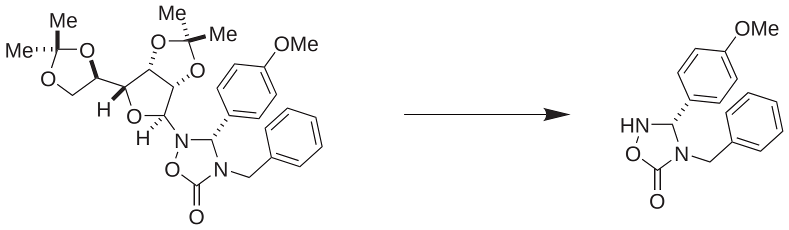
(*S*)-4-Benzyl-2-((3a*R*,4*R*,6a*R*)-2,2-dimethyl-tetrahydro-furo[3,4-*d*][1,3]dioxol-4-yl)-3-(4-methoxy-phenyl)-[1,2,4]oxadiazolidin-5-one (XX)



To nitrone **Q** (984 mg, 3.35 mmol, 1.00 equiv) in CH_2Cl_2 (1.7 ml) at 23 °C is added benzyl isocyanate (446 mg, 3.35 mmol, 1.00 equiv). The solution is heated to reflux and kept at this temperature for 46 h. After cooling, the suspension is concentrated *in vacuo* to afford an off-white solid. NMR analysis of the crude material indicated a 10:1 ratio of diastereomers. The solid is triturated with methanol for 5 h, filtered off, washed with hexane, and dried *in vacuo* to afford the target compound as a colorless solid (83% yield, > 99:1 dr).

R*f* = 0.46 (2:1 hexane/EtOAc). Melting Point (methanol): mp 125 °C. Specific Rotation $[\alpha]_{33.3}$ $_{D}$ −40° (c 1.05, $CHCl_3$). NMR Spectroscopy: ^1H NMR (300 MHz, $CDCl_3$) δ: 7.37–7.31 (m, 3H), 7.20–7.14 (m, 4H), 6.93–6.91 (m, 2H), 5.28 (s, 1H), 4.89 (d, *J* = 6.2 Hz, 1H), 4.84–4.75 (m, 2H), 4.60 (s, 1H), 3.89 (d, *J* = 10.3 Hz, 1H), 3.83 (s, 3H), 3.69–3.64 (m, 2H), 1.46 (s, 3H), 1.31 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 160.5, 156.0, 134.5, 128.9, 128.5, 128.2, 128.2, 127.4, 114.4, 112.3, 98.3, 83.4, 80.0, 77.4, 74.0, 55.4, 45.9, 26.2, 24.6. IR Spectroscopy (thin film) 2937, 1768, 1612, 1514, 1409, 1374, 1252, 1057, 912, 772 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{23}H_{26}N_2O_6Na$, 449.1689. Found, 449.1678. Combustion Analysis: Anal. calcd for $C_{23}H_{26}N_2O_6$: C, 64.78; H, 6.14; N, 6.57. Found C, 64.56; H, 6.00; N, 6.58.

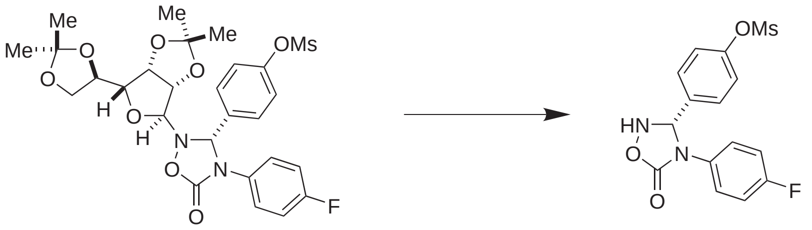
(*R*)-4-Benzyl-3-(4-methoxy-phenyl)-[1,2,4]oxadiazolidin-5-one (XXI)



To oxadiazolidinone **XIV** (52.7 mg, 0.100 mmol, 1.00 equiv) in methanol/ water (6:1) (1.9 ml) at 23 °C is added 4-toluenesulfonic acid hydrate (190 mg, 1.00 mmol, 10.0 equiv). The solution is heated at reflux and kept at this temperature for 2 h. After cooling, $Na_3PO_4{}^x12\ H_2O$ (228 mg, 0.600 mmol, 6.00 equiv) is added and the suspension is concentrated *in vacuo* to a quarter of the original volume. To this suspension is added EtOAc and water. The phases are separated and the aqueous phase is extracted with EtOAc. The combined organic phases are washed with brine, dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the crude product by chromatography on silica gel (eluent hexane/EtOAc 3:2) afford the target compound as a colorless oil (88% yield, ee > 99%).

R*f* = 0.32 (3:2 hexane/EtOAc). Specific Rotation $[\alpha]_{35\cdot0}$ *D* +170° (c 0.98, $CHCl_3$). NMR Spectroscopy: ^1H NMR (300 MHz, $CDCl_3$) δ: 7.32–7.25 (m, 5H), 7.13- 7.07 (m, 2H), 6.99–6.94 (m, 2H), 5.35 (s, 1H), 4.77 (d, *J* = 14.6 Hz, 1H), 3.85 (s, 3H), 3.78 (d, *J* = 14.6 Hz, 1H)). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 161.3, 159.3, 134.3, 129.2, 128.7, 128.6, 128.3, 128.2, 114.8, 76.5, 55.5, 46.3. IR Spectroscopy (thin film) 3218, 2935, 1760, 1613, 1516, 1397, 1254, 1177, 1030, 834, 703 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{16}H_{16}N_2O_3Na$, 307.1059. Found, 307.1048. Chiral HPLC (Daicel Chiralpak AD-H, hexane/*i*- PrOH = 4:1, flow rate = 1.00 ml/min) t_R = 18.2 min (major), t_R = 12.4 min (minor).

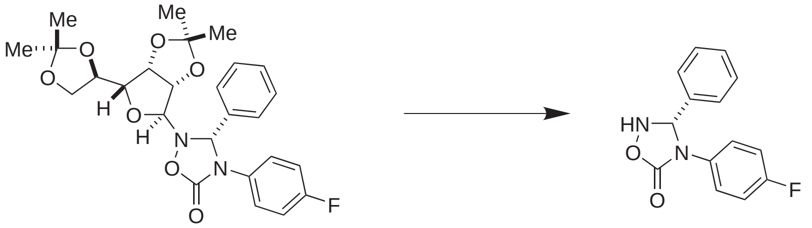
Methanesulfonic acid 4-[(*R*)-4-(4-fluoro-phenyl)-5-oxo-[1,2,4]oxadiazolidin-3-yl]-phenyl ester (XXII)



To oxadiazolidinone **VI** (280mg, 0.566mmol, 1.00 equiv) inmethanol/ water (6:1) (5.6 ml) at 23 °C is added 4-toluenesulfonic acid hydrate (1.08 g, 5.66 mmol, 10.0 equiv). The solution is heated at reflux and kept at this temperature for 1.5 h. After cooling, $Na_3PO_4{}^{x}12\ H_2O$ is added and the suspension is concentrated *in vacuo* to a quarter of the original volume. To this suspension is added EtOAc and water. The phases are separated and the aqueous phase is extracted with EtOAc. The combined organic phases are washed with brine, dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the crude product by chromatography on silica gel (eluent hexane/EtOAc 2:3) afford the target compound as a colorless solid (91% yield, ee > 99%).

R*f* = 0.41 (2:3 hexane/EtOAc). Melting Point (toluene): mp 104 °C. Specific Rotation $[\alpha]_{33.0}\ _{D}$ +112° (c 0.60, $CHCl_3$). NMR Spectroscopy: ^1H NMR (300 MHz, methanol-d_4, 52 °C) δ: 7.56-7.53 (m, 2H), 7.37-7.32 (m, 4H), 7.07-7.01 (m, 2H), 6.37 (s, 1H), 3.29 (s, 3H). ^{13}C NMR (75 MHz, methanol-d_4, 52 °C) δ: 160.2 (d, *J* = 247 Hz), 156.8, 150.3, 132.5, 131.5, 131.5, 129.0, 123.1 (d, *J* = 9 Hz), 122.9, 116.1, (d, *J* = 23 Hz), 77.5, 38.0. IR Spectroscopy (KBr) 3645, 3230, 3029, 2939, 1762, 1606, 1513, 1368, 1232, 1152, 973, 873, 834, 786, 744, 684, 622 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{15}H_{13}FN_2O_5SNa$, 375.0427. Found, 375.0416. Combustion Analysis: Anal. calcd for $C_{15}H_{13}NF_2O_5S$: C, 51.13; H, 3.72; N, 7.95. Found C, 51.33; H, 3.81; N, 7.84. Chiral HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 7:3, flow rate = 1.00 ml/min) t_R = 20.4 min (major), t_R = 25.7 min (minor).

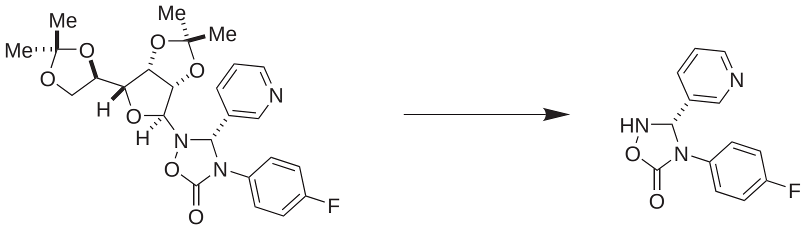
(*R*)-4-(4-Fluoro-phenyl)-3-phenyl-[1,2,4]oxadiazolidin-5-one (XXIII)



To oxadiazolidinone **IV** (900 mg, 1.80 mmol, 1.00 equiv) in methanol/ water (6:1) (36 ml) at 23 °C is added 4-toluenesulfonic acid hydrate (3.42 g, 18.0 mmol, 10.0 equiv). The solution is heated at reflux and kept at this temperature for 2 h. After cooling, $Na_3PO_4{}^x12\ H_2O$ (4.10 g, 10.8 mmol, 6.00 equiv) is added and the suspension is concentrated *in vacuo* to a quarter of the original volume. To this suspension is added EtOAc and water. The phases are separated and the aqueous phase is extracted with EtOAc. The combined organic phases are washed with brine, dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the crude product by chromatography on silica gel (eluent hexane/EtOAc 3:2) afford the target compound as a colorless solid (81% yield, ee > 99%).

R*f* = 0.47 (3:2 hexane/EtOAc). Specific Rotation $[\alpha]_{35\cdot5}$ *D* +142° (c 0.53, $CHCl_3$). NMR Spectroscopy: ^1H NMR (300 MHz, $CDCl_3$, 52 °C) δ: 7.42 (m, 5H), 7.26–7.21 (m, 2H), 7.00–6.94 (m, 2H), 6.18 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, 52 °C) δ: 160.1 (d, *J* = 247 Hz), 157.2, 133.0, 131.8, 131.8, 130.5, 129.4, 123.2 (d, *J* = 9 Hz), 115.9, (d, *J* = 23 Hz), 78.6. IR Spectroscopy (thin film) 3220, 3068, 1761, 1512, 1387, 1232, 1132, 834, 759, 702 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{14}H_{11}FN_2O_2Na$, 281.0703. Found, 281.0693. Combustion Analysis: Anal. calcd for $C_{14}H_{11}NF_2O_2$: C, 65.11; H, 4.29; N, 10.85. Found C, 64.96; H, 4.34; N, 10.86.Chiral HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 9:1, flow rate = 1.00 ml/min) t_R = 34.5 min (major).

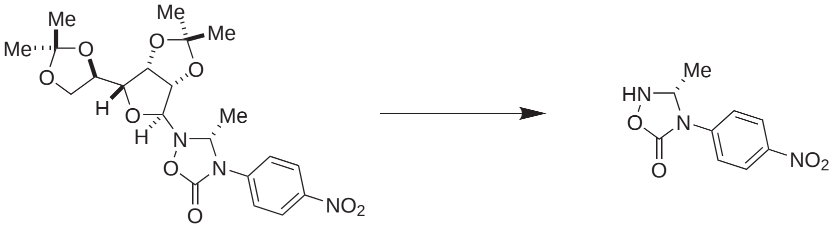
(*R*)-4-(4-Fluoro-phenyl)-3-pyridin-3-yl-[1,2,4]oxadiazolidin-5-one (XXIV)



To oxadiazolidinone **VII** (1.25 g, 2.49 mmol, 1.00 equiv) in methanol/ water (6:1) (49 ml) at 23 °C is added 4-toluenesulfonic acid hydrate (4.74 g, 24.9 mmol, 10.0 equiv). The solution is heated at reflux and kept at this temperature for 3 h. After cooling, $Na_3PO_4{}^x12\ H_2O$ (5.68 g, 14.9 mmol, 6.00 equiv) is added and the suspension is concentrated *in vacuo* to a quarter of the original volume. To this suspension is added EtOAc and water. The phases are separated and the aqueous phase is extracted with EtOAc. The combined organic phases are washed with brine, dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the crude produc by chromatography on silica gel (eluent EtOAc 3:2) afford the target compound as a colorless solid (65% yield, ee > 99%).

R*f* = 0.44 (EtOAc). Melting Point (toluene): mp 136 °C. Specific Rotation $[\alpha]_{35.5}$ *D* +126° (c 0.53, CH_2Cl_2). NMR Spectroscopy: ^{1}H NMR (300 MHz, $CDCl_3$, 52 °C) δ: 8.67 (m, 2H), 7.77–7.74 (m, 1H), 7.36–7.32 (m, 1H), 7.26–7.22 (m, 2H), 7.03–6.98 (m, 2H), 6.24 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, 52 °C) δ: 160.3 (d, *J* = 246 Hz), 156.6, 151.6, 148.9, 134.5, 131.2, 123.9, 123.3 (d, *J* = 9 Hz), 116.3, (d, *J* = 23 Hz), 76.4. IR Spectroscopy (thin film) 3214, 1759, 1512, 1433, 1386, 1231, 1125, 835, 747, 711 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{13}H_{10}FN_3O_2HNa$, 260.0836. Found, 260.0826. Combustion Analysis: Anal. calcd for $C_{13}H_{10}FN_3O_2$: C, 60.23; H, 3.89; N, 16.21. Found C, 60.11; H, 4.02; N, 16.18. Chiral HPLC (Daicel Chiralpak AD-H, hexane/*i*- PrOH = 9:1, flow rate = 1.00 ml/min) t_R = 60.9 min (major), t_R = 78.1 min (minor).

(*R*)-3-Methyl-4-(4-nitro-phenyl)-[1,2,4]oxadiazolidin-5-one (XXV)

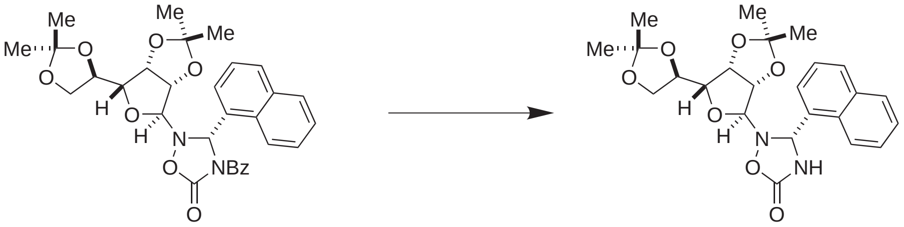


To oxadiazolidinone **XV** (325 mg, 0.698 mmol, 1.00 equiv) in methanol/ water (6:1) (14 ml) at 23 °C is added 4-toluenesulfonic acid hydrate (1.33 g, 6.98 mmol, 10.0 equiv). The solution is heated at reflux and kept at this temperature for 1.5 h. After cooling, $Na_3PO_4{}^x12\ H_2O$ (1.59 g, 4.12 mmol, 6.00 equiv) is added and the suspension is concentrated *in vacuo* to a quarter of the original volume. To this suspension is added EtOAc and water. The phases are separated and the aqueous phase is extracted with EtOAc. The combined organic phases are washed with brine, dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the crude product by chromatography on silica gel (eluent EtOAc/hexane 3:2) afford the target compound as a colorless solid (65% yield, ee > 99%).

R*f* = 0.35 (1:1 hexane/EtOAc). Melting Point (methanol): mp 107 °C. Specific Rotation $[\alpha]_{33.0\ D}$ −58° (c 0.10, $CHCl_3$). NMR Spectroscopy: ^1H NMR (300 MHz, acetone-d_6) δ: 8.33–8.29 (m, 2H), 7.98–7.85 (m, 2H), 6.01 (q, *J* = 5.9 Hz, 1H), 5.98 (s, 1H), 1.56 (d, *J* = 5.9 Hz, 3H). ^{13}C NMR (75 MHz, acetone-d_6) δ: 143.8, 143.0, 125.5, 119.2, 118.6, 72.6, 20.7. IR Spectroscopy (thin film) 3237, 3123, 1760, 1598, 1516, 1504, 1386, 1338, 1204,11139, 854, 750 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_9H_9N_3O_4HNa$, 246.0491. Found, 246.0482. Combustion Analysis: Anal. calcd for $C_9H_9N_3O_2$: C, 48.43; H, 4.06; N, 18.83. Found

C, 48.63; H, 4.26; N, 18.69. Chiral HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 4/1, flow rate = 1.00 ml/min) t_R = 12.4 min (major), t_R = 15.5 min (minor).

Oxadiazolidinone (XXVIa)

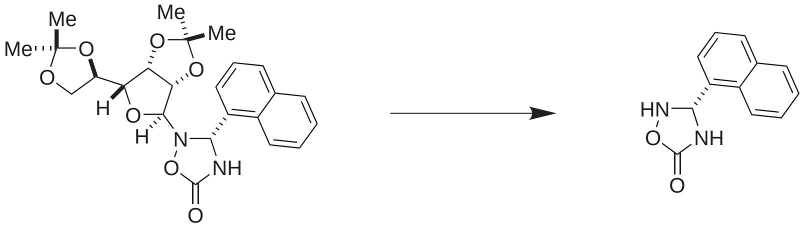


To oxadiazolidinone **XII** (220 mg, 0.392 mmol, 1.00 equiv) in methanol (1.5 ml) at 23 °C is added K_2CO_3 (5.4 mg, 39 μmol, 0.10 equiv). The solution is stirred for 30 min, then diluted with aqueous NH_4Cl, H_2O, and EtOAc. The phases are separated and the aqueous phase is extracted with EtOAc. The combined organic phases are washed with brine, dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the crude product by chromatography on silica gel (eluent hexane/EtOAc 3:2) affords the debenzoylated oxadiazolidinone **230** as a colorless solid (85% yield).

R*f* = 0.32 (3:2 hexane/EtOAc). Melting Point (toluene): mp 197 °C. Specific Rotation $[\alpha]_{35.0}$ $_D$ +37° (c 0.59, $CHCl_3$). NMR Spectroscopy: ^1H NMR (300 MHz, $CDCl_3$) δ: 8.15 (d, *J* = 8.4 Hz, 1H), 7.92–7.88 (m, 2H), 7.72–7.44 (m, 4H), 6.55 (s, 1H), 6.38 (s, 1H), 5.04 (s, 1H), 4.95 (d, *J* = 6.2 Hz, 1H), 4.75 (dd, *J* = 5.9 Hz, 3.7 Hz, 1H), 4.48–4.42 (m, 1H), 4.32 (dd, *J* = 5.1 Hz, 3.9 Hz, 1H), 4.09 (d, *J* = 6.0 Hz, 2H), 1.51 (s, 3H), 1.46 (s, 3H), 1.42 (s, 3H), 1.32 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 158.3, 133.9, 131.5, 130.3, 129.0, 127.5, 126.3, 125.1, 123.5, 122.1, 112.9, 108.8, 97.9, 84.1, 83.0, 79.8, 73.7, 72.0, 65.7, 26.8, 26.0, 25.2, 24.4. IR Spectroscopy (thin film) 3263, 2988, 1779, 1526, 1374, 1350, 1212, 1067, 754 (cm^{-1}). Mass

Spectrometry HRMS-ESI (m/z): Calcd for $C_{24}H_{28}N_2O_7Na$, 479.1795. Found, 479.1784. Combustion Analysis: Anal. Calcd for $C_{24}H_{28}N_2O_7$: C, 63.15; H, 6.18; N, 6.14. Found C, 62.88; H, 6.31; N, 6.27.

(*R*)-3-Naphthalen-1-yl-[1,2,4]oxadiazolidin-5-one (XXVI)

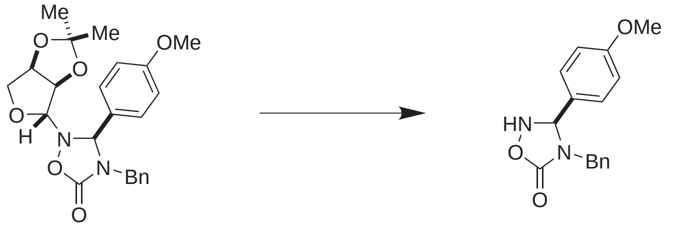


To oxadiazolidinone **XXVIa** (125mg, 0.274mmol, 1.00 equiv) inmethanol/ water (6:1) (7.0 ml) at 23 °C is added 4-toluenesulfonic acid hydrate (520 mg, 274 mmol, 10.0 equiv). The solution is heated to 40 °C and kept at this temperature for 6 h. After cooling, $Na_3PO_4{}^{x}12\ H_2O$ (625 mg, 1.64 mmol, 6.00 equiv) is added and the suspension is concentrated *in vacuo* to a quarter of the original volume. To this suspension is added EtOAc and water. The phases are separated and the aqueous phase is extracted with EtOAc. The combined organic phases are washed with brine, dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the crude product by chromatography on silica gel (eluent EtOAc 1:1) afford the target compound as a colorless solid (35% yield, ee > 99%).

R*f* = 0.24 (hexane/EtOAc 1:1). Melting Point (toluene): mp 136 °C. Specific Rotation $[\alpha]_{35\cdot 8\ D}$ +180° (c 0.40, CH_2Cl_2). NMR Spectroscopy: ^1H NMR (300 MHz, methanol-*d*$_4$, 54 °C) δ: 9.10 (s, 1H), 8.55–8.52 (m, 1H), 8.03–7.92 (m, 3H), 7.65–7.51 (m, 3H). ^{13}C NMR (75 MHz, methanol-*d*$_4$, 54 °C) δ: 154.8, 134.9, 132.7, 131.8, 129.4, 128.2, 127.2, 127.1, 125.8, 124.8. IR Spectroscopy (thin film) 3214, 1759, 1512, 1433, 1386, 1231, 1125, 835, 747, 711 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z):

Calcd for $C_{13}H_{10}FN_3O_2HNa$, 237.0640. Found, 237.0631. Chiral HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 9:1, flow rate = 1.00 ml/min) t_R = 50.9 min (major), t_R = 54.1 min (minor).

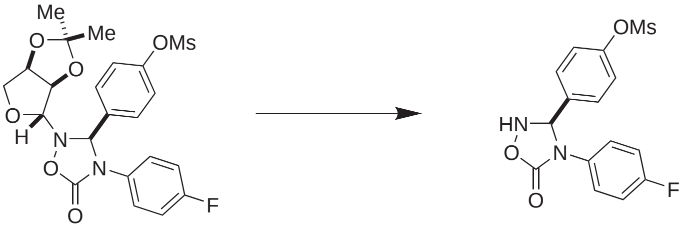
(*S*)-4-Benzyl-3-(4-methoxy-phenyl)-[1,2,4]oxadiazolidin-5-one (XXVII)



To oxadiazolidinone **XX** (166mg, 0.389mmol, 1.00 equiv) inmethanol/ water (6:1) (4.3 ml) at 23 °C is added 4-toluenesulfonic acid hydrate (740 mg, 3.89 mmol, 10.0 equiv). The solution is heated at reflux and kept at this temperature for 2 h. After cooling, $Na_3PO_4{}^x12\ H_2O$ is added and the suspension is concentrated *in vacuo* to a quarter of the original volume. To this suspension is added EtOAc and water. The phases are separated and the aqueous phase is extracted with EtOAc. The combined organic phases are washed with brine, dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the crude product by chromatography on silica gel (eluent hexane/EtOAc 3:2) afford the target compound as a colorless oil (86% yield, ee > 99%).

R*f* = 0.32 (3:2 hexane/EtOAc). Specific Rotation $[\alpha]_{34.2\ D}$ −180° (c 0.34, $CHCl_3$). NMR Spectroscopy: ^1H NMR (300 MHz, $CDCl_3$) δ: 7.32–7.25 (m, 5H), 7.13–7.07 (m, 2H), 6.99–6.94 (m, 2H), 5.35 (s, 1H), 4.77 (d, *J* = 14.6 Hz, 1H), 3.85 (s, 3H), 3.78 (d, *J* = 14.6 Hz, 1H)). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 161.3, 159.3, 134.3, 129.2, 128.7, 128.6, 128.3, 128.2, 114.8, 76.5, 55.5, 46.3. IR Spectroscopy (thin film) 3218, 2935, 1760, 1613, 1516, 1397, 1254, 1177, 1030, 834, 703 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{16}H_{16}N_2O_3Na$, 307.1059. Found, 307.1049. Combustion Analysis: Anal. Calcd for $C_{16}H_{16}N_2O_3$: C, 67.59; H, 5.67; N, 9.85. Found C, 67.41; H, 5.64; N, 9.92. Chiral HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 4:1, flow rate = 1.00 ml/min) t_R = 12.4 min (major), t_R = 18.2 min (minor).

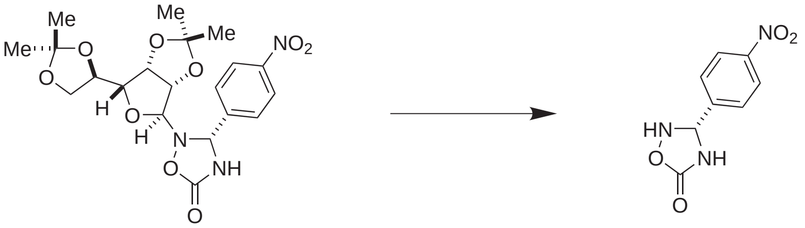
Methanesulfonic acid 4-[(*S*)-4-(4-fluoro-phenyl)-5-oxo-[1,2,4]oxadiazolidin-3- yl]-phenyl ester (XXVII)



To oxadiazolidinone **XIX** (1.60 g, 2.69 mmol, 1.00 equiv) in methanol/ water (6:1) (49 ml) at 23 °C is added 4-toluenesulfonic acid hydrate (5.12 g, 26.9 mmol, 10.0 equiv). The solution is heated at reflux and kept at this temperature for 2 h. After cooling, Na_3PO_4x12 H_2O (6.13 g, 16.1 mmol, 6.00 equiv) is added and the suspension is concentrated *in vacuo* to a quarter of the original volume. To this suspension is added EtOAc and water. The phases are separated and the aqueous phase is extracted with EtOAc. The combined organic phases are washed with brine, dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the crude product by chromatography on silica gel (eluent hexane/EtOAc 2:3) afford the target compound as a colorless solid (87% yield, ee > 99%).

R*f* = 0.41 (2:3 hexane/EtOAc). Melting Point (benzene): mp 104 °C. Specific Rotation $[\alpha]_{32.0\,D}$ −114° (c 0.60, $CHCl_3$). NMR Spectroscopy: ^1H NMR (300 MHz, methanol-d_4, 52 °C) δ: 7.56–7.53 (m, 2H), 7.37–7.32 (m, 4H), 7.07–7.01 (m, 2H), 6.37 (s, 1H), 3.29 (s, 3H). ^{13}C NMR (75 MHz, methanol-d_4, 52 °C) δ: 160.2 (d, *J* = 247 Hz), 156.8, 150.3, 132.5, 131.5, 131.5, 129.0, 123.1 (d, *J* = 9 Hz), 122.9, 116.1, (d, *J* = 23 Hz), 77.5, 38.0. IR Spectroscopy (KBr) 3645, 3230, 3029, 2939, 1762, 1606, 1513, 1368, 1232, 1152, 973, 873, 834, 786, 744, 684, 622 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{15}H_{13}FN_2O_5SNa$, 375.0427. Found, 375.0418. Combustion Analysis: Anal. calcd for $C_{15}H_{13}NF_2O_5S$: C, 51.13; H, 3.72; N, 7.95. Found C, 51.04; H, 3.92; N, 7.73. Chiral HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 7/3, flow rate = 1.00 ml/min) t_R = 26.3 min (major), t_R = 21.6 min (minor).

(*R*)-3-(4-Nitro-phenyl)-[1,2,4]oxadiazolidin-5-one (XXIX)

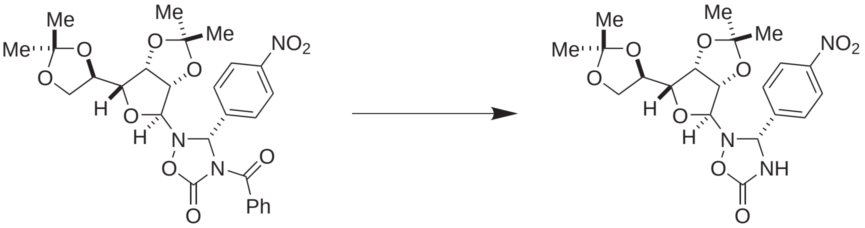


To oxadiazolidinone **14** (135mg, 0.299mmol, 1.00 equiv) inmethanol/ water (6:1) (7.0 ml) at 23 $^\circ$C is added 4-toluenesulfonic acid hydrate (572 mg, 2.99

mmol, 10.0 equiv). The solution is heated at reflux and kept at this temperature for 2 h. After cooling, $Na_3PO_4{}^x12\ H_2O$ (684 mg, 1.80 mmol, 6.00 equiv) is added and the suspension is concentrated *in vacuo* to a quarter of the original volume. To this suspension is added EtOAc and water. The phases are separated and the aqueous phase is extracted with EtOAc. The combined organic phases are washed with brine, dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the crude product by chromatography on silica gel (eluent EtOAc) afford the target compound as a colorless solid (58% yield, ee > 99%).

R*f* = 0.55 (EtOAc). Specific Rotation $[\alpha]_{35.8}\ _{D}$ +150° (c 0.30, CH_2Cl_2). NMR Spectroscopy: ^{1}H NMR (300MHz, acetone-d_6) δ: 8.70–8.48 (m, 2H), 7.64–7.76 (m, 2H), 6.26–6.19 (m, 1H). ^{13}C NMR (75 MHz, acetone-d_6) δ: 128.5, 124.3. IR Spectroscopy (thin film) 3214, 1759, 1512, 1433, 1386, 1231, 1125, 835, 747, 711 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for 2x[$C_8H_7N_3O_4$]Na, 441.0772. Found, 441.0759. Chiral HPLC (Daicel Chiralpak AD-H, hexane/*i*- PrOH = 2:1, flow rate = 1.00 ml/min) t_R = 31.5 min (major), t_R = 35.6 min (minor).

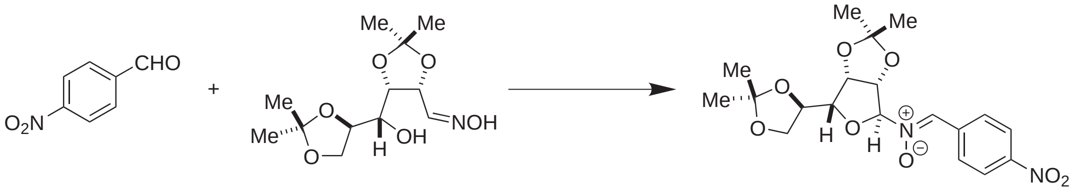
(*R*)-2-[(3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-Dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyltetrahydro-furo[3,4-*d*][1,3]dioxol-4-yl]-3-(4-nitro-phenyl)-[1,2,4]oxadiazolidin-5-one (14)



To oxadiazolidinone **XI** (200 mg, 0.360 mmol, 1.00 equiv) in 10% aqueous methanol (1.8 ml) at 23 °C is added K_2CO_3 (50.0 mg, 0.360 mmol, 1.00 equiv). The suspension is stirred at 23 ° for 10 min and then diluted with saturated aqueous NH_4Cl and EtOAc. The phases are separated and the aqueous phase is extracted with EtOAc. The combined organic layers are washed with brine, dried (Na_2SO_4) and concentrated *in vacuo* to afford a yellow oil. Purification of this oil by chromatography on silica gel (1:1 hexane/EtOAc) afforded the target compound as a colorless solid (83% yield).

R*f* = 0.38 (1:1 hexane/EtOAc). Melting Point: mp 108 °C. Specific Rotation $[\alpha]_{36.3\ D}$ −26° (c 0.42, $CHCl_3$). NMR Spectroscopy: ^1H NMR (300 MHz, $CDCl_3$) δ: 8.30–8.27 (m, 2H), 7.58–7.55 (m, 2H), 6.88 (s, 1H), 5.84 (s, 1H), 4.90 (d, *J* = 5.9 Hz, 1H), 4.85 (s, 1H), 4.80 (dd, *J* = 5.9 Hz, 3.7 Hz, 1H), 4.41–4.35 (m, 1H), 4.06–3.99 (m, 2H), 3.87 (dd, *J* = 6.2 Hz, 4.7 Hz, 1H), 1.48 (s, 3H), 1.40 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 157.3, 148.4, 144.2, 127.2, 124.3, 113.0, 109.0, 97.5, 83.5, 82.7, 79.7, 74.1, 73.0, 65.9, 26.8, 25.9, 25.0, 24.4. IR Spectroscopy (thin film) 3279, 2988, 1782, 1526, 1374, 1350, 1211, 1067, 857, 753 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{20}H_{25}N_3O_9Na$, 474.1489. Found, 474.1489. Combustion Analysis: Anal. Calcd for $C_{20}H_{25}N_3O_9$: C, 53.21; H, 5.58; N, 9.31. Found C, 53.22; H, 5.68; N, 9.17.

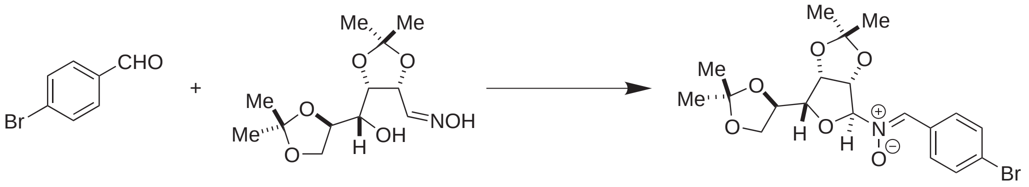
[(3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-Dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyltetrahydro- furo[3,4-*d*][1,3]dioxol-4-yl]-[1-(4-nitro-phenyl)-meth-(*E*)-ylidene]-amine *N*-oxide (A)



To 4-nitrobenzaldehyde (5.07 g, 33.5 mmol, 1.00 equiv) and 2,3:5,6-*O*isopropylidene- D-mannose oxime (9.24 g, 33.5 mmol, 1.00 equiv) is added toluene (67 ml). Upon heating to reflux, all solids dissolve and the resulting solution is kept at reflux for 24 h. Water is continuously removed from the reaction mixture using a Dean-Stark trap. The stirred solution is cooled and the crystals formed are filtered off, washed with hexane, and dried *in vacuo* to afford the target compound as yellow crystals (76% yield).

R*f* = 0.34 (2:1 hexane/EtOAc). Melting Point (toluene): mp 142 °C. Specific Rotation $[\alpha]_{37.6\ D}$ +38° (c 1.0, $CHCl_3$). NMR Spectroscopy: ^1H NMR (300 MHz, $CDCl_3$) δ: 8.41–8.38 (m, 2H), 8.27–8.24 (m, 2H), 7.72 (s, 1H), 5.49 (s, 1H), 5.31 (d, *J* = 5.9 Hz, 1H), 4.98 (dd, *J* = 5.7 Hz, 3.8 Hz, 1H), 4.61 (dd, *J* = 6.9 Hz, 3.8 Hz, 1H), 4.45–4.41 (m, 1H), 4.16–4.09 (m, 2H), 1.53 (s, 3H), 1.46 (s, 3H), 1.38 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 148.0, 134.9, 130.6, 129.2, 123.7, 113.5, 109.3, 103.9, 85.6, 84.5, 80.1, 73.1, 66.4, 26.9, 26.1, 25.2, 24.5. IR Spectroscopy (thin film) 2988, 1598, 1520, 1374, 1343, 1211, 1154, 1103, 1068, 863, 732 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{19}H_{24}N_2O_8Na$, 431.1431. Found, 431.1419. Combustion Analysis: Anal. Calcd for $C_{19}H_{24}N_2O_8$: C, 55.88; H, 5.92; N, 6.86. Found C, 55.95; H, 5.99; N, 6.57.

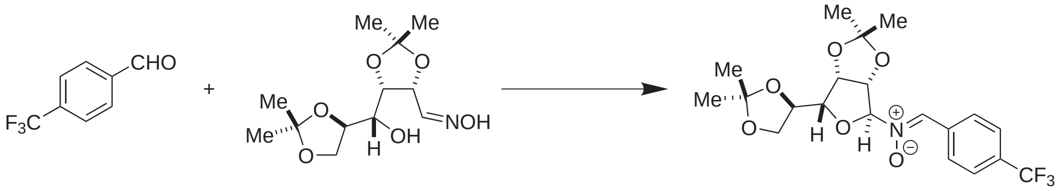
[1-(4-Bromo-phenyl)-meth-(*E*)-ylidene]-[(3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyl-tetrahydro-furo[3,4-*d*][1,3]dioxol-4-yl]-amine *N*-oxide (B)



To 4-bromobenzaldehyde (3.75 g, 20.3 mmol, 1.00 equiv) and 2,3:5,6-*O*isopropylidene-D-mannose oxime (5.58 g, 20.3 mmol, 1.00 equiv) is added toluene (40 ml). Upon heating to reflux, all solids dissolve and the resulting solution is kept at reflux for 20 h. Water is continuously removed from the reactionmixture using a Dean-Stark trap. The stirred solution is cooled and the crystals formed are filtered off, washed with hexane, and dried *in vacuo* to afford the target compound as colorless crystals (80% yield).

R*f* = 0.36 (2:1 hexane/EtOAc). Melting Point (toluene): mp 185 °C. Specific Rotation $[\alpha]_{33.7\ D}$ +50° (c 1.1, $CHCl_3$). NMR Spectroscopy: ^1H NMR (300 MHz, $CDCl_3$) δ: 8.12–8.09 (m, 2H), 7.56–7.53 (m, 2H), 5.44 (s, 1H), 5.31 (d, *J* = 6.2 Hz, 1H), 4.97 (dd, *J* = 5.9 Hz, 3.7 Hz, 1H), 4.64 (dd, *J* = 7.1 Hz, 3.9 Hz, 1H), 4.42–4.36 (m, 1H), 4.12–4.07 (m, 2H), 1.51 (s, 3H), 1.45 (s, 3H), 1.37 (s, 3H), 1.35 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 132.0, 131.8, 130.1, 128.3, 125.0, 113.3, 109.3, 103.5, 85.6, 84.5, 80.3, 73.2, 66.5, 26.9, 26.1, 25.3, 24.5. IR Spectroscopy (thin film) 2988, 2950, 2896, 1576, 1456, 1385, 1279, 1209, 1147, 1064, 842, 742 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{19}H_{24}BrNO_6Na$, 464.0685. Found, 464.0685. Combustion Analysis: Anal. calcd for $C_{19}H_{24}BrNO_6$: C, 51.60; H, 5.47; N, 3.17. Found C, 51.69; H, 5.57; N, 3.13.

[(3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-Dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyltetrahydro-furo[3,4-*d*][1,3]dioxol-4-yl]-[1-(4-trifluoromethyl-phenyl)-meth-(*E*)- ylidene]-amine *N*-oxide (C)

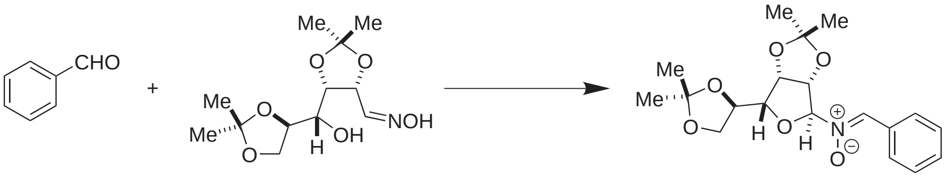


To 4-trifluoromethylbenzaldehyde (4.06 g, 19.4 mmol, 1.00 equiv) and 2,3:5,6-*O*-isopropylidene-D-mannose oxime (5.35 g, 19.4 mmol, 1.00 equiv) is added toluene (20 ml). Upon heating to reflux, all solids dissolve and the resulting solution is kept at reflux for 16 h. Water is continuously removed from the reaction mixture using a Dean-Stark trap. The stirred solution is cooled and the crystals formed are filtered off, washed with hexane, and dried *in vacuo* to afford the target compound as colorless crystals (84% yield).

R*f* = 0.36 (2:1 hexane/EtOAc). Melting Point (toluene): mp 138 °C. Specific Rotation $[\alpha]_{33.7\ D}$ +48° (c 0.93, $CHCl_3$). NMR Spectroscopy: ^1H NMR (300 MHz, $CDCl_3$) δ: 8.33 (d, *J* = 8.1 Hz, 2H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.64 (s, 1H), 5.48 (s, 1H), 5.33 (d, *J* = 6.0 Hz, 1H), 4.98 (dd, *J* = 6.0 Hz, 3.9 Hz, 1H), 4.64 (dd, *J* = 7.1 Hz, 3.9 Hz, 1H), 4.45–4.39 (m, 1H), 4.16–4.07 (m, 2H), 1.53 (s, 3H), 1.46 (s, 3H), 1.38 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 132.5, 132.0

(q, *J* = 32 Hz), 131.1, 128.8, 125.4 (q, *J* = 3 Hz), 123.6 (q, *J* = 277 Hz), 113.4, 109.3, 103.7, 85.6, 84.6, 80.2, 73.2, 66.5, 26.9, 26.1, 25.2, 24.5. IR Spectroscopy (thin film) 2989, 2939, 1581, 1457, 1413, 1374, 1326, 1167, 1129, 1067, 854, 732 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{20}H_{24}F_3NO_6Na$, 454.1454. Found, 454.1449. Combustion Analysis: Anal. calcd for $C_{20}H_{24}F_3NO_6$: C, 55.68; H, 5.61; N, 3.25. Found C, 55.56; H, 5.66; N, 3.19.

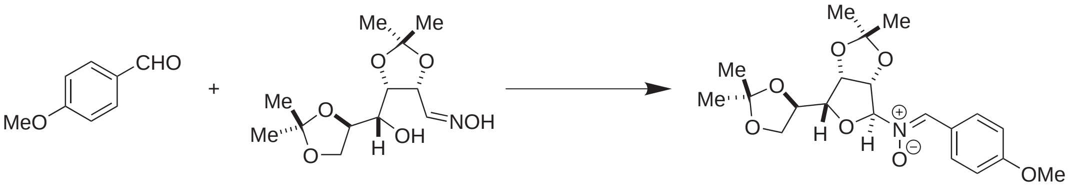
[(3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-Dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyltetrahydro-furo[3,4-*d*][1,3]dioxol-4-yl]-[1-phenyl-meth-(*E*)-ylidene]-amine *N*-oxide (D)



To benzaldehyde (738 mg, 6.95 mmol, 1.10 equiv) and 2,3:5,6-*O*-isopropylidene-D-mannose oxime (1.74 g, 6.32 mmol, 1.00 equiv) is added toluene (6.0 ml). Upon heating to reflux, all solids dissolve and the resulting solution is kept at reflux for 7 h. Water is continuously removed from the reaction mixture using a Dean-Stark trap. The stirred solution is cooled and the crystals formed are filtered off, washed with hexane, and dried *in vacuo* to afford the target compound as colorless crystals (65% yield).

R*f* = 0.65 (1:1 hexane/EtOAc). Melting Point (toluene): mp 181 °C. Specific Rotation $[\alpha]_{27.4\ D}$ +67° (c 1.10, $CHCl_3$). NMR Spectroscopy: ^1H NMR (300 MHz, $CDCl_3$) δ: 8.25–8.22 (m, 2H), 7.57 (s, 1H), 7.47–7.42 (m, 3H), 5.47 (s, 1H), 5.35 (d, *J* = 5.9 Hz, 1H), 5.00 (dd, *J* = 5.9 Hz, 3.9 Hz, 1H), 4.68 (dd, *J* = 7.2 Hz, 4.0 Hz, 1H), 4.44–4.37 (m, 1H), 4.16–4.08 (m, 2H), 1.53 (s, 3H), 1.46 (s, 3H), 1.39 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 133.2, 131.0, 129.3, 128.9, 128.5, 113.2, 109.3, 103.3, 85.6, 84.5, 80.3, 73.2, 66.5, 26.9, 26.1, 25.3, 24.5. IR Spectroscopy (thin film) 2987, 1580, 1454, 1379, 1218, 1088, 1065, 847, 772 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{19}H_{25}NO_6Na$, 386.1580. Found, 386.1569. Combustion Analysis: Anal. calcd for $C_{19}H_{25}NO_6$: C, 62.80; H, 6.93; N, 3.85. Found C, 62.59; H, 7.01; N, 3.77.

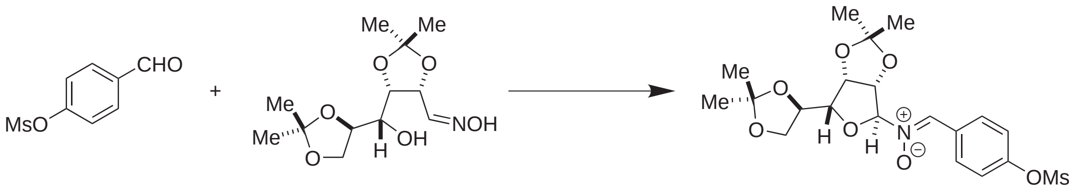
[(3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-Dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyltetrahydro-furo[3,4-*d*][1,3]dioxol-4-yl]-[1-(4-methoxy-phenyl)-meth-(*E*)-ylidene]-amine *N*-oxide (E)



To 4-methoxybenzaldehyde (1.48 g, 10.9 mmol, 1.20 equiv) and 2,3:5,6-*O*-isopropylidene-D-mannose oxime (2.50 g, 9.08 mmol, 1.00 equiv) is added toluene (10 ml). Upon heating to reflux, all solids dissolve and the resulting solution is kept at reflux for 16 h. Water is continuously removed from the reaction mixture using a Dean-Stark trap. The stirred solution is cooled and the crystals formed are filtered off, washed with hexane, and dried *in vacuo* to afford the target compound as colorless crystals (86% yield).

R*f* = 0.28 (1:1 hexane/EtOAc). Melting Point (toluene): mp 154 °C. Specific Rotation $[\alpha]_{33.7}$ *D* +68° (c 1.00, $CHCl_3$). NMR Spectroscopy: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.25–8.21 (m, 2H), 7.47 (s, 1H), 6.96–6.92 (m, 2H), 5.43 (s, 1H), 5.33 (d, *J* = 6.0 Hz, 1H), 5.00 (dd, *J* = 5.9 Hz, 4.0 Hz, 1H), 4.69 (dd, *J* = 7.3 Hz, 4.0 Hz, 1H), 4.42–4.36 (m, 1H), 4.14–4.08 (m, 2H), 1.52 (s, 3H), 1.45 (s, 3H), 1.38 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 161.4, 132.9, 130.9, 122.3, 113.9, 113.1, 109.2, 103.0, 85.6, 84.4, 80.4, 73.3, 66.6, 55.4, 26.9, 26.1, 25.3, 24.5. IR Spectroscopy (thin film) 2974, 2945, 2893, 1606, 1566, 1510, 1443, 1379, 1258, 1209, 1139, 1119, 1053, 848 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{20}H_{24}F_3NO_6Na$, 454.1454. Found, 454.1449. Combustion Analysis: Anal. calcd for $C_{20}H_{27}NO_7$: C, 61.06; H, 6.92; N, 3.56. Found C, 61.04; H, 6.88; N, 3.54.

Methanesulfonic acid 4-[(*E*)-(3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyl-tetrahydro-furo[3,4-*d*][1,3]dioxol-4-yliminoN-oxide]-methyl-phenyl ester (F)

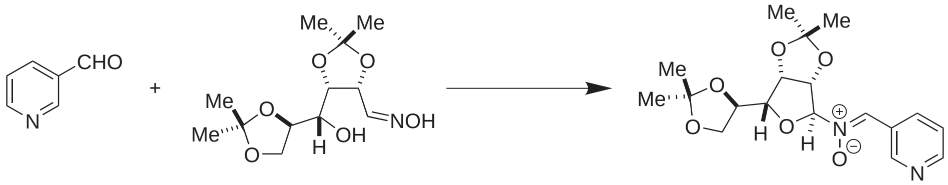


To 4-methanesulfonyloxybenzaldehyde (11.0 g, 40.0 mmol, 1.00 equiv) and 2,3:5,6-*O*-isopropylidene-D-mannose oxime (8.00 g, 40.0 mmol, 1.00 equiv) is added toluene (80 ml). Upon heating to reflux, all solids dissolve and the resulting solution is kept at reflux for 22 h. Water is continuously removed from the reaction mixture using a Dean-Stark trap. The stirred solution is cooled and the crystals formed are filtered off, washed with hexane, and dried *in vacuo* to afford the target compound as colorless crystals (82% yield).

R*f* = 0.35 (2:3 hexane/EtOAc). Melting Point (toluene): mp 143 °C. Specific Rotation $[\alpha]_{33.6\ D}$ +47° (c 1.79, $CHCl_3$). NMR Spectroscopy: ^1H NMR (500 MHz, $CDCl_3$) δ: 8.34–8.32 (m, 2H), 7.61 (s, 1H), 7.36–7.34 (m, 2H), 5.48 (s, 1H), 5.33 (d, *J* = 6.0 Hz, 1H), 4.99 (dd, *J* = 6.0 Hz, 3.9 Hz, 1H), 4.64 (dd, *J* = 7.1 Hz, 3.9 Hz, 1H), 4.42 (ddd, *J* = 7.1 Hz, 6.2 Hz, 4.9 Hz, 1H), 4.13 (dd, *J* = 8.8 Hz, 6.2 Hz, 1H), 4.10

(dd, *J* = 8.8 Hz, 4.9 Hz, 1H), 3.17 (s, 3H), 1.53 (s, 3H), 1.46 (s, 3H), 1.39 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 150.2, 131.6, 130.7, 128.8, 122.2, 113.4, 109.3, 103.6, 85.6, 84.5, 80.3, 73.2, 66.5, 37.7, 26.8, 26.0, 25.2, 24.5. IR Spectroscopy (thin film) 2988, 2938, 1498, 1371, 1209, 1150, 1067, 866, 756 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{20}H_{27}NO_9SNa$, 480.1305. Found, 480.1292. Combustion Analysis: Anal. Calcd for $C_{20}H_{27}NO_9S$: C, 52.51; H, 5.95; N, 3.06. Found C, 52.43; H, 6.04; N, 3.05.

[(3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-Dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyltetrahydro-furo[3,4-*d*][1,3]dioxol-4-yl]-[1-pyridin-3-yl-meth-(*E*)-ylidene]-amine*N*-oxide (G)

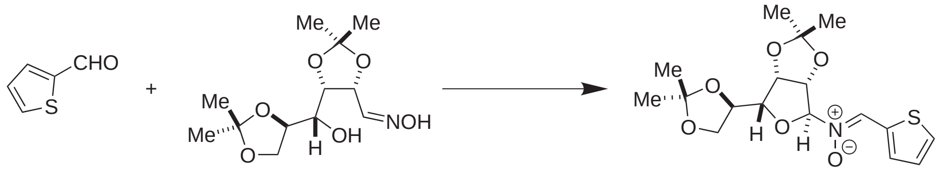


To 3-pyridinecarboxaldehyde (2.65 g, 24.7 mmol, 1.00 equiv) and 2,3:5,6-*O*-isopropyl-idene-D-mannose oxime (6.80 g, 24.7 mmol, 1.00 equiv) is added toluene (25 ml). Upon heating to reflux, all solids dissolve and the resulting solution is kept at reflux for 13 h. Water is continuously removed from the reaction mixture using a Dean-Stark trap. The stirred solution is cooled and the crystals formed are filtered off, washed with hexane, and dried *in vacuo*. The crystals are dissolved in $CHCl_3$ and then concentrated *in vacuo* to azeotrop residual toluene to afford the target compound as a colorless solid (85% yield).

R*f* = 0.26 (EtOAc). Melting Point (toluene): mp 147 °C. Specific Rotation $[\alpha]_{27.4\ D}$ +50° (c 1.40, $CHCl_3$). NMR Spectroscopy: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.00 (d, *J* = 1.4 Hz, 1H), 8.99–8.96 (m, 1H), 8.63 (dd,

J = 4.9 Hz, 1.5 Hz, 1H), 7.64 (s, 1H), 7.39 (dd, *J* = 8.1 Hz, 4.9 Hz, 1H), 5.49 (s, 1H), 5.31 (d, *J* = 6.0 Hz, 1H), 4.98 (dd, *J* = 5.9 Hz, 3.9 Hz, 1H), 4.63 (dd, *J* = 7.0 Hz, 3.9 Hz, 1H), 4.44–4.38 (m, 1H), 4.15–4.07 (m, 2H), 1.52 (s, 3H), 1.46 (s, 3H), 1.38 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 150.6, 149.7, 135.0, 129.9, 126.1, 123.6, 113.4, 109.3, 103.5, 85.6, 84.5, 80.2, 73.2, 66.4, 26.9, 26.1, 25.2, 24.5. IR Spectroscopy (thin film) 2987, 1560, 1373, 1210, 1067, 846, 705. (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{18}H_{24}N_2O_7Na$, 387.1532. Found, 387.1552. Combustion Analysis: Anal. calcd for $C_{18}H_{24}N_2O_7$: C, 59.33; H, 6.64; N, 7.69. Found C, 59.17; H, 6.64; N, 7.65.

[(3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-Dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyltetrahydro-furo[3,4-*d*][1,3]dioxol-4-yl]-[1-thiophen-2-yl-meth-(*E*)-ylidene]-amine *N*-oxide (H)

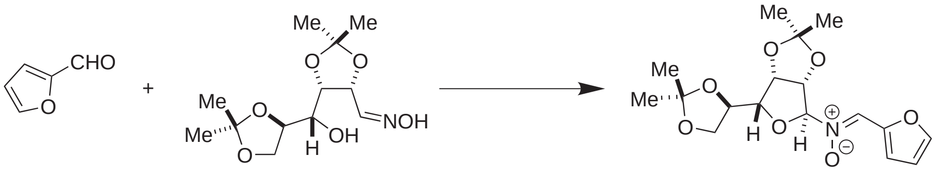


To thiophene-2-carbaldehyde (1.24 g, 11.1 mmol, 1.20 equiv) and 2,3:5,6-*O*-isopropyl-idene-D-mannose oxime (2.54 g, 9.23 mmol, 1.00 equiv) is added toluene (9.0 ml). Upon heating to reflux, all solids dissolve and the resulting solution is kept at reflux for 28 h. Water is continuously removed from the reaction mixture using a Dean-Stark trap. The stirred solution is cooled and the crystals formed are filtered off, washed with hexane, and dried *in vacuo* to afford the target compound as colorless crystals (75% yield).

R*f* = 0.52 (1:1 hexane/EtOAc). Melting Point (toluene): mp 163 °C. Specific Rotation $[\alpha]_{28.2\ D}$ +62° (c 0.60, $CHCl_3$). NMR Spectroscopy: ^{1}H

NMR (300 MHz, $CDCl_3$) δ: 8.05 (s, 1H), 7.56–7.51 (m, 2H), 7.18 (dd, *J* = 5.0 Hz, 4.0 Hz, 1H), 5.51 (s, 1H), 5.35 (d, *J* = 5.9 Hz, 1H), 5.01 (dd, *J* = 5.9 Hz, 3.7 Hz, 1H), 4.58 (dd, *J* = 7.2 Hz, 3.7 Hz, 1H), 4.45–4.37 (m, 1H), 4.15–4.06 (m, 2H), 1.53 (s, 3H), 1.46 (s, 3H), 1.39 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 131.1, 130.9, 130.0, 129.0, 126.7, 113.2, 109.3, 101.7, 85.3, 84.3, 80.2, 73.2, 66.5, 26.9, 26.0, 25.2, 24.4. IR Spectroscopy (thin film) 2987, 1578, 1373, 1254, 1211, 1116, 1091, 1067, 848, 772 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{17}H_{23}NO_5SNa$, 392.1144. Found, 392.1142. Combustion Analysis: Anal. Calcd for $C_{19}H_{25}NO_5S$: C, 55.27; H, 6.27; N, 3.79. Found C, 55.38; H, 6.44; N, 3.78.

[(3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-Dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyltetrahydro-furo[3,4-*d*][1,3]dioxol-4-yl]-[1-furan-2-yl-meth-(*E*)-ylidene]-amine *N*-oxide (J)

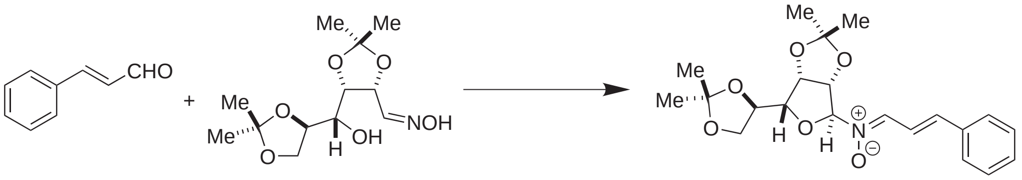


To furan-2-carbaldehyde (859 mg, 8.94 mmol, 1.20 equiv) and 2,3:5,6-*O*isopropylidene-D-mannose oxime (2.05 g, 7.45 mmol, 1.00 equiv) is added toluene (7.0 ml). Upon heating to reflux, all solids dissolve and the resulting solution is kept at reflux for 29 h. Water is continuously removed from the reaction mixture using a Dean-Stark trap. The stirred solution is cooled and the crystals formed are filtered off, washed with hexane, and dried *in vacuo* to afford the target compound as colorless crystals (83% yield).

R*f* = 0.49 (1:1 hexane/EtOAc). Melting Point (toluene): mp 170 °C. Specific Rotation $[\alpha]_{27\cdot 8}$ *D* +63° (c 1.15, $CHCl_3$). NMR Spectroscopy: ^1H

NMR (300 MHz, $CDCl_3$) δ: 7.79 (d, *J* = 3.7 Hz, 1H), 7.75 (s, 1H), 7.53 (d, *J* = 1.2 Hz, 1H), 6.58 (dd, *J* = 3.7 Hz, 1.2 Hz, 1H), 5.47 (s, 1H), 5.33 (d, *J* = 5.9 Hz, 1H), 4.97 (dd, *J* = 5.9 Hz, 3.7 Hz, 1H), 4.58 (dd, *J* = 7.2 Hz, 3.7 Hz, 1H), 4.44–4.37 (m, 1H), 4.15–4.05 (m, 2H), 1.52 (s, 3H), 1.46 (s, 3H), 1.39 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 146.0, 144.4, 124.1, 116.3, 113.3, 112.5, 109.3, 102.1, 85.3, 84.3, 80.2, 73.2, 66.5, 26.9, 26.1, 25.3, 24.5. IR Spectroscopy (thin film) 2990, 2894, 1590, 1481, 1380, 1219, 1159, 1113, 1089, 1061, 938, 850, 759 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{17}H_{23}NO_7Na$, 376.1373. Found, 386.0000. Combustion Analysis: Anal. calcd for $C_{19}H_{25}NO_6$: C, 57.78; H, 6.56; N, 3.96. Found C, 57.21; H, 6.28; N, 3.83.

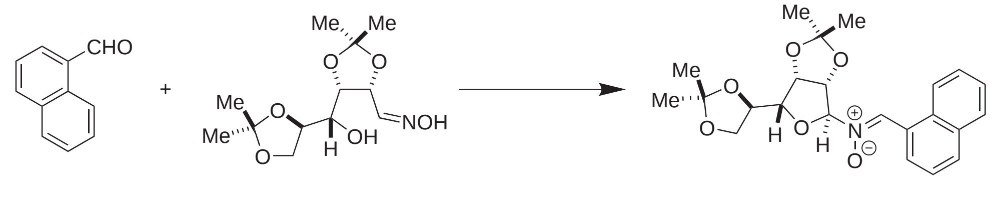
[(3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-Dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyltetrahydro-furo[3,4-*d*][1,3]dioxol-4-yl]-[(*E*)-3-phenyl-prop-2-en-(*E*)-ylidene]-amine *N*-oxide (K)



To cinnamaldehyde (1.45 g, 11.0 mmol, 1.10 equiv) and 2,3:5,6-*O*-isopropylidene-D-mannose oxime (2.75 g, 10.0 mmol, 1.00 equiv) is added toluene (10 ml). Upon heating to reflux, all solids dissolve and the resulting solution is kept at reflux for 9 h. Water is continuously removed from the reaction mixture using a Dean-Stark trap. The stirred solution is cooled and the crystals formed are filtered off, washed with hexane, and dried *in vacuo* to afford the target compound as colorless crystals (82% yield).

R*f* = 0.47 (2:3 hexane/EtOAc). Melting Point (toluene): mp 176 °C. Specific Rotation $[\alpha]_{34.0\,D}$ +67° (c 1.76, $CHCl_3$). NMR Spectroscopy: ^1H NMR (300 MHz, $CDCl_3$) δ: 7.53–7.31 (m, 7H), 7.10 (d, *J* = 14.9 Hz, 1H), 5.36 (s, 1H), 5.29 (d, *J* = 5.9 Hz, 1H), 4.96 (dd, *J* = 5.9 Hz, 3.7 Hz, 1H), 4.56 (dd, *J* = 7.2 Hz, 3.7 Hz, 1H), 4.43–4.36 (m, 1H), 4.15–4.07 (m, 2H), 1.52 (s, 3H), 1.46 (s, 3H), 1.38 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 140.2, 135.7, 135.5, 130.0, 128.8, 127.4, 117.1, 113.2, 109.3, 102.0, 85.4, 84.4, 80.2, 73.2, 66.6, 26.9, 26.1, 25.3, 24.6. IR Spectroscopy (thin film) 2988, 2936, 1542, 1381, 1258, 1210, 1126, 1088, 1066, 970, 844 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{21}H_{27}NO_6Na$, 412.1736. Found, 412.1736. Combustion Analysis: Anal. Calcd for $C_{21}H_{27}NO_6$: C, 64.77; H, 6.99; N, 3.60. Found C, 64.71; H, 7.03; N, 3.53.

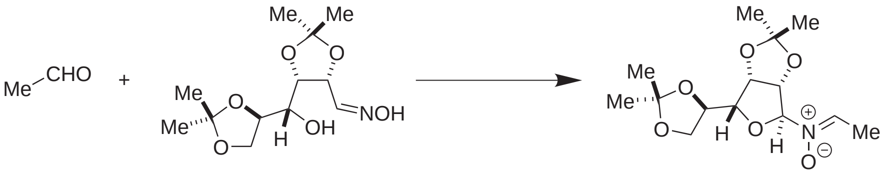
[(3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-Dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyltetrahydro-furo[3,4-*d*][1,3]dioxol-4-yl]-[1-naphthalen-1-yl-meth-(*E*)-ylidene]-amine *N*-oxide (L)



To α-naphthylcarboxaldehyde (1.99 g, 12.7 mmol, 1.00 equiv) and 2,3:5,6-*O*-isopropylidene-D-mannose oxime (3.51 g, 12.7 mmol, 1.00 equiv) is added toluene (13 ml). Upon heating to reflux, all solids dissolve and the resulting solution is kept at reflux for 15 h. Water is continuously removed from the reaction mixture using a Dean-Stark trap. The stirred solution is cooled and the crystals formed are filtered off, washed with hexane, and dried *in vacuo* to afford the target compound as colorless crystals (79% yield).

R*f* = 0.45 (3:2 hexane/EtOAc). Melting Point (toluene): mp 153 °C. Specific Rotation $[\alpha]_{34.2\ D}$ +52° (c 0.92, $CHCl_3$). NMR Spectroscopy: ^1H NMR (300 MHz, CD_2Cl_2) δ: 9.50 (d, *J* = 9.5 Hz, 1H), 8.44 (s, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.99–7.89 (m, 2H), 7.64–7.52 (m, 3H), 5.59 (s, 1H), 5.38 (d, *J* = 6.0 Hz, 1H), 4.96 (dd, *J* = 5.9 Hz, 3.9 Hz, 1H), 4.69 (dd, *J* = 7.0 Hz, 3.9 Hz, 1H), 4.47–4.40 (m, 1H), 4.18–4.12 (m, 2H), 1.54 (s, 3H), 1.45 (s, 3H), 1.38 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ: 133.7, 131.5, 130.9, 129.4, 128.0, 127.3, 126.9, 126.2, 152.7, 125.0, 121.8, 113.5, 109.2, 104.2, 85.6, 85.0, 80.6, 73.6, 66.7, 26.9, 26.3, 25.3, 24.8. IR Spectroscopy (thin film) 2988, 2938, 1511, 1456, 1373, 1211, 1068, 859, 843, 770, 756 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $2x[C_{23}H_{27}NO_6]Na$, 849.3574. Found, 849.3558. Combustion Analysis: Anal. calcd for $C_{19}H_{25}NO_6$: C, 66.81; H, 6.58; N, 3.39. Found C, 66.79; H, 6.65; N, 3.32.

[(3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-Dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyltetrahydro-furo[3,4-*d*][1,3]dioxol-4-yl]-eth-(*E*)-ylidene-amine *N*-oxide (M)

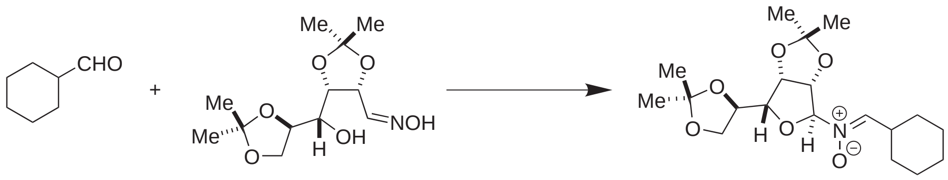


To 2,3:5,6-*O*-isopropylidene-D-mannose oxime (8.33 g, 30.2 mmol, 1.00 equiv) in CH_2Cl_2 (60 ml) are added Na_2SO_4 (1.29 g, 15.4 mmol, 0.51 equiv), $NaHCO_3$ (2.19 g, 15.4 mmol, 0.51 equiv), and acetaldehyde (4.00 g, 90.1 mmol, 3.00 equiv). The suspension is stirred at 23 °C for 6 h, then filtered over a plug of celite eluting with CH_2Cl_2. The filtrate is concentrated to afford a colorless solid which is recrystallized from EtOAc/Et_2O 1:2 to afford the title compound as colorless crystals (78% yield).

R*f* = 0.05 (EtOAc). Melting Point (EtOAc/Et_2O 1:2): mp 137 °C. Specific Rotation $[\alpha]_{33\cdot 8}$

$_D$ +42° (c 1.17, $CHCl_3$). NMR Spectroscopy: ^1H NMR (300 MHz, $CDCl_3$) δ: 7.00 (q, *J* = 5.8 Hz, 1H), 5.28 (s, 1H), 5.23 (d, *J* = 6.0 Hz, 1H), 4.92 (dd, *J* = 5.9 Hz, 3.9 Hz, 1H), 4.54 (dd, *J* = 7.2 Hz, 3.9 Hz, 1H), 4.39–4.33 (m, 1H), 4.11–4.02 (m, 2H), 2.02 (d, *J* = 5.8 Hz, 3H), 1.49 (s, 3H), 1.43 (s, 3H), 1.36 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 134.3, 113.4, 109.5, 102.3, 85.5, 84.5, 80.4, 73.4, 66.7, 27.0, 26.2, 25.4, 24.6, 12.3. IR Spectroscopy (thin film) 3386, 2987, 2937, 1373, 1210, 1068, 848, 755. (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{14}H_{23}NO_6Na$, 324.1423. Found, 324.1423. Combustion Analysis: Anal. calcd for $C_{14}H_{23}NO_6$: C, 55.80; H, 7.69; N, 4.65. Found C, 55.94; H, 7.74; N, 4.64.

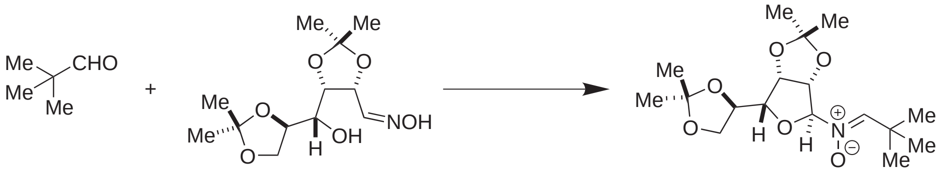
[1-Cyclohexyl-meth-(*E*)-ylidene]-[(3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyl-tetrahydro-furo[3,4-*d*][1,3]dioxol-4-yl]-amine *N*-oxide (N)



To 2,3:5,6-*O*-isopropylidene-D-mannose oxime (5.56 g, 20.2 mmol, 1.00 equiv) in CH_2Cl_2 (40 ml) are added $MgSO_4$ (7.30 g, 60.6 mmol, 3.00 equiv), and cyclohexane carboxaldehyde (4.54 g, 40.4 mmol, 2.00 equiv). The suspension is stirred at 23 °C for 18 h, then filtered over a plug of celite eluting with CH_2Cl_2. The filtrate is concentrated to afford a colorless solid which is recrystallized from 40 ml EtOAc/hexane 4:1 to afford the title compound as colorless crystals (82% yield).

R*f* = 0.43 (1:2 hexane/EtOAc). Melting Point (EtOAc/Et_2O 1:2): mp 174 °C. Specific Rotation $[\alpha]_{33.9\,D}$ +68° (c 1.60, $CHCl_3$). NMR Spectroscopy: ^1H NMR (300 MHz, $CDCl_3$) δ: 6.70 (d, *J* = 7.5 Hz, 1H), 5.24 (s, 1H), 5.22 (d, *J* = 5.9 Hz, 1H), 4.95 (dd, *J* = 5.9 Hz, 4.0 Hz, 1H), 4.62 (dd, *J* = 7.5 Hz, 4.0 Hz, 1H), 4.39–4.33 (m, 1H), 4.12–4.03 (m, 2H), 3.02–2.87 (m, 1H), 1.91–1.81 (m, 2H), 1.78–1.63 (m, 3H), 1.41–1.09 (m, 5H), 1.50 (s, 3H), 1.44 (s, 3H), 1.37 (s, 3H), 1.35 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 142.6, 113.0, 109.2, 102.3, 85.6, 84.4, 80.3, 73.2, 66.6, 34.6, 29.0, 25.6, 26.8, 26.0, 25.9, 25.2, 24.5. IR Spectroscopy (thin film) 2984, 2923, 2851, 1581, 1452, 1369, 1209, 1162, 1118, 1069, 866, 734 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{19}H_{31}NO_6Na$, 392.2049. Found, 392.2039. Combustion Analysis: Anal. Calcd for $C_{19}H_{31}NO_6$: C, 61.77; H, 8.46; N, 3.79. Found C, 61.96; H, 8.59; N, 3.68.

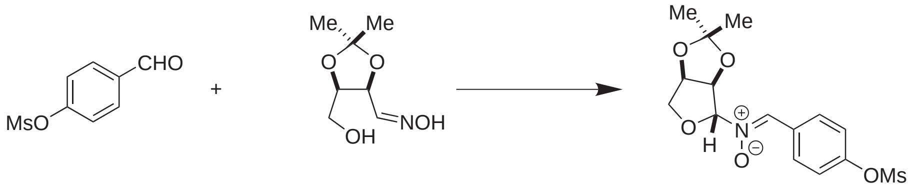
[(3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-Dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyltetrahydro-furo[3,4-*d*][1,3]dioxol-4-yl]-[2,2-dimethyl-prop-(*E*)-ylidene]-amine *N*-oxide (O)



To 2,3:5,6-*O*-isopropylidene-D-mannose oxime (2.75 g, 10.0 mmol, 1.00 equiv) in CH_2Cl_2 (20 ml) are added $MgSO_4$ (3.61 g, 30.0 mmol, 3.00 equiv), and pivalaldehyde (5.16 g, 60.0 mmol, 6.00 equiv). The suspension is stirred at 23 °C for 6 d, then filtered over a plug of celite eluting with CH_2Cl_2. The filtrate is concentrated to afford a colorless solid which is recrystallized from EtOAc to afford the title compound as colorless crystals (45% yield).

R*f* = 0.47 (1:1 hexane/EtOAc). Melting Point (EtOAc): mp 150 °C. Specific Rotation $[\alpha]_{31.9\,D}$ +61° (c 1.00, $CHCl_3$). NMR Spectroscopy: ^1H NMR (300 MHz, CD_2Cl_2) δ: 6.65 (s, 1H), 5.20 (s, 1H), 5.13 (d, J = 6.5 Hz, 1H), 4.88 (dd, J = 5.9 Hz, 3.7 Hz, 1H), 4.60 (dd, J = 6.5 Hz, 3.7 Hz, 1H), 4.34–4.28 (m, 1H), 4.08–3.95 (m, 2H), 1.47 (s, 3H), 1.40 (s, 3H), 1.33 (s, 3H), 1.33 (s, 3H), 1.24 (s, 9H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ: 143.7, 113.2, 109.0, 103.4, 85.9, 85.0, 80.7, 73.6, 66.7, 32.7, 26.8, 24.2, 26.0, 25.3, 24.6. IR Spectroscopy (thin film) 2985, 2936, 2882, 1570, 1368, 1277, 1209, 1163, 1116, 1065, 940, 867, 796, 729 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{17}H_{29}NO_6Na$, 344.2074. Found, 344.2070. Combustion Analysis: Anal. calcd for $C_{17}H_{29}NO_6$: C, 59.46; H, 8.51; N, 4.08. Found C, 59.50; H, 8.45; N, 4.09.

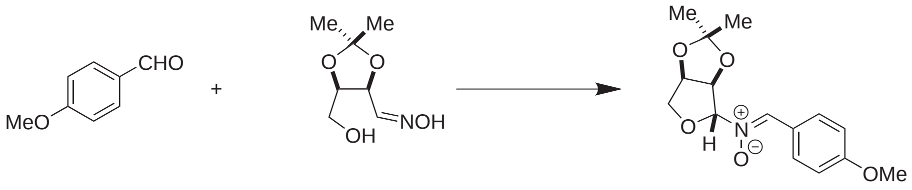
Methanesulfonic acid 4-[(*E*)-(3a*R*,4*R*,6a*R*)-2,2-dimethyl-tetrahydro-furo[3,4-*d*][1,3]dioxol-4-ylimino *N*-oxide]-methyl-phenyl ester (P)



To 4-methanesulfonyloxybenzaldehyde (7.41 g, 37.0 mmol, 1.00 equiv) and 2,3-*O*-isopropylidene-D-erythrose oxime (6.48 g, 37.0 mmol, 1.00 equiv) is added toluene (37 ml). Upon heating to reflux, all solids dissolve and the resulting solution is kept at reflux for 17 h. Water is continuously removed from the reaction mixture using a Dean-Stark trap. The stirred solution is cooled and the crystals formed are filtered off, washed with hexane, and dried *in vacuo* to afford the target compound as colorless crystals (87% yield).

R*f* = 0.35 (2:3 hexane/EtOAc). Melting Point (toluene): mp 154 °C. Specific Rotation $[\alpha]_{34.2}$ *D* -60° (c 1.0, $CHCl_3$). NMR Spectroscopy: ^1H NMR (300 MHz, $CDCl_3$) δ: 8.36-8.31 (m, 2H), 7.63 (s, 1H), 7.38-7.32 (m, 2H), 5.49 (s, 1H), 5.30 (d, *J* = 5.9 Hz, 1H), 4.99 (dd, *J* = 5.9 Hz, 3.7 Hz, 1H), 4.46 (dd, *J* = 10.0 Hz, 3.7 Hz, 1H), 4.32 (d, *J* = 10.0 Hz), 3.16 (s, 3H), 1.54 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 150.0, 131.0, 130.6, 128.7, 122.1, 113.0, 104.0, 84.4, 80.4, 37.7, 26.4, 24.8. IR Spectroscopy (thin film) 2938, 1598, 1498, 1369, 1208, 1150, 1102, 1055, 973, 858, 775 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for $C_{15}H_{19}NO_7SNa$, 380.0780. Found, 380.0774. Combustion Analysis: Anal. calcd for $C_{15}H_{19}NO_7S$: C, 50.41; H, 5.36; N, 3.92. Found C, 50.61; H, 5.46; N, 3.91.

((3a*R*,4*R*,6a*R*)-2,2-Dimethyl-tetrahydro-furo[3,4-*d*][1,3]dioxol-4-yl)-[1-(4- methoxy-phenyl)-meth-(*E*)-ylidene]-amine *N*-oxide (Q)

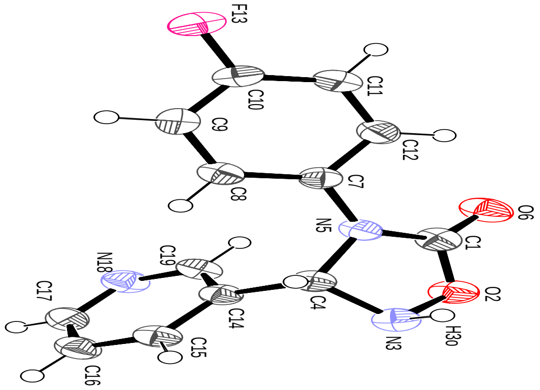


To 4-methoxybenzaldehyde (3.27 g, 24.0 mmol, 1.20 equiv) and 2,3-*O*isopropylidene-D-erythrose oxime (3.50 g, 20.0 mmol, 1.00 equiv) is added toluene (20 ml). Upon heating to reflux, all solids dissolve and the resulting solution is kept at reflux for 17 h. Water is continuously removed from the reaction mixture using a Dean-Stark trap. The stirred solution is cooled and the crystals formed are filtered off, washed with hexane, and dried *in vacuo* to afford the target compound as colorless crystals (79% yield).

R*f* = 0.43 (2:3 hexane/EtOAc). Melting Point (toluene): mp 136 °C. Specific Rotation $[\alpha]_{34.1}$ *D* -132° (c 1.56, $CHCl_3$). NMR Spectroscopy: ^1H

NMR (300 MHz, $CDCl_3$) δ: 8.25-8.21 (m, 2H), 7.52 (s, 1H), 6.69-6.91 (m, 2H), 5.47 (s, 1H), 5.22 (d, *J* = 5.9 Hz, 1H), 5.02 (dd, *J* = 5.9 Hz, 3.7 Hz, 1H), 4.52 (dd, *J* = 10.0 Hz, 3.7 Hz, 1H), 4.29 (d, *J* = 10.0 Hz), 3.85 (s, 3H), 1.53 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 161.5, 132.7, 131.0, 122.4, 113.9, 112.8, 103.7, 84.4, 80.6, 77.2, 55.4, 26.5, 24.8. IR Spectroscopy (thin film) 2987, 1603, 1508, 1257, 1100, 1055, 858, 773 (cm^{-1}). Mass Spectrometry HRMS-ESI (m/z): Calcd for 2x[$C_{15}H_{19}NO_5$]Na, 609.2424. Found, 609.2411. Combustion Analysis: Anal. calcd for $C_{15}H_{19}NO_5$: C, 61.42; H, 6.53; N, 4.78. Found C, 61.17; H, 6.68; N, 4.76.

Crystallographic Data for oxadiazolidinone **XXIV**



ORTEP drawing of oxadiazolidinone **XXIV**

CCDC 249665 contains the supplementary crystallographic data for this paper. These data can be obtained online free of charge (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Crystal data at 173 K for 'C13 H10 F N3 O2' [Mr = 259.24].

Monoclinic space group 'P 21' , Dc = 1.455 g/cm**3, Z = 2 , a = 7.1795(4) , b = 6.4404(4) , c = 12.7937(7) Ang., alfa = 90.00, beta = 90.688(3), gamma = 90.00 deg., V = 591.52(6) Ang.**3.

Bruker-Nonius Kappa-CCD, Mokalfa radiation, lamda = 0.7107 Ang.

The structure was solved by direct methods [iii] and refined by full-matrix least-squares analysis [iv] including an isotropic extinction correction. All heavy atoms were refined anisotropically, H-atoms isotropic, whereby H-positions are based on stereochemical considerations, except H3O which was located from a difference-density map and refined without restraints. Final R(F) = 0.0457, wR(F**2) = 0.0968 for 186 parameters and 1988 reflections with I >2sigma(I) and theta < 27.50 deg.

[iii] A. Altomare, M. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.*, **1999**, *32*, 115.

[iv] G.M. Sheldrick, 1997, SHELXL-97 Program for the Refinement of Crystal Structures. University of Goettingen, Germany.