A Palladium Catalyzed Enantioselective Alkylative Desymmetrization of *meso*-Succinic Anhydrides

Eric A. Bercot and Tomislav Rovis*

*Department of Chemistry, Colorado State University
Fort Collins, Colorado 80523*

Supporting Information

General Methods. All reactions were carried out under an atmosphere of argon in flame-dried glassware with magnetic stirring. Tetrahydrofuran, diethylether, and dichloromethane were degassed with argon and passed through two columns of neutral alumina. Toluene was degassed with argon and passed through one column of neutral alumina and one column of Q5 reactant. Column chromatography was performed on EM Science silica gel 60 (230-400 mesh). Thin layer chromatography was performed on EM Science 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light, KMnO_4 , aqueous ceric ammonium molybdate, or bromocresol green dips followed by heating.

$\text{Pd}(\text{OAc})_2$ was purchased from Aldrich Chemical Co. and used without further purification. Ligands **4**, **5**, and **6** were provided by Solvias and are available from Strem Chemical, Inc. Diphenylzinc was purchased from Strem Chemical, Inc.

Melting points were measured with a MelTemp II melting point apparatus outfitted with a Fluke 51 thermocouple and are uncorrected. Infrared spectra were obtained on a Nicolet Avatar 320 FT-IR spectrometer. ^1H NMR and spectra were recorded on a Varian 300, 400, or 500 MHz spectrometer at ambient temperature. Data are reported as follows: chemical shift in parts per million (δ , ppm) from an internal standard [tetramethylsilane (TMS) or deuterated chloroform (CDCl_3)], multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), integration, and coupling constant (Hz). ^{13}C NMR were recorded on a Varian 75, 100, or 125 MHz spectrometer at ambient temperature. Chemical shifts are reported in ppm from (CDCl_3) taken as 77.0 ppm. Mass spectra were obtained on Fisons VG Autospec. Analytical high performance liquid chromatography (HPLC) was performed on a Dynamax model SD-200 HPLC equipped with a Dynamax model UV-1 variable wavelength UV detector using Chiralcel chiral columns as indicated. Gas chromatography was performed on a Varian Cp 3800 gas chromatograph equipped with a flame ionization detector using a Chiraldex B-DM or Chiraldex B-PH capillary column. Optical rotations were measured on an Autopol III automatic polarimeter in a 1 dm cell.

General procedure for the enantioselective desymmetrization of cyclic anhydrides:

A flame-dried round bottom flask was charged with $\text{Pd}(\text{OAc})_2$ (0.05 eq), (R)-(-)-1-[(S)-2-diphenylphosphino)ferrocenyl]-ethylidicyclohexylphosphine [(R,S)-JOSIPHOS] (0.06 eq), and diphenylzinc (1.1 eq.) in an inert atmosphere (N_2) glove box. Upon removal from the glove box, 1.0 ml THF was added via syringe and the solution was stirred at ambient

temperature for 15 minutes. Anhydride (1 eq) in THF (1 mL, typically 0.03-0.003 M in substrate) was then added via cannula and the reaction was stirred for the time and temperature indicated. The reaction mixture was then diluted with 10 ml of ether and quenched with 10 mL 1M aq. HCl. The layers were separated and the aqueous layer extracted with ether (2 X 10 mL). Organic layers were combined and extracted with 1M aq. Na₂CO₃ (2 X 5 mL), the basic layers were combined and brought to pH = 1-2 with concentrated HCl. The acidified aqueous layer was extracted with Et₂O (3 X 10 mL). The combined organic extracts were then washed with brine, dried over MgSO₄, filtered, and concentrated *in vacuo*. For analytical analysis the corresponding methyl ester was generated by treatment with TMSCHN₂ (2.0M in Et₂O or Hexanes) in 2-4 mL of MeOH/PhH (1:1) at 23 °C for 5 min. followed by quenching with AcOH and purification.

(1S, 6R) 6-benzoyl-cyclohex-3-enecarboxylic acid (2). According to the general procedure, 3.5 mg (0.016 mmol) of Pd(OAc)₂, 11.1 mg (0.019 mmol) of (*R,S*)-JOSIPHOS, and 85.0 mg of diphenylzinc (0.387 mmol) in 2 mL of THF was treated with 51.0 mg (0.335 mmol) of anhydride **1** in 0.25 mL THF. The reaction was stirred for 16 h at 23 °C. Standard work-up provided 60 mg crude acid that was purified by column chromatography (98:2 CH₂Cl₂/MeOH) providing 53.0 mg (69 %) of known acid **2** as an off white solid (mp = 106-108 °C, CH₂Cl₂/MeOH; Lit: mp = 130-131 °C, rac. Et₂O/Pet ether).¹ The corresponding methyl ester was used for ee determination. HPLC analysis (Chiralcel OD-H, 97:3 hex/*i*-PrOH, 0.5 mL/min, 254 nm; tr (minor) = 31.9 min., tr (major) = 36.1 min.) gave the isomeric composition of the product: 91% ee. [α]_D²³ (acid) = -31.9° (c = 0.48, CHCl₃).

(1S, 6R) 6-benzoyl-3,4-dimethyl-cyclohex-3-enecarboxylic acid (8). According to the general procedure, 3.9 mg (0.017 mmol) of Pd(OAc)₂, 11.5 mg (0.019 mmol) of (*R,S*)-JOSIPHOS, and 81.0 mg of diphenylzinc (0.369 mmol) in 2 mL of THF was treated with 58.0 mg (0.322 mmol) of anhydride **7** in 0.25 mL THF. The reaction was stirred for 22 h at 23 °C. Standard work-up provided 87.0 mg (87 %) of the desired acid **8** as a white solid (mp = 168-170 °C, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.85-7.87 (m, 2H), 7.53-7.57 (m, 1H), 7.43-7.47 (m, 2H), 3.90 (ddd, 1H, *J* = 6.4, 6.4, 3.8 Hz), 3.00 (ddd, 1H, *J* = 7.2, 7.2, 3.8 Hz), 2.66-2.72 (m, 1H), 2.33-2.39 (m, 3H), 1.65 (s, 3H), 1.55 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 202.5, 178.5, 136.3, 132.8, 128.6, 128.3, 124.6, 122.8, 42.6, 40.3, 32.8, 32.1, 18.9; IR (NaCl, dep from CHCl₃), 3429, 2920, 2858, 1700, 1676, 1445, 1327, 1225, 1180 cm⁻¹; HRMS (FAB+) calcd for C₁₆H₁₉O₃, 259.1334. Found 259.1338; [α]_D²³ = -55.6° (c = 0.16, CHCl₃). The product acid was converted the corresponding methyl ester for ee determination. HPLC analysis (Chiralcel OD-H, 97:3 hex/*i*-PrOH, 0.5 mL/min, 254 nm; tr (minor) = 22.8 min., tr (major) = 27.0 min.) gave the isomeric composition of the product: 90 % ee.

¹ (a) Fieser, L. F.; Novello, F. *J. Am Chem. Soc.* **1942**, *64*, 802-809; (b) Sugita, K.; Tamura, S. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2866-2867.

(2S, 3R) 3-benzoyl-1,2,3,4-tetrahydro-naphthalene-2-carboxylic acid (10). According to the general procedure, 4.1 mg (0.018 mmol) of Pd(OAc)₂, 11.7 mg (0.020 mmol) of (*R,S*)-JOSIPHOS, and 81.0 mg of diphenylzinc (0.369 mmol) in 2 mL of THF was treated with 65.0 mg (0.321 mmol) of anhydride **9** in 0.25 mL THF. The reaction was stirred for 22 h at 23 °C. Standard work-up provided 76.0 mg (84 %) of the desired acid as a white crystalline solid (mp = 174-176 °C, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.88-7.90 (m, 2H), 7.45-7.59 (m, 3H), 7.00-7.17 (m, 4H), 4.12 (ddd, 1H, *J* = 7.0, 7.0, 3.6 Hz), 3.47 (dd, 1H, *J* = 16.2, 6.0 Hz), 3.16-3.27 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 201.8, 177.3, 136.0, 134.2, 133.1, 129.0, 128.7, 128.4, 126.4, 126.0, 42.7, 40.3, 30.6, 29.9; IR (NaCl, dep from CHCl₃) 3408, 2924, 2849, 1691, 1676, 1551, 1155, 1115 cm⁻¹; HRMS (FAB+) calcd for C₁₈H₁₇O₃, 281.1178. Found 281.1178; [α]_D²³ = -61.0° (c = 0.20, CHCl₃). The corresponding methyl ester was used for ee determination. HPLC analysis (Chiralcel OD-H, 95:5 hex/*i*-PrOH, 1.0 mL/min, 254 nm; tr (minor) = 25.4 min., tr (major) = 27.2 min.) gave the isomeric composition of the product: 95 % ee.

(1S, 2R) 2-benzoyl-cyclohexanecarboxylic acid (12). According to the general procedure, 3.7 mg (0.017 mmol) of Pd(OAc)₂, 11.5 mg (0.019 mmol) of (*R,S*)-JOSIPHOS, and 82.0 mg of diphenylzinc (0.373 mmol) in 10 mL of THF was treated with 52.0 mg (0.373 mmol) of anhydride **11** in 0.25 mL THF. The reaction was stirred for 16 h at 23 °C. Standard work-up provided 70.0 mg (89 %) of the known acid **12** as a white solid (mp = 114-115 °C, CH₂Cl₂, Lit = 130-132 °C, rac. from PhH).² The corresponding methyl ester was used for ee determination.³ HPLC analysis (Chiralcel OD-H, 97:3 hex/*i*-PrOH, 0.5 mL/min, 254 nm; tr (minor) = 21.7 min., tr (major) = 23.5 min.) gave the isomeric composition of the product: 94 % ee. [α]_D²³ (acid) = +4.9° (c = 0.35, CHCl₃).

(2S, 3R, 5S, 6R) 6-benzoyl-2,2-dimethyl-hexahydro-benzo[1,3]dioxole-5-carboxylic acid methyl ester (14). According to the general procedure, 3.9 mg (0.017 mmol) of Pd(OAc)₂, 12.3 mg (0.021 mmol) of (*R,S*)-JOSIPHOS, and 83.0 mg of diphenylzinc (0.378 mmol) in 2 mL of THF was treated with 75.0 mg (0.332 mmol) of anhydride **13** in 0.25 mL THF. The reaction was stirred for 17 h at 23 °C. The reaction was allowed to cool to room temperature before diluting the reaction mixture with diethylether (10 ml) and quenched with 1M aq. citric acid (10 ml). The organic layer was separated and the aqueous layer extracted with ether (2 X 10 ml). The organics were combined, washed with brine, dried over MgSO₄, filtered and concentrated. The crude brown oil was then taken up in MeOH/PhH (1:1) and treated with TMSCHN₂. Purification by column chromatography (4:1 Hex/EtOAc) yielded 88.0 mg (83 %) of the product ester **14** as a colorless oil. HPLC analysis (Chiralcel AD, 97:3

² (a) Fieser, L. F.; Novello, F. *J. Am. Chem. Soc.* **1942**, *64*, 802-809; (b) Van der Mey, M.; Hatzelmann, A.; Van Klink, G. P. M.; Van der Laan, I. J.; Strek, G. J.; Thibaut, U.; Ulrich, W. R.; Timmerman, H. *J. Med. Chem.* **2001**, *44*, 2523-2535; (c) Available from Acros Organics, cat. num. 298600025.

³ For ¹H and ¹³C spectra, see: Bercot, E. A.; Rovis, T. *J. Am. Chem. Soc.* **2002**, *124*, 174.

hex/*i*-PrOH, 1.0 mL/min, 254 nm; tr (major) = 20.8 min., tr (minor) = 23.8 min.) gave the isomeric composition of the product: 97% ee. R_f = 0.14 (4:1 Hex/EtOAc); ¹H NMR (300 MHz, CDCl₃) δ 7.88-7.92 (m, 2H), 7.53-7.59 (m, 1H), 7.43-7.48 (m, 2H), 4.38 (ddd, 1H, *J* = 10.6, 10.6, 4.8 Hz), 4.08 (ddd, 1H, *J* = 10.3, 10.3, 4.4 Hz), 3.54 (s, 3H), 3.09 (ddd, 1H, *J* = 10.3, 5.1, 5.1 Hz), 2.01-2.32 (m, 4H), 1.54 (s, 3H), 1.36 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 201.9, 173.8, 136.2, 132.9, 128.6, 128.1, 107.9, 72.2, 72.0, 51.6, 40.1, 38.4, 28.1, 28.0, 27.8, 25.5; IR (NaCl, neat) 2985, 2949, 1736, 1682, 1597, 1448, 1381, 1204, 1041 cm⁻¹; HRMS (FAB+) calcd for C₁₈H₂₃O₅, 319.1545. Found 319.1554; [α]_D²³ = +15.7° (c = 0.76, CHCl₃).

(1S, 2R) 2-benzoyl-cyclopentanecarboxylic acid methyl ester (16).

According to the general procedure, 4.2 mg (0.019 mmol) of Pd(OAc)₂, 12.1 mg (0.020 mmol) of (*R,S*)-JOSIPHOS, and 81.0 mg of diphenylzinc (0.369 mmol) in 2 mL of THF was treated with 46.0 mg (0.328 mmol) of anhydride **15** in 0.25 mL THF. The reaction was stirred for 18 h at 40 °C. Standard work-up provided 64.0 mg (89 %) of the desired acid. The product acid was converted the corresponding methyl ester. Purification by column chromatography (9:1 Hex/EtOAc) yielded 57.0 mg (74 %) of product ester **16** as a colorless oil. HPLC analysis (Chiralcel OB-H, 95:5 hex/*i*-PrOH, 1.0 mL/min, 254 nm; tr (major) = 25.1 min., tr (minor) = 31.4 min.) gave the isomeric composition of the product: 89% ee. R_f = 0.20 (4:1 Hex/EtOAc); ¹H NMR (300 MHz, CDCl₃) δ 7.94-7.91 (m, 2H), 7.57-7.52 (m, 1H), 7.48-7.42 (m, 2H), 4.11 (ddd, 1H, *J* = 8.1, 5.5, 5.5 Hz), 3.52 (s, 3H), 3.07 (ddd, 1H, *J* = 8.1, 8.1, 8.1 Hz), 2.26-1.62 (m, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 200.6, 174.1, 136.4, 132.7, 128.4, 128.3, 51.4, 48.9, 47.6, 30.1, 28.3, 24.2; IR (NaCl, neat) 2591, 2874, 1738, 1682, 1597, 1448, 1209, 1001 cm⁻¹; HRMS (FAB+) calcd for C₁₄H₁₇O₃, 233.1178. Found 233.1176; [α]_D²³ = +6.3° (c = 0.63, CHCl₃).

(2S, 3R) 2,3-dimethyl-4-oxo-4-phenylbutyric acid (18). According to the general procedure, 3.7 mg (0.017 mmol) of Pd(OAc)₂, 10.7 mg (0.018 mmol) of (*R,S*)-JOSIPHOS, and 81.0 mg of diphenylzinc (0.369 mmol) in 2 mL of THF was treated with 42.0 mg (0.324 mmol) of anhydride **17** in 0.25 mL THF. The reaction was stirred for 18 h at 80 °C. Standard work-up provided 48.0 mg (72 %) of the known acid **18** as a white solid (mp = 49-51 °C, CH₂Cl₂).⁴ The corresponding methyl ester was used for ee determination. HPLC analysis (Chiralcel OB-H, 97:3 hex/*i*-PrOH, 0.5 mL/min, 254 nm; tr (minor) = 21.0 min., tr (major) = 22.2 min.) gave the isomeric composition of the product: 92% ee. [α]_D²³ = -29.5° (c = 0.21, CH₃Cl).

(5S, 6R) 5-benzoyl-6-methoxycarbonyl-decanedioic acid diethyl ester (20). According to the general procedure, 3.7 mg (0.017 mmol) of Pd(OAc)₂, 10.7 mg (0.018 mmol) of (*R,S*)-JOSIPHOS, and 83.0 mg of diphenylzinc (0.378 mmol) in 2 mL of THF was treated with 105.0 mg (0.320 mmol) of

⁴ Schreiber, S. L.; Klimas, M. T.; Sammakia, T. *J. Am. Chem. Soc.* **1987**, *109*, 5749-5759.

anhydride **19** in 0.25 mL THF. The reaction was stirred for 17 h at 40 °C. The reaction was allowed to cool to room temperature before diluting the reaction mixture with diethylether (10 mL) and quenched with 1M aq. citric acid (10 mL). The organic layer was separated and the aqueous layer extracted with ether (2 X 10 mL). The organics were combined, washed with brine, dried over MgSO₄, filtered and concentrated. The crude brown oil was then taken up in MeOH/PhH (1:1) and treated with TMSCHN₂. Purification by column chromatography (4:1 Hex/EtOAc) yielded 82.0 mg (61 %) of the product ester **20** as a colorless oil. HPLC analysis (Chiralcel AD, 97:3 hex/*i*-PrOH, 1.0 mL/min, 254 nm; tr (min.) = 33.5 min., tr (maj.) = 51.6 min.) gave the isomeric composition of the product: 89% ee. R_f = 0.14 (4:1 Hex/EtOAc); ¹H NMR (300 MHz, CDCl₃) δ 7.98-7.94 (m, 2H), 7.62-7.56 (m, 1H), 7.50-7.46 (m, 2H), 4.05 (q, 2H, *J* = 7.0 Hz), 4.04 (q, 2H, *J* = 7.0 Hz), 3.77 (ddd, 1H, *J* = 9.2, 9.2, 2.9 Hz), 3.70 (s, 3H), 2.87 (ddd, 1H, *J* = 9.9, 9.9, 3.3 Hz), 1.78-1.30 (m, 8H), 1.19 (t, 3H, *J* = 7.0 Hz), 1.18 (t, 3H, *J* = 7.0 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 202.0, 174.7, 172.8, 172.7, 137.6, 133.4, 128.7, 128.2, 60.3, 51.7, 48.1, 47.5, 34.3, 33.9, 31.1, 30.5, 23.1, 22.4, 14.2; IR (NaCl, neat) 2953, 2872, 1738, 1682, 1695, 1579, 1448, 1159 cm⁻¹; HRMS (FAB+) calcd for C₂₃H₃₃O₇, 421.2226. Found 421.2228; [α]_D²³ = -10.0° (c = 0.51, CHCl₃).

(1S, 6R) 6-Acetyl-cyclohex-3-enecarboxylic acid (21).⁵ According to the general procedure, 3.7 mg (0.016 mmol) of Pd(OAc)₂, 7.9 mg (0.013 mmol) of (*R,S*)-JOSIPHOS in 2 mL of THF was treated with 0.2 mL of dimethylzinc (0.4 mmol, 2.0M in PhMe) before adding 10 μL of 4-fluorostyrene (0.084 mmol) via syringe. After 15 min. an additional 8 mL of THF were added. To the resulting dark brown reaction solution was added 50.0 mg (0.329 mmol) of anhydride **1** in 0.25 mL THF. The reaction was stirred for 22 h at 23 °C. Standard work-up provided crude acid that was purified by column chromatography (98:2 CH₂Cl₂/MeOH) to provide 33 mg (60 %) of the desired acid as a colorless oil. R_f = 0.14 (95:5 CH₂Cl₂/MeOH); ¹H NMR (400 MHz, CDCl₃) δ 5.68 (s, 2H), 3.05-3.07 (m, 1H), 2.87-2.90 (m, 1H), 2.32-2.62 (m, 4H), 2.18 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 208.9, 179.6, 125.7, 124.5, 47.0, 39.2, 27.7, 26.0, 25.4; IR (NaCl, neat) 3400, 3030, 2920, 1709, 1657, 1435, 1356, 1250, 1194, 933 cm⁻¹; HRMS (FAB+) calcd for C₉H₁₃O₃, 169.0865. Found 169.0865; [α]_D²³ = +21.7° (c = 1.43, CHCl₃). The corresponding benzyl ester was used for ee determination. HPLC analysis (Chiralcel OD-H, 97:3 hex/*i*-PrOH, 0.5 mL/min, 254 nm; tr (min.) = 24.9 min., tr (maj.) = 26.2 min.) gave the isomeric composition of the product: 91% ee.

DETERMINATION OF ABSOLUTE STEREOCHEMISTRY

(1S, 2S, 4R, 5R) 2-Benzoyl-4-iodo-6-oxa-bicyclo[3.2.1]octan-7-one.

A flame-dried round bottom flask was charged with 53 mg (0.230 mmol, 91 % ee) of acid **2** in 2 mL of CH₂Cl₂ and 3 mL of 0.5M aq. NaHCO₃. A solution of 312 mg (1.23 mmol) of I₂ and 330 mg (1.99 mmol) of KI in 2

⁵ This procedure is highly reproducible when using 0.8 eq. of ligand to metal. A 1:1 stoichiometry has been found to be capricious.

mL of water was added dropwise to the reaction mixture and the resulting deep red biphasic mixture was stirred in the dark for 17 h. The reaction was quenched with 15 mL of sat. aq. NaHSO₃. The organic layer was separated and the remaining aqueous layer extracted with CH₂Cl₂ (2 X 20 mL). Organics were combined, washed with sat. aq. NaHCO₃, brine, dried over MgSO₄, filtered and concentrated *in vacuo* to provide a crude white solid. Column chromatography (4:1 Hex/EtOAc) provided 69.0 mg (84 %) of the desired iodolactonized products as a white crystalline solid: mp = 144 °C (dec). X-ray quality crystals were derived from slow evaporation of a methylene chloride solution. R_f = 0.50 (1:1 Hex/EtOAc); ¹H NMR (400 MHz, CDCl₃) δ 7.92-7.91 (m, 2H), 7.62-7.58 (m, 1H), 7.52-7.48 (m, 2H), 4.87 (dd, 1H, *J* = 4.7, 4.7 Hz), 4.63 (dd, 1H, *J* = 4.5, 4.5 Hz), 3.87 (ddd, 1H, *J* = 12.2, 4.4 0.0 Hz), 3.04-2.98 (m, 2H), 2.82 (ddd, 1H, *J* = 17.1, 12.4, 5.5 Hz), 2.53 (ddd, 1H, *J* = 11.5, 5.5, 5.5 Hz), 2.31 (ddd, 1H, *J* = 16.6, 4.1, 0.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 196.9, 174.3, 134.9, 133.6, 128.9, 128.3, 79.3, 41.6, 40.8, 34.6, 32.0, 22.6; HRMS (FAB+) calcd for C₁₄H₁₄IO₃, 356.9988. Found 356.9996; [α]_D²³ = +27.0° (c = 0.64, CHCl₃).

^1H and ^{13}C for compound **2**:

^1H and ^{13}C for compound **8**:

^1H and ^{13}C for compound **10**:

^1H and ^{13}C spectra for **12**.

^1H and ^{13}C spectra for **14**:

^1H and ^{13}C spectra for **16**:

^1H and ^{13}C spectra for **18**.

^1H and ^{13}C spectra for **20**:

^1H and ^{13}C spectra for **21**:

^1H and ^{13}C spectra for the iodolactonized product of **2**:

X-Ray data for iodolactone derived from **2**:

Table 1. Crystal data and structure refinement for rovis8m.

Identification code	rovis8m	
Empirical formula	C ₁₄ H ₁₃ I O ₃	
Formula weight	356.14	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 7.3666(8) Å	α = 90°.
	b = 5.9287(7) Å	β = 101.328(2)°.
	c = 15.0952(17) Å	γ = 90°.
Volume	646.43(13) Å ³	
Z	2	
Density (calculated)	1.830 Mg/m ³	
Absorption coefficient	2.474 mm ⁻¹	
F(000)	348	
Crystal size	0.40 x 0.25 x 0.20 mm ³	
Theta range for data collection	2.75 to 28.28°.	
Index ranges	-9 ≤ h ≤ 9, -7 ≤ k ≤ 7, -19 ≤ l ≤ 18	
Reflections collected	6024	
Independent reflections	3094 [R(int) = 0.0191]	

Completeness to theta = 28.28°	98.5 %
Absorption correction	SADABS
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3094 / 1 / 166
Goodness-of-fit on F ²	1.078
Final R indices [I>2sigma(I)]	R1 = 0.0338, wR2 = 0.0612
R indices (all data)	R1 = 0.0387, wR2 = 0.0627
Absolute structure parameter	0.03(2)
Largest diff. peak and hole	0.995 and -0.498 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

for rovis8m. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	7381(5)	9898(7)	5589(3)	37(1)
C(2)	6988(5)	11439(8)	4882(3)	43(1)
C(3)	7202(5)	10813(13)	4025(2)	51(1)
C(4)	7822(6)	8689(9)	3877(3)	53(1)
C(5)	8182(6)	7156(8)	4567(3)	49(1)
C(6)	7929(6)	7741(7)	5426(3)	44(1)
C(7)	7236(5)	10749(10)	6509(3)	41(1)
C(8)	7081(5)	9029(6)	7254(3)	35(1)
C(9)	5917(5)	10075(7)	7884(2)	41(1)
C(10)	6070(6)	8894(7)	8792(3)	41(1)
C(11)	8013(6)	8084(7)	9154(3)	47(1)
C(12)	8739(6)	6579(6)	8497(3)	43(1)
C(13)	9022(5)	8335(6)	7798(3)	39(1)
C(14)	9878(6)	10216(7)	8418(3)	49(1)
I(1)	4194(1)	6041(1)	8730(1)	49(1)
O(1)	7269(5)	12740(6)	6668(2)	60(1)
O(2)	10963(5)	11652(5)	8304(3)	67(1)
O(3)	9227(4)	10084(5)	9200(2)	58(1)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for rovis8m.

C(1)-C(6)	1.378(6)
C(1)-C(2)	1.391(5)
C(1)-C(7)	1.500(6)
C(2)-C(3)	1.385(6)
C(3)-C(4)	1.373(9)
C(4)-C(5)	1.369(6)
C(5)-C(6)	1.389(6)
C(7)-O(1)	1.204(7)
C(7)-C(8)	1.539(6)
C(8)-C(9)	1.531(5)
C(8)-C(13)	1.559(5)
C(9)-C(10)	1.524(5)
C(10)-C(11)	1.507(6)
C(10)-I(1)	2.175(4)
C(11)-O(3)	1.479(5)
C(11)-C(12)	1.508(6)
C(12)-C(13)	1.525(5)
C(13)-C(14)	1.512(6)
C(14)-O(2)	1.203(5)
C(14)-O(3)	1.361(6)
C(6)-C(1)-C(2)	119.8(4)
C(6)-C(1)-C(7)	123.7(4)
C(2)-C(1)-C(7)	116.5(4)
C(3)-C(2)-C(1)	119.7(5)
C(4)-C(3)-C(2)	120.1(5)
C(5)-C(4)-C(3)	120.4(4)
C(4)-C(5)-C(6)	120.2(4)
C(1)-C(6)-C(5)	119.8(4)
O(1)-C(7)-C(1)	120.8(4)
O(1)-C(7)-C(8)	120.3(4)
C(1)-C(7)-C(8)	118.8(4)
C(9)-C(8)-C(7)	108.5(3)

C(9)-C(8)-C(13)	110.3(3)
C(7)-C(8)-C(13)	111.6(3)
C(10)-C(9)-C(8)	114.9(3)
C(11)-C(10)-C(9)	111.7(3)
C(11)-C(10)-I(1)	108.6(3)
C(9)-C(10)-I(1)	112.6(3)
O(3)-C(11)-C(12)	102.5(3)
O(3)-C(11)-C(10)	106.5(3)
C(12)-C(11)-C(10)	112.6(3)
C(11)-C(12)-C(13)	99.5(3)
C(14)-C(13)-C(12)	100.0(3)
C(14)-C(13)-C(8)	111.1(3)
C(12)-C(13)-C(8)	108.0(3)
O(2)-C(14)-O(3)	121.5(4)
O(2)-C(14)-C(13)	129.9(5)
O(3)-C(14)-C(13)	108.6(4)
C(14)-O(3)-C(11)	108.5(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for rovis8m. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	31(2)	40(2)	40(2)	3(2)	6(2)	-3(2)
C(2)	41(2)	40(4)	47(2)	5(2)	6(2)	2(2)
C(3)	54(2)	59(3)	37(2)	6(3)	2(2)	0(3)
C(4)	50(3)	69(3)	40(2)	-6(2)	7(2)	-9(2)
C(5)	52(2)	46(2)	50(2)	-16(2)	14(2)	-7(2)
C(6)	48(2)	39(2)	45(2)	4(2)	11(2)	0(2)
C(7)	45(2)	37(3)	41(2)	6(2)	11(1)	4(2)
C(8)	38(2)	32(2)	35(2)	-2(2)	8(2)	-3(2)
C(9)	41(2)	41(2)	40(2)	0(2)	9(2)	6(2)
C(10)	46(2)	47(2)	33(2)	-6(2)	11(2)	1(2)
C(11)	49(2)	53(3)	33(2)	1(2)	-5(2)	-5(2)
C(12)	39(2)	37(3)	53(2)	6(2)	5(2)	2(1)
C(13)	35(2)	35(2)	48(2)	-1(2)	9(2)	2(2)
C(14)	38(2)	44(2)	59(3)	-1(2)	-1(2)	-2(2)
I(1)	44(1)	59(1)	46(1)	9(1)	15(1)	-3(1)
O(1)	94(3)	36(2)	54(2)	1(2)	25(2)	-6(2)
O(2)	54(2)	52(3)	91(2)	-5(2)	9(2)	-18(2)
O(3)	56(2)	61(2)	51(2)	-11(1)	-1(2)	-17(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)
for rovis8m.

	x	y	z	U(eq)
H(2)	6583	12884	4985	52
H(3)	6924	11832	3549	61
H(4)	8000	8290	3304	64
H(5)	8596	5718	4461	58
H(6)	8130	6681	5889	52
H(8)	6447	7679	6973	42
H(9A)	6287	11637	7992	49
H(9B)	4629	10068	7578	49
H(10)	5750(60)	9990(70)	9220(30)	50
H(11)	8117	7364	9746	56
H(12A)	7842	5442	8240	52
H(12B)	9892	5855	8774	52
H(13)	9846	7798	7407	47