Palladium-Catalyzed Diastereo- and Enantioselective Formal [3+2]-Cycloadditions of Substituted Vinylcyclopropanes

SUPPORTING INFORMATION

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General Information

Glassware was oven-dried for at least 6 h at 110 °C or flame dried prior to use. All reactions were performed under inert atmosphere (dry nitrogen or argon) unless otherwise noted. Analytical thin-layer chromatography was performed using 0.25 nm coated commercial silica gel plates (EMD Chemicals, silica gel 60 F254). Silica gel flash chromatography was performed using Silicycle silica gel (230-400 Mesh). Proton and carbon nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were acquired on a Inova-300 (300 MHz), Mercury 400 (400 MHz), or Varian Unity Inova-500 (500 MHz) spectrometer. Chemical shifts are reported in parts per million (ppm) relative to deuterochloroform (7.26 ppm for ^{1}H NMR and 77.23 ppm for ^{13}C NMR). Coupling constants (*J*) are quoted in Hz to the nearest 0.5 Hz. Splitting patterns are reported as: s, singlet; d, doublet; t, triplet; q, quartet, m, multiplet, etc. Melting points (uncorrected) were measured using a Thomas Hoover Capillary Melting Point Analysis. Infrared (IR) spectra were recorded as a thin film on NaCl plates with a Thermo Scientific Nicolet IR 100 FT-IR. Chiral HPLC analyses were performed on a Thermo Separation Products spectra series P-100 or P-200 pump and a UV100 detector (254 nm or 220 nm) using a Chiralpak IA. IB, or IC column eluted with the indicated solvent mixture and a flow rate of 1 mL min^{-1}. Optical rotations were measured on a Jasco DIP-1000 digital polarimeter using 5 cm cells and the sodium D line (589 nm) at ambient temperature in methylene chloride. High resolution mass spectra were obtained from Stanford University using positive electrospray ionization (ESI+).

Materials

Dioxane and toluene were distilled from sodium metal under nitrogen prior to use. Dichloroethane was distilled from calcium hydride under nitrogen. Other reaction solvents were dried using J.C. Meyer's Solvent Purification System by passing them through activated alumina prior to use.

$Pd_2dba_3{\cdot}CHCl_3$ was prepared by the procedure of Ibers.[1]

Trost Ligands $\mathbf{L_1}$, $\mathbf{L_2}$, $\mathbf{L_3}$, and $\mathbf{L_4}$ were prepared according to literature procedures.[2]

Dimethyl 2-vinylcyclopropane-1,1-dicarboxylate **1** was purified according to the procedure of Johnson *et al.*[3] Spectral data were in accordance with the literature values.

Meldrum's acid alkylidenes **4**,[4] **8c**,[5] **8e**,[6] **8f**,[7] **8g**[8] and **8j**[9] were prepared by Dr. Pekka Joensuu at Stanford University according to the procedure of Sartori *et al.*[10] Spectral data were in accordance with the literature values.

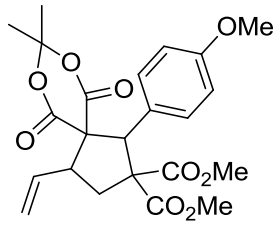
(*Z*)-4-Benzylidene-2-phenyloxazol-5(4*H*)-one **14a** was purchased from Sigma Aldrich and used without purification.

Azlactone alkylidene (*Z*)-4-(4-nitrobenzylidene)-2-phenyloxazol-5(4*H*)-one **14g**[11] was prepared by Dr Benjamin Taft at Stanford University according to General Procedure C reported by Chavez *et al.*[16] Spectral data were in accordance with the literature values.

All other reagents were purchased from commercial sources and used without prior purification, unless otherwise noted.

Compound Synthesis

Dimethyl 1-(4-methoxyphenyl)-8,8-dimethyl-6,10-dioxo-4-vinyl-7,9-dioxaspiro[4.5]decane-2,2-dicarboxylate **5a**

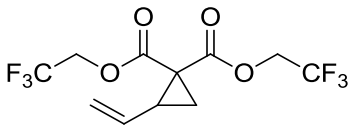


5a

An oven-dried reaction tube equipped with a stir bar was charged with palladium dibenzylideneacetone-chloroform complex (2.0 mg, 0.002 mmol) and (*R*,*R*)-**L**$_1$ chiral ligand, (4.0 mg, 0.006 mmol). A second reaction tube, also equipped with a stir bar, was charged with dimethyl 2-vinylcyclopropane-1,1-dicarboxylate **1** (20.0 mg, 0.109 mmol), 5-(4-methoxybenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione **4** (35.0 mg, 0.133 mmol) and 1,3,5-trimethoxybenzene (5.0 mg, 0.03 mmol). Both tubes were sealed with a septum, evacuated, and backfilled with dry nitrogen. Toluene (degassed by sparging with nitrogen for 30 min) was added to the first tube (1 mL) and second tube (1 mL), and the tubes were for stirred 20 min. The contents of the first reaction tube were transferred to the second test tube *via* syringe, and the mixture was stirred at room temperature for 14 h and the solvent was removed *in vacuo*. ^{1}H NMR spectroscopy of the crude product reveals a

97% yield (internal standard 1,3,5-trimethoxybenzene) and a 1.5:1 diastereomeric ratio. The product was purified by flash column chromatography (10% to 40% diethyl ether in petroleum ether) to give the title compound **5a** as a waxy solid, as a 1.5:1 mixture of diastereomers, with a 39% e.e. for the major diastereomer and a 72% e.e. for the minor diastereomer (by chiral HPLC, Chiralpak IC column, 10% isopropanol, 90% heptanes, UV wavelength 254 nm; retention times: 15.9 min (minor enantiomer, minor diastereomer), 18.0 min (minor enantiomer, major diastereomer), 19.6 min (major enantiomer, major diastereomer), 35.6 min (major enantiomer, minor diastereomer)); ^{1}H NMR (500 MHz, $CDCl_3$, 1.5:1 mixture of diastereomers): δ = 7.30–7.15 (m, 4H, both diastereomers), 5.82–5.69 (m, 1H, both diastereomers), 5.35 (s, 1H, minor diastereomer), 5.34–5.27 (m, 1H, both diastereomers), 5.25–5.19 (m, 1H, both diastereomers), 4.95 (s, 1H, major diastereomer), 4.24 (td, *J* = 7.9, 12.0 Hz, 1H, major diastereomer), 3.86 (t, *J* = 14.0 Hz, 1H, minor diastereomer), 3.80 (s, 3H, both diastereomers), 3.78 (s, 3H, minor diastereomer), 3.77 (s, 3H, major diastereomer), 3.45 (m, 1H, minor diastereomer), 3.40 (s, 3H, minor diastereomer), 3.38 (s, 3H, major diastereomer), 3.05 (dd, *J* = 13.5, 7.0 Hz, 1H, major diastereomer), 2.69 (t, *J* = 13.0 Hz, 1H, major diastereomer), 2.42 (dd, *J* = 14.0, 6.0 Hz, 1H, minor diastereomer), 1.62 (s, 3H, major diastereomer), 1.56 (s, 3H, minor diastereomer), 1.51 (s, 3H, major diastereomer), 0.85 (s, 3H, minor diastereomer); ^{13}C NMR (100 MHz, $CDCl_3$, 1.5:1 mixture of diastereomers) 172.8, 171.3, 170.0, 168.6, 159.7, 134.5, 133.1, 132.7, 131.8, 120.5, 114.1, 113.7, 66.9, 66.2, 65.1, 63.7, 60.6, 55.4, 55.4, 55.2, 54.0, 53.7, 52.7, 52.6, 39.9, 39.2, 29.5, 29.5, 29.4, 29.2; HRMS (ESI+): observed 469.1464; calculated 469.1469 ($C_{23}H_{26}NaO_9$, $[M+Na]^+$).

Bis(2,2,2-trifluoroethyl) 2-vinylcyclopropane-1,1-dicarboxylate **6**

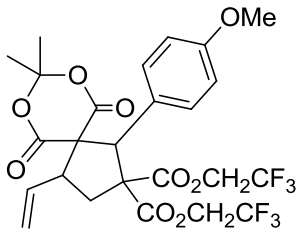


6

A stirred mixture of bis(2,2,2-trifluoroethyl)malonate[12] (893 mg, 3.33 mmol), 1,4-dibromobut-2-ene (705 mg, 3.33 mmol) and cesium carbonate (2.70 g, 8.29 mmol) in tetrahydrofuran (20 mL) was heated under reflux at 60 °C for 16 h. The reaction mixture was then allowed to cool, filtered, and the filtrate diluted with diethyl ether. The organic phase was washed successively with sat. aq. sodium bicarbonate, water, brine, and dried ($MgSO_4$). The organic layers were concentrated *in vacuo* to give the crude product, which was purified by silica gel chromatography (10% to 20% methylene

chloride in petroleum ether) to afford the title compound **6** as a colorless oil (600 mg, 56% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.46 (ddd, *J* = 17.0, 10.0, 8.0 Hz, 1H), 5.35 (d, *J* = 17.0 Hz, 1H), 5.23 (d, *J* = 10.0 Hz, 1H), 4.53 (m, 4H), 2.74 (dd, *J* = 9.0, 9.0 Hz, 1H), 1.90 (dd, *J* = 8.0, 5.0 Hz, 1H), 1.73 (dd, *J* = 9.0, 5.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.7, 165.4, 131.5, 122.8 (q, $J_{C\text{-}F}$ = 275 Hz, 2C), 120.5, 61.5 (q, $J_{C\text{-}F}$ =37 Hz), 61.3 (q, $J_{C\text{-}F}$ = 37 Hz), 35.2, 33.1, 21.7; ^{19}F NMR (479 MHz, $CDCl_3$): δ = −74.2 (t, *J* = 8.0 Hz, 3F), −74.4 (t, *J* = 8.5 Hz, 3F); IR (cm^{-1}): 2979, 1747, 1640, 1414, 1280, 1168, 1120, 978, 926, 842, 780; HRMS (ESI+): observed 321.0557; calculated 321.0562 ($C_{11}H_{11}F_6O_4$, $[M+H]^+$).

Bis(2,2,2-trifluoroethyl) 1-(4-methoxyphenyl)-8,8-dimethyl-6,10-dioxo-4-vinyl-7,9-dioxaspiro[4.5]decane-2,2-dicarboxylate **5b**

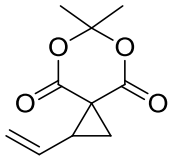


5b

An oven-dried reaction tube equipped with a stir bar was charged with palladium dibenzylideneacetone-chloroform complex (2.5 mg, 0.002 mmol) and (*R*,*R*)-$\mathbf{L_1}$ chiral ligand, (5.0 mg, 0.009 mmol). A second reaction tube, also equipped with a stir bar, was charged with bis(2,2,2-trifluoroethyl) 2-vinylcyclopropane-1,1-dicarboxylate **6** (25.0 mg, 0.078 mmol), 5-(4-methoxybenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione **4** (30.0 mg, 0.114 mmol) and 1,3,5-trimethoxybenzene (5.0 mg, 0.03 mmol). Both tubes were sealed with a septum, evacuated, and backfilled with dry nitrogen. Toluene (degassed by sparging with nitrogen for 30 min) was added to the first tube (1 mL) and second tube (1 mL), and the tubes were for stirred 20 min. The contents of the first reaction tube were transferred to the second test tube *via* syringe, and the mixture was stirred at room temperature for 14 h and the solvent was removed *in vacuo*. ^{1}H NMR spectroscopy of the crude product reveals a 84% yield (internal standard 1,3,5-trimethoxybenzene) and a 2.1:1 diastereomeric ratio. The product was purified by flash column chromatography (10% to 40% diethyl ether in petroleum ether) to give the title compound **5b** as a waxy solid, as a 2.1:1 mixture of diastereomers, with a 29% e.e. for the major diastereomer and a 79% e.e. for the minor diastereomer (by chiral HPLC, Chiralpak IC column, 1% isopropanol, 99% heptanes, UV wavelength 254 nm;

retention times: 12.4 min (major enantiomer, major diastereomer), 13.4 min (major enantiomer, minor diastereomer), 14.7 min (minor enantiomer, minor diastereomer), 21.1 min (minor enantiomer, major diastereomer)); ^{1}H NMR (500 MHz, $CDCl_3$, 2.1:1 mixture of diastereomers): δ =7.22 (d, *J* = 9.0 Hz, 2H, major diastereomer), 7.14 (d, *J* = 9.0 Hz, 2H, minor diastereomer), 6.84-6.75 (m, 2H, both diastereomers), 5.77 (ddd, *J* = 17.0, 10.0, 8.5 Hz, 1H, major diastereomer), 5.71 (ddd, *J* = 17.5, 10.5, 9.0 Hz, 1H, minor diastereomer), 5.35-5.30 (m, 1H, both diastereomers), 5.32 (s, 1H, minor diastereomer), 5.27 (d, *J* = 10.5 Hz, 1H, minor diastereomer), 5.24 (d, *J* = 10.5 Hz, 1H, major diastereomer), 4.94 (s, 1 H, major diastereomer), 4.65-4.37 (m, 4H, both diastereomers), 4.21 (dq, *J* = 12.0, 8.0 Hz, 1H, major diastereomer), 3.96-3.83 (m, 1H, minor diastereomer), 3.79 (s, 3H, major diastereomer), 3.78 (s, 3H, minor diastereomer), 3.46 (dd, *J* = 13.5, 7.0 Hz, 1H, minor diastereomer), 3.11 (dd, *J* = 13.5, 8.0 Hz, 1H, major diastereomer), 2.72 (dd, *J* = 13.5, 12.0 Hz, 1H, major diastereomer), 2.44 (dd, *J* = 14.0, 7.0 Hz, 1H, minor diastereomer), 1.61 (s, 3H, major diastereomer), 1.58 (s, 3H, minor diastereomer), 1.50 (s, 9H, both diastereomers); ^{13}C NMR (75 MHz, $CDCl_3$, 2.1:1 mixture of diastereomers): δ = 168.7, 168.3, 167.6, 166.6, 160.1, 133.9, 132.6, 132.3, 131.7, 125.3, 121.1, 114.5, 114.0, 105.7, 66.5, 65.9, 64.8, 63.6, 62.2 (q, *J* = 21.3 Hz), 61.6 (q, *J* = 20.4), 55.5, 54.0, 39.3; 19F NMR (376 MHz, $CDCl_3$): δ = −74.05-−75.51 (m, 6F); IR (cm^{-1}): 1756, 1612, 1516, 1414, 1263, 1254, 1170, 1035, 938, 839, 734; HRMS (ESI+): observed 605.1228; calculated 605.1217 ($C_{25}H_{24}F_6NaO_9$, $[M+Na]^+$).

6,6-Dimethyl-1-vinyl-5,7-dioxaspiro[2.5]octane-4,8-dione **7**

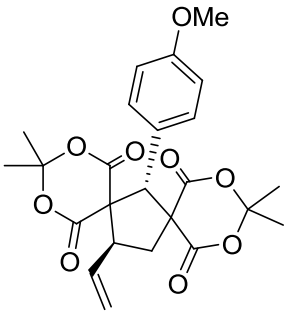


7

To a stirred suspension of Meldrum's acid (565 mg, 3.92 mmol) in DMF (4 mL) at 0 °C was added potassium carbonate (677 mg, 4.90 mmol). The reaction was stirred for 10 min, then 1,4-dibromobut-2-ene (1.00 g, 4.70 mmol) was added in a single portion and the reaction stirred for a 1 h at 0 °C and a further 2 h at room temperature. A further portion of potassium carbonate (677 mg, 4.90 mmol) was added, and the reaction was stirred for a further 16 h at room temperature. The reaction was poured into 1 M aqueous HCl (25 mL) and extracted with ethyl acetate (3 x 25 mL). The combined organic layers were washed successively with brine (25 mL), water (25 mL), dried

($MgSO_4$) and concentrated *in vacuo* to give the crude product, which was purified by flash column chromatography (4:1 petrol:diethyl ether) to give the title compound **7** as a waxy solid (299 mg, 1.52 mmol, 39%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.75 (ddd, *J* = 17.0, 10.5, 9.5 Hz, 1H), 5.46 (dd, *J* = 17.0, 1.0 Hz, 1H), 5.32 (dd, *J* = 10.5, 1.0 Hz, 1H), 2.76 (dd, *J* = 9.0, 9.0 Hz, 1H), 2.36 (dd, *J* = 9.0, 4.5 Hz, 1H), 2.21 (dd, *J* = 8.5, 4.5 Hz, 1H), 1.76 (d, *J* = 0.5 Hz, 3H), 1.72 (d, *J* = 0.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 167.8, 165.5, 131.6, 122.2, 105.4, 43.3, 31.8, 27.9, 27.8, 24.9; IR (cm^{-1}): 3101, 1745, 1394, 1327, 1284, 1200, 1046, 967, 930, 881, 831, 740, 690; spectral data in accordance with the literature.[13]

(7*R*,14*S*)-1,5,9,13-Tetraoxy-3,3,11,11-tetramethyl-7-(4-methoxyphenyl)-14-vinyl-2,4,10,12-tetraoxadispiro[5.1.5.2]pentadecane **5c**



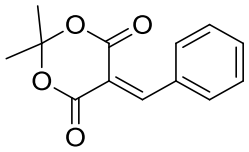
5c

An oven-dried reaction tube equipped with a stir bar was charged with palladium dibenzylideneacetone-chloroform complex (4.0 mg, 0.004 mmol) and (*R*,*R*)-**L$_3$** chiral ligand, (8.0 mg, 0.010 mmol). A second reaction tube, also equipped with a stir bar, was charged with 6,6-dimethyl-1-vinyl-5,7-dioxaspiro[2.5]octane-4,8-dione **7** (35.0 mg, 0.178 mmol) and 5-(4-methoxybenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione **4** (60.0 mg, 0.229 mmol). Both tubes were sealed with a septum, evacuated, and backfilled with dry nitrogen. Dioxane (degassed by sparging with nitrogen for 30 min) was added to the first tube (1 mL) and second tube (2 mL), and the tubes were for stirred 20 min. The contents of the first reaction tube were transferred to the second test tube *via* syringe, and the mixture was stirred at room temperature for 16 h. The reaction mixture was poured into sat. aq. sodium bicarbonate solution, and extracted with methylene chloride. The combined organic extracts were dried ($MgSO_4$) and the solvent was removed *in vacuo* to give the crude product, which was purified by flash column chromatography (30% to 35% diethyl ether in petroleum ether) to give the title compound **5c** as a white solid (50.8 mg, 0.111 mmol, 62%), as a 17:1 mixture of

diastereomers (by crude ^{1}H NMR) and with a 96% e.e. for the major diastereomer (by chiral HPLC, Chiralpak IC column, 0.7% ethanol, 27% methylene chloride, 72.3% heptanes, UV wavelength 254 nm; retention times: 7.83 min (minor enantiomer, major diastereomer), 10.07 min (minor diastereomer), 10.60 min (minor diastereomer), 12.54 min (major enantiomer, major diastereomer)); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.26 (d, *J* = 6.5 Hz, 2H), 6.81 (d, *J* = 6.5 Hz, 2H), 5.80 (ddd, *J* = 17.5, 10.5, 8.5 Hz, 1H), 5.35 (d, *J* = 17.5 Hz, 1H), 5.23 (d, *J* = 10.5 Hz, 1H), 4.94 (ddd, *J* = 13.0, 8.5, 6.0 Hz, 1H), 4.86 (s, 1H), 3.78 (s, 3H), 3.19 (dd, *J* = 13.0, 12.5 Hz, 1H), 2.47 (dd, *J* = 12.5, 6.0 Hz, 1H), 1.63 (s, 3H), 1.57 (s, 3H), 1.19 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.4, 170.1, 167.1, 166.6, 160.6, 133.9, 132.9, 125.0, 121.2, 114.6, 105.6, 105.3, 66.2, 64.7, 62.1, 56.2, 55.5, 42.2, 29.6, 29.4, 29.3, 28.5; IR (cm^{-1}): 3583, 3001, 2944, 1769, 1746, 1609, 1514, 1393, 1382, 1275, 1205, 1186, 1091, 1029, 929, 732; HRMS (ESI+) observed 481.1468; calculated 481.1479 ($C_{24}H_{26}NaO_9$, $[M+Na]^+$); $[\alpha]^{23}_D$ = +27.55° (c = 1.0, CH_2Cl_2); m.p. 148 °C (decomposes).

The compound was recrystallized by vapor diffusion of hexanes into chloroform at room temperature, to obtain X-ray quality crystals. The X-ray crystallographic report for this compound is in **Appendix A**.

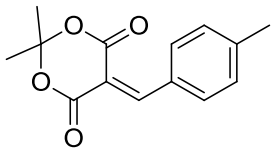
5-Benzylidene-2,2-dimethyl-1,3-dioxane-4,6-dione **8a**



8a

To a stirred solution of benzaldehyde (1.06 g, 10.0 mmol) and Meldrum's acid (1.58 g, 10.9 mmol) in benzene (50 mL) was added pyrrolidinium acetate (2.0 mL of a 0.5 M solution in benzene, 1.00 mmol). The reaction was stirred at room temperature for 16 h, then diluted with ethyl acetate, and washed with sat. aq. sodium bicarbonate. The organic phase was dried ($MgSO_4$) and concentrated *in vacuo* to give the crude product, which was purified by flash column chromatography (20%-30% diethyl ether in petroleum ether) to give the title compound **8a** as a yellow liquid which crystalizes upon standing (830 mg, 3.57 mmol, 36%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.43 (s, 1H), 8.05 (d, *J* = 7.5 Hz, 2H), 7.60-7.54 (m, 1H), 7.50 (dd, *J* = 7.5, 7.5 Hz, 2H), 1.81 (s, 6H); m.p. 72-74 °C (lit. 74.5-75.5 °C); spectral data in accordance with the literature.[14]

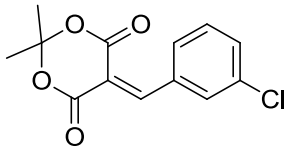
2,2-Dimethyl-5-(4-methylbenzylidene)-1,3-dioxane-4,6-dione **8b**



8b

To a stirred solution of 4-methylbenzaldehyde (1.20 g, 10.0 mmol) and Meldrum's acid (1.58 g, 10.9 mmol) in benzene (50 mL) was added pyrrolidinium acetate (2.0 mL of a 0.5 M solution in benzene, 1.00 mmol). The reaction was heated under reflux at 50 °C for 16 h, then allowed to cool, diluted with ethyl acetate, and washed with sat. aq. sodium bicarbonate. The organic phase was dried ($MgSO_4$) and concentrated *in vacuo* to give the crude product, which was recrystallized from hot ethanol to give the title compound **8b** as a white solid (1.23 g, 50.0 mmol, 50%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (s, 1H), 8.05 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H), 1.80 (s, 6H); m.p. 110-114 °C (lit. 116-118 °C); spectral data in accordance with the literature.[15]

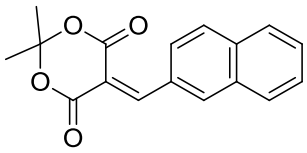
5-(3-Chlorobenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione **8d**



8d

To a stirred solution of 3-chlorobenzaldehyde (1.40 g, 10.0 mmol) and Meldrum's acid (1.58 g, 10.9 mmol) in benzene (50 mL) was added pyrrolidinium acetate (2.0 mL of a 0.5 M solution in benzene, 1.00 mmol). The reaction was heated under reflux at 50 °C for 16 h, then allowed to cool, diluted with ethyl acetate, and washed with sat. aq. sodium bicarbonate. The organic phase was dried ($MgSO_4$) and concentrated *in vacuo* to give the crude product, which was recrystallized from hot ethanol to give the title compound **8d** as a white solid (1.40 g, 52.5 mmol, 53%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (s, 1H), 8.03 (s, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.41 (dd, *J* = 8.0 Hz, 1H), 1.80 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.0, 159.6, 156.3, 134.9, 133.5, 133.4, 132.8, 131.6, 130.1, 116.5, 105.1, 27.9; IR (cm^{-1}): 1731, 1612, 1562, 1472, 1424, 1381, 1283, 1188, 1032, 935, 798, 674; m.p. 104-107 °C (lit. 115-116 °C); spectral data in accordance with the literature.[4]

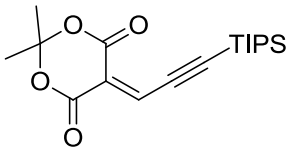
2,2-Dimethyl-5-(naphthalen-2-ylmethylene)-1,3-dioxane-4,6-dione **8h**



8h

To a stirred solution of 2-naphthaldehyde (1.55 g, 10.0 mmol) and Meldrum's acid (1.58 g, 10.9 mmol) in benzene (50 mL) was added pyrrolidinium acetate (2.0 mL of a 0.5 M solution in benzene, 1.00 mmol). The reaction was heated under reflux at 50 °C for 16 h, then allowed to cool, diluted with ethyl acetate, and washed with sat. aq. sodium bicarbonate. The organic phase was dried ($MgSO_4$) and concentrated *in vacuo* to give the crude product, which was recrystallized from hot ethanol to give the title compound **8d** as a white solid (1.50 g, 53.1 mmol, 53%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.60 (s, 1H), 8.57 (s, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 7.0 Hz, 1H), 7.63 (dd, *J* = 7.0, 7.0 Hz, 1H), 7.56 (dd, *J* = 8.5, 7.0 Hz, 1H), 1.86 (s, 6H); m.p. 148-149 °C (lit. 150.8-151.5 °C); spectral data in accordance with the literature.[14]

2,2-Dimethyl-5-(3-(triisopropylsilyl)prop-2-yn-1-ylidene)-1,3-dioxane-4,6-dione **8i**

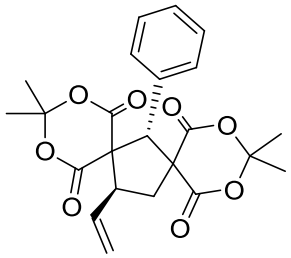


8i

To a stirred solution of triisopropylsilylacetylene (522 mg, 2.87 mmol) in tetrahydrofuran (10 mL) at -78 °C was added *n*-butyllithium (2.5 M in hexanes, 1 mL, 2.5 mmol) *via* syringe. The flask was allowed to warm to -20 °C, and stirred for 10 min, then recooled to –78 °C. A solution of 5-(dimethylaminomethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione (440 mg, 2.05 mmol) in tetrahydrofuran (25 mL) was then added slowly via syringe at –78 °C. The solution was then allowed to slowly warm to room temperature over 1.5 h. The solution was then poured into 1 M HCl, and quickly extracted with dichloromethane. The organic phase was dried ($MgSO_4$) and concentrated *in vacuo* to give the crude product, which was purified by flash column chromatography (20% diethyl ether in petroleum ether) to give the title compound **8i** as a pale yellow oil (682 mg, 2.03 mmol, 99%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (s, 1H), 1.75 (s, 6H), 1.14 (sp, *J* = 5.5 Hz, 3H), 1.10 (d,

J = 5.5 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.7, 158.1, 137.2, 126.1, 124.4, 105.2, 102.8, 28.1, 18.7, 11.4; IR (cm^{-1}): 2944, 2866, 2129, 2030, 1741, 1595, 1463, 1383, 1347, 1285, 1203, 1080, 1022, 925, 883, 794, 678; HRMS (ESI+) observed 359.1649; calculated 359.1655 ($C_{18}H_{29}NaO_4Si$, $[M+Na]^+$).

(7*R*,14*S*)-1,5,9,13-Tetraoxy-3,3,11,11-tetramethyl-7-phenyl-14-vinyl-2,4,10,12-tetraoxadispiro[5.1.5.2]pentadecane **9a**

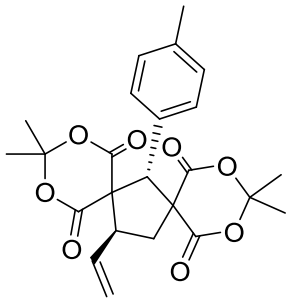


9a

An oven-dried reaction tube equipped with a stir bar was charged with palladium dibenzylideneacetone-chloroform complex (3.0 mg, 0.003 mmol) and (*R*,*R*)-**L$_3$** chiral ligand, (6.0 mg, 0.075 mmol). A second reaction tube, also equipped with a stir bar, was charged with 6,6-dimethyl-1-vinyl-5,7-dioxaspiro[2.5]octane-4,8-dione **7** (36.0 mg, 0.178 mmol) and 5-benzylidene-2,2-dimethyl-1,3-dioxane-4,6-dione **8a** (50.0 mg, 0.215 mmol). Both tubes were sealed with a septum, evacuated, and backfilled with dry nitrogen. Dioxane (degassed by sparging with nitrogen for 30 min) was added to the first tube (1 mL) and second tube (3 mL), and the tubes were for stirred 20 min. The contents of the first reaction tube were transferred to the second test tube *via* syringe, and the mixture was stirred at room temperature for 16 h. The reaction mixture was poured into sat. aq. sodium bicarbonate solution, and extracted with methylene chloride. The combined organic extracts were dried ($MgSO_4$) and the solvent was removed *in vacuo* to give the crude product, which was purified by flash column chromatography (20% to 40% diethyl ether in petroleum ether) to give the title compound **9a** as a white solid (59.5 mg, 0.139 mmol, 78%), as a 8:1 mixture of diastereomers (by crude ^{1}H NMR) and with a 89% e.e. for the major diastereomer (by chiral HPLC, Chiralpak IC column, 3% isopropanol, 10% methylene chloride, 87% heptanes, UV wavelength 254 nm; retention times: 11.5 min (minor enantiomer, major diastereomer), 14.2 min (minor diastereomer), 15.3 min (minor diastereomer), 16.6 min (major enantiomer, major diastereomer)); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.45–7.25 (m, 5H), 5.82 (ddd, J = 17.0, 10.0, 8.5 Hz, 1H), 5.38 (d, J =

17.0 Hz, 1H), 5.28 (d, *J* = 10.0 Hz, 1H), 4.98 (ddd, *J* = 13.0, 8.0, 6.0 Hz, 1H), 4.91 (s, 1H), 3.19 (dd, *J* = 13.0, 12.5 Hz, 1H), 2.48 (dd, *J* = 12.5, 6.0 Hz, 1H), 1.61 (s, 3H), 1.56 (s, 3H), 1.14 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.3, 169.9, 133.9, 133.2, 131.6, 129.9, 129.6, 121.4, 105.7, 105.4, 66.7, 64.6, 62.1, 56.4, 44.2, 29.5, 29.4, 29.3, 28.4; IR (cm^{-1}) 2999, 1746, 1456, 1394, 1277, 1205, 1097, 1022, 930, 730, 704; HRMS (ESI+) observed 451.1364; calculated 451.1369 ($C_{23}H_{24}NaO_8$, $[M+Na]^+$); $[\alpha]^{23}_D$ = +23.38° (c = 1.0, CH_2Cl_2); m.p. 154 °C (decomposes).

(7*R*,14*S*)-1,5,9,13-Tetraoxy-3,3,11,11-tetramethyl-7-tolyl-14-vinyl-2,4,10,12-tetraoxadispiro[5.1.5.2]pentadecane **9b**

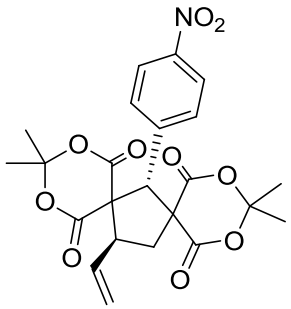


9b

An oven-dried reaction tube equipped with a stir bar was charged with palladium dibenzylideneacetone-chloroform complex (3.0 mg, 0.003 mmol) and (*R*,*R*)-**L$_3$** chiral ligand, (6.0 mg, 0.075 mmol). A second reaction tube, also equipped with a stir bar, was charged with 6,6-dimethyl-1-vinyl-5,7-dioxaspiro[2.5]octane-4,8-dione **7** (37.0 mg, 0.189 mmol) and 2,2-dimethyl-5-(4-methylbenzylidene)-1,3-dioxane-4,6-dione **8b** (60.0 mg, 0.244 mmol). Both tubes were sealed with a septum, evacuated, and backfilled with dry nitrogen. Dioxane (degassed by sparging with nitrogen for 30 min) was added to the first tube (1 mL) and second tube (3 mL), and the tubes were for stirred 20 min. The contents of the first reaction tube were transferred to the second test tube *via* syringe, and the mixture was stirred at room temperature for 16 h. The reaction mixture was poured into sat. aq. sodium bicarbonate solution, and extracted with methylene chloride. The combined organic extracts were dried ($MgSO_4$) and the solvent was removed *in vacuo* to give the crude product, which was purified by flash column chromatography (20% to 40% diethyl ether in petroleum ether) to give the title compound **9b** as a white solid (63.6 mg, 0.144 mmol, 76%), as a 12:1 mixture of diastereomers (by crude ^{1}H NMR) and with a 95% e.e. for the major diastereomer (by chiral HPLC, Chiralpak IC column, 3% isopropanol, 10% methylene chloride, 87% heptanes, UV wavelength 254

nm; retention times: 11.1 min (minor enantiomer, major diastereomer), 13.9 min (minor diastereomer), 17.8 min (minor diastereomer), 20.3 min (major enantiomer, major diastereomer)); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.21 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 5.81 (ddd, *J* = 17.5, 10.5, 8.5 Hz, 1H), 5.36 (d, *J* = 17.5 Hz, 1H), 5.23 (d, *J* = 10.5 Hz, 1H), 4.96 (ddd, *J* = 13.0, 8.5, 6.5 Hz, 1H), 4.86 (s, 1H), 3.20 (dd, *J* = 13.0, 13.0 Hz, 1H), 2.48 (dd, *J* = 13.0, 6.5 Hz, 1H), 2.29 (s, 3H), 1.63 (s, 3H), 1.58 (s, 3H), 1.19 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.4, 170.1, 167.1, 166.5, 139.9, 134.0, 131.4, 130.2, 130.1, 121.3, 105.6, 105.4, 66.5, 64.7, 62.0, 56.3, 44.2, 29.6, 29.5, 29.4, 28.4, 21.3; IR (cm^{-1}) 3000, 2946, 1769, 1747, 1516, 1393, 1276, 1205, 1091, 1045, 930, 792, 736, 703; HRMS (ESI+) observed 465.1520; calculated 465.1525 ($C_{24}H_{26}O_8Na$, $[M+Na]^+$); $[\alpha]^{23}_D$ = +30.50° (c = 1.0, CH_2Cl_2); m.p. 145 °C (decomposes).

(7*R*,14*S*)-1,5,9,13-Tetraoxy-3,3,11,11-tetramethyl-7-(4-nitrophenyl)-14-vinyl-2,4,10,12-tetraoxadispiro[5.1.5.2]pentadecane **9c**

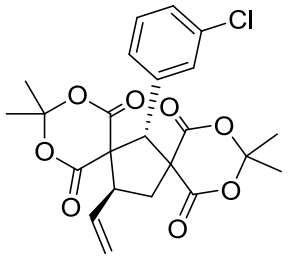


9c

An oven-dried reaction tube equipped with a stir bar was charged with palladium dibenzylideneacetone-chloroform complex (4.0 mg, 0.004 mmol) and (*R*,*R*)-**L$_3$** chiral ligand, (8.0 mg, 0.010 mmol). A second reaction tube, also equipped with a stir bar, was charged with 6,6-dimethyl-1-vinyl-5,7-dioxaspiro[2.5]octane-4,8-dione **7** (35.0 mg, 0.178 mmol) and 2,2-dimethyl-5-(4-nitrobenzylidene)-1,3-dioxane-4,6-dione **8c** (60.0 mg, 0.216 mmol). Both tubes were sealed with a septum, evacuated, and backfilled with dry nitrogen. Dioxane (degassed by sparging with nitrogen for 30 min) was added to the first tube (1 mL) and second tube (2 mL), and the tubes were for stirred 20 min. The contents of the first reaction tube were transferred to the second test tube *via* syringe, and the mixture was stirred at room temperature for 16 h. The reaction mixture was poured into sat. aq. sodium bicarbonate solution, and extracted with methylene chloride. The combined organic extracts were dried ($MgSO_4$) and the solvent was removed *in vacuo* to give the crude product,

which was purified by flash column chromatography (30% to 35% diethyl ether in petroleum ether) to give the title compound **9c** as a white solid (59.0 mg, 0.125 mmol, 70%), as a 10:1 mixture of diastereomers (by crude ^{1}H NMR) and with a 85% e.e. for the major diastereomer (by chiral HPLC, Chiralpak IC column, 2% isopropanol, 20% methylene chloride, 78% heptanes, UV wavelength 254 nm; retention times: 12.0 min (minor enantiomer, major diastereomer), 12.6 min (minor diastereomer), 14.0 min (minor diastereomer), 16.3 min (major enantiomer, major diastereomer)); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.15 (dd, *J* = 6.5, 2.0 Hz, 2H), 7.57 (dd, *J* = 6.5, 2.0 Hz, 2H), 5.77 (ddd, *J* = 17.0, 10.0, 8.5 Hz, 1H), 5.37 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.27 (dd, *J* = 10.5, 1.5 Hz, 1H), 5.12 (s, 1H), 4.85 (ddd, *J* = 13.0, 8.5, 6.5 Hz, 1H), 3.17 (dd, *J* = 13.0, 13.0 Hz, 1H), 2.52 (dd, *J* = 13.0, 6.5 Hz, 1H), 1.67 (s, 3H), 1.58 (s, 3H), 1.19 (s, 3H), 1.10 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.8, 169.3, 166.6, 166.2, 148.5, 140.2, 133.2, 132.7, 124.3, 122.1, 105.7, 105.6, 64.9, 64.3, 61.8, 56.4, 44.2, 29.7, 29.4, 29.3, 28.7; IR (cm^{-1}): 3490, 3082, 3001, 2946, 1770, 1746, 1604, 1525, 1393, 1351, 1278, 1204, 1046, 1024, 929, 732; HRMS (ESI+): observed 496.1214; calculated 496.1220 ($C_{23}H_{23}NNaO_{10}$, $[M+Na]^+$); $[\alpha]^{23}_D$ = + 30.39° (c = 1.0, CH_2Cl_2); m.p. 147 °C (decomposes).

(7*R*,14*S*)-1,5,9,13-Tetraoxy-3,3,11,11-tetramethyl-7-(3-chlorophenyl)-14-vinyl-2,4,10,12-tetraoxadispiro[5.1.5.2]pentadecane **9d**

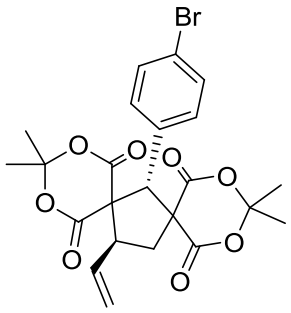


9d

An oven-dried reaction tube equipped with a stir bar was charged with palladium dibenzylideneacetone-chloroform complex (3.0 mg, 0.003 mmol) and (*R*,*R*)-**L$_3$** chiral ligand, (6.0 mg, 0.075 mmol). A second reaction tube, also equipped with a stir bar, was charged with 6,6-dimethyl-1-vinyl-5,7-dioxaspiro[2.5]octane-4,8-dione **7** (39.0 mg, 0.198 mmol) and 5-(3-chlorobenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione **8d** (60.0 mg, 0.225 mmol). Both tubes were sealed with a septum, evacuated, and backfilled with dry nitrogen. Dioxane (degassed by sparging with nitrogen for 30 min) was added to the first tube (1 mL) and second tube (3 mL), and the tubes were for stirred 20 min. The contents of the first reaction tube were transferred to the second test tube *via*

syringe, and the mixture was stirred at room temperature for 16 h. The reaction mixture was poured into sat. aq. sodium bicarbonate solution, and extracted with methylene chloride. The combined organic extracts were dried ($MgSO_4$) and the solvent was removed *in vacuo* to give the crude product, which was purified by flash column chromatography (20% to 40% diethyl ether in petroleum ether) to give the title compound **9d** as a white solid (59.7 mg, 0.129 mmol, 65%), as a 6:1 mixture of diastereomers (by crude ^{1}H NMR) and with a 89% e.e. for the major diastereomer (by chiral HPLC, Chiralpak IC column, 3% isopropanol, 10% methylene chloride, 87% heptanes, UV wavelength 254 nm; retention times: 10.5 min (minor enantiomer, major diastereomer), 15.0 min (minor diastereomer), 16.3 min (major enantiomer, major diastereomer), 22.0 min (minor diastereomer)); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.37-7.24 (m, 4H), 5.81 (ddd, *J* = 17.0, 10.0, 8.5 Hz, 1H), 5.38 (d, *J* = 17.0 Hz, 1H), 5.27 (d, *J* = 10.0 Hz, 1H), 4.92 (s, 1H), 4.94-4.88 (m, 1H), 3.19 (dd, *J* = 13.0, 13.0 Hz, 1H), 2.51 (dd, *J* = 13.0, 6.5 Hz, 1H), 1.67 (s, 3H), 1.61 (s, 3H), 1.24 (s, 3H), 1.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.1, 169.7, 166.8, 166.3, 135.3, 135.1, 133.6, 131.7, 130.8, 130.1, 129.6, 131.7, 105.7, 105.5, 65.6, 64.4, 61.8, 56.4, 44.2, 29.6, 29.4, 29.3, 28.6; IR (cm^{-1}) 3000, 1770, 1746, 1383, 1277, 1205, 1092, 1023, 932, 735; HRMS (ESI+), observed 485.0975; calculated 485.0979 ($C_{23}H_{23}ClNaO_8$, $[M+Na]^+$); $[\alpha]^{23}_D$ = +27.61° (c = 1.0, CH_2Cl_2); m.p. 156 °C (decomposes).

(7*R*,14*S*)-1,5,9,13-Tetraoxy-3,3,11,11-tetramethyl-7-(4-bromophenyl)-14-vinyl-2,4,10,12-tetraoxadispiro[5.1.5.2]pentadecane **9e**

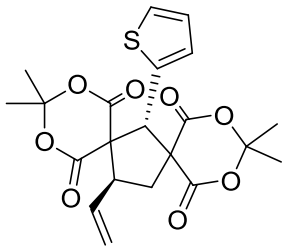


9e

An oven-dried reaction tube equipped with a stir bar was charged with palladium dibenzylideneacetone-chloroform complex (4.0 mg, 0.004 mmol) and (*R*,*R*)-**L$_3$** chiral ligand, (7.8 mg, 0.010 mmol). A second reaction tube, also equipped with a stir bar, was charged with 6,6-dimethyl-1-vinyl-5,7-dioxaspiro[2.5]octane-4,8-dione **7** (29.4 mg, 0.150 mmol) and 5-(4-bromobenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione **8e** (52.9 mg, 0.170 mmol). Both tubes were sealed with a

septum, evacuated, and backfilled with dry nitrogen. Dioxane (degassed by sparging with nitrogen for 30 min) was added to the first tube (1 mL) and second tube (2 mL), and the tubes were for stirred 20 min. The contents of the first reaction tube were transferred to the second test tube *via* syringe, and the mixture was stirred at room temperature for 16 h. The reaction mixture was poured into sat. aq. sodium bicarbonate solution, and extracted with methylene chloride. The combined organic extracts were dried ($MgSO_4$) and the solvent was removed *in vacuo* to give the crude product, which was purified by flash column chromatography (30% diethyl ether in petroleum ether) to give the title compound **9e** as a white solid (54.8 mg, 0.108 mmol, 70%), as a 6:1 mixture of diastereomers (by crude ^{1}H NMR) and with a 92% e.e. for the major diastereomer (by chiral HPLC, Chiralpak IC column, 2% isopropanol, 20% methylene chloride, 78% heptanes, UV wavelength 254 nm; retention times: 10.0 min (minor enantiomer, major diastereomer), 11.1 min (minor diastereomer), 16.5 min (minor diastereomer), 18.1 min (major enantiomer, major diastereomer)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 5.77 (ddd, *J* = 17.0, 10.0, 8.5 Hz, 1H), 5.34 (d, *J* = 17.0 Hz, 1H), 5.23 (d, *J* = 10.0 Hz, 1H), 4.92-4.83 (1H, m), 4.89 (s, 1H), 3.16 (dd, *J* = 13.0, 12.5 Hz, 1H), 2.47 (dd, *J* = 12.5, 6.0 Hz, 1H), 1.64 (s, 3H), 1.57 (s, 3H), 1.19 (s, 3H), 1.01 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.1, 169.7, 168.9, 163.4, 133.6, 133.2, 132.6, 132.1, 124.4, 131.6, 105.6, 105.5, 65.6, 64.4, 61.9, 56.4, 44.1, 29.7, 29.4, 29.3, 28.6; IR (cm^{-1}) ; HRMS (ESI+): observed 529.0465; calculated 529.0469 ($C_{23}H_{23}{}^{79}BrNaO_8$, $[M+Na]^+$); $[\alpha]^{23}_D$ = +26.96° (c = 1.0, CH_2Cl_2); m.p. 134 °C (decomposes).

(7*R*,14*S*)-1,5,9,13-Tetraoxy-3,3,11,11-tetramethyl-7-(2-thienyl)-14-vinyl-2,4,10,12-tetraoxadispiro[5.1.5.2]pentadecane **9f**

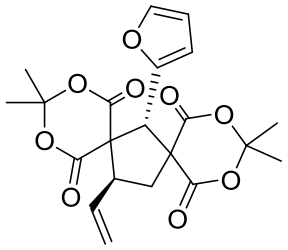


9f

An oven-dried reaction tube equipped with a stir bar was charged with palladium dibenzylideneacetone-chloroform complex (4.0 mg, 0.004 mmol) and (*R*,*R*)-**L$_3$** chiral ligand, (8.0 mg, 0.010 mmol). A second reaction tube, also equipped with a stir bar, was charged with 6,6-dimethyl-

1-vinyl-5,7-dioxaspiro[2.5]octane-4,8-dione **7** (35.0 mg, 0.178 mmol) and 2,2-dimethyl-5-(thiophen-2-ylmethylene)-1,3-dioxane-4,6-dione **8f** (60.0 mg, 0.252 mmol). Both tubes were sealed with a septum, evacuated, and backfilled with dry nitrogen. Dioxane (degassed by sparging with nitrogen for 30 min) was added to the first tube (1 mL) and second tube (3 mL), and the tubes were for stirred 20 min. The contents of the first reaction tube were transferred to the second test tube *via* syringe, and the mixture was stirred at room temperature for 16 h. The reaction mixture was poured into sat. aq. sodium bicarbonate solution, and extracted with methylene chloride. The combined organic extracts were dried ($MgSO_4$) and the solvent was removed *in vacuo* to give the crude product, which was purified by flash column chromatography (30% to 35% diethyl ether in petroleum ether) to give the title compound **9f** as a white solid (25.0 mg, 0.058 mmol, 32%), as a 8:1 mixture of diastereomers (by crude ^{1}H NMR) and with a 96% e.e. for the major diastereomer (by chiral HPLC, Chiralpak IC column, 0.5% ethanol, 20% methylene chloride, 79.5% heptanes, UV wavelength 254 nm; retention times: 14.6 min (minor enantiomer, major diastereomer), 20.9 min (major enantiomer, major diastereomer), 23.1 min (minor diastereomer, overlapping)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.16 (dd, *J* = 4.0, 1.0 Hz, 1H), 6.97 (dd, *J* = 5.0, 4.0 Hz, 1H), 5.75 (ddd, *J* = 17.0, 10.0, 8.5 Hz, 1H), 5.34 (d, *J* = 17.0 Hz, 1H), 5.23 (d, *J* = 10.0 Hz, 1H), 5.22 (s, 1H), 4.87 (ddd, *J* = 13.0, 8.5, 6.0 Hz, 1H), 3.15 (dd, *J* = 13.0, 13.0 Hz, 1H), 2.46 (dd, *J* = 13.0, 6.0 Hz, 1H), 1.66 (s, 3H) 1.60 (s, 3H), 1.30 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.1, 169.8, 166.9, 166.4, 133.6, 133.5, 131.6, 128.7, 127.0, 121.6, 105.7, 105.5, 64.6, 62.6, 60.0, 56.6, 44.4, 29.7, 29.3, 29.2, 28.7; IR (cm^{-1}): 3485, 2998, 1769, 1744, 1395, 1384, 1277, 1247, 1203, 831, 703; HRMS (ESI+) observed 457.0927; calculated 457.0933 ($C_{21}H_{22}NaO_8S$, $[M+Na]^+$); $[\alpha]^{23}_D$ = +26.95° (c = 1.0, CH_2Cl_2); m.p. 154 °C (decomposes).

(7*R*,14*S*)-1,5,9,13-Tetraoxy-3,3,11,11-tetramethyl-7-(2-furyl)-14-vinyl-2,4,10,12-tetraoxadispiro[5.1.5.2]pentadecane **9g**

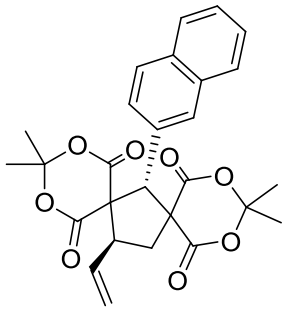


9g

An oven-dried reaction tube equipped with a stir bar was charged with palladium dibenzylideneacetone-chloroform complex (4.0 mg, 0.004 mmol) and (*R*,*R*)-$\mathbf{L_3}$ chiral ligand, (8.0 mg, 0.010 mmol). A second reaction tube, also equipped with a stir bar, was charged with 6,6-dimethyl-1-vinyl-5,7-dioxaspiro[2.5]octane-4,8-dione **7** (35.0 mg, 0.178 mmol) and 5-(furan-2-ylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione **8g** (55.0 mg, 0.248 mmol). Both tubes were sealed with a septum, evacuated, and backfilled with dry nitrogen. Dioxane (degassed by sparging with nitrogen for 30 min) was added to the first tube (1 mL) and second tube (3 mL), and the tubes were for stirred 20 min. The contents of the first reaction tube were transferred to the second test tube *via* syringe, and the mixture was stirred at room temperature for 16 h. The reaction mixture was poured into sat. aq. sodium bicarbonate solution, and extracted with methylene chloride. The combined organic extracts were dried ($MgSO_4$) and the solvent was removed *in vacuo* to give the crude product, which was purified by flash column chromatography (30% to 35% diethyl ether in petroleum ether) to give the title compound **9g** as a white solid (39.0 mg, 0.093 mmol, 52%), as a 7:1 mixture of diastereomers (by crude ^{1}H NMR) and with a 85% e.e. for the major diastereomer (by chiral HPLC, Chiralpak IC column, 0.5% ethanol, 20% methylene chloride, 79.5% heptanes, UV wavelength 254 nm; retention times: 15.6 min (minor enantiomer, major diastereomer), 21.7 min (minor diastereomer, overlapping), 26.2 min (major enantiomer, major diastereomer)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (d, *J* = 2.0 Hz, 1H), 6.44 (d, *J* = 3.5 Hz, 1H), 6.33 (dd, *J* = 3.5, 2.0 Hz, 1H), 5.71 (ddd, *J* = 17.0, 10.0, 8.5 Hz, 1H), 5.32 (d, *J* = 17.0 Hz, 1H), 5.22 (d, *J* = 10.0 Hz, 1H), 5.11 (s, 1H), 4.82 (ddd, *J* = 13.0, 8.5, 6.0 Hz, 1H), 3.18 (dd, *J* = 13.0, 13.0 Hz, 1H), 2.46 (dd, *J* = 13.0, 6.0 Hz, 1H), 1.68 (s, 3H), 1.61 (s, 3H), 1.33 (s, 3H), 1.17 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.7, 169.6, 166.4, 165.7, 147.0, 142.3, 133.1, 121.7, 113.9, 112.4, 105.6, 105.5, 63.5, 60.8, 58.1, 56.4, 44.7, 29.3, 29.1, 29.0, 28.7; IR (cm^{-1}): 3489, 1772, 1746, 1394, 1277, 1249, 1205, 1016, 943; HRMS (ESI+),

observed 441.1158; calculated 441.1162 ($C_{21}H_{22}NaO_9$, $[M+Na]^+$); $[\alpha]^{23}_D$ = +22.09° (c = 1.0, CH_2Cl_2); m.p. 143 °C (decomposes).

(7*R*,14*S*)-1,5,9,13-Tetraoxy-3,3,11,11-tetramethyl-7-(2-naphthyl)-14-vinyl-2,4,10,12-tetraoxadispiro[5.1.5.2]pentadecane **9h**

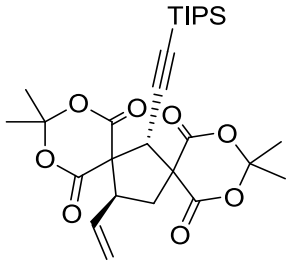


9h

An oven-dried reaction tube equipped with a stir bar was charged with palladium dibenzylideneacetone-chloroform complex (3.0 mg, 0.003 mmol) and (*R*,*R*)-**L$_3$** chiral ligand, (6.0 mg, 0.075 mmol). A second reaction tube, also equipped with a stir bar, was charged with 6,6-dimethyl-1-vinyl-5,7-dioxaspiro[2.5]octane-4,8-dione **7** (36.0 mg, 0.183 mmol) and 2,2-dimethyl-5-(naphthalen-2-ylmethylene)-1,3-dioxane-4,6-dione **8h** (55.0 mg, 0.195 mmol). Both tubes were sealed with a septum, evacuated, and backfilled with dry nitrogen. Dioxane (degassed by sparging with nitrogen for 30 min) was added to the first tube (1 mL) and second tube (3 mL), and the tubes were for stirred 20 min. The contents of the first reaction tube were transferred to the second test tube *via* syringe, and the mixture was stirred at room temperature for 16 h. The reaction mixture was poured into sat. aq. sodium bicarbonate solution, and extracted with methylene chloride. The combined organic extracts were dried ($MgSO_4$) and the solvent was removed *in vacuo* to give the crude product, which was purified by flash column chromatography (20% to 40% diethyl ether in petroleum ether) to give the title compound **9h** as a white solid (60.4 mg, 0.126 mmol, 69%), as a 8:1 mixture of diastereomers (by crude ^{1}H NMR) and with a 93% e.e. for the major diastereomer (by chiral HPLC, Chiralpak IC column, 3% isopropanol, 10% methylene chloride, 87% heptanes, UV wavelength 254 nm; retention times: 10.2 min (minor enantiomer, major diastereomer), 14.5 min (minor diastereomer), 16.2 min (major enantiomer, major diastereomer), 21.2 min (minor diastereomer)); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.86-7.67 (m, 4H), 7.58-7.35 (m, 3H), 5.82 (ddd, *J* = 17.0, 10.5, 8.5 Hz, 1H), 5.38 (d, *J* = 17.0 Hz, 1H), 5.25 (d, *J* = 10.5 Hz, 1H), 5.16 (s, 1H), 5.01

(ddd, J = 13.5, 8.0, 6.0 Hz, 1H), 3.24 (dd, J = 13.5, 12.5 Hz, 1H), 2.52 (dd, J = 12.5, 6.0 Hz, 1H), 1.57 (s, 3H), 1.53 (s, 3H), 1.07 (s, 3H), 0.73 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.4, 170.0, 167.1, 166.6, 133.9, 133.5, 133.2, 131.7, 130.5, 129.4, 128.7, 128.1, 127.8, 127.5, 126.9, 121.4, 105.6, 105.4, 66.7, 64.7, 62.0, 56.4, 44.4, 29.6, 29.4, 29.3, 28.4; IR (cm^{-1}) 3060, 3001, 1746, 1444, 1382, 1274, 1204, 1093, 1046, 930, 805, 737, 703; HRMS (ESI+) observed 501.1522; calculated 501.1525 ($C_{27}H_{26}NaO_8$, $[M+Na]^+$); $[\alpha]^{23}_D$ = +26.95° (c = 1.0, CH_2Cl_2); m.p. 105 °C.

(7*R*,14*S*)-1,5,9,13-Tetraoxy-3,3,11,11-tetramethyl-7-(triisopropylsilylethynyl)-14-vinyl-2,4,10,12-tetraoxadispiro[5.1.5.2]pentadecane **9i**

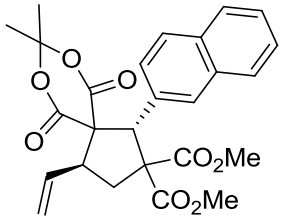


9i

An oven-dried reaction tube equipped with a stir bar was charged with palladium dibenzylideneacetone-chloroform complex (2.0 mg, 0.002 mmol) and (*R*,*R*)-**L$_3$** chiral ligand, (4.0 mg, 0.005 mmol). A second reaction tube, also equipped with a stir bar, was charged with 6,6-dimethyl-1-vinyl-5,7-dioxaspiro[2.5]octane-4,8-dione **7** (35.0 mg, 0.178 mmol) and 2,2-dimethyl-5-(3-(triisopropylsilyl)prop-2-yn-1-ylidene)-1,3-dioxane-4,6-dione **8i** (70.0 mg, 0.208 mmol). Both tubes were sealed with a septum, evacuated, and backfilled with dry nitrogen. Dioxane (degassed by sparging with nitrogen for 30 min) was added to the first tube (1 mL) and second tube (3 mL), and the tubes were for stirred 20 min. The contents of the first reaction tube were transferred to the second test tube *via* syringe, and the mixture was stirred at room temperature for 16 h. The reaction mixture was poured into sat. aq. sodium bicarbonate solution, and extracted with methylene chloride. The combined organic extracts were dried ($MgSO_4$) and the solvent was removed *in vacuo* to give the crude product, which was purified by flash column chromatography (10% to 20% to 40% diethyl ether in petroleum ether) to give the title compound **9i** as a white solid (72.0 mg, 0.135 mmol, 76%), as a 12:1 mixture of diastereomers (by crude ^{1}H NMR) and with a 89% e.e. for the major diastereomer (by chiral HPLC, Chiralpak IC column, 2% isopropanol, 20% methylene chloride, 78% heptanes, UV wavelength 254 nm; retention times: 5.8 min (minor enantiomer, major

diastereomer), 9.2 min (minor diastereomer, overlapping), 9.8 min (major enantiomer, major diastereomer); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.66 (ddd, *J* = 17.5, 10.5, 8.5 Hz, 1H), 5.30 (d, *J* = 17.5 Hz, 1H), 5.18 (d, *J* = 10.5 Hz, 1H), 4.66 (ddd, *J* = 13.5, 8.5, 6.0 Hz, 1H), 4.51 (s, 1H), 3.14 (dd, *J* = 13.5, 12.5 Hz, 1H), 2.41 (dd, *J* = 12.5, 6.0 Hz, 1H), 1.77 (s, 3H), 1.76 (s, 3H), 1.75 (s, 3H), 1.69 (s, 3H), 1.05-0.97 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.8, 168.8, 165.8, 164.3, 132.6, 121.8, 105.4, 99.0, 94.5, 91.5, 63.2, 60.4, 56.0, 51.9, 44.7, 30.4, 29.5, 29.2, 28.9, 18.6, 11.3; IR (cm^{-1}) 3001, 2944, 2866, 2173, 1754, 1639, 1463, 1384, 1276, 1205, 1077, 1020, 924, 883, 735, 679; HRMS (ESI+) observed 555.2384; calculated 555.2390 ($C_{28}H_{40}NaO_8Si$, $[M+Na]^+$); $[\alpha]^{23}_D$ = +30.32° (c = 1.0, CH_2Cl_2); m.p. 114 °C (decomposes).

(1*R*,4*S*)-Dimethyl 8,8-dimethyl-1-(naphthalen-2-yl)-6,10-dioxo-4-vinyl-7,9-dioxaspiro[4.5]decane-2,2-dicarboxylate **10**

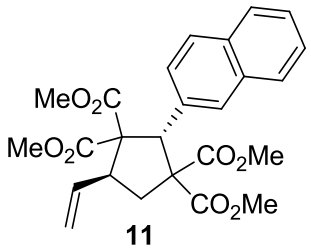


10

To a stirred solution of (7*R*,14*S*)-1,5,9,13-tetraoxy-3,3,11,11-tetramethyl-7-(2-naphthyl)-14-vinyl-2,4,10,12-tetraoxadispiro[5.1.5.2]pentadecane **9h** (56.0 mg, 0.117 mmol) in anhydrous methanol (2 mL) was added a solution of sodium methoxide (200 μL, 0.58 M in methanol, 0.117 mmol). The reaction was stirred for 1 h at room temperature, then quenched by addition of excess aqueous 1 M sodium bisulfate solution. The reaction mixture was extracted twice with methylene chloride, and the combined organic extracts concentrated *in vacuo*. The crude residue was dissolved in a mixture of dimethoxyethane (1 mL) and methanol (1 mL). Trimethylsilyldiazomethane (200 μL, 2 M in diethyl ether, 0.400 mmol) was added. The reaction was allowed to stir for 20 min, then quenched by dropwise addition of acetic acid until no further effervescence was observed. The reaction mixture was diluted with diethyl ether and washed with sat. aq. sodium bicarbonate solution. The organic layer was dried (Na_2SO_4) and concentrated *in vacuo* to give the crude product, which was purified by flash column chromatography (20% to 30% diethyl ether in petroleum ether) to give the title compound **10** as a waxy solid (51.2 mg, 0.110 mmol, 94%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.81-7.36 (m, 4H), 7.47-7.45 (m, 2H), 7.39 (dd, *J* = 8.5, 1.5 Hz, 1H), 5.78 (ddd, *J* = 17.5, 10.5, 8.5 Hz,

1H), 5.33 (d, *J* = 17.5 Hz, 1H), 5.20 (d, *J* = 10.5 Hz, 1H), 5.14 (s, 1H), 4.32 (ddd, *J* = 12.0, 8.5, 8.0 Hz, 1H), 3.74 (s, 3H), 3.20 (s, 3H), 3.09 (dd, *J* = 13.5, 8.0 Hz, 1H), 2.73 (dd, *J* = 13.5, 12.0 Hz, 1H), 1.56 (s, 3H), 1.44 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.4, 170.1, 168.6, 166.6, 134.4, 133.2, 133.1, 132.2, 131.2, 128.5, 127.9, 127.7, 126.9, 126.5, 120.6, 105.5, 66.3, 65.1, 61.2, 54.4, 53.7, 53.6, 52.7, 39.4, 29.6, 29.3; IR (cm^{-1}): 3581, 2950, 1736, 1432, 1391, 1380, 1249, 1203, 1151, 1091, 1021; HRMS (ESI+) observed 467.1699; calculated 467.1706 ($C_{26}H_{27}O_8$, $[M+H]^+$); $[\alpha]^{23}_D$ = +24.04° (c = 1.0, CH_2Cl_2).

(2*R*,4*S*)-Tetramethyl 2-(naphthalen-2-yl)-4-vinylcyclopentane-1,1,3,3-tetracarboxylate **11**

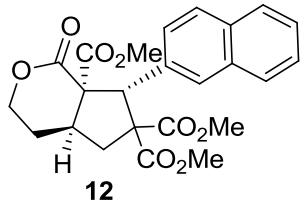


11

To a stirred solution of (7*R*,14*S*)-1,5,9,13-tetraoxy-3,3,11,11-tetramethyl-7-(2-naphthyl)-14-vinyl-2,4,10,12-tetraoxadispiro[5.1.5.2]pentadecane **9h** (83 mg, 0.173 mmol) in anhydrous methanol (2 mL) was added a solution of sodium methoxide (750 μl, 0.58 M in methanol, 0.435 mmol). The reaction was stirred at room temperature for 1 h, then quenched by addition of excess aqueous 1 M sodium bisulfate. The reaction mixture was extracted twice with methylene chloride, and the combined organic extracts concentrated *in vacuo*. The crude residue was dissolved in a mixture of dimethoxyethane (1 mL) and methanol (1 mL). Trimethylsilyldiazomethane (0.20 mL, 2 M in diethyl ether, 0.400 mmol) was added and the reaction was allowed to stir for 20 min, then quenched by dropwise addition of acetic acid until no further effervescence was observed. The reaction mixture was diluted with diethyl ether, washed with sat. aq. sodium bicarbonate solution and the organic layer was dried (Na_2SO_4) and concentrated *in vacuo* to give the crude product, which was purified by flash column chromatography gave the title compound **11** as a waxy solid (61.6 mg, 0.136 mmol, 78%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.78-7.65 (m, 4H), 7.43-7.40 (m, 2H), 7.26-7.23 (m, 1H), 5.95 (ddd, *J* = 17.5, 10.5, 6.5 Hz, 1H), 5.28 (s, 1H), 5.24 (d, *J* = 17.5 Hz, 1H), 5.16 (d, *J* = 10.5 Hz, 1H), 4.14-4.07 (m, 1H), 3.79 (s, 3H), 3.66 (s, 3H), 2.95 (s, 3H), 2.86 (dd, *J* = 13.5, 6.5 Hz, 1H), 2.81 (s, 3H), 2.12 (dd, *J* = 13.5, 13.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.7, 171.2, 170.8, 169.7, 136.2, 135.9, 133.1, 132.5, 128.5, 128.3, 127.6, 127.3, 126.3, 126.2, 116.8, 69.5, 65.4, 56.5, 53.3,

52.5, 52.4, 52.1, 49.8, 36.1; IR (cm^{-1}): 2950, 1733, 1432, 1245, 1203, 1178, 1116, 1093, 1061, 935, 748, 700; HRMS (ESI+): observed 455.1701; calculated 455.1706 ($C_{25}H_{27}O_8$, $[M+H]^+$); $[\alpha]^{23}_D$ = +36.04° (c = 1.0, CH_2Cl_2).

(4*aS*,7*R*,7*aR*)-Trimethyl 7-(naphthalen-2-yl)-1-oxohexahydrocyclopenta[*c*]pyran-6,6,7*a*(1*H*)-tricarboxylate **12**



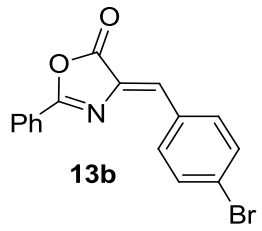
12

A solution of (2*R*,4*S*)-tetramethyl 2-(naphthalen-2-yl)-4-vinylcyclopentane-1,1,3,3-tetracarboxylate **11** (42.0 mg, 0.092 mmol) and dicyclohexylborane (21.0 mg, 0.118 mmol) in tetrahydrofuran (0.5 mL) was stirred at room temperature for 14 h. Aqueous sodium acetate (1.0 mL, 5.0 M, 5.0 mmol) was added, followed by hydrogen peroxide (1.0 mL, 30% in water). The reaction was allowed to stir for 6 h, and then quenched by addition to aqueous sodium bicarbonate solution. The mixture was extracted with diethyl ether, and the organic extracts washed with water, dried (Na_2SO_4) and concentrated *in vacuo* to give the crude product, which was purified by flash column chromatography (20% - 50% ethyl acetate in petroleum ether) to give the corresponding primary alcohol as a colorless oil (20 mg, 0.042 mmol, 46%), which was used directly in the next step.

A stirred solution of the alcohol (20 mg, 0.042 mmol, 46%) and p-toluenesulfonic acid monohydrate (10.0 mg, 0.05 mmol) in chloroform (1 mL) heated to 60 °C for 4 h, after which time thin layer chromatography showed complete consumption of the intermediate alcohol (R_f = 0.3 in 50% ethyl acetate/petroleum ether), and formation of a new product (R_f = 0.6 in 50% ethyl acetate/petroleum ether). The solvent was removed *in vacuo*, and the crude reaction mixture purified by flash column chromatography (30% ethyl acetate in petroleum ether) to give the title compound **12** as a colorless oil (16.1 mg, 0.037 mmol, 87%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.81-7.71 (m, 4H), 7.47-7.42 (m, 2H), 7.28 (dd, *J* = 8.5, 2.0 Hz, 1H), 5.51 (s, 1H), 4.31 (ddd, *J* = 11.5, 5.5, 2.5 Hz, 1H), 4.17-4.08 (m, 2H), 3.74 (s, 3H), 3.15 (s, 3H), 3.05 (dd, *J* = 13.5, 8.5 Hz, 1H), 3.03 (s, 3H), 2.37 (ddd, *J* = 13.5, 9.0, 2.5 Hz, 1H), 1.92 (dd, *J* = 14.0, 10.5 Hz, 1H), 1.90-1.83 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.3, 170.3, 169.9, 168.9, 134.6, 133.2, 132.7, 129.3, 128.3, 127.6, 127.6, 126.4, 126.3, 91.2, 67.3, 66.2, 65.4, 57.5, 53.5, 53.2, 52.5, 41.1, 39.5, 28.3; IR (cm^{-1}) 2950, 2917, 1732, 1432, 1260, 1234, 1166,

1136, 1083, 1070; HRMS (ESI+), observed 441.1543; calculated 441.1549 ($C_{24}H_{25}O_8$, $[M+H]^+$); $[\alpha]^{23}_D = -11.16°$ (c = 0.5, CH_2Cl_2).

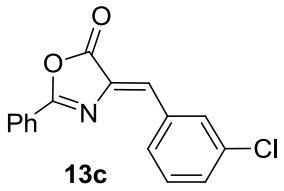
(*Z*)-4-(4-Bromobenzylidene)-2-phenyloxazol-5(4*H*)-one **13b**



13b

According to General Procedure A reported by Chavez *et al.*[16] A stirred solution of 4-bromobenzaldehyde (2.40 g, 13.0 mmol), hippuric acid (2.85 g, 15.9 mmol), acetic anhydride (4.87 g, 48 mmol, 4.5 mL) and diisopropylethylamine (1.03 g, 8.0 mmol, 1.5 mL) was heated to 40 °C under reflux for 40 min. The reaction was allowed to cool to room temperature, diluted with 50% aqueous ethanol solution (15 mL), and then cooled to -20 °C in the freezer for 30 min. The resulting solid was filtered to and recrystallized from hot toluene to give the title compound **13b** as a powdery yellow solid (1.73 g, 5.27 mmol, 41%); ^{1}H NMR (400MHz, $CDCl_3$) δ = 8.20-8.16 (m, 2H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.67-7.58 (m, 3H), 7.54 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.17 (s, 1H); m.p. 188 °C (lit. 197-199 °C); spectral data in accordance with the literature.[11]

(*Z*)-4-(4-Chlorobenzylidene)-2-phenyloxazol-5(4*H*)-one **13c**

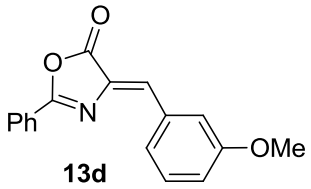


13c

According to General Procedure A reported by Chavez *et al.*[16] A stirred solution of 3-chlorobenzaldehyde (1.80 g, 13.0 mmol), hippuric acid (2.85 g, 15.9 mmol), acetic anhydride (4.87 g, 48 mmol, 4.5 mL) and diisopropylethylamine (1.03 g, 8.0 mmol, 1.5 mL) was heated to 40 °C under reflux for 40 min. The reaction was allowed to cool to room temperature, diluted with 50% aqueous ethanol solution (15 mL), and then cooled to -20 °C in the freezer for 30 min. The resulting solid was filtered to and recrystallized from hot toluene to give the title compound **13c** as a feathery yellow solid (1.15 g, 4.05 mmol, 31%); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.31 (s, 1H), 8.20 (dd, *J* =

8.5, 1.0 Hz, 2H), 8.04-7.98 (m, 1H), 7.64 (tt, *J* = 7.0, 1.0 Hz, 1H), 7.58-7.52 (m, 2H), 7.45-7.40 (m, 2H), 7.17 (s, 1H); m.p. 163-165 °C (lit. 166 °C); spectral data in accordance with the literature.[17]

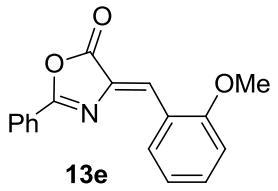
(*Z*)-4-(3-Methoxybenzylidene)-2-phenyloxazol-5(4*H*)-one **13d**



13d

According to General Procedure A reported by Chavez *et al.*[16] To a stirred solution of 3-methoxybenzaldehyde (2.10 g, 15.0 mmol), hippuric acid (3.00 g, 16.7 mmol), acetic anhydride (3.30 g, 32 mmol, 3.1 mL) in tetrahydrofuran (24 mL) was added sodium acetate (820 mg, 10.0 mmol). The reaction mixture was heated to 60 °C under reflux for 3 h, then allowed to cool to room temperature and the solvent removed *in vacuo*. The resulting solid was filtered, washed on the filter successively with water, sat. aq. sodium bicarbonate, water and ethanol to give the crude product, which was recrystallized from hot ethanol to give the title compound **13d** as a yellow solid (1.39 g, 4.98 mmol, 33%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (dd, *J* = 8.5, 1.0 Hz, 2H), 7.94 (s, 1H), 7.68 (d, *J* = 7.5 Hz, 1H), 7.62 (dd, *J* = 7.0 Hz, 1H), 7.58-7.48 (m, 2H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.23 (s, 1H), 7.06-6.92 (m, 1H), 3.92 (s, 3H); m.p. 99–102 °C (lit. 103.5-104 °C); spectral data in accordance with the literature.[18]

(*Z*)-4-(2-Methoxybenzylidene)-2-phenyloxazol-5(4*H*)-one **13e**

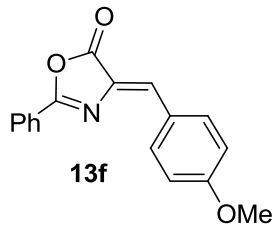


13e

According to General Procedure A reported by Chavez *et al.*[16] To a stirred solution of 2-methoxybenzaldehyde (1.60 g, 11.0 mmol), hippuric acid (2.70 g, 15.1 mmol), acetic anhydride (4.20 g, 41 mmol, 4.0 mL) in tetrahydrofuran (20 mL) was added sodium acetate (300 mg, 3.60 mmol). The reaction mixture was heated to 60 °C under reflux for 3 h, then allowed to cool to room temperature and the solvent removed *in vacuo*. The resulting solid was filtered, washed on the filter successively with water, sat. aq. sodium bicarbonate, water and ethanol to give the crude

product, which was recrystallized from hot ethanol to give the title compound **13e** as an off-white solid (2.57 g, 9.20 mmol, 84%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (dd, *J* = 8.0, 1.0 Hz, 2H), 7.57-7.50 (m, 1H), 7.50-7.37 (m, 4H), 7.31 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.99-6.85 (m, 2H), 3.93 (s, 3H); m.p. 156–157 °C (lit. 154 °C); spectral data in accordance with the literature.[19]

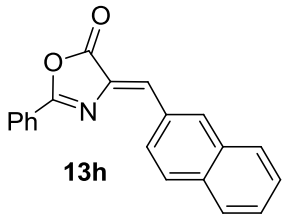
(*Z*)-4-(4-Methoxybenzylidene)-2-phenyloxazol-5(4*H*)-one **13f**



13f

To a stirred solution of 4-methoxybenzaldehyde (1.20 g, 8.80 mmol), hippuric acid (2.70 g, 15.1 mmol), acetic anhydride (5.40 g, 53 mmol, 5.0 mL) in tetrahydrofuran (20 mL) was added sodium acetate (300 mg, 3.60 mmol). The reaction mixture was heated to 60 °C under reflux for 3 h, then allowed to cool to room temperature and the solvent removed *in vacuo*. The resulting solid was filtered, washed on the filter successively with water, sat. aq. sodium bicarbonate, water and ethanol to give the crude product, which was recrystallized from hot ethanol to give the title compound **13f** as an off-white solid (1.36 g, 48.7 mmol, 55%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.24-8.14 (m, 4H), 7.59 (dd, *J* = 7.0, 7.0 Hz, 1H), 7.58-7.49 (m, 2H), 7.23 (s, 1H), 7.01 (d, *J* = 9.0 Hz, 2H), 3.90 (s, 3H); m.p. 145-147 °C (lit. 143 °C); spectral data in accordance with the literature.[11]

(*Z*)-4-(Naphthalen-2-ylmethylene)-2-phenyloxazol-5(4*H*)-one **13h**

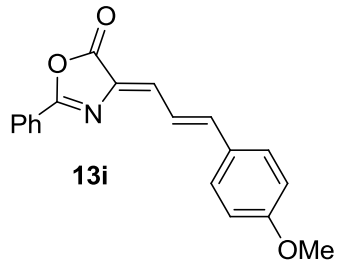


13h

According to General Procedure A reported by Chavez *et al.*[16] To a stirred solution of 2-naphthaldehyde (1.80 g, 12.0 mmol), hippuric acid (2.70 g, 15.1 mmol), acetic anhydride (5.40 g, 53 mmol, 5.0 mL) in tetrahydrofuran (20 mL) was added sodium acetate (300 mg, 3.60 mmol). The reaction mixture was heated to 60 °C under reflux for 3 h, then allowed to cool to room temperature and the solvent removed *in vacuo*. The resulting solid was filtered, washed on the filter successively

with water, sat. aq. sodium bicarbonate, water and ethanol to give the crude product, which was recrystallized from hot ethanol to give the title compound **13h** as a bright yellow solid (1.72 g, 5.74 mmol, 48%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.54 (d, *J* = 8.5 Hz, 1H), 8.48 (s, 1H), 8.25-8.21 (m, 2H), 7.97-7.90 (m, 2H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.63 (tt, *J* = 7.0, 1.5 Hz, 1H), 7.60-7.51 (m, 4H), 7.42 (s, 1H); m.p. 135-138 °C (lit. 154 °C); spectral data in accordance with the literature.[20]

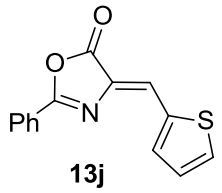
(*Z*)-4-((*E*)-3-(4-Methoxyphenyl)allylidene)-2-phenyloxazol-5(4*H*)-one **13i**



13i

According to General Procedure A reported by Chavez *et al.*[16] To a stirred solution of (*E*)-3-(4-methoxyphenyl)acrylaldehyde (2.00 g, 12.0 mmol), hippuric acid (2.70 g, 15.1 mmol), acetic anhydride (4.20 g, 41 mmol, 4.0 mL) in tetrahydrofuran (20 mL) was added sodium acetate (300 mg, 3.60 mmol). The reaction mixture was heated to 60 °C under reflux for 3 h, then allowed to cool to room temperature and poured into sat. aq. sodium bicarbonate solution and diluted with diethyl ether. The organic phase was washed successively with water, and brine, leading to the formation of an emulsion, which was collected by suction filtration and recrystallized from hot ethanol to give the title compound **13i** as a bright orange solid (400 mg, 1.31 mmol, 11%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (dd, *J* = 7.0, 1.5 Hz, 2H), 7.59-7.51 (m, 6H), 7.14 (dd, *J* = 11.5, 1.0 Hz, 1H), 7.09 (d, *J* = 15.0 Hz, 1H), 6.93 (dt, *J* = 8.5, 1.5 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.2, 161.8, 161.5, 144.3, 134.0, 133.1, 133.1, 130.0, 129.2, 129.1, 128.2, 126.0, 121.6, 114.7, 55.7; IR (cm^{-1}): 1777, 1645, 1594, 1569, 1509, 1337, 1306, 1254, 1167, 1029, 967, 875, 817, 695, 680; HRMS (ESI+): observed 328.0945; calculated 328.0950 ($C_{19}H_{15}NNaO_3$, $[M+Na]^+$); m.p. 156-158 °C.

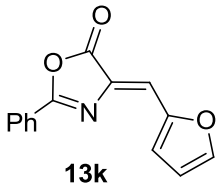
(*Z*)-2-Phenyl-4-(thiophen-2-ylmethylene)oxazol-5(4*H*)-one **13j**



13j

To a stirred solution of 2-thiophenecarboxaldehyde (1.20 g, 10.7 mmol), hippuric acid (2.70 g, 15.1 mmol), acetic anhydride (5.40 g, 53 mmol, 5.0 mL) in tetrahydrofuran (20 mL) was added sodium acetate (300 mg, 3.60 mmol). The reaction mixture was heated to 60 °C under reflux for 3 h, then allowed to cool to room temperature and the solvent removed *in vacuo*. The resulting solid was filtered, washed on the filter successively with water, sat. aq. sodium bicarbonate, water and ethanol to give the crude product, which was recrystallized from hot ethanol to give the title compound **13j** as a bright yellow feathery solid (820 mg, 3.21 mmol, 30%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.20-8.15 (m, 2H), 7.73 (d, *J* = 5.0 Hz, 1H), 7.64 (d, *J* = 3.5 Hz, 1H), 7.62-7.57 (m, 1H), 7.57-7.48 (m, 3H), 7.17 (dd, *J* = 5.0, 4.0 Hz, 1H); m.p. 161–164 °C (lit. 176-178 °C); spectral data in accordance with the literature.[21]

(*Z*)-4-(Furan-2-ylmethylene)-2-phenyloxazol-5(4*H*)-one **13k**

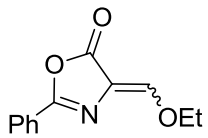


13k

According to General Procedure A reported by Chavez *et al.*[16] To a stirred solution of 2-furancarboxaldehyde (1.20 g, 12.5 mmol), hippuric acid (2.70 g, 15.1 mmol), acetic anhydride (5.40 g, 53 mmol, 5.0 mL) in tetrahydrofuran (20 mL) was added sodium acetate (300 mg, 3.60 mmol). The reaction mixture was heated to 60 °C under reflux for 3 h, then allowed to cool to room temperature and the solvent removed *in vacuo*. The resulting solid was filtered, washed on the filter successively with water, sat. aq. sodium bicarbonate, water and ethanol to give the crude product, which was recrystallized from hot ethanol to give the title compound **13k** as a bright yellow feathery solid (1.76 g, 7.36 mmol, 59%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.20-8.13 (m, 2H), 7.69 (dd, *J* = 1.5,

0.5 Hz, 1H), 7.64-7.56 (m, 2H), 7.56-7.49 (m, 2H), 7.19 (s, 1H), 6.67 (ddt, *J* = 2.5, 1.5, 0.5 Hz, 1H); m.p. 158-160 °C (lit. 168-169 °C);[21] spectral data in accordance with the literature.[22]

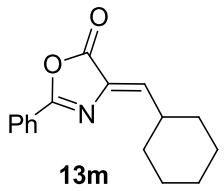
4-(Ethoxymethylene)-2-phenyloxazol-5(4*H*)-one **13l**



13l

According to the procedure of Stammer *et al.*[23] A stirred solution of hippuric acid (9.00 g, 50.0 mmol) and triethylorthoformate (8.90 g, 60 mmol, 10.0 mL) in acetic anhydride (20 mL) under a nitrogen atmosphere was heated under reflux to 135 °C for 45 min; a red-brown solution formed. The reaction was then allowed to cool and poured into a mizture of diethyl ether and sat. aq. sodium bicarbonate solution. The organic layer was carefully washed twice with saturated aqueous sodium bicarbonate, dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was crystallized from hot isopropanol (50 mL) to give a brown solid, which was filtered and washed on the filter with water to give the title compound **13l** as an off-white solid (4.90 g, 22.6 mmol, 45%, 3:1 mixture of *E*/*Z* isomers) which was used directly without further purification; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09-8.04 (m, 2H), 7.53 (tt, *J*= 9.0, 1.5 Hz, 1H), 7.49-7.43 (m, 2H), 7.35 (s, 1H), 4.43 (q, *J* = 7.0 Hz, 2H), 1.49 (t, *J* = 7.0 Hz, 3H); m.p. 94-96 °C (lit. 94-95 °C); spectral data in accordance with the literature.[23]

(*Z*)-4-(Cyclohexylmethylene)-2-phenyloxazol-5(4*H*)-one **13m**

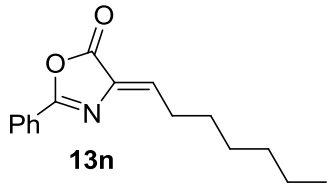


13m

According to General Procedure A reported by Chavez *et al.*[16] To a stirred solution of cyclohexanecarboxaldehyde (1.80 g, 16.0 mmol), hippuric acid (2.70 g, 15.1 mmol), acetic anhydride (5.40 g, 53 mmol, 5.0 mL) in tetrahydrofuran (20 mL) was added sodium acetate (300 mg, 3.60 mmol). The reaction mixture was heated to 60 °C under reflux for 3 h, then allowed to cool to room temperature and the solvent removed *in vacuo*. The resulting solid was filtered, washed on the

filter successively with water, sat. aq. sodium bicarbonate, water and ethanol to give the crude product, which was recrystallized from hot ethanol to give the title compound **13m** as an off-white solid (1.45 g, 5.68 mmol, 36%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (dd, *J* = 7.0, 1.0 Hz, 2H), 7.61-7.55 (m, 1H), 7.53-7.47 (m, 2H), 6.55 (d, *J* = 10.0 Hz, 1H), 3.03 (td, *J* = 10.5, 3.5 Hz, 1H), 1.88-1.69 (m, 5H), 1.48-1.18 (m, 5H); m.p. 94-98 °C (lit. 114 °C); spectral data in accordance with the literature.[24]

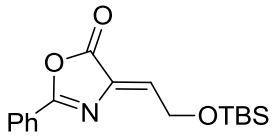
(*Z*)-4-Heptylidene-2-phenyloxazol-5(4*H*)-one **13n**



13n

According to the procedure reported by Paradisi *et al.*[25] A suspension of 2-phenyloxazol-5(4*H*)-one (107 mg, 0.660 mmol), heptaldehyde (81 mg, 0.720 mmol) and alumina (1.00 g, Brockmann Grade I, basic) in methylene chloride (1.0 mL) was stirred vigorously for 5 min at room temperature. The reaction was concentrated *in vacuo*, petroleum ether (3 mL) was added and the resulting slurry was purified by silica gel chromatography (10% to 20% to 40% methylene chloride in petroleum ether) to give the title compound **13n** as a viscous liquid (46 mg, 0.179 mmol, 27%); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.10 (dd, *J* = 8.5, 1.0 Hz, 2H), 7.64-7.56 (m, 1H), 7.56-7.44 (m, 2H), 6.72 (t, *J* = 8.0 Hz, 1H), 2.70 (dt, *J* = 8.0, 8.0 Hz, 2H), 1.70-1.49 (m, 2H), 1.46-1.27 (m, 6H), 0.91 (t, *J* = 7.5 Hz, 3H); spectral data in accordance with the literature.[26]

(*Z*)-4-(2-((*tert*-Butyldimethylsilyl)oxy)ethylidene)-2-phenyloxazol-5(4*H*)-one **13o**

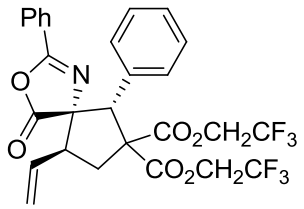


13o

According to the procedure reported by Paradisi *et al.*[25] A suspension of 2-phenyloxazol-5(4*H*)-one (550 mg, 3.41 mmol), 2-((*tert*-butyldimethylsilyl)oxy)acetaldehyde (470 mg, 2.70 mmol) and alumina (5.00 g, Brockmann Grade I, basic) in methylene chloride (10.0 mL) was stirred vigorously for 2 h at room temperature. The reaction was filtered to remove the alumina, concentrated *in vacuo* and

purified by silica gel chromatography (5% diethyl ether in petroleum ether) to give the title compound **13o** as a viscous liquid (107 mg, 0.337 mmol, 13%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 7.0 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 2H), 6.70 (t, *J* = 6.0 Hz, 1H), 4.80 (d, *J* = 6.5 Hz, 2H), 0.93 (s, 9H), 0.12 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.1, 143.3, 137.4, 133.7, 129.2, 128.5, 128.3, 125.6, 60.2, 26.1, 18.5, -5.0; IR (cm^{-1}): 2954, 2929, 2857, 1801, 1677, 1593, 1569, 1450, 1326, 1255, 1177, 1104, 1059, 871, 836, 778, 689; HRMS (ESI+): observed 340.1336; calculated 340.1345 ($C_{17}H_{23}NNaO_3Si$, $[M+Na]^+$).

(5*S*,6*R*,9*S*)-Bis(2,2,2-trifluoroethyl) 4-oxo-2,6-diphenyl-9-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7,7-dicarboxylate **14a**

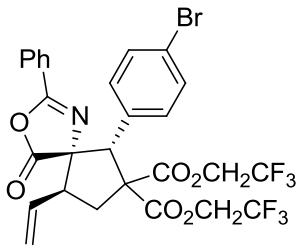


14a

An oven-dried reaction tube equipped with a stir bar was charged with palladium dibenzylideneacetone-chloroform complex (4 mg, 0.004 mmol) and (*S*,*S*)-$\mathbf{L_1}$ chiral ligand, (8 mg, 0.010 mmol). A second reaction tube, also equipped with a stir bar, was charged with bis(2,2,2-trifluoroethyl) 2-vinylcyclopropane-1,1-dicarboxylate (40 mg, 0.12 mmol) and (*Z*)-4-benzylidene-2-phenyloxazol-5(4H)-one **13a** (40 mg, 0.160 mmol). Both tubes were sealed with a septum, evacuated, and backfilled with dry nitrogen. Toluene (degassed by sparging with nitrogen for 30 min, 1 mL) was added to each tube, and the tubes were for stirred 20 min. The contents of the first reaction tube were transferred to the second test tube *via* syringe, and the mixture was stirred at room temperature for 16 h. The solvent was removed *in vacuo* to give the crude product, which was purified by flash column chromatography (5% to 10% diethyl ether in petroleum ether) to give the title compound **14a** as a colorless oil (45 mg, 0.079 mmol, 66%), as a 19:1 mixture of diastereomers (by crude ^{1}H NMR) and with a 96% e.e. for the major diastereomer (by chiral HPLC, Chiralpak OD-H column, 5% isopropanol, 95% heptanes, UV wavelength 254 nm; retention times: 5.74 min (major enantiomer), 7.30 min (minor enantiomer)); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.89 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 2H), 7.36 (m, 2H), 7.22 (m, 3H), 5.79 (ddd, *J* = 17.5, 10.5, 8.0 Hz, 1H), 5.23 (d, *J* = 17.5 Hz, 1H), 5.21 (d, *J* = 10.5 Hz, 1H), 4.78 (s, 1H), 4.66 (dq, *J* = 12.5, 8.0 Hz, 1H), 4.43 (dq, *J* = 12.5, 8.0 Hz, 1H), 4.40 (dq, *J* = 12.5, 8.0 Hz, 1H), 3.66 (ddd,

J = 9.5, 8.0, 6.5 Hz, 1H), 3.41 (dq, J = 12.5, 8.0 Hz, 1H), 3.19 (dd, J = 13.5, 6.5 Hz, 1H), 2.51 (dd, J = 13.5, 9.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 178.6, 169.1, 168.1, 160.3, 136.4, 134.0, 133.3, 133.1, 131.2, 128.9, 128.3, 128.1, 125.7, 122.7 (q, $J_{C\text{-}F}$ = 276 Hz), 122.4 (q, $J_{C\text{-}F}$ = 276 Hz), 120.5, 91.2, 80.3, 78.6, 65.1, 61.7 (q, $J_{C\text{-}F}$ = 36 Hz), 61.5 (q, $J_{C\text{-}F}$ = 37 Hz), 58.1, 53.4, 38.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −74.20-−74.24 (m, 3F), −74.30-−74.35 (m, 3F); IR(cm^{-1}): 2965, 1812, 1752, 1652, 1495, 1451, 1413, 1283, 1236, 1168, 871, 697; HRMS (ESI+): observed 570.1336; calculated 570.1351 ($C_{27}H_{22}F_6NO_6$, $[M+H]^+$); $[\alpha]^{23}_D$ = +15.61° (c = 1.0, CH_2Cl_2).

(5*S*,6*R*,9*S*)-Bis(2,2,2-trifluoroethyl) 6-(4-bromophenyl)-4-oxo-2-phenyl-9-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7,7-dicarboxylate **14b**

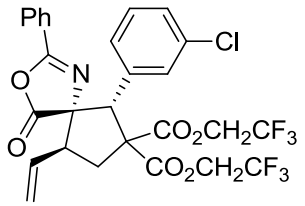


14b

An oven-dried reaction tube equipped with a stir bar was charged with palladium dibenzylideneacetone-chloroform complex (2 mg, 0.002 mmol) and (*S*,*S*)-$\mathbf{L_1}$ chiral ligand, (4 mg, 0.006 mmol). A second reaction tube, also equipped with a stir bar, was charged with bis(2,2,2-trifluoroethyl) 2-vinylcyclopropane-1,1-dicarboxylate (30 mg, 0.093 mmol) and (*Z*)-4-(4-bromobenzylidene)-2-phenyloxazol-5(4*H*)-one **13b** (30 mg, 0.094 mmol). Both tubes were sealed with a septum, evacuated, and backfilled with dry nitrogen. Toluene (degassed by sparging with nitrogen for 30 min, 1 mL) was added to each tube, and the tubes were for stirred 20 min. The contents of the first reaction tube were transferred to the second test tube *via* syringe, and the mixture was stirred at room temperature for 16 h. The solvent was removed *in vacuo* to give the crude product, which was purified by flash column chromatography (5% to 10% diethyl ether in petroleum ether) to give the title compound **14b** as a colorless oil (47 mg, 0.072 mmol, 78%), as a 19:1 mixture of diastereomers (by crude ^{1}H NMR) and with a 98% e.e. for the major diastereomer (by chiral HPLC, Chiralpak OD-H column, 2% isopropanol, 98% heptanes, UV wavelength 254 nm; retention times: 8.03 min (major enantiomer), 9.27 min (minor enantiomer)); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.90 (dd, J = 8.0, 1.0, 2H), 7.56 (td, J = 7.0, 1.0 Hz, 1H), 7.47 (t, J = 8.5 Hz, 2H),

7.38 (d, J = 8.5 Hz, 2H), 7.25 (m, 2H), 5.77 (ddd, J = 17.0, 10.0, 8.0 Hz, 1H), 5.22 (d, J = 17.0 Hz, 1H), 5.21 (d, J = 10.0 Hz, 1H), 4.71 (s, 1H), 4.71-4.62 (m, 1H), 4.53-4.36 (m, 2H), 3.70-3.62 (m, 2H), 3.14 (dd, J = 13.5, 6.5 Hz, 1H), 2.49 (dd, J = 13.5, 10.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 178.4, 168.9, 167.9, 160.6, 133.3, 133.0, 132.9, 132.1, 131.6, 131.2, 129.1, 129.0, 128.3, 125.4, 122.8, 122.7 (q, $J_{C\text{-}F}$ =275 Hz), 122.3 (q, $J_{C\text{-}F}$ = 276 Hz), 120.7, 80.0, 64.9, 61.9 (q, $J_{C\text{-}F}$ = 37.1 Hz), 61.5 (q, $J_{C\text{-}F}$ = 37.2 Hz), 57.5, 53.5, 38.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −74.18 Hz-−74.28 Hz (m, 6F); IR (cm^{-1}): 1812, 1752, 1650, 1489, 1450, 1413, 1283, 1236, 1169, 971, 883, 699; HRMS (ESI+): observed 648.0449; calculated 648.0456 ($C_{27}H_{21}{}^{79}BrF_6NO_6$, $[M+H]^+$); $[\alpha]^{26}_D$ = −3.14° (c = 1.0, CH_2Cl_2).

(5*S*,6*R*,9*S*)-Bis(2,2,2-trifluoroethyl) 6-(3-chlorophenyl)-4-oxo-2-phenyl-9-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7,7-dicarboxylate **14c**

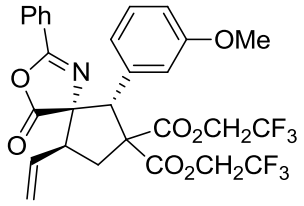


14c

An oven-dried reaction tube equipped with a stir bar was charged with palladium dibenzylideneacetone-chloroform complex (2.5 mg, 0.0024 mmol) and (*S*,*S*)-$\mathbf{L_1}$ chiral ligand, (5 mg, 0.007 mmol). A second reaction tube, also equipped with a stir bar, was charged with bis(2,2,2-trifluoroethyl) 2-vinylcyclopropane-1,1-dicarboxylate (52 mg, 0.160 mmol) and (*Z*)-4-(3-chlorobenzylidene)-2-phenyloxazol-5(4*H*)-one **13c** (45 mg, 0.160 mmol). Both tubes were sealed with a septum, evacuated, and backfilled with dry nitrogen. Toluene (degassed by sparging with nitrogen for 30 min, 2 mL) was added to each tube, and the tubes were for stirred 20 min. The contents of the first reaction tube were transferred to the second test tube *via* syringe, and the mixture was stirred at room temperature for 16 h. The solvent was removed *in vacuo* to give the crude product, which was purified by flash column chromatography (5% to 10% diethyl ether in petroleum ether) to give the title compound **14c** as a colorless oil (68 mg, 0.113 mmol, 70%), as a 19:1 mixture of diastereomers (by crude ^{1}H NMR) and with a 93% e.e. for the major diastereomer (by chiral HPLC, Chiralpak OD-H column, 2% isopropanol, 98% heptanes, UV wavelength 254 nm; retention times: 7.80 min (major enantiomer), 8.87 min (minor enantiomer)); ^{1}H NMR (500

MHz, $CDCl_3$): δ = 7.90 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.56 (dd, *J* = 7.0, 7.0 Hz, 1H), 7.45 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.42 (dd, *J* = 1.5, 1.5 Hz, 1H), 7.27 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.21 (dt, *J* = 8.0, 1.5 Hz, 1H), 7.18 (dd, *J* = 8.0, 7.5 Hz, 1H), 5.78 (ddd, *J* = 17.0, 10.0, 8.0 Hz, 1H), 5.23 (d, *J* = 17.0 Hz, 1H), 5.21 (d, *J* = 10.0 Hz, 1H), 4.72 (s, 1H), 4.65 (dq, *J* = 12.5, 8.0 Hz, 1H), 4.46 (dq, *J* = 12.5, 8.0 Hz, 1H), 4.45 (dq, *J* = 12.5, 8.0 Hz, 1H), 3.69-3.57 (m, 2H), 3.15 (dd, *J* = 13.5, 6.5 Hz, 1H), 2.49 (dd, *J* = 13.5, 10.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 178.4, 168.8, 167.9, 160.5, 135.8, 133.8, 133.3, 133.1, 131.3, 129.5, 129.3, 129.1, 128.6, 128.3, 125.4, 122.7 (q, $J_{C\text{-}F}$ = 275 Hz), 122.3 (q, $J_{C\text{-}F}$ = 276 Hz), 120.7, 79.9, 65.1, 61.9 (q, $J_{C\text{-}F}$ = 46 Hz), 61.6 (q, $J_{C\text{-}F}$ = 46 Hz), 57.7, 53.5, 38.2; ^{19}F NMR (470 MHz, $CDCl_3$): δ = −74.2 (m, 3F), −74.3 (m, 3F); IR (cm^{-1}): 1813, 1752, 1651, 1596, 1572, 1450, 1413, 1283, 1237, 1169, 1124, 1086, 971, 884, 779, 693; HRMS (ESI+): observed 604.0948; calculated 604.0961 ($C_{27}H_{21}ClF_6NO_6$, $[M+H]^+$); $[\alpha]^{23}_D$ = +14.16° (c = 1.0, CH_2Cl_2).

(5*S*,6*R*,9*S*)-Bis(2,2,2-trifluoroethyl) 6-(3-methoxyphenyl)-4-oxo-2-phenyl-9-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7,7-dicarboxylate **14d**

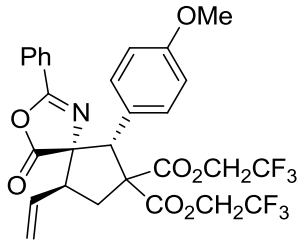


14d

An oven-dried reaction tube equipped with a stir bar was charged with palladium dibenzylideneacetone-chloroform complex (2 mg, 0.002 mmol) and (*S*,*S*)-$\mathbf{L_1}$ chiral ligand, (4 mg, 0.006 mmol). A second reaction tube, also equipped with a stir bar, was charged with bis(2,2,2-trifluoroethyl) 2-vinylcyclopropane-1,1-dicarboxylate (40 mg, 0.125 mmol) and (*Z*)-4-(3-Methoxybenzylidene)-2-phenyloxazol-5(4*H*)-one **13d** (50 mg, 0.180 mmol). Both tubes were sealed with a septum, evacuated, and backfilled with dry nitrogen. Toluene (degassed by sparging with nitrogen for 30 min, 1 mL) was added to each tube, and the tubes were for stirred 20 min. The contents of the first reaction tube were transferred to the second test tube *via* syringe, and the mixture was stirred at room temperature for 16 h. The solvent was removed *in vacuo* to give the crude product, which was purified by flash column chromatography (5% to 10% diethyl ether in petroleum ether) to give the title compound **14d** as a colorless oil (63 mg, 0.105 mmol, 84%), as a 19:1 mixture of diastereomers (by crude ^{1}H NMR) and with a 94% e.e. for the major diastereomer

(by chiral HPLC, Chiralpak OD-H column, 2% isopropanol, 98% heptanes, UV wavelength 254 nm; retention times: 7.84 min (major enantiomer), 9.63 min (minor enantiomer)); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.90 (dd, *J* = 7.5, 1.5 Hz, 2H), 7.54 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.43 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.13 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.96-6.91 (m, 2H), 6.75 (dd, *J* = 8.0, 2.5 Hz, 1H), 5.80 (ddd, *J* = 17.5, 10.0, 8.0 Hz, 1H), 5.21 (d, *J* = 17.5 Hz, 1H), 5.20 (d, *J* = 10.0 Hz, 1H), 4.74 (s, 1H), 4.66 (dq, *J* = 12.5, 8.0 Hz, 1H), 4.44 (dq, *J* = 12.5, 8.0 Hz, 1H), 4.43 (dq, *J* = 12.5, 8.0 Hz, 1H), 3.71 (s, 3H), 3.60 (ddd, *J* = 9.0, 8.0, 7.0 Hz, 1H), 3.47 (dq, *J* = 12.5, 8.0 Hz, 1H), 3.22 (dd, *J* = 13.5, 7.0 Hz, 1H), 2.49 (dd, *J* = 13.5, 9.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 178.4, 169.1, 168.1, 160.3, 159.3, 135.3, 133.3, 133.2, 129.0, 128.8, 128.3, 125.7, 123.4, 122.8 (q, $J_{C\text{-}F}$ = 278 Hz), 122.4 (q, $J_{C\text{-}F}$ = 276 Hz), 120.4, 116.6, 114.2, 80.4, 65.0, 61.8 (q, $J_{C\text{-}F}$ = 36.6 Hz), 61.5 (q, $J_{C\text{-}F}$ = 37 Hz), 58.0, 55.4, 53.5, 38.2; ^{19}F NMR (376 Hz, $CDCl_3$): δ = −74.19-−74.23 (m, 3F), −74.31-−74.35 (m, 3F); IR (cm^{-1}): 1813, 1752, 1652, 1600, 1451, 1413, 1283, 1236, 1168, 971, 696; HRMS (ESI+): observed 600.1461; calculated 600.1457 ($C_{28}H_{24}F_6O_7N$, $[M+H]^+$); $[\alpha]^{24}_D$ = +23.87° (c = 1.0, CH_2Cl_2).

(5*S*,6*R*,9*S*)-Bis(2,2,2-trifluoroethyl) 6-(4-methoxyphenyl)-4-oxo-2-phenyl-9-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7,7-dicarboxylate **14f**

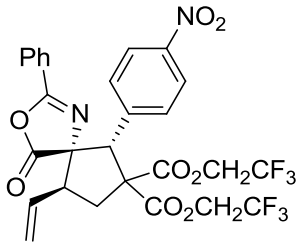


14f

An oven-dried reaction tube equipped with a stir bar was charged with palladium dibenzylideneacetone-chloroform complex (2 mg, 0.002 mmol) and (*S*,*S*)-$\mathbf{L_1}$ chiral ligand, (4 mg, 0.006 mmol). A second reaction tube, also equipped with a stir bar, was charged with bis(2,2,2-trifluoroethyl) 2-vinylcyclopropane-1,1-dicarboxylate (31 mg, 0.096 mmol) and (*Z*)-4-(4-methoxybenzylidene)-2-phenyloxazol-5(4*H*)-one **13f** (31 mg, 0.111 mmol). Both tubes were sealed with a septum, evacuated, and backfilled with dry nitrogen. Toluene (degassed by sparging with nitrogen for 30 min, 1 mL) was added to each tube, and the tubes were for stirred 20 min. The contents of the first reaction tube were transferred to the second test tube *via* syringe, and the mixture was stirred at room temperature for 16 h. The solvent was removed *in vacuo* to give the

crude product, which was purified by flash column chromatography (5% to 10% diethyl ether in petroleum ether) to give the title compound **14f** as a colorless oil (21 mg, 0.035 mmol, 36%), as a >19:1 mixture of diastereomers (by crude ^{1}H NMR) and with a 99% e.e. for the major diastereomer (by chiral HPLC, Chiralpak OD-H column, 2% isopropanol, 98% heptanes, UV wavelength 254 nm; retention times: 10.53 min (major enantiomer), 12.20 min (minor enantiomer)); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.90 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.56 (tt, *J* = 7.5, 1.0 Hz, 1H), 7.52-7.42 (m, 2H), 7.32-7.29 (m, 2H), 6.75 (td, *J* = 9.0, 2.0 Hz, 2H), 5.82 (ddd, *J* = 17.0, 10.0, 8.5 Hz, 1H), 5.23 (d, *J* = 17.5 Hz, 1H), 5.22 (d, *J* = 10.0 Hz, 1H), 4.74 (s, 1H), 4.71-4.61 (m, 1H), 4.52-4.40 (m, 2H), 3.76 (s, 3H), 3.69-3.55 (m, 2H), 3.20 (dd, *J* = 14.0, 7.0 Hz, 1H), 2.49 (dd, *J* = 14.0, 9.5 Hz, 1H); ^{13}C NMR (101MHz, $CDCl_3$): δ = 178.6, 169.1, 168.2, 160.2, 159.5, 133.5, 133.1, 132.3, 128.9, 128.3, 125.7, 125.7, 122.7, (q, $J_{C\text{-}F}$ = 275 Hz, 1C), 122.4 (q, $J_{C\text{-}F}$ =276 Hz, 1C), 120.3, 113.4, 80.4, 64.9, 61.6 (q, $J_{C\text{-}F}$ = 37 Hz, 1C), 61.6 (q, $J_{C\text{-}F}$ = 37 Hz, 1C), 57.7, 55.4, 53.3, 38.2, 29.9; ^{19}F NMR (376 MHz, $CDCl_3$): −74.2-−74.3 (m, 6F); IR (cm^{-1}): 2967, 1813, 1753, 1652, 1612, 1581, 1451, 1414, 1285, 1251. 1180, 1035, 971, 884, 695; HRMS (ESI+): observed 600.1438; calculated 600.1457 ($C_{28}H_{24}ClF_6NO_7$, $[M+H]^+$); $[\alpha]^{24}_D$ = +9.46° (c = 0.46, CH_2Cl_2).

(5*S*,6*R*,9*S*)-Bis(2,2,2-trifluoroethyl) 6-(4-nitrophenyl)-4-oxo-2-phenyl-9-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7,7-dicarboxylate **14g**

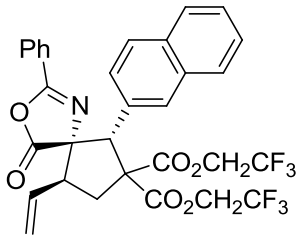


14g

An oven-dried reaction tube equipped with a stir bar was charged with palladium dibenzylideneacetone-chloroform complex (2 mg, 0.002 mmol) and (*S*,*S*)-$\mathbf{L_1}$ chiral ligand, (4 mg, 0.006 mmol). A second reaction tube, also equipped with a stir bar, was charged with bis(2,2,2-trifluoroethyl) 2-vinylcyclopropane-1,1-dicarboxylate (40 mg, 0.125 mmol) and (*Z*)-4-(4-nitrobenzylidene)-2-phenyloxazol-5(4*H*)-one **13g** (40 mg, 0.136 mmol). Both tubes were sealed with a septum, evacuated, and backfilled with dry nitrogen. Toluene (degassed by sparging with nitrogen for 30 min, 1 mL) was added to each tube, and the tubes were for stirred 20 min. The contents of

the first reaction tube were transferred to the second test tube *via* syringe, and the mixture was stirred at room temperature for 16 h. The solvent was removed *in vacuo* to give the crude product, which was purified by flash column chromatography (5% to 10% diethyl ether in petroleum ether) to give the title compound **14g** as a colorless oil (53 mg, 0.086 mmol, 69%), as a 8:1 mixture of diastereomers (by crude ^{1}H NMR) and with a 85% e.e. for the major diastereomer (by chiral HPLC, Chiralpak OD-H column, 2% isopropanol, 98% heptanes, UV wavelength 220 nm; retention times: 25.29 min (major enantiomer), 30.09 min (minor enantiomer)); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 9.0 Hz, 2H), 7.88 (dd, *J* = 8.0, 1.0 Hz, 2H), 7.63-7.54 (m, 3H), 7.45 (dd, *J* = 8.0, 8.0 Hz, 2H), 5.76 (ddd, *J* = 17.0, 10.5, 8.5 Hz, 1H), 5.25 (d, *J* = 17.0 Hz, 1H), 5.23 (d, *J* = 10.5 Hz, 1H), 4.84 (s, 1H), 4.64 (dq, *J* = 12.5, 8.0 Hz, 1H), 4.50 (dq, *J* = 12.5, 8.0 Hz, 1H), 4.39 (dq, *J* = 12.5, 8.0 Hz, 1H), 3.80-3.67 (m, 2H), 3.14 (dd, *J* = 13.5, 7.0 Hz), 2.53 (dd, *J* = 13.5, 10.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.2, 168.5, 167.7, 160.9, 147.8, 141.3, 133.5, 132.7, 132.4, 129.1, 128.3, 125.1, 123.0, 122.6 (q, $J_{C\text{-}F}$ = 275 Hz), 122.2 (q, $J_{C\text{-}F}$ = 276 Hz), 121.1, 79.8, 65.1, 62.0 (q, $J_{C\text{-}F}$ = 37.2 Hz), 61.6 (q, $J_{C\text{-}F}$ = 38.7 Hz), 57.5, 53.7, 38.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ −74.19-−74.25 (m, 6F); IR (cm^{-1}): 2976, 1814, 1752, 1651, 1602, 1524, 1450, 1413, 1349, 1284, 1238, 1170, 1126, 974, 883, 699; HRMS (ESI+): observed 637.1008; calculated 637.1022 ($C_{27}H_{20}F_6N_2NaO_8$, $[M+Na]^+$); $[\alpha]^{26}_D$ = −6.32°, (c = 1.0, CH_2Cl_2).

(5*S*,6*R*,9*S*)-Bis(2,2,2-trifluoroethyl) 6-(naphthalen-2-yl)-4-oxo-2-phenyl-9-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7,7-dicarboxylate **14h**

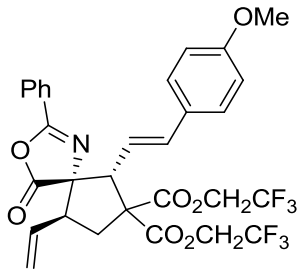


14h

An oven-dried reaction tube equipped with a stir bar was charged with palladium dibenzylideneacetone-chloroform complex (3 mg, 0.003 mmol) and (*S*,*S*)-$\mathbf{L_1}$ chiral ligand, (6 mg, 0.009 mmol). A second reaction tube, also equipped with a stir bar, was charged with bis(2,2,2-trifluoroethyl) 2-vinylcyclopropane-1,1-dicarboxylate (40 mg, 0.125 mmol) and (*Z*)-4-(4-methoxybenzylidene)-2-phenyloxazol-5(4*H*)-one **13h** (50 mg, 0.167 mmol). Both tubes were sealed with a septum, evacuated, and backfilled with dry nitrogen. Toluene (degassed by sparging with

nitrogen for 30 min, 1 mL) was added to each tube, and the tubes were for stirred 20 min. The contents of the first reaction tube were transferred to the second test tube *via* syringe, and the mixture was stirred at room temperature for 16 h. The solvent was removed *in vacuo* to give the crude product, which was purified by flash column chromatography (5% to 10% diethyl ether in petroleum ether) to give the title compound **14h** as a colorless oil (64 mg, 0.103 mmol, 83%), as a >19:1 mixture of diastereomers (by crude ^{1}H NMR) and with a 94% e.e. for the major diastereomer (by chiral HPLC, Chiralpak OD-H column, 2% isopropanol, 98% heptanes, UV wavelength 220 nm; retention times: 7.63 min (major enantiomer), 9.02 min (minor enantiomer)); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.88-7.83 (m, 3H), 7.79-7.72 (m, 2H), 7.70 (d, *J* = 9.0 Hz, 1H), 7.52-7.43 (m, 4H), 7.40 (dd, *J* = 8.0, 8.0 Hz, 2H), 5.84 (ddd, *J* = 17.5, 10.0, 8.0 Hz, 1H), 5.26 (d, *J* = 17.5 Hz, 1H), 5.23 (d, *J* = 10.5 Hz, 1H), 4.96 (s, 1H), 4.68 (dq, *J* = 12.5, 8.0 Hz, 1H), 4.40 (dq, *J* = 12.5, 8.0 Hz, 1H), 4.39 (dq, *J* = 12.5, 8.0 Hz, 1H), 3.77-3.71 (m, 1H), 3.31 (dq, *J* = 12.5, 8.0 Hz, 1H), 3.23 (dd, *J* = 13.5, 7.0 Hz, 1H), 2.56 (dd, *J* = 14.0, 10.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 178.7, 169.1, 168.2, 160.4, 133.3, 133.1, 133.0, 131.4, 131.0, 128.9, 128.3, 128.3, 127.6, 127.2, 126.6, 126.4, 125.6, 122.7 (q, $J_{C\text{-}F}$ = 276 Hz), 122.2 (q, $J_{C\text{-}F}$ = 276 Hz), 120.6, 80.5, 65.0, 61.9 (q, $J_{C\text{-}F}$ = 37 Hz), 61.3 (q, $J_{C\text{-}F}$ = 36 Hz), 58.5, 53.6, 38.2; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −74.1-−74.2 (m, 3F), −74.3-−74.5 (m, 3F); IR (cm^{-1}): 3061, 2970, 1812, 1752, 1650, 1450, 1413, 1283, 1236, 1169, 1123, 1087, 972, 884, 693, 648; HRMS (ESI+): observed 620.1508; calculated 620.1508 ($C_{31}H_{24}F_6O_6N$, $[M+H]^+$); $[\alpha]^{26}_D$ = −26.95° (c = 1.0, CH_2Cl_2).

(5*S*,6*R*,9*S*)-Bis(2,2,2-trifluoroethyl) 6-((E)-4-methoxystyryl)-4-oxo-2-phenyl-9-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7,7-dicarboxylate **14i**

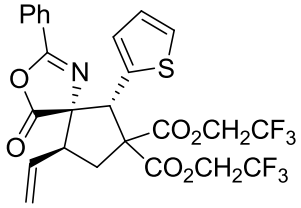


14i

An oven-dried reaction tube equipped with a stir bar was charged with palladium dibenzylideneacetone-chloroform complex (3 mg, 0.003 mmol) and (*S*,*S*)-$\mathbf{L_1}$ chiral ligand, (6 mg, 0.009 mmol). A second reaction tube, also equipped with a stir bar, was charged with bis(2,2,2-

trifluoroethyl) 2-vinylcyclopropane-1,1-dicarboxylate (40 mg, 0.125 mmol) and (*Z*)-4-((*E*)-3-(4-methoxyphenyl)allylidene)-2-phenyloxazol-5(4*H*)-one **13i** (50 mg, 0.164 mmol). Both tubes were sealed with a septum, evacuated, and backfilled with dry nitrogen. Toluene (degassed by sparging with nitrogen for 30 min, 1 mL) was added to each tube, and the tubes were for stirred 20 min. The contents of the first reaction tube were transferred to the second test tube *via* syringe, and the mixture was stirred at room temperature for 16 h. The solvent was removed *in vacuo* to give the crude product, which was purified by flash column chromatography (5% to 10% diethyl ether in petroleum ether) to give the title compound **14i** as a colorless oil (40 mg, 0.064 mmol, 51%), as a >19:1 mixture of diastereomers (by crude ^{1}H NMR) and with a 94% e.e. for the major diastereomer (by chiral HPLC, Chiralpak OD-H column, 2% isopropanol, 98% heptanes, UV wavelength 220 nm; retention times: 12.20 min (major enantiomer), 13.84 min (minor enantiomer)); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 8.5 Hz, 2H), 7.55 (dddd, *J* = 7.5, 7.5, 1.0, 1.0 Hz, 1H), 7.47-7.43 (m, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 6.79 (d, *J* = 8.5 Hz, 2H), 6.50 (d, *J* = 16.0 Hz, 1H), 6.00 (dd, *J* = 16.0, 10.0 Hz, 1H), 5.81 (ddd, *J* = 17.0, 10.5, 9.0 Hz), 5.15 (d, *J* = 17.0 Hz, 1H), 5.14 (d, *J* = 10.0 Hz, 1H), 4.64-4.46 (m, 4H), 4.03 (d, *J* = 10.0 Hz, 1H), 3.76 (s, 3H), 3.48-3.36 (m, 1H), 3.01 (dd, *J* = 13.5, 7.5 Hz, 1H), 2.32 (dd, *J* = 13.5, 11.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 178.0, 168.4, 167.8, 160.7, 159.8, 135.9, 134.3, 133.2, 129.2, 129.0, 128.4, 128.2, 125.6, 122.9 (q, $J_{C\text{-}F}$ = 275 Hz), 122.7 (q, $J_{C\text{-}F}$ = 276 Hz), 119.8, 118.8, 114.1, 80.7, 63.7, 61.7(q, $J_{C\text{-}F}$ = 37 Hz, 2C), 58.1, 55.5, 51.9, 39.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −73.75 (t, *J* = 8.6 Hz, 3F), −74.20 (t, *J* = 7.5 Hz, 3F); IR (cm^{-1}): 1814, 1753, 1649, 1511, 1450, 1412, 1284, 1248, 1172, 1112, 969, 698; HRMS (ESI+): observed 626.1614; calculated 626.1613 ($C_{30}H_{26}F_6NO_7$, $[M+H]^+$); $[\alpha]^{25}_D$ = +106.5° (c = 1.0, CH_2Cl_2).

(5*S*,6*R*,9*S*)-Bis(2,2,2-trifluoroethyl) 4-oxo-2-phenyl-6-(thiophen-2-yl)-9-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7,7-dicarboxylate **14j**

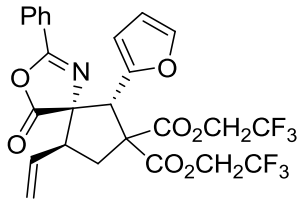


14j

An oven-dried reaction tube equipped with a stir bar was charged with palladium dibenzylideneacetone-chloroform complex (3 mg, 0.003 mmol) and (*S*,*S*)-$\mathbf{L_1}$ chiral ligand, (6 mg,

0.009 mmol). A second reaction tube, also equipped with a stir bar, was charged with bis(2,2,2-trifluoroethyl) 2-vinylcyclopropane-1,1-dicarboxylate (40 mg, 0.125 mmol) and (*Z*)-2-phenyl-4-(thiophen-2-ylmethylene)oxazol-5(4*H*)-one **13j** (35 mg, 0.137 mmol). Both tubes were sealed with a septum, evacuated, and backfilled with dry nitrogen. Toluene (degassed by sparging with nitrogen for 30 min, 1 mL) was added to each tube, and the tubes were for stirred 20 min. The contents of the first reaction tube were transferred to the second test tube *via* syringe, and the mixture was stirred at room temperature for 16 h. The solvent was removed *in vacuo* to give the crude product, which was purified by flash column chromatography (5% to 10% diethyl ether in petroleum ether) to give the title compound **14j** as a colorless oil (28 mg, 0.049 mmol, 39%), as a >19:1 mixture of diastereomers (by crude ^{1}H NMR) and with a 95% e.e. for the major diastereomer (by chiral HPLC, Chiralpak OD-H column, 2% isopropanol, 98% heptanes, UV wavelength 220 nm; retention times: 12.36 min (major enantiomer), 18.64 min (minor enantiomer)); ^{1}H NMR (500MHz ,$CDCl_3$) δ = 7.98 (d, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.48 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.14 (d, *J* = 5.0 Hz, 1H), 7.10 (d, *J* = 3.5 Hz, 1H), 6.87 (dd, *J* = 5.0, 3.5 Hz, 1H), 5.88 (ddd, *J* = 17.0, 10.5, 8.5 Hz, 1H), 5.21 (d, *J* = 10.5 Hz, 1H), 5.16 (d, *J* = 17.0 Hz, 1H), 4.70 (dq, *J* = 12.5, 8.0 Hz, 1H), 4.55 (dq, *J* = 12.5, 8.0 Hz, 1H), 4.41 (dq, *J* = 12.5, 8.0 Hz, 1H), 3.72 (dq, *J* = 12.5, 8.0 Hz, 1H), 3.45 (ddd, *J* = 8.5, 7.5, 7.0 Hz, 1H), 3.32 (dd, *J* = 14.0, 7.0 Hz, 1H), 2.40 (dd, *J* = 14.0, 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 177.3, 169.1, 167.4, 161.3, 134.3, 133.7, 133.3, 130.1, 129.1, 128.6, 127.1, 126.6, 126.5 125.7, 122.7 (q, $J_{C\text{-}F}$ = 276 Hz), 122.5 (q, $J_{C\text{-}F}$ = 276 Hz) 120.1, 80.3, 64.8, 61.8 (q, $J_{C\text{-}F}$ = 37.5 Hz), 61.7 (q, $J_{C\text{-}F}$ = 36 Hz), 53.7, 52.8, 38.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −74.16-−74.23 (m, 6F); IR (cm^{-1}): 1815, 1752, 1649, 1413, 1283, 1232, 1168, 963, 702; HRMS (ESI+): observed 576.0923; calculated 576.0910 ($C_{25}H_{20}F_6NO_6S$, $[M+H]^+$); $[\alpha]^{26}_D$ = +74.1° (c = 1.0, CH_2Cl_2).

(5*S*,6*R*,9*S*)-Bis(2,2,2-trifluoroethyl) 6-(furan-2-yl)-4-oxo-2-phenyl-9-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7,7-dicarboxylate **14k**

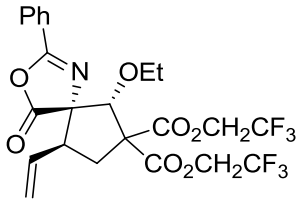


14k

An oven-dried reaction tube equipped with a stir bar was charged with palladium dibenzylideneacetone-chloroform complex (2.5 mg, 0.0024 mmol) and (*S*,*S*)-$\mathbf{L_1}$ chiral ligand, (5 mg, 0.007 mmol). A second reaction tube, also equipped with a stir bar, was charged with bis(2,2,2-trifluoroethyl) 2-vinylcyclopropane-1,1-dicarboxylate (40 mg, 0.125 mmol) and (*Z*)-4-(furan-2-ylmethylene)-2-phenyloxazol-5(4*H*)-one **13k** (35 mg, 0.146 mmol). Both tubes were sealed with a septum, evacuated, and backfilled with dry nitrogen. Toluene (degassed by sparging with nitrogen for 30 min, 1 mL) was added to each tube, and the tubes were for stirred 20 min. The contents of the first reaction tube were transferred to the second test tube *via* syringe, and the mixture was stirred at room temperature for 16 h. The solvent was removed *in vacuo* to give the crude product, which was purified by flash column chromatography (5% to 10% diethyl ether in petroleum ether) to give the title compound **14k** as a colorless oil (60.5 mg, 0.108 mmol, 87%), as a >19:1 mixture of diastereomers (by crude ^{1}H NMR) and with a 95% e.e. for the major diastereomer (by chiral HPLC, Chiralpak OD-H column, 5% isopropanol, 95% heptanes, UV wavelength 254 nm; retention times: 5.95 min (major enantiomer), 7.94 min (minor enantiomer)); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.89 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.56 (tt, *J* = 8.0, 1.5 Hz, 1H), 7.44 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.34 (dd, *J* = 2.0, 1.0, Hz, 1H), 6.24 (dd, *J* = 3.0, 2.0 Hz, 1H), 6.22 (dd, *J* = 3.0, 1.0 Hz, 1H), 5.71 (ddd, *J* = 17.0, 10.5, 8.0 Hz, 1H), 5.22 (d, *J* = 17.0 Hz, 1H), 5.18 (d, *J* = 10.5 Hz, 1H), 4.86 (s, 1H), 4.63 (dq, *J* = 12.5, 8.0 Hz, 1H), 4.55 (dq, *J* = 12.5, 8.0 Hz, 1H), 4.54 (dq, *J* = 12.5, 8.0 Hz, 1H), 3.89 (dq, *J* = 12.5, 8.0 Hz, 1H), 3.70 (ddd, *J* = 10.5, 8.0, 7.0 Hz, 1H), 3.17 (dd, *J* = 13.5, 7.0 Hz, 1H), 2.50 (dd, *J* = 13.5, 10.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 178.0, 168.5, 167.5, 161.1, 148.3, 143.0, 133.3, 133.0, 129.0, 128.4, 125.6, 122.7 (q, $J_{C\text{-}F}$ = 276 Hz), 122.5 (q, $J_{C\text{-}F}$ = 276 Hz), 120.7, 110.9, 110.7, 80.0, 63.1, 62.0 (q, $J_{C\text{-}F}$ = 37 Hz, 2C), 52.3, 51.5, 37.2; ^{19}F NMR (376 MHz, $CDCl_3$): −74.20-−74.26 (m, 6F); IR (cm^{-1}): 2976, 1815, 1758, 1654, 1451, 1414, 1289, 1233, 1171, 973, 931, 885, 740, 695, 664;

HRMS (ESI+): observed 582.0953; calculated 582.0963 ($C_{25}H_{19}F_6NNaO_7$); $[\alpha]^{26}_D$ = −19.2° (c = 1.0, CH_2Cl_2).

(5*S*,6*R*,9*S*)-Bis(2,2,2-trifluoroethyl) 6-ethoxy-4-oxo-2-phenyl-9-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7,7-dicarboxylate **14l**

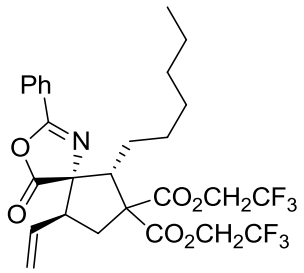


14l

An oven-dried reaction tube equipped with a stir bar was charged with palladium dibenzylideneacetone-chloroform complex (3 mg, 0.003 mmol) and (*S*,*S*)-$\mathbf{L_1}$ chiral ligand, (6 mg, 0.009 mmol). A second reaction tube, also equipped with a stir bar, was charged with bis(2,2,2-trifluoroethyl) 2-vinylcyclopropane-1,1-dicarboxylate (30 mg, 0.093 mmol) and 4-(ethoxymethylene)-2-phenyloxazol-5(4*H*)-one **13l** (40 mg, 0.184 mmol, 3:1 mixture of *E*/*Z* isomers). Both tubes were sealed with a septum, evacuated, and backfilled with dry nitrogen. Toluene (degassed by sparging with nitrogen for 30 min, 1 mL) was added to each tube, and the tubes were for stirred 20 min. The contents of the first reaction tube were transferred to the second test tube *via* syringe, and the mixture was stirred at room temperature for 16 h. The solvent was removed *in vacuo* to give the crude product, which was purified by flash column chromatography (5% to 10% diethyl ether in petroleum ether) to give the title compound **14l** as a colorless oil (38 mg, 0.071 mmol, 76%), as a 10:1 mixture of diastereomers (by crude ^{1}H NMR) and with a 63% e.e. for the major diastereomer (by chiral HPLC, Chiralpak OD-H column, 5% isopropanol, 95% heptanes, UV wavelength 254 nm; retention times: 6.31 min (major enantiomer), 7.29 min (minor enantiomer)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (dd, *J* = 7.5, 1.0 Hz, 2H), 7.59 (tt, *J* = 7.5, 1.0 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 5.58 (ddd, *J* = 17.0, 10.0, 8.0 Hz, 1H), 5.20 (d, *J* = 17.0 Hz, 1H), 5.14 (d, *J* = 10.0 Hz, 1H), 4.82 (s, 1H), 4.63-4.53 (m, 3H), 4.47 (dq, *J* = 9.5, 7.0 Hz, 1H), 3.78 (dq, *J* = 9.5, 7.0 Hz, 1H), 3.56 (dq, *J* = 9.5, 7.0 Hz, 1H), 3.55 (dq, *J* = 9.5, 7.0 Hz, 1H), 3.03 (dd, *J* = 14.0, 7.5 Hz, 1H), 2.43 (dd, *J* = 14.0, 11.5 Hz, 1H), 1.13 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 177.1, 168.1, 166.2, 161.6. 133.3, 132.6, 129.1, 128.4, 125.6, 122.8 (q, $J_{C\text{-}F}$ = 272 Hz, 2C), 120.8, 86.0, 81.1, 69.5, 64.2, 61.9 (q, $J_{C\text{-}F}$ = 36.6 Hz), 61.8 (q, $J_{C\text{-}F}$ = 36.6 Hz), 49.9, 34.1, 15.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −74.12 (t, *J*

= 9.7 Hz, 3F), −74.23 (t, *J* = 8.6 Hz); IR (cm^{-1}): 2976, 1812, 1759, 1649, 1450, 1412, 1284, 1235, 1168, 976, 897; HRMS (ESI+): observed 560.1115; calculated 560.1120 ($C_{23}H_{21}F_6NNaO_7$, $[M+Na]^+$); $[\alpha]^{24}_D = -4.08°$ (c = 1.0, CH_2Cl_2).

(5*S*,6*R*,9*S*)-Bis(2,2,2-trifluoroethyl) 6-hexyl-4-oxo-2-phenyl-9-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7,7-dicarboxylate **14n**

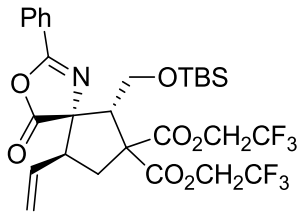


14n

An oven-dried reaction tube equipped with a stir bar was charged with palladium dibenzylideneacetone-chloroform complex (2 mg, 0.002 mmol) and (*S*,*S*)-$\mathbf{L_1}$ chiral ligand, (4 mg, 0.006 mmol). A second reaction tube, also equipped with a stir bar, was charged with bis(2,2,2-trifluoroethyl) 2-vinylcyclopropane-1,1-dicarboxylate (30 mg, 0.093 mmol) and (*Z*)-4-heptylidene-2-phenyloxazol-5(4*H*)-one **13n** (20 mg, 0.078 mmol). Both tubes were sealed with a septum, evacuated, and backfilled with dry nitrogen. Toluene (degassed by sparging with nitrogen for 30 min, 1 mL) was added to each tube, and the tubes were for stirred 20 min. The contents of the first reaction tube were transferred to the second test tube *via* syringe, and the mixture was stirred at room temperature for 16 h. The solvent was removed *in vacuo* to give the crude product, which was purified by flash column chromatography (5% to 10% diethyl ether in petroleum ether) to give the title compound **14n** as a colorless oil (28 mg, 0.048 mmol, 63%), as a 8:1 mixture of diastereomers (by crude ^{1}H NMR) and with a 77% e.e. for the major diastereomer (by chiral HPLC, Chiralpak OD-H column, 2% isopropanol, 98% heptanes, UV wavelength 254 nm; retention times: 9.49 min (major enantiomer), 14.45 min (minor enantiomer)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (dd, *J* = 1.5, 8.0 Hz, 2H), 7.58 (tt, *J* = 8.0, 1.5 Hz, 1H), 7.48 (dd, *J* = 8.0, 8.0, 2H), 5.76 (ddd, *J* = 17.0, 10.5, 9.0 Hz, 1H), 5.10 (d, *J* = 10.5 Hz, 1H), 5.09 (d, *J* = 17.0 Hz, 1H), 4.71 (dq, *J* = 12.5, 8.5 Hz, 1H), 4.65-4.46 (m, 3H), 3.39 (ddd, *J* = 11.5, 9.0, 7.0 Hz, 1H), 3.26 (dd, *J* = 10.0, 5.0 Hz, 1H), 2.80 (dd, *J* = 13.0, 7.0 Hz, 1H), 2.15 (dd, *J* = 13.0, 11.5 Hz, 1H), 1.64-1.47 (m, 2H), 1.21-0.96 (m, 8H), 0.73 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 179.4, 168.8, 168.1, 160.4, 134.5, 133.1, 129.0, 128.3,

125.7, 122.9 (q, $J_{C\text{-}F}$ = 275 Hz), 122.8 (q, $J_{C\text{-}F}$ = 276 Hz), 119.8, 79.4, 62.9, 61.5 (q, $J_{C\text{-}F}$ = 37.1 Hz), 61.4 (q, $J_{C\text{-}F}$ =37 Hz), 54.9, 52.6, 40.1, 31.4, 29.2, 27.9, 27.2, 22.5, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −73.84 (t, *J* = 8.6 Hz, 3F), −74.26 (t, *J* = 8.6 Hz, 3F); IR (cm^{-1}): 2921, 2856, 1813, 1753, 1649, 1451, 1411, 1283, 1233, 1168, 1098, 963, 880, 699; HRMS (ESI+): observed 600.1793; calculated 600.1797 ($C_{27}H_{29}F_6NNaO_6$, $[M+Na]^+$); $[\alpha]^{26}_D$ = +23.96° (c = 1.0, CH_2Cl_2).

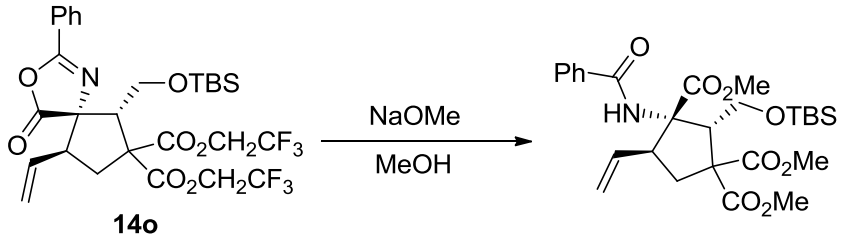
(5*S*,6*R*,9*S*)-Bis(2,2,2-trifluoroethyl) 6-(((*tert*-butyldimethylsilyl)oxy)methyl)-4-oxo-2-phenyl-9-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7,7-dicarboxylate **14o**



14o

An oven-dried reaction tube equipped with a stir bar was charged with palladium dibenzylideneacetone-chloroform complex (2 mg, 0.002 mmol) and (*S*,*S*)-$\mathbf{L_1}$ chiral ligand, (4 mg, 0.006 mmol). A second reaction tube, also equipped with a stir bar, was charged with bis(2,2,2-trifluoroethyl) 2-vinylcyclopropane-1,1-dicarboxylate (39 mg, 0.121 mmol) and (*Z*)-4-(2-((*tert*-butyldimethylsilyl)oxy)ethylidene)-2-phenyloxazol-5(4*H*)-one **13o** (40 mg, 0.126 mmol). Both tubes were sealed with a septum, evacuated, and backfilled with dry nitrogen. Toluene (degassed by sparging with nitrogen for 30 min, 1 mL) was added to each tube, and the tubes were for stirred 20 min. The contents of the first reaction tube were transferred to the second test tube *via* syringe, and the mixture was stirred at room temperature for 16 h. The solvent was removed *in vacuo* to give the crude product, which was purified by flash column chromatography (5% to 10% diethyl ether in petroleum ether) to give the title compound **14o** as a colorless oil (49 mg, 0.077 mmol, 64%), as a 3:1 mixture of diastereomers which were inseparable by chiral HPLC [derivatization, shown below, estimates the e.e. for the major diastereomer to be 77%]; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.99-7.95 (m, 2H), 7.54 (tt, *J* = 7.5, 1.0 Hz, 1H), 7.46 (dd, *J* = 7.5, 7.5 Hz, 2H), 5.83 (ddd, *J* = 17.0, 10.0, 9.0 Hz, 1H), 5.10 (d, *J* = 10.0 Hz, 1H), 5.08 (d, *J* = 17.0 Hz, 1H), 4.78 (dq, *J* = 12.5, 8.5 Hz, 1H), 4.63 (dq, *J* = 12.5, 8.5 Hz, 1H), 4.60 (dq, *J* = 12.5, 8.5 Hz, 1H), 4.43 (dq, *J* = 12.5, 8.5 Hz, 1H), 3.80 (dd, *J* = 10.0, 4.5 Hz, 1H), 3.70 (dd, *J* = 10.5, 10.0 Hz, 1H), 3.48 (dd, *J* = 10.5, 4.5 Hz, 1H), 3.38-3.27 (m, 1H), 2.92 (dd, *J* = 13.0, 7.5 Hz, 1H), 2.13 (dd, *J* = 13.0, 11.0 Hz, 1H), 0.73 (s, 9H), −0.08 (s, 3H),

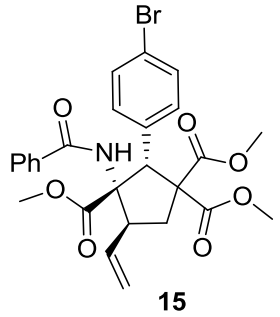
−0.25 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 178.2, 168.2, 167.3, 160.8, 134.8, 132.9, 128.9, 128.3, 126.1, 122.8 (q, $J_{C\text{-}F}$ = 274 Hz), 122.7 (q, $J_{C\text{-}F}$ = 276 Hz), 99.4, 78.0, 61.5 (q, $J_{C\text{-}F}$ = 36.5 Hz, 2C), 60.7, 59.7, 57.2, 51.8, 40.7, 25.7, 18.2, -5.8, -5.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −73.83 (t, *J* = 8.5 Hz, 3F), −74.33 (t, *J* = 7.0 Hz, 3F); IR (cm^{-1}): 2931, 2859, 1819, 1759, 1651, 1451, 1411, 1284, 1173, 1098, 966, 884, 840, 799, 700, 666; HRMS (ESI+): observed 660.1805; calculated 660.1828 ($C_{28}H_{33}F_6NNaO_7Si$, $[M+Na]^+$); $[\alpha]^{24}_D$ = +34.05° (c = 1.0, CH_2Cl_2).



14o

For the purposes of e.e. determination, **14o** (approx. 10 mg) was dissolved in methanol (2 mL), and sodium methoxide (approx. 100 mg, excess) was added. The mixture was stirred at room temperature for 1 h, then quenched by addition of aqueous sodium bicarbonate, extracted into methylene chloride. The organic phase was dried ($MgSO_4$) and the solvent was removed *in vacuo*. The crude compound was filtered through a silica plug (100% diethyl ether) to obtain the derivative which showed an e.e. of 77% (by chiral HPLC, Chiralpak IA column, 10% isopropanol, 90% heptanes, UV wavelength 254 nm; retention times: 9.51 min (major enantiomer), 12.55 min (minor enantiomer); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (dd, *J* = 7.0, 1.0 Hz, 2H), 7.50 (t, *J* = 7.0 Hz, 1H), 7.42 (dd, *J* = 7.0, 7.0 Hz, 2H), 5.70 (ddd, *J* = 17.0, 10.5, 7.5 Hz, 1H), 5.13 (d, *J* = 17.0 Hz, 1H), 5.11 (d, *J* = 10.5 Hz, 1H), 3.91-3.75 (m, 3H), 3.81 (s, 3H), 3.78 (s, 3H), 3.74 (s, 3H), 2.84 (dd, *J* = 13.0, 6.5 Hz, 1H), 2.18 (dd, *J* = 13.0, 12.0 Hz, 1H), 0.79 (s, 9H), -0.08 (s, 3H), -0.10 (s, 3H); IR (cm^{-1}): 2926, 2852, 1734, 1669, 1520, 1487, 1434, 1254, 1090, 837.

(2*R*,3*S*,4*S*)-Trimethyl 3-benzamido-2-(4-bromophenyl)-4-vinylcyclopentane-1,1,3-tricarboxylate **15**

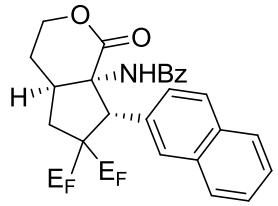


15

A solution of (5*S*,6*R*,9*S*)-bis(2,2,2-trifluoroethyl) 6-(4-bromophenyl)-4-oxo-2-phenyl-9-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7,7-dicarboxylate **14b** (49 mg, 0.075 mmol) and sodium methoxide (150 mg, 3.75 mmol) in methanol (4 mL) was stirred for 1 h at room temperature. The reaction was quenched by the addition of aqueous sodium bicarbonate, then extracted twice with diethyl ether, the organic layers combined, dried (Na_2SO_4) and the solvent removed *in vacuo* to give the crude product, which was purified by flash column chromatography (50% diethyl in petroleum ether) to give the title compound **15** as a white solid (35 mg, 0.065 mmol, 86%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45-7.40 (m, 1H) 7.37-7.27 (m, 6H), 7.14 (d, *J* = 8.5 Hz, 2H), 6.25 (s, 1H), 5.65 (ddd, *J* = 17.0, 10.0, 8.0 Hz, 1H), 5.45 (s, 1H), 5.38 (d, *J* = 17.0, 1H), 5.27 (d, *J* = 10.0 Hz, 1H), 3.82 (s, 3H), 3.70 (s, 3H), 3.41 (ddd, *J* = 12.5, 8.0, 7.5, Hz, 1H), 3.10 (s, 3H), 2.81 (dd, *J* = 13.5, 7.5 Hz, 1H), 2.26 (dd, *J* = 13.5, 12.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.1, 171.5, 171.3, 167.3, 136.8, 134.6, 133.9, 132.7, 131.9, 130.6, 128.7, 126.8, 121.3, 119.6, 70.4, 65.4, 56.4, 55.9, 53.4, 52.8, 52.7, 35.9; IR (cm^{-1}): 3359, 2949, 1731, 1641, 1579, 1526, 1488, 1433, 1238, 1210, 1121, 1074, 1009, 912, 842, 792, 731; HRMS (ESI+): observed 566.0780; calculated 566.0790 ($C_{26}H_{26}{}^{79}BrNNaO_7$, $[M+Na]^+$); $[\alpha]^{25}{}_D$ = +68.9° (c = 1.0, CH_2Cl_2); m.p. 148-149 °C.

The compound was recrystallized by vapor diffusion of pentanes into ethyl acetate at -20 °C, to obtain X-ray quality crystals. The X-ray crystallographic report for this compound is in **Appendix B**.

(4*aS*,7*R*,7*aS*)-Bis(2,2,2-trifluoroethyl) 7*a*-benzamido-7-(naphthalen-2-yl)-1-oxohexahydrocyclopenta[*d*]pyran-6,6(1*H*)-dicarboxylate **16**

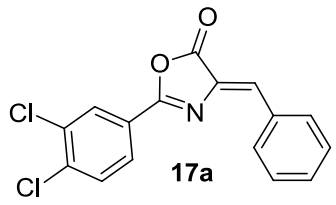


$E_F = CO_2CH_2CF_3$

16

To dicyclohexylborane (15.0 mg, 0.083 mmol) in a sealed vial equipped with a stir bar under a nitrogen atmosphere was added a solution of (5*S*,6*R*,9*S*)-bis(2,2,2-trifluoroethyl) 6-(naphthalen-2-yl)-4-oxo-2-phenyl-9-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7,7-dicarboxylate **14h** (35.0 mg, 0.056 mmol) in tetrahydrofuran (1 mL). The reaction was stirred at room temperature for 16 h, then a solution of *meta*-chloroperoxybenzoic acid (130 mg, 75% by weight, 0.540 mmol) in tetrahydrofuran (2.5 mL) was added by syringe. The reaction was stirred for a further 4 h, then diluted with ethyl acetate. The solution was washed successively with 1 M aq. sodium bisulfate solution and sat. aq. sodium bicarbonate solution, then dried (Na_2SO_4), and the solvent was removed *in vacuo* to give the crude product, which was purified by flash column chromatography (20% to 40% to 100% ethyl acetate in petroleum ether), to give the title compound **16** as a waxy solid (25.2 mg, 0.040 mmol, 71%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.94 (s, 1H), 7.90-7.79 (m, 3H), 7.75 (dd, *J* = 7.0, 1.0 Hz, 2H), 7.55-7.41 (m, 7H), 4.98 (s, 1H), 4.89-4.75 (m, 2H), 4.58-4.48 (m, 2H), 4.39 (dq, *J* = 12.5, 8.0 Hz, 1H), 3.54 (dq, *J* = 12.5, 8.0 Hz, 1H), 3.34 (dd, *J* = 14.5, 8.0 Hz, 1H), 3.27 (dt, *J* = 12.5, 6.0 Hz, 1H), 2.40 (dd, *J* = 14.5, 1.5 Hz, 1H), 2.11-2.04 (m, 1H), 2.04-1.94 (m, 1H); ^{13}C NMR (500 MHz, $CDCl_3$): δ = 170.5, 170.1, 169.3, 167.8, 133.4, 133.3, 133.2, 132.5, 130.2, 130.1, 129.0, 128.9, 128.4, 127.8, 127.3, 127.2, 127.0, 126.8, 122.6 (q, $J_{C\text{-}F}$ = 275 Hz), 122.1 (q, $J_{C\text{-}F}$ = 276 Hz), 68.7, 67.3, 64.3, 62.0 (q, $J_{C\text{-}F}$ = 37 Hz), 61.8 (q, $J_{C\text{-}F}$ = 37 Hz), 56.3, 44.3, 39.5, 27.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −74.12 (t, *J* = 8.6 Hz, 3F), −74.40 (t, *J* = 7.5 Hz, 3F); IR (cm^{-1}): 3300, 3059, 2976, 1753, 1664, 1601, 1522, 1481, 1446, 1413, 1284, 1241, 1169, 1073, 965, 738, 712, 650; HRMS (ESI+): observed 660.1437; calculated 660.1433 ($C_{31}H_{25}F_6NNaO_7$, $[M+Na]^+$); $[\alpha]^{24}_D$ = +116.27° (c = 1.0, CH_2Cl_2).

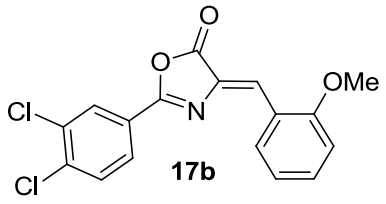
(*Z*)-4-Benzylidene-2-(3,4-dichlorophenyl)oxazol-5(4*H*)-one **17a**



17a

To a stirred mixture of 2-(3,4-dichlorobenzamido)acetic acid (860 mg, 3.46 mmol) and benzaldehyde (800 mg, 7.54 mmol) were added acetic anhydride (15 mL) and sodium acetate (500 mg, 12.5 mmol). The resulting solution was heated under reflux to 90 °C under a nitrogen atmosphere for 2.5 h, resulting in the formation of a yellow precipitate. The solution was allowed to cool, filtered, and the filter cake washed successively with water (10 mL), cold ethanol (10 mL). The yellow solid product dried *in vacuo* for 16 h to give the title compound **17a** as a yellow solid (485 mg, 1.52 mmol, 44%) which was used without further purification; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.27 (d, *J* = 2.0 Hz, 1H), 8.20 (dd, *J* = 7.5, 2.0 Hz, 2H), 8.00 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.55-7.49 (m, 3H), 7.31 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 167.2, 161.8, 138.1, 134.0, 133.5, 133.5, 132.9, 132.9, 131.9, 131.4, 130.1, 129.3, 127.4, 125.7; IR (cm^{-1}): 1797, 1774, 1658, 1449, 1390, 1306, 1278, 1246, 1164, 1108, 994, 892, 865, 892, 765, 829, 765, 722, 681, 558; HRMS (ESI+): observed 318.0082; calculated 318.0083 ($C_{16}H_{10}Cl_2NO_2$, $[M+H]^+$); m.p. 261-263 °C.

(*Z*)-2-(3,4-Dichlorophenyl)-4-(2-methoxybenzylidene)oxazol-5(4*H*)-one **17b**

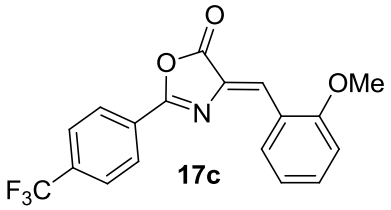


17b

To a stirred mixture of 2-(3,4-dichlorobenzamido)acetic acid (1.50 g, 6.05 mmol), 2-methoxybenzaldehyde (1.00 g, 7.34 mmol), and sodium acetate (300 mg, 3.65 mmol) was added acetic anhydride (10 mL). The mixture was heated under reflux at 90 °C for 2 h and allowed to cool. The yellow precipitate was filtered off, then washed on the filter successively with water (40 mL), aqueous sodium bicarbonate (20 mL) and ethanol (10 mL). The solid was dried under vacuum (<1 Torr) over 16 h, to obtain the title compound **17b** as a yellow solid (970 mg, 2.79 mmol, 46%) which was used without further purification; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.80 (d, *J* = 7.0 Hz, 1H),

8.25 (s, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.92 (s, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.45 (dd, J = 8.0, 8.0 Hz, 1H), 7.11 (dd, J = 8.0, 8.0 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.5, 161.2, 159.7, 137.8, 133.9, 133.8, 133.2, 132.1, 131.4, 130.0, 127.7, 127.3, 126.0, 122.6, 121.3, 111.1, 56.0; IR(cm^{-1}): 1792, 1774, 1649, 1571, 1462, 1389, 1304, 1255, 1223, 1180, 1165, 1029, 997, 892, 870, 826, 747, 718; HRMS (ESI+): observed 348.0177; calculated 348.0189 ($C_{17}H_{12}Cl_2NO_3$, $[M+H]^+$); m.p. 208-210 °C.

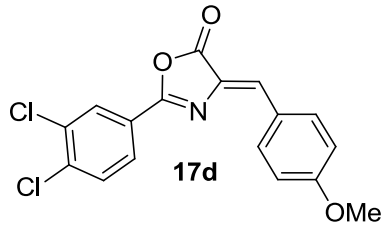
(*Z*)-4-(2-Methoxybenzylidene)-2-(4-(trifluoromethyl)phenyl)oxazol-5(4*H*)-one **17c**



17c

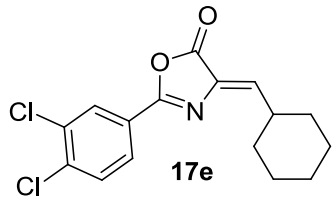
To a stirred solution of glycine *tert*-butyl ester (262 mg, 2.00 mmol) in a biphasic mixture of dichloromethane (5 mL) and sat. aq. sodium bicarbonate solution (5 mL) was added 4-trifluromethylbenzoic anhydride (869 mg, 2.40 mmol). The reaction was stirred for 20 min, the layers were separated and the aqueous layer extracted with dichloromethane (20 mL). The combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo* to give a white solid (618 mg), which was re-dissolved in trifluoroacetic acid (2 mL) and stirred at room temperature for 30 min. The solvent was removed *in vacuo* and co-evaporated with toluene to remove residual traces, to give a white solid (471 mg). The solid was resuspended in acetic anhydride, sodium acetate (492 mg, 6.00 mmol) and *o*-anisaldehyde (454 mg, 4.00 mmol) were added and the mixture was heated under reflux at 90 °C for 2 h, then allowed to cool. The resulting solid was filtered and washed on the filter with di-isopropylether (50 mL), then purified by flash column chromatography (1:1 petroleum ether:ethyl acetate) to give the title compound **17c** as a yellow solid (172 mg, 0.495 mmol, 50% over three steps); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81 (dd, J = 8.0, 1.0 Hz, 1H), 8.25 (d, J = 8.0 Hz, 2H), 7.92 (s, 1H), 7.76 (d, J = 8.0 Hz, 2H), 7.44 (dd, J = 7.5, 7.5 Hz, 1H), 7.09 (dd, J = 7.5, 7.5 Hz, 1H), 6.93 (d, J = 8.5 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.5, 161.8, 159.7, 137.7, 133.8, 133.2, 130.7 (q, $J_{C\text{-}F}$ = 275 Hz), 128.7, 128.0 (q, $J_{C\text{-}F}$ = 27.5 Hz), 127.9, 126.1 (q, $J_{C\text{-}F}$ = 3.7 Hz), 122.6, 121.3, 111.1, 55.9; ^{19}F NMR: (376 MHz, $CDCl_3$): δ = −63.53 (s, 3F); IR (cm^{-1}): 1795, 1776, 1650, 1614, 1485, 1321, 1252, 1164, 1066, 856; HRMS (ESI+): observed 348.0830; calculated 348.0842 ($C_{18}H_{13}F_3NO_3$, $[M+H]^+$); m.p. 162-163 °C.

(*Z*)-2-(3,4-Dichlorophenyl)-4-(4-methoxybenzylidene)oxazol-5(4*H*)-one **17d**



To a stirred mixture of 2-(3,4-dichlorobenzamido)acetic acid (1.46 g, 5.89 mmol), 4-methoxybenzaldehyde (1.00 g, 7.35 mmol), and sodium acetate (400 mg, 4.88 mmol) was added acetic anhydride (15 mL). The reaction mixture was heated under reflux at 90 °C for 2 h under an atmosphere of nitrogen. After 2 h, the reaction mixture was allowed to cool to room temperature, and yellow precipitate was filtered off, then washed on the filter successively with water (40 mL), aqueous sodium bicarbonate (20 mL) and ethanol (10 mL). The solid was dried under vacuum (<1 Torr) over 16 h, to obtain the title compound **17d** as a yellow solid (801 mg, 2.31 mmol, 39%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (s, 1H), 8.18 (d, *J* = 8.5 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.5 Hz, 1H), 7.26 (s, 1H), 7.01 (d, *J* = 8.5 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.6, 162.8, 160.7, 137.7, 135.1, 133.9, 133.6, 131.4, 130.7, 129.9, 127.2, 126.5, 126.0, 114.9, 55.8; IR(cm^{-1}): 1795, 1771, 1699, 1649, 1602, 1561, 1512, 1463, 1430, 1389, 1311, 1263, 1181, 1162, 1023, 894, 861, 800, 759, 717; HRMS (ESI+): observed 348.0184; calculated 348.0189 ($C_{17}H_{12}Cl_2NO_3$, $[M+H]^+$); m.p. 203-205 °C.

(*Z*)-4-(Cyclohexylmethylene)-2-(3,4-dichlorophenyl)oxazol-5(4*H*)-one **17e**

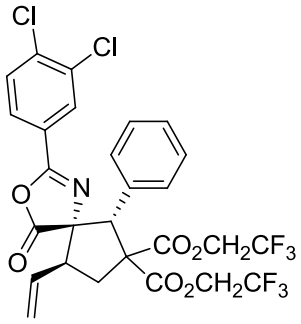


To a stirred solution of 2-(3,4-dichlorobenzamido)acetic acid (1.30 g, 5.24 mmol) in methylene chloride (50 mL) was added 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (1.11 g, 1.1 mmol). The reaction was stirred for 1 h, then water (50 mL) was added. The reaction mixture was washed with water, the organic phase was dried ($MgSO_4$), and the solvent removed *in vacuo* to give 2-(3,4-dichlorophenyl)oxazol-5(4*H*)-one as a white solid (621 mg, 2.70 mmol, 51%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 (s, 1H), 7.85 (d, *J* = 8.5 Hz, 1H), 7.58 (d, *J* = 8.5 Hz, 1H), 4.46 (s, 2H); ^{13}C NMR (125

MHz, $CDCl_3$): δ = 133.5, 131.3, 129.9, 127.8, 127.1, 55.3; m.p. 129-133 °C. The intermediate azlactone was used without further purification.

A vial equipped with a stir bar was charged with a solution of 2-(3,4-dichlorophenyl)oxazol-5(4H)-one (100 mg, 0.430 mmol) and cyclohexanecarboxaldehyde (100 mg, 0.89 mmol) in methylene chloride (4 mL), then alumina (Brockmann grade I, basic, 2.00 g) was added. The vial was sealed and stirred vigorously for 2 h. The crude product was purified by flash column chromatography (10% diethyl ether in petroleum ether) to give the title compound **17e** (42 mg, 0.130 mmol, 30%); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.18 (d, *J* = 2.0 Hz, 1H), 7.89 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.58 (d, *J* = 8.5 Hz, 1H), 6.61 (d, *J* = 10.0 Hz, 1H), 3.01 (dtt, *J* = 10.0, 10.0, 3.0 Hz, 1H), 1.95-1.65 (m, 5H), 1.46-1.16 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.2, 160.8, 146.3, 137.8, 134.3, 133.8, 131.3, 129.9, 127.2, 125.9, 38.3, 32.0, 25.9, 25.4; IR (cm^{-1}): 2928, 2852, 1811, 1671, 1596, 1551, 1463, 1393, 1308, 1244, 1180, 1142, 1104, 1032, 960, 883, 726; HRMS (ESI+): observed 324.0553; calculated 324.0553 ($C_{16}H_{16}Cl_2NO_2$, $[M+H]^+$); m.p. 107-109 °C.

(5*S*,6*R*,9*S*)-Bis(2,2,2-trifluoroethyl) 2-(3,4-dichlorophenyl)-4-oxo-6-phenyl-9-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7,7-dicarboxylate **18a**

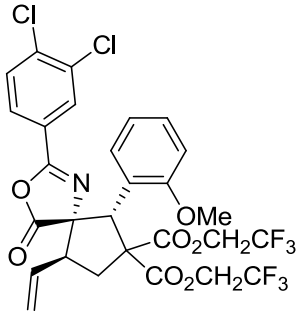


18a

An oven-dried reaction tube equipped with a stir bar was charged with palladium dibenzylideneacetone-chloroform complex (2.5 mg, 0.0025 mmol) and (*S*,*S*)-$\mathbf{L_1}$ chiral ligand, (5 mg, 0.0072 mmol). A second reaction tube, also equipped with a stir bar, was charged with bis(2,2,2-trifluoroethyl) 2-vinylcyclopropane-1,1-dicarboxylate (30 mg, 0.093 mmol) and (*Z*)-4-benzylidene-2-(3,4-dichlorophenyl)oxazol-5(4*H*)-one **17a** (30 mg, 0.094 mmol). Both tubes were sealed with a septum, evacuated, and backfilled with dry nitrogen. Toluene (degassed by sparging with nitrogen for 30 min, 1 mL) was added to each tube, and the tubes were for stirred 20 min. The contents of the first reaction tube were transferred to the second test tube *via* syringe, and the mixture was

stirred at room temperature for 16 h. The solvent was removed *in vacuo* to give the crude product, which was purified by flash column chromatography (5% to 10% diethyl ether in petroleum ether) to give the title compound **18a** as a colorless oil (41 mg, 0.064 mmol, 68%), as a 10:1 mixture of diastereomers (by crude ^{1}H NMR) and with a 96% e.e. for the major diastereomer (by chiral HPLC, Chiralpak OD-H column, 2% isopropanol, 98% heptanes, UV wavelength 254 nm; retention times: 10.94 min (minor enantiomer), 12.92 min (major enantiomer)); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 2.0 Hz, 1H), 7.72 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.53 (d, *J* = 8.5 Hz, 1H), 7.32-7.41 (m, 2H), 7.20-7.32 (m, 3H), 5.78 (ddd, *J* = 17.0, 10.0, 8.5 Hz, 1H), 5.25 (d, *J* = 17.0 Hz, 1H), 5.23 (d, *J* = 10.0 Hz, 1H), 4.79 (s, 1H), 4.68 (dq, *J* = 12.5, 8.5 Hz, 1H), 4.45 (dq, *J* = 12.5, 8.5 Hz, 1H), 4.43 (dq, *J* = 12.5, 8.5 Hz, 1H), 3.68 (ddd, *J* = 10.0, 8.5, 7.0 Hz, 1H), 3.44 (dq, *J* = 12.5, 8.5 Hz, 1H), 3.19 (dd, *J* = 13.5, 7.0, Hz, 1H), 2.52 (dd, *J* = 13.5, 10.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 177.9, 168.9, 168.0, 158.7, 137.8, 133.8, 133.7, 133.0, 131.2, 131.1, 130.0, 128.5, 128.2, 127.2, 125.5, 122.9 (q, $J_{C\text{-}F}$ = 227 Hz), 122.5 (q, $J_{C\text{-}F}$ = 227 Hz), 120.8, 80.5, 65.1, 61.8 (q, $J_{C\text{-}F}$ =37 Hz, 1C), 61.6 (q, $J_{C\text{-}F}$ = 37 Hz, 1C), 61.3, 58.2, 53.6; ^{19}F NMR (376 MHz, $CDCl_3$): −74.23 (t, *J* = 8.6 Hz, 3F), −74.32 (t, *J* = 7.1 Hz, 3F); IR(cm^{-1}): 2972, 1822, 1753, 1654, 1472, 1454, 1284, 1240, 1171, 1124, 1091, 974, 898, 744, 706, 651; HRMS (ESI+): observed 638.0557; calculated 638.0566 ($C_{27}H_{20}Cl_2F_6NO_6$, $[M+H]^+$); $[\alpha]^{25}_D$ = −37.5° (c = 1.0, CH_2Cl_2).

(5*S*,6*R*,9*S*)-Bis(2,2,2-trifluoroethyl) 2-(3,4-dichlorophenyl)-6-(2-methoxyphenyl)-4-oxo-9-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7,7-dicarboxylate **18b**

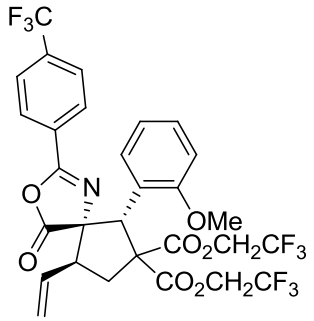


18b

An oven-dried reaction tube equipped with a stir bar was charged with palladium dibenzylideneacetone-chloroform complex (3 mg, 0.003 mmol) and (*S*,*S*)-$\mathbf{L_1}$ chiral ligand, (6 mg, 0.009 mmol). A second reaction tube, also equipped with a stir bar, was charged with bis(2,2,2-trifluoroethyl) 2-vinylcyclopropane-1,1-dicarboxylate (30 mg, 0.093 mmol) and (*Z*)-2-(3,4-

dichlorophenyl)-4-(2-methoxybenzylidene)oxazol-5(4*H*)-one **17b** (53 mg, 0.152 mmol). Both tubes were sealed with a septum, evacuated, and backfilled with dry nitrogen. Toluene (degassed by sparging with nitrogen for 30 min, 1 mL) was added to each tube, and the tubes were for stirred 20 min. The contents of the first reaction tube were transferred to the second test tube *via* syringe, and the mixture was stirred at room temperature for 16 h. The solvent was removed *in vacuo* to give the crude product, which was purified by flash column chromatography (5% to 10% diethyl ether in petroleum ether) to give the title compound **18b** as a colorless oil (18 mg, 0.027 mmol, 29%), as a >19:1 mixture of diastereomers (by crude ^{1}H NMR) and with a 92% e.e. for the major diastereomer (by chiral HPLC, Chiralpak AD-H column, 2% isopropanol, 98% heptanes, UV wavelength 254 nm; retention times: 14.09 min (major enantiomer), 15.09 min (minor enantiomer)); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.90 (d, *J* = 2.0 Hz, 1H), 7.64 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.29 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.22-7.15 (m, 1H), 6.87-6.77 (m, 2H), 5.70 (ddd, *J* = 17.0, 10.0, 8.0 Hz, 1H), 5.39 (s, 1H), 5.27-5.13 (m, 2H), 4.74-4.55 (m, 1H), 4.55-4.32 (m, 2H), 3.76 (s, 3H), 3.66 (dt, *J* = 11.0, 7.5 Hz, 1H), 3.61-3.42 (m, 2H), 3.08 (dd, *J* = 13.5, 7.5 Hz, 1H), 2.59 (dd, *J* = 13.5, 11.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.5, 168.5, 168.3, 158.6, 158.0, 143.6, 137.5, 133.0, 131.7, 130.7, 129.9, 129.4, 129.2, 128.6, 127.1, 121.3 (q, *J* = 284 Hz, 2C), 120.9, 111.0, 80.4, 64.5, 61.8 (q, J_{C-F} = 29.2), 61.4 (q, J_{C-F} = 29.1), 55.8, 53.1, 50.0, 37.9; ^{19}F NMR (376 MHz, $CDCl_3$): −74.27 (t, *J* = 7.5 Hz, 6F); IR(cm^{-1}): 2924, 2852, 1820, 1755, 1654, 1494, 1466, 1413, 1283, 1249, 1169, 1127, 1085, 974, 897; HRMS (ESI+): observed 668.0665; calculated 668.0672 ($C_{28}H_{22}Cl_2F_6NO_7$, $[M+H]^+$); $[\alpha]^{25}_D$ = +16.21° (c = 0.46, CH_2Cl_2).

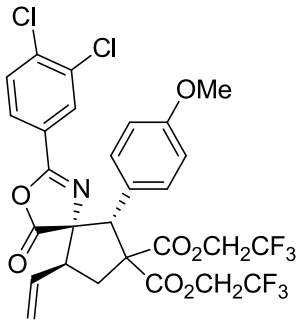
(5*S*,6*R*,9*S*)-Bis(2,2,2-trifluoroethyl) 6-(2-methoxyphenyl)-4-oxo-2-(4-(trifluoromethyl)phenyl)-9-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7,7-dicarboxylate **18c**



18c

An oven-dried reaction tube equipped with a stir bar was charged with palladium dibenzylideneacetone-chloroform complex (3 mg, 0.003 mmol) and (*S*,*S*)-$\mathbf{L_1}$ chiral ligand, (6 mg, 0.009 mmol). A second reaction tube, also equipped with a stir bar, was charged with bis(2,2,2-trifluoroethyl) 2-vinylcyclopropane-1,1-dicarboxylate (30 mg, 0.093 mmol) and (*Z*)-4-(2-methoxybenzylidene)-2-(4-(trifluoromethyl)phenyl)oxazol-5(4*H*)-one **17c** (53 mg, 0.152 mmol). Both tubes were sealed with a septum, evacuated, and backfilled with dry nitrogen. Toluene (degassed by sparging with nitrogen for 30 min, 1 mL) was added to each tube, and the tubes were for stirred 20 min. The contents of the first reaction tube were transferred to the second test tube *via* syringe, and the mixture was stirred at room temperature for 16 h. The solvent was removed *in vacuo* to give the crude product, which was purified by flash column chromatography (5% to 10% diethyl ether in petroleum ether) to give the title compound **18c** as a colorless oil (40 mg, 0.060 mmol, 64%), as a >19:1 mixture of diastereomers (by crude ^{1}H NMR) and with a 99% e.e. for the major diastereomer (by chiral HPLC, Chiralpak IA column, 2% isopropanol, 98% heptanes, UV wavelength 254 nm; retention times: 9.57 min (major enantiomer), 11.88 min (minor enantiomer)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 9.0 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.31 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.23-7.11 (m, 1H), 6.84 (t, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 8.5 Hz, 1H), 5.72 (ddd, *J* = 17.5, 10.0, 8.5 Hz, 1H), 5.40 (s, 1H), 5.21 (d, *J* = 17.5 Hz, 1H), 5.18 (d, *J* = 10.0 Hz, 1H), 4.61 (dq, *J* = 16.0, 8.0, 1H), 4.53-4.35 (m, 2H), 3.76 (s, 3H), 3.69 (ddd, *J* = 11.5, 8.5, 7.0 Hz, 1H), 3.56 (dq, *J* = 16.0, 8.0, 1H), 3.10 (dd, *J* = 13.5, 7.0 Hz, 1H), 2.61 (dd, *J* = 13.5, 11.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.5, 168.5, 168.3, 159.2, 158.0, 133.0, 131.7, 129.4, 128.5, 125.9, 125.8, 124.1 (q, $J_{C\text{-}F}$ = 349 Hz, 1C), 122.8, 122.7 (q, $J_{C\text{-}F}$ = 276 Hz, 1C), 122.4 (q, $J_{C\text{-}F}$ = 276 Hz, 1C), 120.8, 119.7, 111.0, 80.4, 64.5, 61.7 (q, $J_{C\text{-}F}$= 39.9 Hz, 1C), 61.5 (q, $J_{C\text{-}F}$ = 37.2 Hz, 1C), 55.8, 53.1, 50.1, 37.9, 29.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −63.63 (s, 3F), −74.27 (t, *J* = 8.6 Hz, 6F); IR(cm^{-1}): 2947, 1818, 1756, 1654, 1495, 1414, 1324, 1285, 1169, 1130, 966, 854, 756; HRMS (ESI+): observed 668.1316; calculated 668.1325 ($C_{28}H_{23}F_9NO_7$, $[M+H]^+$); $[\alpha]^{25}_D$ = +5.70° (c = 0.46, CH_2Cl_2).

(5*S*,6*R*,9*S*)-Bis(2,2,2-trifluoroethyl) 2-(3,4-dichlorophenyl)-6-(4-methoxyphenyl)-4-oxo-9-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7,7-dicarboxylate **18d**

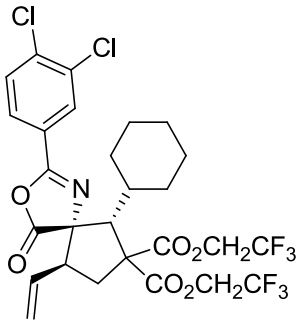


18d

An oven-dried reaction tube equipped with a stir bar was charged with palladium dibenzylideneacetone-chloroform complex (3 mg, 0.003 mmol) and (*S*,*S*)-$\mathbf{L_1}$ chiral ligand, (8 mg, 0.011 mmol). A second reaction tube, also equipped with a stir bar, was charged with bis(2,2,2-trifluoroethyl) 2-vinylcyclopropane-1,1-dicarboxylate (34 mg, 0.098 mmol) and (*Z*)-2-(3,4-dichlorophenyl)-4-(4-methoxybenzylidene)oxazol-5(4*H*)-one **17d** (34 mg, 0.097 mmol). Both tubes were sealed with a septum, evacuated, and backfilled with dry nitrogen. Toluene (degassed by sparging with nitrogen for 30 min, 1 mL) was added to each tube, and the tubes were for stirred 20 min. The contents of the first reaction tube were transferred to the second test tube *via* syringe, and the mixture was stirred at room temperature for 16 h. The solvent was removed *in vacuo* to give the crude product, which was purified by flash column chromatography (5% to 10% diethyl ether in petroleum ether) to give the title compound **18d** as a colorless oil (53 mg, 0.079 mmol, 81%), as a >19:1 mixture of diastereomers (by crude ^{1}H NMR) and with a 95% e.e. for the major diastereomer (by chiral HPLC, Chiralpak OD-H column, 2% isopropanol, 98% heptanes, UV wavelength 254 nm; retention times: 9.59 min (minor enantiomer), 13.27 min (major enantiomer)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 2.0 Hz, 1H), 7.71 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.56-7.46 (m, 1H), 7.28-7.18 (m, 2H), 6.74 (d, *J* = 9.0 Hz, 2H), 5.76 (ddd, *J* = 16.5, 10.5, 8.5 Hz, 1H), 5.21 (d, *J* = 16.5 Hz, 1H), 5.19 (d, *J* = 10.5 Hz, 1H), 4.72 (s, 1H), 4.69-4.58 (m, 1H), 4.51-4.40 (m, 2H), 3.73 (s, 3H), 3.66-3.48 (m, 2H), 3.16 (dd, *J* = 13.5, 7.0 Hz, 1H), 2.46 (dd, *J* = 13.5, 9.5 Hz, 1H);. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.9, 169.0, 168.1, 159.6, 158.6, 137.7, 133.7, 133.2, 132.3, 131.1, 129.9, 127.2, 125.5, 125.4, 122.7 (q, $J_{C\text{-}F}$ = 275 Hz, 1C), 122.4 (q, $J_{C\text{-}F}$ = 275 Hz, 1C), 120.6, 113.5, 80.6, 64.9, 62.0 (q, $J_{C\text{-}F}$ = 37 Hz, 1C), 61.6 (q, $J_{C\text{-}F}$ = 37 Hz, 1C), 57.8, 55.4, 53.4, 38.2; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −74.20-−74.27 (m, 6F); IR (cm^{-1}): 2924, 1821, 1753, 1652, 1611, 1514, 1469, 1414, 1283, 1251, 1170,

1033, 975, 897; HRMS (ESI+): observed 668.0662; calculated 668.0672 ($C_{28}H_{22}Cl_2F_6NO_7$); $[\alpha]^{25}_D$ = −21.06° (c = 1.0, CH_2Cl_2).

(5*S*,6*R*,9*S*)-Bis(2,2,2-trifluoroethyl) 6-cyclohexyl-2-(3,4-dichlorophenyl)-4-oxo-9-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7,7-dicarboxylate **18e**



18e

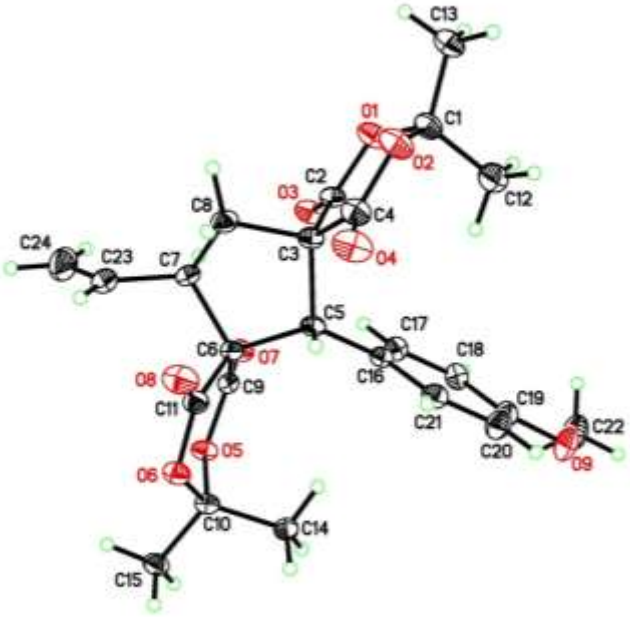
An oven-dried reaction tube equipped with a stir bar was charged with palladium dibenzylideneacetone-chloroform complex (3 mg, 0.003 mmol) and (*S*,*S*)-$\mathbf{L_1}$ chiral ligand, (6 mg, 0.009 mmol). A second reaction tube, also equipped with a stir bar, was charged with bis(2,2,2-trifluoroethyl) 2-vinylcyclopropane-1,1-dicarboxylate (30 mg, 0.093 mmol) and (*Z*)-4-(cyclohexylmethylene)-2-(3,4-dichlorophenyl)oxazol-5(4*H*)-one **17e** (42 mg, 0.130 mmol). Both tubes were sealed with a septum, evacuated, and backfilled with dry nitrogen. Toluene (degassed by sparging with nitrogen for 30 min, 1 mL) was added to each tube, and the tubes were for stirred 20 min. The contents of the first reaction tube were transferred to the second test tube *via* syringe, and the mixture was stirred at room temperature for 16 h. The solvent was removed *in vacuo* to give the crude product, which was purified by flash column chromatography (5% to 10% diethyl ether in petroleum ether) to give the title compound **18e** as a gummy solid (18 mg, 0.028 mmol, 31%), as a >19:1 mixture of diastereomers (by crude ^{1}H NMR) and with a 70% e.e. for the major diastereomer (by chiral HPLC, Chiralpak AD-H column, 2% isopropanol, 98% heptanes, UV wavelength 254 nm; retention times: 9.4 min (major enantiomer), 10.3 min (minor enantiomer)); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 1.5 Hz, 1H), 7.80 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.59 (d, *J* = 8.5 Hz, 1H), 5.75 (dt, *J* = 16.5, 9.5 Hz, 1H), 5.13 (d, *J* = 10.0 Hz, 1H), 5.07 (d, *J* = 16.5 Hz, 1H), 4.76 (dq, *J* = 12.5, 8.5 Hz, 1H), 4.70-4.58 (m, 2H), 4.53 (dq, *J* = 12.5, 8.5 Hz, 1H), 3.16 (d, *J* = 11.0 Hz, 1H), 3.09-2.96 (m, 1H), 2.84 (dd, *J* = 12.5, 6.5 Hz, 1H), 2.14 (t, *J* = 12.5 Hz, 1H), 1.93 (q, *J* = 11.0 Hz, 1H), 1.80 (d, *J* = 12.5 Hz, 2H), 1.73-1.62 (m, 1H), 1.29-1.13 (m, 3H), 1.09-1.01 (m, 2H), 0.96-0.84 (m, 3H); ^{13}C

NMR (125 MHz, $CDCl_3$): δ = 178.3, 169.6, 167.6, 158.7, 137.8, 134.2, 133.8, 131.3, 130.0, 127.2, 125.5, 123.1 (q, $J_{C\text{-}F}$= 275 Hz, 1C), 122.7 (q, $J_{C\text{-}F}$= 275 Hz, 1C), 120.4, 79.2, 62.1, 61.7 (q, $J_{C\text{-}F}$ = 28.5 Hz, 2C), 53.2, 42.1, 32.1, 32.0, 30.0, 26.3, 26.1, 26.0; ^{19}F (376 MHz, $CDCl_3$): δ = −73.23-−74.86 (m, 6F); IR (cm^{-1}): 2935, 2858 1758, 1730, 1283, 1168, 976; HRMS (ESI+): observed 644.1045; calculated ($C_{27}H_{24}Cl_2F_6NO_6$, $[M+H]^+$); $[\alpha]^{25}_D$ = +2.80° (c = 0.5, CH_2Cl_2).

Appendix A – Crystal Structure of compound 5c

The compound crystallizes as colorless rod-like crystals from a chloroform / hexanes solution. There are three crystallographically independent, yet chemically identical, molecules of the compound in the asymmetric unit of the primitive, acentric, orthorhombic space group $P2_12_12_1$. The correct enantiomorph and handedness of the molecules was determined by comparison with the known handedness and by comparison of intensities of Friedel pairs of reflections. Both techniques agree and the correct configuration is depicted in the Figures. The Flack analysis, determined by comparison of intensities of Friedel pairs of reflections yields a Flack *x* parameter of -0.01(6); a value of zero indicates the correct enantiomorph, a value of one the inverted absolute structure. Bayesian statistical analysis was also performed on the data yielding a Hooft *y* parameter of -0.021(16), with values of zero representing the correct configuration and one the inverted absolute configuration. P2(true) and P3(true) values of 1.000 and 1.000 are also reported. These values are a measure of enantiopurity of the sample analyzed. A value of one indicates an enantiopure crystal.

The structure of the compound is as expected. The three independent molecules all exhibit the same configuration at C5 (C29, C53). The primary difference between all three molecules is that one molecule has adopted an opposite direction to the partial boat conformation of one of the rings (molecule 1 adopts the opposite geometry, see Figures). Otherwise the three molecules are essentially identical and their derived parameters (bond distances and angles) are well within statistical error and support this.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O1
C1
O2
C2
O3
C8
C4
C12
C24
C23
C7
C3
O4
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C17
C6
O7
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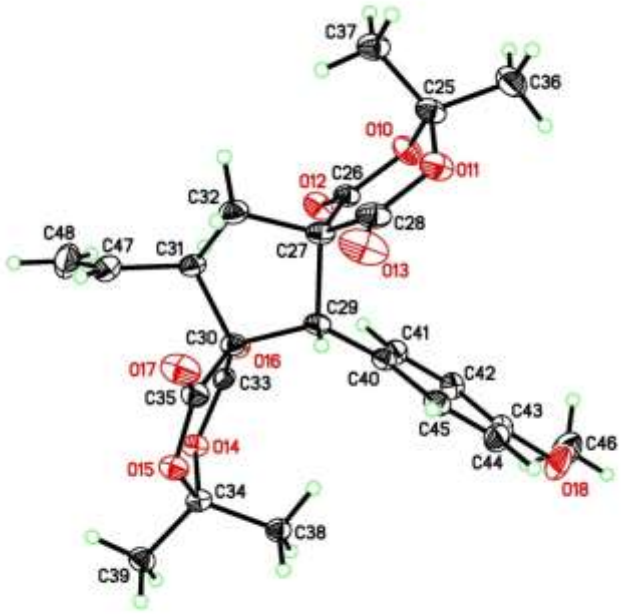
C22
O5
C20
O9
O6
C10
C14
C15


C37
C25
C36
O10
O11
O12
C26
C32
C28
C48
C47
C31
C27
O13
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C41
O17
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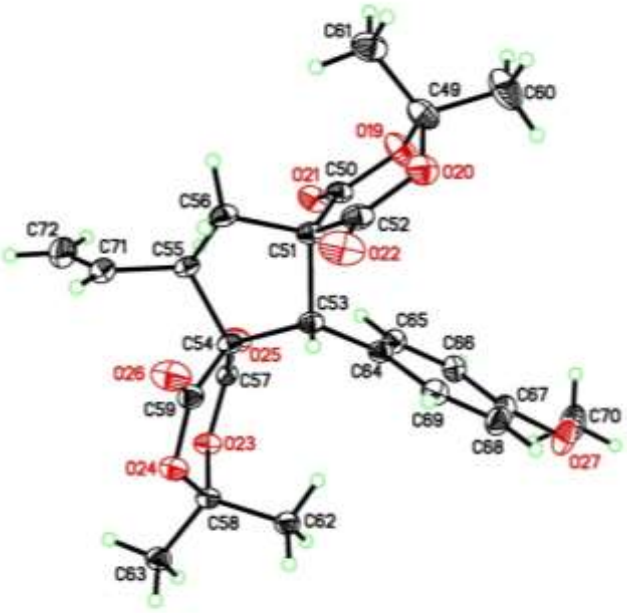
O14
C46
O15
C44
O18
C34
C38
C39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C51
O22
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C54
O25
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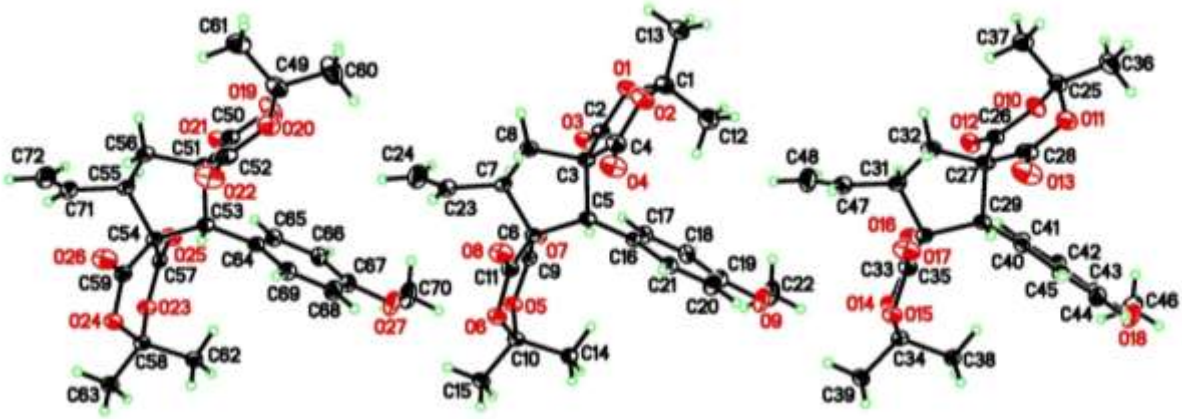
C68
O27
O24
C58
C62
C63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O21
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C51
C52
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C55
O22
C71
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C66
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C32
C28
C48
C31
C27
O13
C47
C29
C41
O16
O17
C42
C33
C35
C40
C43
O14
O15
C45
C46
C44
O18
C34
C38
C39

CRYSTAL SUMMARY

Crystal data for $C_{24}H_{26}O_9$; M_r = 458.45; Orthorhombic; space group $P2_12_12_1$; *a* = 6.9048(2) Å; *b* = 30.4010(9) Å; *c* = 32.6302(9) Å; α = 90°; β = 90°; γ = 90°; V = 6849.5(3) $Å^3$; Z = 12; T = 120(2) K; λ(Cu-Kα) = 1.54184 Å; μ(Cu-Kα) = 0.860 mm^{-1}; d_{calc} = 1.334g.cm^{-3}; 136106 reflections collected; 12961 unique (R_{int} = 0.0306); giving R_1 = 0.0296, wR_2 = 0.0800 for 12840 data with [I>2σ(I)] and R_1 = 0.0299, wR_2 = 0.0803 for all 12961 data. Residual electron density ($e^-.Å^{-3}$) max/min: 0.395/-0.168.

An arbitrary sphere of data were collected on a colorless rod-like crystal, having approximate dimensions of 0.38 × 0.22 × 0.14 mm, on a Bruker APEX-II diffractometer using a combination of ω- and φ-scans of 0.5°. Data were corrected for absorption and polarization effects and analyzed for space group determination. The structure was solved by direct methods and expanded routinely. The model was refined by full-matrix least-squares analysis of F^2 against all reflections. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Thermal parameters for the hydrogens were tied to the isotropic thermal parameter of the atom to which they are bonded (1.5 × for methyl, 1.2 × for all others).

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G. M. Sheldrick, *Acta Cryst.*, **2008**, *A64*, 112.

R. W. W. Hooft, L. H. Straver & A. L. Spek, *J. Appl. Cryst.*, **2008**, *41*, 96.

H. D. Flack, *Acta Cryst.*, **1983**, *A39*, 876.

Table 1. Crystal data and structure refinement for su1211.

Identification code	su1211	
Empirical formula	$C_{24}H_{26}O_9$	
Formula weight	458.45	
Temperature	120(2) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 6.9048(2) Å	α = 90°
	b = 30.4010(9) Å	β = 90°
	c = 32.6302(9) Å	γ = 90°
Volume	6849.5(3) $Å^3$	
Z	12	
Density (calculated)	1.334 $g.cm^{-3}$	
Absorption coefficient (μ)	0.860 mm^{-1}	
F(000)	2904	
Crystal color, habit	colorless, rod	
Crystal size	0.38 × 0.22 × 0.14 mm^3	
θ range for data collection	1.99 to 71.34°	
Index ranges	$-8 \leq h \leq 6$, $-37 \leq k \leq 37$, $-39 \leq l \leq 40$	

Reflections collected	136106
Independent reflections	12961 [R_{int} = 0.0306]
Completeness to θ = 71.34°	97.5 %
Absorption correction	Numerical
Max. and min. transmission	1.0000 and 0.9014
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12961 / 0 / 907
Goodness-of-fit on F^2	1.064
Final R indices [I>2σ(I)]	R_1 = 0.0296, wR_2 = 0.0800
R indices (all data)	R_1 = 0.0299, wR_2 = 0.0803
Absolute structure parameter	-0.01(6)
Largest diff. peak and hole	0.395 and -0.168 $e^-.Å^{-3}$

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$)

for su1211. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	0.92908(14)	0.51349(3)	0.69247(3)	0.026(1)
O(2)	0.67122(14)	0.50295(3)	0.73869(3)	0.027(1)
O(3)	0.90451(13)	0.55112(3)	0.63592(3)	0.024(1)
O(4)	0.37732(14)	0.52795(4)	0.72671(3)	0.030(1)
O(5)	0.39260(13)	0.61534(3)	0.55006(2)	0.018(1)
O(6)	0.14637(13)	0.62718(3)	0.59868(2)	0.019(1)
O(7)	0.68576(13)	0.59524(3)	0.56595(3)	0.022(1)
O(8)	0.20051(15)	0.62236(3)	0.66458(3)	0.028(1)
O(9)	0.42256(16)	0.39107(3)	0.54984(3)	0.030(1)
C(1)	0.8329(2)	0.48265(4)	0.71915(4)	0.022(1)
C(2)	0.82439(18)	0.53758(4)	0.66577(3)	0.018(1)
C(3)	0.61911(18)	0.55042(4)	0.67821(3)	0.017(1)
C(4)	0.5417(2)	0.52534(4)	0.71550(4)	0.022(1)
C(5)	0.46449(17)	0.54898(4)	0.64292(3)	0.016(1)
C(6)	0.46142(17)	0.59666(4)	0.62242(3)	0.016(1)
C(7)	0.61668(19)	0.62348(4)	0.64781(4)	0.020(1)

C(8)	0.62459(19)	0.60033(4)	0.68947(4)	0.021(1)
C(9)	0.52264(17)	0.60071(4)	0.57759(3)	0.015(1)
C(10)	0.18847(18)	0.61145(4)	0.55795(3)	0.016(1)
C(11)	0.25894(18)	0.61583(4)	0.63052(4)	0.018(1)
C(12)	0.7665(2)	0.44371(5)	0.69415(4)	0.035(1)
C(13)	0.9769(2)	0.47116(4)	0.75183(4)	0.027(1)
C(14)	0.12776(18)	0.56410(4)	0.55238(3)	0.018(1)
C(15)	0.08876(19)	0.64251(4)	0.52892(4)	0.021(1)
C(16)	0.46551(18)	0.50783(4)	0.61666(3)	0.016(1)
C(17)	0.60851(18)	0.49723(4)	0.58789(4)	0.019(1)
C(18)	0.59939(19)	0.45836(4)	0.56519(4)	0.021(1)
C(19)	0.4471(2)	0.42953(4)	0.57098(4)	0.022(1)
C(20)	0.3043(2)	0.43902(4)	0.59997(4)	0.025(1)
C(21)	0.31417(19)	0.47772(4)	0.62220(4)	0.020(1)
C(22)	0.5680(2)	0.37929(5)	0.52097(5)	0.034(1)
C(23)	0.5855(2)	0.67237(4)	0.65011(4)	0.030(1)
C(24)	0.7104(3)	0.70066(5)	0.63458(5)	0.044(1)
O(10)	0.91339(14)	0.14994(3)	0.67854(3)	0.025(1)
O(11)	0.64828(14)	0.13760(3)	0.72204(3)	0.027(1)
O(12)	0.92231(14)	0.20198(3)	0.63212(3)	0.025(1)
O(13)	0.38622(16)	0.17860(4)	0.72041(3)	0.039(1)

O(14)	0.41129(13)	0.27554(3)	0.54947(2)	0.019(1)
O(15)	0.16577(13)	0.28315(3)	0.59909(3)	0.020(1)
O(16)	0.70389(13)	0.25290(3)	0.56320(3)	0.024(1)
O(17)	0.22904(15)	0.27689(4)	0.66449(3)	0.032(1)
O(18)	0.41877(16)	0.05387(3)	0.53313(3)	0.033(1)
C(25)	0.85547(19)	0.13898(4)	0.71966(4)	0.023(1)
C(26)	0.83436(18)	0.18539(4)	0.65979(3)	0.018(1)
C(27)	0.63607(18)	0.20109(4)	0.67410(3)	0.020(1)
C(28)	0.5463(2)	0.17233(5)	0.70775(4)	0.025(1)
C(29)	0.48143(18)	0.20241(4)	0.63806(3)	0.017(1)
C(30)	0.48248(18)	0.25128(4)	0.62029(3)	0.018(1)
C(31)	0.6424(2)	0.27531(4)	0.64655(4)	0.022(1)
C(32)	0.6481(2)	0.25021(4)	0.68715(4)	0.024(1)
C(33)	0.54184(18)	0.25814(4)	0.57559(4)	0.017(1)
C(34)	0.20718(18)	0.27100(4)	0.55723(3)	0.016(1)
C(35)	0.28296(19)	0.27095(4)	0.62991(4)	0.020(1)
C(36)	0.9272(2)	0.09277(5)	0.72725(4)	0.032(1)
C(37)	0.9334(2)	0.17218(4)	0.74976(4)	0.026(1)
C(38)	0.14587(18)	0.22428(4)	0.54838(4)	0.019(1)
C(39)	0.10743(19)	0.30468(4)	0.53082(4)	0.022(1)
C(40)	0.47974(18)	0.16320(4)	0.60933(3)	0.017(1)

C(41)	0.62024(19)	0.15458(4)	0.57965(4)	0.021(1)
C(42)	0.6050(2)	0.11827(4)	0.55374(4)	0.022(1)
C(43)	0.4485(2)	0.09004(4)	0.55736(4)	0.023(1)
C(44)	0.3085(2)	0.09755(4)	0.58724(4)	0.025(1)
C(45)	0.32481(19)	0.13361(4)	0.61273(4)	0.021(1)
C(46)	0.5658(3)	0.04274(5)	0.50473(5)	0.040(1)
C(47)	0.6182(2)	0.32441(5)	0.64923(4)	0.033(1)
C(48)	0.7318(3)	0.35166(5)	0.62872(5)	0.042(1)
O(19)	0.84728(16)	0.82916(3)	0.68393(3)	0.033(1)
O(20)	0.57391(15)	0.82109(3)	0.72637(3)	0.028(1)
O(21)	0.88005(14)	0.88113(3)	0.63816(3)	0.025(1)
O(22)	0.32488(15)	0.86586(4)	0.72324(3)	0.036(1)
O(23)	0.38180(13)	0.94490(3)	0.54522(2)	0.019(1)
O(24)	0.13351(13)	0.96035(3)	0.59254(2)	0.021(1)
O(25)	0.67614(13)	0.92880(3)	0.56363(3)	0.024(1)
O(26)	0.18216(15)	0.95913(4)	0.65857(3)	0.031(1)
O(27)	0.41424(17)	0.72498(3)	0.54420(3)	0.032(1)
C(49)	0.7818(2)	0.81881(5)	0.72446(4)	0.026(1)
C(50)	0.78235(18)	0.86550(4)	0.66461(3)	0.019(1)
C(51)	0.58239(19)	0.88276(4)	0.67641(3)	0.019(1)
C(52)	0.4835(2)	0.85670(4)	0.71085(4)	0.023(1)

C(53)	0.43575(18)	0.88199(4)	0.63887(3)	0.017(1)
C(54)	0.44366(17)	0.92977(4)	0.61867(3)	0.017(1)
C(55)	0.5984(2)	0.95538(4)	0.64512(4)	0.021(1)
C(56)	0.5936(2)	0.93236(4)	0.68698(4)	0.022(1)
C(57)	0.51066(17)	0.93307(4)	0.57410(3)	0.016(1)
C(58)	0.17683(18)	0.94244(4)	0.55278(3)	0.016(1)
C(59)	0.24281(18)	0.95032(4)	0.62525(4)	0.019(1)
C(60)	0.8376(3)	0.77165(5)	0.73175(5)	0.042(1)
C(61)	0.8673(2)	0.85031(5)	0.75530(4)	0.031(1)
C(62)	0.11100(18)	0.89529(4)	0.54912(4)	0.019(1)
C(63)	0.08199(19)	0.97267(4)	0.52225(4)	0.021(1)
C(64)	0.44373(18)	0.84085(4)	0.61273(3)	0.017(1)
C(65)	0.59069(19)	0.83081(4)	0.58479(4)	0.020(1)
C(66)	0.5867(2)	0.79241(4)	0.56154(4)	0.021(1)
C(67)	0.4340(2)	0.76313(4)	0.56604(4)	0.022(1)
C(68)	0.2872(2)	0.77190(4)	0.59426(4)	0.025(1)
C(69)	0.29289(19)	0.81013(4)	0.61718(4)	0.021(1)
C(70)	0.5642(3)	0.71376(5)	0.51644(5)	0.038(1)
C(71)	0.5740(2)	1.00451(4)	0.64721(4)	0.030(1)
C(72)	0.7034(3)	1.03184(5)	0.63190(5)	0.041(1)
H(5)	0.3382	0.5473	0.6578	0.019

H(7)	0.7449	0.6187	0.6343	0.024
H(8A)	0.5120	0.6085	0.7066	0.025
H(8B)	0.7452	0.6078	0.7043	0.025
H(12A)	0.6780	0.4537	0.6726	0.052
H(12B)	0.6995	0.4227	0.7120	0.052
H(12C)	0.8791	0.4294	0.6816	0.052
H(13A)	1.0963	0.4604	0.7391	0.041
H(13B)	0.9229	0.4482	0.7696	0.041
H(13C)	1.0056	0.4974	0.7682	0.041
H(14A)	0.1559	0.5548	0.5243	0.027
H(14B)	-0.0114	0.5613	0.5576	0.027
H(14C)	0.1994	0.5455	0.5716	0.027
H(15A)	0.1159	0.6337	0.5006	0.031
H(15B)	0.1367	0.6725	0.5335	0.031
H(15C)	-0.0513	0.6416	0.5338	0.031
H(17)	0.7137	0.5169	0.5837	0.023
H(18)	0.6978	0.4517	0.5458	0.025
H(20)	0.2008	0.4190	0.6044	0.030
H(21)	0.2158	0.4840	0.6417	0.023
H(22A)	0.5357	0.3508	0.5086	0.052
H(22B)	0.6934	0.3771	0.5349	0.052

H(22C)	0.5752	0.4018	0.4995	0.052
H(23)	0.4722	0.6832	0.6632	0.036
H(24A)	0.8244	0.6903	0.6214	0.053
H(24B)	0.6863	0.7314	0.6366	0.053
H(29)	0.3543	0.2003	0.6526	0.021
H(31)	0.7691	0.2698	0.6326	0.026
H(32A)	0.5370	0.2584	0.7048	0.029
H(32B)	0.7699	0.2562	0.7022	0.029
H(36A)	0.8645	0.0726	0.7080	0.048
H(36B)	0.8957	0.0840	0.7554	0.048
H(36C)	1.0678	0.0917	0.7233	0.048
H(37A)	1.0746	0.1738	0.7472	0.039
H(37B)	0.8990	0.1632	0.7777	0.039
H(37C)	0.8772	0.2011	0.7439	0.039
H(38A)	0.1724	0.2173	0.5196	0.028
H(38B)	0.0069	0.2211	0.5538	0.028
H(38C)	0.2184	0.2041	0.5661	0.028
H(39A)	0.1351	0.2986	0.5019	0.032
H(39B)	0.1548	0.3341	0.5379	0.032
H(39C)	-0.0327	0.3033	0.5355	0.032
H(41)	0.7281	0.1738	0.5771	0.025

H(42)	0.7017	0.1129	0.5336	0.026
H(44)	0.2022	0.0780	0.5901	0.031
H(45)	0.2287	0.1385	0.6331	0.025
H(46A)	0.5294	0.0158	0.4902	0.060
H(46B)	0.6879	0.0380	0.5194	0.060
H(46C)	0.5818	0.0668	0.4850	0.060
H(47)	0.5187	0.3361	0.6661	0.039
H(48A)	0.8318	0.3404	0.6117	0.051
H(48B)	0.7132	0.3825	0.6310	0.051
H(53)	0.3051	0.8807	0.6521	0.020
H(55)	0.7282	0.9495	0.6327	0.025
H(56A)	0.4791	0.9417	0.7030	0.026
H(56B)	0.7121	0.9390	0.7029	0.026
H(60A)	0.7710	0.7528	0.7119	0.062
H(60B)	0.8003	0.7631	0.7596	0.062
H(60C)	0.9780	0.7684	0.7285	0.062
H(61A)	1.0089	0.8495	0.7534	0.047
H(61B)	0.8271	0.8417	0.7830	0.047
H(61C)	0.8214	0.8802	0.7495	0.047
H(62A)	-0.0293	0.8937	0.5534	0.029
H(62B)	0.1769	0.8774	0.5698	0.029

H(62C)	0.1426	0.8842	0.5217	0.029
H(63A)	0.1115	0.9626	0.4944	0.031
H(63B)	0.1313	1.0026	0.5260	0.031
H(63C)	-0.0585	0.9724	0.5265	0.031
H(65)	0.6959	0.8507	0.5816	0.024
H(66)	0.6880	0.7863	0.5427	0.026
H(68)	0.1836	0.7517	0.5977	0.030
H(69)	0.1926	0.8158	0.6364	0.025
H(70A)	0.5341	0.6856	0.5034	0.057
H(70B)	0.6870	0.7113	0.5313	0.057
H(70C)	0.5752	0.7366	0.4954	0.057
H(71)	0.4616	1.0162	0.6600	0.035
H(72A)	0.8166	1.0207	0.6190	0.049
H(72B)	0.6834	1.0627	0.6337	0.049

Table 3. Anisotropic displacement parameters ($Å^2$) for su1211.

The anisotropic displacement factor exponent takes the form:

$-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	0.0193(5)	0.0350(5)	0.0230(4)	0.0104(4)	0.0015(4)	0.0038(4)
O(2)	0.0267(5)	0.0362(5)	0.0194(4)	0.0073(4)	0.0050(4)	0.0074(4)
O(3)	0.0176(5)	0.0342(5)	0.0192(4)	0.0072(4)	0.0025(3)	0.0012(4)
O(4)	0.0221(5)	0.0468(6)	0.0223(4)	0.0069(4)	0.0067(4)	0.0023(4)
O(5)	0.0122(4)	0.0258(4)	0.0159(4)	0.0044(3)	0.0009(3)	-0.0010(3)
O(6)	0.0174(4)	0.0249(4)	0.0158(4)	-0.0024(3)	-0.0003(3)	0.0056(3)
O(7)	0.0154(5)	0.0320(5)	0.0201(4)	0.0014(3)	0.0018(3)	0.0028(4)
O(8)	0.0276(5)	0.0409(5)	0.0162(4)	-0.0070(4)	0.0015(4)	0.0105(4)
O(9)	0.0349(6)	0.0199(4)	0.0361(5)	-0.0088(4)	0.0062(4)	-0.0045(4)
C(1)	0.0235(7)	0.0256(6)	0.0161(5)	0.0048(4)	0.0022(5)	0.0025(5)
C(2)	0.0174(6)	0.0227(5)	0.0134(5)	0.0004(4)	-0.0017(4)	0.0005(4)
C(3)	0.0162(6)	0.0220(5)	0.0141(5)	0.0008(4)	-0.0007(4)	0.0004(4)
C(4)	0.0237(7)	0.0272(6)	0.0143(5)	0.0006(4)	0.0027(5)	0.0028(5)
C(5)	0.0150(6)	0.0207(5)	0.0123(5)	0.0008(4)	-0.0005(4)	0.0006(4)
C(6)	0.0139(6)	0.0194(5)	0.0139(5)	-0.0015(4)	-0.0015(4)	0.0015(4)

C(7)	0.0223(6)	0.0205(5)	0.0173(5)	-0.0029(4)	-0.0057(5)	-0.0016(5)
C(8)	0.0239(7)	0.0243(6)	0.0151(5)	-0.0035(4)	-0.0038(5)	0.0015(5)
C(9)	0.0154(6)	0.0161(5)	0.0148(5)	-0.0010(4)	-0.0007(4)	-0.0009(4)
C(10)	0.0133(6)	0.0213(5)	0.0128(5)	0.0000(4)	0.0006(4)	0.0009(4)
C(11)	0.0188(6)	0.0210(5)	0.0150(5)	-0.0033(4)	-0.0014(4)	0.0027(4)
C(12)	0.0451(9)	0.0287(7)	0.0310(7)	-0.0002(5)	-0.0096(6)	0.0034(6)
C(13)	0.0298(7)	0.0301(6)	0.0217(6)	0.0063(5)	-0.0019(5)	0.0042(5)
C(14)	0.0150(6)	0.0202(5)	0.0187(5)	0.0000(4)	0.0000(4)	-0.0007(4)
C(15)	0.0186(6)	0.0224(5)	0.0217(6)	0.0055(4)	-0.0032(5)	0.0002(5)
C(16)	0.0154(6)	0.0184(5)	0.0146(5)	0.0014(4)	-0.0010(4)	0.0007(4)
C(17)	0.0183(6)	0.0197(5)	0.0189(5)	0.0016(4)	0.0025(4)	-0.0007(5)
C(18)	0.0234(6)	0.0195(5)	0.0195(5)	0.0009(4)	0.0039(5)	0.0018(5)
C(19)	0.0261(7)	0.0173(5)	0.0213(6)	-0.0011(4)	-0.0005(5)	0.0007(5)
C(20)	0.0221(7)	0.0231(6)	0.0288(6)	0.0000(5)	0.0034(5)	-0.0051(5)
C(21)	0.0158(6)	0.0232(5)	0.0195(5)	0.0022(4)	0.0021(4)	0.0001(5)
C(22)	0.0412(9)	0.0241(6)	0.0380(8)	-0.0119(6)	0.0098(7)	-0.0009(6)
C(23)	0.0381(8)	0.0233(6)	0.0276(6)	-0.0053(5)	-0.0136(6)	0.0019(6)
C(24)	0.0675(12)	0.0257(7)	0.0389(8)	0.0051(6)	-0.0154(8)	-0.0082(7)
O(10)	0.0257(5)	0.0282(4)	0.0197(4)	0.0064(3)	0.0041(4)	0.0064(4)
O(11)	0.0205(5)	0.0355(5)	0.0265(5)	0.0116(4)	-0.0009(4)	-0.0050(4)
O(12)	0.0195(5)	0.0303(4)	0.0244(4)	0.0095(4)	0.0052(4)	0.0000(4)

O(13)	0.0232(6)	0.0674(7)	0.0274(5)	0.0149(5)	0.0090(4)	0.0044(5)
O(14)	0.0146(4)	0.0249(4)	0.0164(4)	0.0037(3)	0.0014(3)	-0.0020(3)
O(15)	0.0190(5)	0.0272(4)	0.0144(4)	-0.0018(3)	0.0004(3)	0.0046(3)
O(16)	0.0163(5)	0.0316(5)	0.0228(4)	0.0006(3)	0.0027(3)	0.0008(4)
O(17)	0.0307(6)	0.0478(6)	0.0161(4)	-0.0068(4)	0.0012(4)	0.0136(4)
O(18)	0.0323(6)	0.0226(4)	0.0432(6)	-0.0118(4)	0.0039(4)	-0.0033(4)
C(25)	0.0196(6)	0.0301(6)	0.0184(6)	0.0088(5)	0.0003(5)	-0.0028(5)
C(26)	0.0172(6)	0.0228(5)	0.0141(5)	0.0024(4)	-0.0006(4)	-0.0009(4)
C(27)	0.0171(6)	0.0268(6)	0.0146(5)	0.0008(4)	-0.0008(4)	0.0001(5)
C(28)	0.0203(7)	0.0381(7)	0.0164(5)	0.0049(5)	-0.0008(5)	-0.0026(5)
C(29)	0.0156(6)	0.0227(6)	0.0137(5)	0.0014(4)	-0.0007(4)	0.0003(4)
C(30)	0.0174(6)	0.0205(5)	0.0146(5)	-0.0022(4)	-0.0014(4)	0.0007(4)
C(31)	0.0231(7)	0.0236(6)	0.0188(6)	-0.0039(5)	-0.0062(5)	0.0008(5)
C(32)	0.0266(7)	0.0279(6)	0.0183(6)	-0.0050(5)	-0.0054(5)	0.0020(5)
C(33)	0.0180(6)	0.0160(5)	0.0167(5)	-0.0014(4)	-0.0016(4)	-0.0029(4)
C(34)	0.0146(6)	0.0216(5)	0.0128(5)	0.0000(4)	0.0018(4)	-0.0019(4)
C(35)	0.0208(7)	0.0239(6)	0.0157(5)	-0.0020(4)	-0.0001(5)	0.0027(5)
C(36)	0.0351(8)	0.0303(7)	0.0303(7)	0.0098(6)	-0.0044(6)	0.0014(6)
C(37)	0.0248(7)	0.0340(7)	0.0201(6)	0.0058(5)	-0.0013(5)	-0.0051(5)
C(38)	0.0169(6)	0.0207(5)	0.0188(5)	0.0009(4)	-0.0002(4)	-0.0011(4)
C(39)	0.0216(7)	0.0221(6)	0.0206(6)	0.0040(4)	-0.0019(5)	0.0007(5)

C(40)	0.0163(6)	0.0196(5)	0.0163(5)	0.0030(4)	-0.0014(4)	0.0006(4)
C(41)	0.0194(6)	0.0209(5)	0.0215(6)	0.0011(4)	0.0015(5)	-0.0011(5)
C(42)	0.0228(7)	0.0204(5)	0.0214(6)	0.0009(4)	0.0030(5)	0.0004(5)
C(43)	0.0248(7)	0.0173(5)	0.0276(6)	-0.0001(5)	-0.0031(5)	0.0013(5)
C(44)	0.0204(7)	0.0227(6)	0.0334(7)	0.0031(5)	0.0007(5)	-0.0037(5)
C(45)	0.0176(6)	0.0230(6)	0.0225(6)	0.0037(4)	0.0012(5)	0.0007(5)
C(46)	0.0370(9)	0.0315(7)	0.0514(9)	-0.0201(7)	0.0041(7)	0.0005(6)
C(47)	0.0406(9)	0.0259(7)	0.0317(7)	-0.0093(5)	-0.0150(6)	0.0037(6)
C(48)	0.0686(12)	0.0210(6)	0.0376(8)	-0.0021(6)	-0.0134(8)	-0.0030(7)
O(19)	0.0399(6)	0.0366(5)	0.0212(4)	0.0116(4)	0.0101(4)	0.0153(5)
O(20)	0.0281(5)	0.0326(5)	0.0229(4)	0.0082(4)	0.0011(4)	-0.0056(4)
O(21)	0.0190(5)	0.0317(5)	0.0253(4)	0.0092(4)	0.0024(4)	0.0000(4)
O(22)	0.0240(5)	0.0587(7)	0.0245(5)	0.0082(4)	0.0071(4)	0.0005(5)
O(23)	0.0140(4)	0.0275(4)	0.0153(4)	0.0022(3)	0.0010(3)	-0.0014(3)
O(24)	0.0193(5)	0.0278(4)	0.0150(4)	-0.0039(3)	-0.0005(3)	0.0057(3)
O(25)	0.0151(5)	0.0339(5)	0.0229(4)	0.0023(4)	0.0025(3)	0.0023(4)
O(26)	0.0280(5)	0.0487(6)	0.0171(4)	-0.0081(4)	0.0015(4)	0.0111(4)
O(27)	0.0367(6)	0.0201(4)	0.0395(5)	-0.0096(4)	0.0055(5)	-0.0045(4)
C(49)	0.0291(7)	0.0312(7)	0.0179(6)	0.0077(5)	0.0044(5)	0.0047(5)
C(50)	0.0194(6)	0.0239(6)	0.0145(5)	0.0019(4)	-0.0026(4)	-0.0004(5)
C(51)	0.0182(6)	0.0245(6)	0.0135(5)	0.0004(4)	-0.0012(4)	-0.0016(5)

C(52)	0.0234(7)	0.0315(6)	0.0151(5)	0.0008(5)	-0.0014(5)	-0.0031(5)
C(53)	0.0160(6)	0.0211(5)	0.0133(5)	0.0009(4)	-0.0003(4)	-0.0021(4)
C(54)	0.0160(6)	0.0201(5)	0.0137(5)	-0.0020(4)	-0.0007(4)	-0.0007(4)
C(55)	0.0238(7)	0.0209(6)	0.0176(6)	-0.0027(4)	-0.0068(5)	-0.0020(5)
C(56)	0.0247(7)	0.0252(6)	0.0160(5)	-0.0033(4)	-0.0054(5)	-0.0005(5)
C(57)	0.0163(6)	0.0155(5)	0.0161(5)	-0.0009(4)	-0.0007(4)	-0.0021(4)
C(58)	0.0144(6)	0.0206(5)	0.0129(5)	-0.0009(4)	0.0005(4)	0.0004(4)
C(59)	0.0198(6)	0.0215(5)	0.0158(5)	-0.0033(4)	-0.0011(4)	0.0009(5)
C(60)	0.0639(11)	0.0337(8)	0.0274(7)	0.0112(6)	0.0075(7)	0.0126(7)
C(61)	0.0277(8)	0.0399(7)	0.0258(6)	0.0094(6)	-0.0013(5)	-0.0041(6)
C(62)	0.0169(6)	0.0207(5)	0.0204(5)	0.0005(4)	-0.0016(4)	-0.0008(4)
C(63)	0.0214(7)	0.0221(5)	0.0194(5)	0.0030(4)	-0.0031(5)	-0.0008(5)
C(64)	0.0175(6)	0.0190(5)	0.0146(5)	0.0012(4)	-0.0012(4)	-0.0010(4)
C(65)	0.0198(6)	0.0204(5)	0.0195(6)	0.0007(4)	0.0017(5)	-0.0020(5)
C(66)	0.0239(7)	0.0199(5)	0.0200(5)	0.0008(4)	0.0032(5)	0.0011(5)
C(67)	0.0264(7)	0.0166(5)	0.0239(6)	-0.0003(4)	-0.0017(5)	0.0005(5)
C(68)	0.0231(7)	0.0213(6)	0.0315(7)	0.0005(5)	0.0013(5)	-0.0050(5)
C(69)	0.0188(6)	0.0235(6)	0.0206(6)	0.0029(4)	0.0024(5)	-0.0014(5)
C(70)	0.0457(10)	0.0240(6)	0.0436(8)	-0.0114(6)	0.0112(7)	-0.0016(6)
C(71)	0.0373(8)	0.0223(6)	0.0290(7)	-0.0050(5)	-0.0135(6)	0.0022(6)
C(72)	0.0562(11)	0.0234(6)	0.0426(8)	0.0041(6)	-0.0174(8)	-0.0059(7)

Table 4. Bond lengths [Å] for su1211.

atom-atom	distance	atom-atom	distance
O(1)-C(2)	1.3482(15)	O(1)-C(1)	1.4416(15)
O(2)-C(4)	1.3547(16)	O(2)-C(1)	1.4260(15)
O(3)-C(2)	1.1934(15)	O(4)-C(4)	1.1954(17)
O(5)-C(9)	1.3456(14)	O(5)-C(10)	1.4376(15)
O(6)-C(11)	1.3427(15)	O(6)-C(10)	1.4421(13)
O(7)-C(9)	1.2003(16)	O(8)-C(11)	1.1987(15)
O(9)-C(19)	1.3680(15)	O(9)-C(22)	1.4228(18)
C(1)-C(13)	1.4993(17)	C(1)-C(12)	1.5088(18)
C(2)-C(3)	1.5252(17)	C(3)-C(4)	1.5321(16)
C(3)-C(8)	1.5614(16)	C(3)-C(5)	1.5709(15)
C(5)-C(16)	1.5162(15)	C(5)-C(6)	1.5964(15)
C(6)-C(9)	1.5277(15)	C(6)-C(11)	1.5377(17)
C(6)-C(7)	1.5813(16)	C(7)-C(23)	1.5035(17)
C(7)-C(8)	1.5318(16)	C(10)-C(15)	1.5042(16)
C(10)-C(14)	1.5101(15)	C(16)-C(17)	1.3999(16)
C(16)-C(21)	1.4010(17)	C(17)-C(18)	1.3960(16)
C(18)-C(19)	1.3819(18)	C(19)-C(20)	1.3965(18)
C(20)-C(21)	1.3838(17)	C(23)-C(24)	1.319(2)
O(10)-C(26)	1.3541(15)	O(10)-C(25)	1.4393(14)
O(11)-C(28)	1.3518(17)	O(11)-C(25)	1.4333(16)
O(12)-C(26)	1.1992(15)	O(13)-C(28)	1.1952(18)
O(14)-C(33)	1.3485(15)	O(14)-C(34)	1.4385(15)
O(15)-C(35)	1.3428(15)	O(15)-C(34)	1.4436(13)
O(16)-C(33)	1.2002(16)	O(17)-C(35)	1.2019(15)
O(18)-C(43)	1.3699(15)	O(18)-C(46)	1.4155(19)
C(25)-C(37)	1.5078(18)	C(25)-C(36)	1.5100(18)

C(26)-C(27)	1.5233(17)	C(27)-C(28)	1.5347(17)
C(27)-C(32)	1.5551(17)	C(27)-C(29)	1.5889(16)
C(29)-C(40)	1.5166(16)	C(29)-C(30)	1.5946(16)
C(30)-C(33)	1.5296(16)	C(30)-C(35)	1.5343(17)
C(30)-C(31)	1.5770(16)	C(31)-C(47)	1.5046(17)
C(31)-C(32)	1.5294(17)	C(34)-C(39)	1.5052(16)
C(34)-C(38)	1.5101(15)	C(40)-C(41)	1.3956(17)
C(40)-C(45)	1.4021(18)	C(41)-C(42)	1.3943(17)
C(42)-C(43)	1.3852(18)	C(43)-C(44)	1.3917(19)
C(44)-C(45)	1.3806(18)	C(47)-C(48)	1.323(2)
O(19)-C(50)	1.3487(15)	O(19)-C(49)	1.4325(15)
O(20)-C(52)	1.3481(17)	O(20)-C(49)	1.4387(18)
O(21)-C(50)	1.1940(16)	O(22)-C(52)	1.2004(18)
O(23)-C(57)	1.3448(15)	O(23)-C(58)	1.4386(15)
O(24)-C(59)	1.3424(15)	O(24)-C(58)	1.4386(13)
O(25)-C(57)	1.1996(16)	O(26)-C(59)	1.1955(15)
O(27)-C(67)	1.3679(15)	O(27)-C(70)	1.4174(19)
C(49)-C(60)	1.5036(19)	C(49)-C(61)	1.509(2)
C(50)-C(51)	1.5263(18)	C(51)-C(52)	1.5355(16)
C(51)-C(56)	1.5486(16)	C(51)-C(53)	1.5893(15)
C(53)-C(64)	1.5149(15)	C(53)-C(54)	1.5960(15)
C(54)-C(57)	1.5297(15)	C(54)-C(59)	1.5361(17)
C(54)-C(55)	1.5786(16)	C(55)-C(71)	1.5047(17)
C(55)-C(56)	1.5350(16)	C(58)-C(63)	1.5054(16)
C(58)-C(62)	1.5082(15)	C(64)-C(65)	1.3977(17)
C(64)-C(69)	1.4066(17)	C(65)-C(66)	1.3928(16)
C(66)-C(67)	1.3875(18)	C(67)-C(68)	1.3954(19)
C(68)-C(69)	1.3824(18)	C(71)-C(72)	1.318(2)
C(5)-H(5)	1.0000	C(7)-H(7)	1.0000
C(8)-H(8A)	0.9900	C(8)-H(8B)	0.9900
C(12)-H(12A)	0.9800	C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800	C(13)-H(13A)	0.9800

C(13)-H(13B)	0.9800	C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800	C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800	C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800	C(15)-H(15C)	0.9800
C(17)-H(17)	0.9500	C(18)-H(18)	0.9500
C(20)-H(20)	0.9500	C(21)-H(21)	0.9500
C(22)-H(22A)	0.9800	C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800	C(23)-H(23)	0.9500
C(24)-H(24A)	0.9500	C(24)-H(24B)	0.9500
C(29)-H(29)	1.0000	C(31)-H(31)	1.0000
C(32)-H(32A)	0.9900	C(32)-H(32B)	0.9900
C(36)-H(36A)	0.9800	C(36)-H(36B)	0.9800
C(36)-H(36C)	0.9800	C(37)-H(37A)	0.9800
C(37)-H(37B)	0.9800	C(37)-H(37C)	0.9800
C(38)-H(38A)	0.9800	C(38)-H(38B)	0.9800
C(38)-H(38C)	0.9800	C(39)-H(39A)	0.9800
C(39)-H(39B)	0.9800	C(39)-H(39C)	0.9800
C(41)-H(41)	0.9500	C(42)-H(42)	0.9500
C(44)-H(44)	0.9500	C(45)-H(45)	0.9500
C(46)-H(46A)	0.9800	C(46)-H(46B)	0.9800
C(46)-H(46C)	0.9800	C(47)-H(47)	0.9500
C(48)-H(48A)	0.9500	C(48)-H(48B)	0.9500
C(53)-H(53)	1.0000	C(55)-H(55)	1.0000
C(56)-H(56A)	0.9900	C(56)-H(56B)	0.9900
C(60)-H(60A)	0.9800	C(60)-H(60B)	0.9800
C(60)-H(60C)	0.9800	C(61)-H(61A)	0.9800
C(61)-H(61B)	0.9800	C(61)-H(61C)	0.9800
C(62)-H(62A)	0.9800	C(62)-H(62B)	0.9800
C(62)-H(62C)	0.9800	C(63)-H(63A)	0.9800
C(63)-H(63B)	0.9800	C(63)-H(63C)	0.9800
C(65)-H(65)	0.9500	C(66)-H(66)	0.9500
C(68)-H(68)	0.9500	C(69)-H(69)	0.9500

C(70)-H(70A)	0.9800	C(70)-H(70B)	0.9800
C(70)-H(70C)	0.9800	C(71)-H(71)	0.9500
C(72)-H(72A)	0.9500	C(72)-H(72B)	0.9500

Symmetry transformations used to generate equivalent atoms:

Table 5. Bond angles [°] for su1211.

atom-atom-atom	angle	atom-atom-atom	angle
C(2)-O(1)-C(1)	119.76(10)	C(4)-O(2)-C(1)	118.97(9)
C(9)-O(5)-C(10)	120.50(9)	C(11)-O(6)-C(10)	120.75(9)
C(19)-O(9)-C(22)	117.49(11)	O(2)-C(1)-O(1)	110.44(10)
O(2)-C(1)-C(13)	107.58(10)	O(1)-C(1)-C(13)	105.99(11)
O(2)-C(1)-C(12)	110.10(12)	O(1)-C(1)-C(12)	108.88(10)
C(13)-C(1)-C(12)	113.77(11)	O(3)-C(2)-O(1)	117.79(12)
O(3)-C(2)-C(3)	124.03(11)	O(1)-C(2)-C(3)	117.74(10)
C(2)-C(3)-C(4)	114.07(10)	C(2)-C(3)-C(8)	106.79(10)
C(4)-C(3)-C(8)	107.77(9)	C(2)-C(3)-C(5)	115.43(9)
C(4)-C(3)-C(5)	109.34(10)	C(8)-C(3)-C(5)	102.48(9)
O(4)-C(4)-O(2)	119.29(11)	O(4)-C(4)-C(3)	122.76(12)
O(2)-C(4)-C(3)	117.62(11)	C(16)-C(5)-C(3)	115.73(9)
C(16)-C(5)-C(6)	120.82(9)	C(3)-C(5)-C(6)	106.90(9)
C(9)-C(6)-C(11)	112.68(10)	C(9)-C(6)-C(7)	105.80(9)
C(11)-C(6)-C(7)	109.32(9)	C(9)-C(6)-C(5)	118.09(9)
C(11)-C(6)-C(5)	106.52(9)	C(7)-C(6)-C(5)	103.87(9)
C(23)-C(7)-C(8)	114.52(10)	C(23)-C(7)-C(6)	116.03(11)
C(8)-C(7)-C(6)	104.60(9)	C(7)-C(8)-C(3)	103.70(9)
O(7)-C(9)-O(5)	117.44(10)	O(7)-C(9)-C(6)	123.47(11)
O(5)-C(9)-C(6)	118.77(10)	O(5)-C(10)-O(6)	109.59(9)
O(5)-C(10)-C(15)	106.52(9)	O(6)-C(10)-C(15)	106.25(9)
O(5)-C(10)-C(14)	109.21(9)	O(6)-C(10)-C(14)	111.78(9)
C(15)-C(10)-C(14)	113.30(10)	O(8)-C(11)-O(6)	118.69(11)
O(8)-C(11)-C(6)	121.88(11)	O(6)-C(11)-C(6)	119.38(10)
C(17)-C(16)-C(21)	117.52(11)	C(17)-C(16)-C(5)	124.90(10)
C(21)-C(16)-C(5)	117.57(10)	C(18)-C(17)-C(16)	121.25(11)

C(19)-C(18)-C(17)	119.92(11)	O(9)-C(19)-C(18)	124.58(12)
O(9)-C(19)-C(20)	115.51(12)	C(18)-C(19)-C(20)	119.91(11)
C(21)-C(20)-C(19)	119.73(12)	C(20)-C(21)-C(16)	121.65(12)
C(24)-C(23)-C(7)	122.11(15)	C(26)-O(10)-C(25)	119.58(10)
C(28)-O(11)-C(25)	118.59(10)	C(33)-O(14)-C(34)	120.40(9)
C(35)-O(15)-C(34)	121.23(9)	C(43)-O(18)-C(46)	117.53(11)
O(11)-C(25)-O(10)	109.54(10)	O(11)-C(25)-C(37)	109.91(11)
O(10)-C(25)-C(37)	110.67(10)	O(11)-C(25)-C(36)	106.94(11)
O(10)-C(25)-C(36)	106.10(11)	C(37)-C(25)-C(36)	113.52(11)
O(12)-C(26)-O(10)	118.08(12)	O(12)-C(26)-C(27)	123.65(11)
O(10)-C(26)-C(27)	118.24(10)	C(26)-C(27)-C(28)	113.82(11)
C(26)-C(27)-C(32)	109.69(10)	C(28)-C(27)-C(32)	111.88(10)
C(26)-C(27)-C(29)	112.65(9)	C(28)-C(27)-C(29)	105.82(10)
C(32)-C(27)-C(29)	102.38(9)	O(13)-C(28)-O(11)	119.15(12)
O(13)-C(28)-C(27)	122.00(13)	O(11)-C(28)-C(27)	118.77(12)
C(40)-C(29)-C(27)	116.28(10)	C(40)-C(29)-C(30)	120.51(9)
C(27)-C(29)-C(30)	106.82(9)	C(33)-C(30)-C(35)	112.48(10)
C(33)-C(30)-C(31)	105.50(10)	C(35)-C(30)-C(31)	109.70(9)
C(33)-C(30)-C(29)	118.35(9)	C(35)-C(30)-C(29)	106.55(9)
C(31)-C(30)-C(29)	103.73(9)	C(47)-C(31)-C(32)	116.57(11)
C(47)-C(31)-C(30)	114.42(11)	C(32)-C(31)-C(30)	104.92(10)
C(31)-C(32)-C(27)	103.90(9)	O(16)-C(33)-O(14)	117.55(11)
O(16)-C(33)-C(30)	123.55(11)	O(14)-C(33)-C(30)	118.49(10)
O(14)-C(34)-O(15)	109.64(9)	O(14)-C(34)-C(39)	106.40(9)
O(15)-C(34)-C(39)	106.09(9)	O(14)-C(34)-C(38)	109.35(10)
O(15)-C(34)-C(38)	111.47(9)	C(39)-C(34)-C(38)	113.71(10)
O(17)-C(35)-O(15)	118.35(12)	O(17)-C(35)-C(30)	121.92(11)
O(15)-C(35)-C(30)	119.71(10)	C(41)-C(40)-C(45)	117.70(11)
C(41)-C(40)-C(29)	124.83(11)	C(45)-C(40)-C(29)	117.47(11)
C(42)-C(41)-C(40)	121.13(11)	C(43)-C(42)-C(41)	119.84(12)
O(18)-C(43)-C(42)	124.40(12)	O(18)-C(43)-C(44)	115.60(12)
C(42)-C(43)-C(44)	120.00(12)	C(45)-C(44)-C(43)	119.71(12)

C(44)-C(45)-C(40)	121.60(12)	C(48)-C(47)-C(31)	121.76(15)
C(50)-O(19)-C(49)	120.44(10)	C(52)-O(20)-C(49)	118.98(11)
C(57)-O(23)-C(58)	121.12(9)	C(59)-O(24)-C(58)	120.94(9)
C(67)-O(27)-C(70)	117.65(11)	O(19)-C(49)-O(20)	110.13(11)
O(19)-C(49)-C(60)	105.96(11)	O(20)-C(49)-C(60)	107.15(13)
O(19)-C(49)-C(61)	110.66(12)	O(20)-C(49)-C(61)	109.31(12)
C(60)-C(49)-C(61)	113.53(12)	O(21)-C(50)-O(19)	118.42(12)
O(21)-C(50)-C(51)	123.82(11)	O(19)-C(50)-C(51)	117.68(11)
C(50)-C(51)-C(52)	114.16(10)	C(50)-C(51)-C(56)	110.21(10)
C(52)-C(51)-C(56)	111.20(10)	C(50)-C(51)-C(53)	112.14(9)
C(52)-C(51)-C(53)	105.86(10)	C(56)-C(51)-C(53)	102.59(9)
O(22)-C(52)-O(20)	118.84(12)	O(22)-C(52)-C(51)	122.18(13)
O(20)-C(52)-C(51)	118.91(12)	C(64)-C(53)-C(51)	115.02(10)
C(64)-C(53)-C(54)	121.18(9)	C(51)-C(53)-C(54)	106.44(9)
C(57)-C(54)-C(59)	112.29(10)	C(57)-C(54)-C(55)	106.43(10)
C(59)-C(54)-C(55)	109.52(9)	C(57)-C(54)-C(53)	117.56(9)
C(59)-C(54)-C(53)	106.35(9)	C(55)-C(54)-C(53)	104.25(9)
C(71)-C(55)-C(56)	114.21(10)	C(71)-C(55)-C(54)	116.00(11)
C(56)-C(55)-C(54)	104.32(10)	C(55)-C(56)-C(51)	104.28(9)
O(25)-C(57)-O(23)	117.36(11)	O(25)-C(57)-C(54)	123.49(11)
O(23)-C(57)-C(54)	118.92(10)	O(24)-C(58)-O(23)	109.84(9)
O(24)-C(58)-C(63)	105.98(9)	O(23)-C(58)-C(63)	106.42(10)
O(24)-C(58)-C(62)	111.63(10)	O(23)-C(58)-C(62)	109.42(10)
C(63)-C(58)-C(62)	113.37(10)	O(26)-C(59)-O(24)	118.38(12)
O(26)-C(59)-C(54)	122.31(11)	O(24)-C(59)-C(54)	119.26(10)
C(65)-C(64)-C(69)	117.38(11)	C(65)-C(64)-C(53)	125.03(11)
C(69)-C(64)-C(53)	117.59(10)	C(66)-C(65)-C(64)	121.60(11)
C(67)-C(66)-C(65)	119.69(12)	O(27)-C(67)-C(66)	124.37(12)
O(27)-C(67)-C(68)	115.69(11)	C(66)-C(67)-C(68)	119.94(11)
C(69)-C(68)-C(67)	119.80(12)	C(68)-C(69)-C(64)	121.57(12)
C(72)-C(71)-C(55)	122.19(15)	C(16)-C(5)-H(5)	103.7
C(3)-C(5)-H(5)	103.7	C(6)-C(5)-H(5)	103.7

C(23)-C(7)-H(7)	107.1	C(8)-C(7)-H(7)	107.1
C(6)-C(7)-H(7)	107.1	C(7)-C(8)-H(8A)	111.0
C(3)-C(8)-H(8A)	111.0	C(7)-C(8)-H(8B)	111.0
C(3)-C(8)-H(8B)	111.0	H(8A)-C(8)-H(8B)	109.0
C(1)-C(12)-H(12A)	109.5	C(1)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5	C(1)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5	H(12B)-C(12)-H(12C)	109.5
C(1)-C(13)-H(13A)	109.5	C(1)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5	C(1)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5	H(13B)-C(13)-H(13C)	109.5
C(10)-C(14)-H(14A)	109.5	C(10)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5	C(10)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5	H(14B)-C(14)-H(14C)	109.5
C(10)-C(15)-H(15A)	109.5	C(10)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5	C(10)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5	H(15B)-C(15)-H(15C)	109.5
C(18)-C(17)-H(17)	119.4	C(16)-C(17)-H(17)	119.4
C(19)-C(18)-H(18)	120.0	C(17)-C(18)-H(18)	120.0
C(21)-C(20)-H(20)	120.1	C(19)-C(20)-H(20)	120.1
C(20)-C(21)-H(21)	119.2	C(16)-C(21)-H(21)	119.2
O(9)-C(22)-H(22A)	109.5	O(9)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5	O(9)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5	H(22B)-C(22)-H(22C)	109.5
C(24)-C(23)-H(23)	118.9	C(7)-C(23)-H(23)	118.9
C(23)-C(24)-H(24A)	120.0	C(23)-C(24)-H(24B)	120.0
H(24A)-C(24)-H(24B)	120.0	C(40)-C(29)-H(29)	103.7
C(27)-C(29)-H(29)	103.7	C(30)-C(29)-H(29)	103.7
C(47)-C(31)-H(31)	106.8	C(32)-C(31)-H(31)	106.8
C(30)-C(31)-H(31)	106.8	C(31)-C(32)-H(32A)	111.0
C(27)-C(32)-H(32A)	111.0	C(31)-C(32)-H(32B)	111.0
C(27)-C(32)-H(32B)	111.0	H(32A)-C(32)-H(32B)	109.0
C(25)-C(36)-H(36A)	109.5	C(25)-C(36)-H(36B)	109.5

H(36A)-C(36)-H(36B)	109.5	C(25)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5	H(36B)-C(36)-H(36C)	109.5
C(25)-C(37)-H(37A)	109.5	C(25)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37B)	109.5	C(25)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37C)	109.5	H(37B)-C(37)-H(37C)	109.5
C(34)-C(38)-H(38A)	109.5	C(34)-C(38)-H(38B)	109.5
H(38A)-C(38)-H(38B)	109.5	C(34)-C(38)-H(38C)	109.5
H(38A)-C(38)-H(38C)	109.5	H(38B)-C(38)-H(38C)	109.5
C(34)-C(39)-H(39A)	109.5	C(34)-C(39)-H(39B)	109.5
H(39A)-C(39)-H(39B)	109.5	C(34)-C(39)-H(39C)	109.5
H(39A)-C(39)-H(39C)	109.5	H(39B)-C(39)-H(39C)	109.5
C(42)-C(41)-H(41)	119.4	C(40)-C(41)-H(41)	119.4
C(43)-C(42)-H(42)	120.1	C(41)-C(42)-H(42)	120.1
C(45)-C(44)-H(44)	120.1	C(43)-C(44)-H(44)	120.1
C(44)-C(45)-H(45)	119.2	C(40)-C(45)-H(45)	119.2
O(18)-C(46)-H(46A)	109.5	O(18)-C(46)-H(46B)	109.5
H(46A)-C(46)-H(46B)	109.5	O(18)-C(46)-H(46C)	109.5
H(46A)-C(46)-H(46C)	109.5	H(46B)-C(46)-H(46C)	109.5
C(48)-C(47)-H(47)	119.1	C(31)-C(47)-H(47)	119.1
C(47)-C(48)-H(48A)	120.0	C(47)-C(48)-H(48B)	120.0
H(48A)-C(48)-H(48B)	120.0	C(64)-C(53)-H(53)	104.1
C(51)-C(53)-H(53)	104.1	C(54)-C(53)-H(53)	104.1
C(71)-C(55)-H(55)	107.3	C(56)-C(55)-H(55)	107.3
C(54)-C(55)-H(55)	107.3	C(55)-C(56)-H(56A)	110.9
C(51)-C(56)-H(56A)	110.9	C(55)-C(56)-H(56B)	110.9
C(51)-C(56)-H(56B)	110.9	H(56A)-C(56)-H(56B)	108.9
C(49)-C(60)-H(60A)	109.5	C(49)-C(60)-H(60B)	109.5
H(60A)-C(60)-H(60B)	109.5	C(49)-C(60)-H(60C)	109.5
H(60A)-C(60)-H(60C)	109.5	H(60B)-C(60)-H(60C)	109.5
C(49)-C(61)-H(61A)	109.5	C(49)-C(61)-H(61B)	109.5
H(61A)-C(61)-H(61B)	109.5	C(49)-C(61)-H(61C)	109.5
H(61A)-C(61)-H(61C)	109.5	H(61B)-C(61)-H(61C)	109.5

C(58)-C(62)-H(62A)	109.5	C(58)-C(62)-H(62B)	109.5
H(62A)-C(62)-H(62B)	109.5	C(58)-C(62)-H(62C)	109.5
H(62A)-C(62)-H(62C)	109.5	H(62B)-C(62)-H(62C)	109.5
C(58)-C(63)-H(63A)	109.5	C(58)-C(63)-H(63B)	109.5
H(63A)-C(63)-H(63B)	109.5	C(58)-C(63)-H(63C)	109.5
H(63A)-C(63)-H(63C)	109.5	H(63B)-C(63)-H(63C)	109.5
C(66)-C(65)-H(65)	119.2	C(64)-C(65)-H(65)	119.2
C(67)-C(66)-H(66)	120.2	C(65)-C(66)-H(66)	120.2
C(69)-C(68)-H(68)	120.1	C(67)-C(68)-H(68)	120.1
C(68)-C(69)-H(69)	119.2	C(64)-C(69)-H(69)	119.2
O(27)-C(70)-H(70A)	109.5	O(27)-C(70)-H(70B)	109.5
H(70A)-C(70)-H(70B)	109.5	O(27)-C(70)-H(70C)	109.5
H(70A)-C(70)-H(70C)	109.5	H(70B)-C(70)-H(70C)	109.5
C(72)-C(71)-H(71)	118.9	C(55)-C(71)-H(71)	118.9
C(71)-C(72)-H(72A)	120.0	C(71)-C(72)-H(72B)	120.0
H(72A)-C(72)-H(72B)	120.0		

Symmetry transformations used to generate equivalent atoms:

Table 6. Torsion angles [°] for su1211.

atom-atom-atom-atom	angle	atom-atom-atom-atom	angle
C(4)-O(2)-C(1)-O(1)	49.80(15)	C(4)-O(2)-C(1)-C(13)	165.05(11)
C(4)-O(2)-C(1)-C(12)	-70.47(14)	C(2)-O(1)-C(1)-O(2)	-48.47(14)
C(2)-O(1)-C(1)-C(13)	-164.71(11)	C(2)-O(1)-C(1)-C(12)	72.53(14)
C(1)-O(1)-C(2)-O(3)	-155.60(11)	C(1)-O(1)-C(2)-C(3)	31.73(15)
O(3)-C(2)-C(3)-C(4)	174.52(12)	O(1)-C(2)-C(3)-C(4)	-13.31(15)
O(3)-C(2)-C(3)-C(8)	-66.54(14)	O(1)-C(2)-C(3)-C(8)	105.64(12)
O(3)-C(2)-C(3)-C(5)	46.63(16)	O(1)-C(2)-C(3)-C(5)	-141.20(11)
C(1)-O(2)-C(4)-O(4)	151.73(12)	C(1)-O(2)-C(4)-C(3)	-34.73(16)
C(2)-C(3)-C(4)-O(4)	-171.98(12)	C(8)-C(3)-C(4)-O(4)	69.64(16)
C(5)-C(3)-C(4)-O(4)	-41.04(16)	C(2)-C(3)-C(4)-O(2)	14.73(15)
C(8)-C(3)-C(4)-O(2)	-103.66(12)	C(5)-C(3)-C(4)-O(2)	145.67(11)
C(2)-C(3)-C(5)-C(16)	47.24(14)	C(4)-C(3)-C(5)-C(16)	-82.97(12)
C(8)-C(3)-C(5)-C(16)	162.89(10)	C(2)-C(3)-C(5)-C(6)	-90.57(11)
C(4)-C(3)-C(5)-C(6)	139.22(10)	C(8)-C(3)-C(5)-C(6)	25.08(11)
C(16)-C(5)-C(6)-C(9)	-18.86(15)	C(3)-C(5)-C(6)-C(9)	116.35(11)
C(16)-C(5)-C(6)-C(11)	109.04(11)	C(3)-C(5)-C(6)-C(11)	-115.75(10)
C(16)-C(5)-C(6)-C(7)	-135.58(11)	C(3)-C(5)-C(6)-C(7)	-0.37(11)
C(9)-C(6)-C(7)-C(23)	82.57(13)	C(11)-C(6)-C(7)-C(23)	-39.02(14)
C(5)-C(6)-C(7)-C(23)	-152.41(11)	C(9)-C(6)-C(7)-C(8)	-150.24(10)
C(11)-C(6)-C(7)-C(8)	88.16(11)	C(5)-C(6)-C(7)-C(8)	-25.22(11)
C(23)-C(7)-C(8)-C(3)	169.94(11)	C(6)-C(7)-C(8)-C(3)	41.83(12)
C(2)-C(3)-C(8)-C(7)	80.49(11)	C(4)-C(3)-C(8)-C(7)	-156.55(10)
C(5)-C(3)-C(8)-C(7)	-41.26(12)	C(10)-O(5)-C(9)-O(7)	163.03(11)
C(10)-O(5)-C(9)-C(6)	-23.32(15)	C(11)-C(6)-C(9)-O(7)	166.24(11)
C(7)-C(6)-C(9)-O(7)	46.84(15)	C(5)-C(6)-C(9)-O(7)	-68.85(15)
C(11)-C(6)-C(9)-O(5)	-7.01(14)	C(7)-C(6)-C(9)-O(5)	-126.41(10)

C(5)-C(6)-C(9)-O(5)	117.90(11)	C(9)-O(5)-C(10)-O(6)	48.17(13)
C(9)-O(5)-C(10)-C(15)	162.72(10)	C(9)-O(5)-C(10)-C(14)	-74.58(12)
C(11)-O(6)-C(10)-O(5)	-44.31(14)	C(11)-O(6)-C(10)-C(15)	-159.03(10)
C(11)-O(6)-C(10)-C(14)	76.91(14)	C(10)-O(6)-C(11)-O(8)	-166.04(12)
C(10)-O(6)-C(11)-C(6)	16.39(16)	C(9)-C(6)-C(11)-O(8)	-167.12(12)
C(7)-C(6)-C(11)-O(8)	-49.78(15)	C(5)-C(6)-C(11)-O(8)	61.87(14)
C(9)-C(6)-C(11)-O(6)	10.38(15)	C(7)-C(6)-C(11)-O(6)	127.71(11)
C(5)-C(6)-C(11)-O(6)	-120.64(11)	C(3)-C(5)-C(16)-C(17)	-71.88(14)
C(6)-C(5)-C(16)-C(17)	59.68(16)	C(3)-C(5)-C(16)-C(21)	106.72(12)
C(6)-C(5)-C(16)-C(21)	-121.72(12)	C(21)-C(16)-C(17)-C(18)	0.78(17)
C(5)-C(16)-C(17)-C(18)	179.39(11)	C(16)-C(17)-C(18)-C(19)	-0.04(18)
C(22)-O(9)-C(19)-C(18)	2.41(19)	C(22)-O(9)-C(19)-C(20)	-177.87(13)
C(17)-C(18)-C(19)-O(9)	178.71(12)	C(17)-C(18)-C(19)-C(20)	-1.00(19)
O(9)-C(19)-C(20)-C(21)	-178.46(12)	C(18)-C(19)-C(20)-C(21)	1.28(19)
C(19)-C(20)-C(21)-C(16)	-0.52(19)	C(17)-C(16)-C(21)-C(20)	-0.50(18)
C(5)-C(16)-C(21)-C(20)	-179.21(11)	C(8)-C(7)-C(23)-C(24)	120.96(15)
C(6)-C(7)-C(23)-C(24)	-116.97(15)	C(28)-O(11)-C(25)-O(10)	-51.28(15)
C(28)-O(11)-C(25)-C(37)	70.52(14)	C(28)-O(11)-C(25)-C(36)	-165.85(11)
C(26)-O(10)-C(25)-O(11)	50.64(15)	C(26)-O(10)-C(25)-C(37)	-70.69(15)
C(26)-O(10)-C(25)-C(36)	165.74(11)	C(25)-O(10)-C(26)-O(12)	157.25(11)
C(25)-O(10)-C(26)-C(27)	-24.63(16)	O(12)-C(26)-C(27)-C(28)	175.44(12)
O(10)-C(26)-C(27)-C(28)	-2.56(16)	O(12)-C(26)-C(27)-C(32)	-58.36(15)
O(10)-C(26)-C(27)-C(32)	123.64(11)	O(12)-C(26)-C(27)-C(29)	54.97(16)
O(10)-C(26)-C(27)-C(29)	-123.03(11)	C(25)-O(11)-C(28)-O(13)	-156.63(13)
C(25)-O(11)-C(28)-C(27)	26.51(17)	C(26)-C(27)-C(28)-O(13)	-175.17(13)
C(32)-C(27)-C(28)-O(13)	59.80(17)	C(29)-C(27)-C(28)-O(13)	-50.93(17)
C(26)-C(27)-C(28)-O(11)	1.59(17)	C(32)-C(27)-C(28)-O(11)	-123.44(13)
C(29)-C(27)-C(28)-O(11)	125.83(12)	C(26)-C(27)-C(29)-C(40)	43.59(14)
C(28)-C(27)-C(29)-C(40)	-81.37(12)	C(32)-C(27)-C(29)-C(40)	161.32(10)
C(26)-C(27)-C(29)-C(30)	-94.22(11)	C(28)-C(27)-C(29)-C(30)	140.82(10)
C(32)-C(27)-C(29)-C(30)	23.51(12)	C(40)-C(29)-C(30)-C(33)	-17.93(16)
C(27)-C(29)-C(30)-C(33)	117.72(11)	C(40)-C(29)-C(30)-C(35)	109.92(12)

C(27)-C(29)-C(30)-C(35)	-114.43(10)	C(40)-C(29)-C(30)-C(31)	-134.32(11)
C(27)-C(29)-C(30)-C(31)	1.33(12)	C(33)-C(30)-C(31)-C(47)	79.46(13)
C(35)-C(30)-C(31)-C(47)	-41.92(15)	C(29)-C(30)-C(31)-C(47)	-155.43(11)
C(33)-C(30)-C(31)-C(32)	-151.54(10)	C(35)-C(30)-C(31)-C(32)	87.07(11)
C(29)-C(30)-C(31)-C(32)	-26.44(12)	C(47)-C(31)-C(32)-C(27)	170.08(12)
C(30)-C(31)-C(32)-C(27)	42.38(12)	C(26)-C(27)-C(32)-C(31)	79.46(12)
C(28)-C(27)-C(32)-C(31)	-153.25(11)	C(29)-C(27)-C(32)-C(31)	-40.36(12)
C(34)-O(14)-C(33)-O(16)	161.64(10)	C(34)-O(14)-C(33)-C(30)	-25.40(15)
C(35)-C(30)-C(33)-O(16)	165.72(11)	C(31)-C(30)-C(33)-O(16)	46.16(15)
C(29)-C(30)-C(33)-O(16)	-69.28(15)	C(35)-C(30)-C(33)-O(14)	-6.79(14)
C(31)-C(30)-C(33)-O(14)	-126.35(10)	C(29)-C(30)-C(33)-O(14)	118.21(11)
C(33)-O(14)-C(34)-O(15)	48.79(13)	C(33)-O(14)-C(34)-C(39)	163.11(10)
C(33)-O(14)-C(34)-C(38)	-73.69(12)	C(35)-O(15)-C(34)-O(14)	-41.15(14)
C(35)-O(15)-C(34)-C(39)	-155.67(11)	C(35)-O(15)-C(34)-C(38)	80.06(14)
C(34)-O(15)-C(35)-O(17)	-170.39(12)	C(34)-O(15)-C(35)-C(30)	11.39(16)
C(33)-C(30)-C(35)-O(17)	-164.50(12)	C(31)-C(30)-C(35)-O(17)	-47.41(16)
C(29)-C(30)-C(35)-O(17)	64.27(15)	C(33)-C(30)-C(35)-O(15)	13.66(15)
C(31)-C(30)-C(35)-O(15)	130.75(11)	C(29)-C(30)-C(35)-O(15)	-117.58(11)
C(27)-C(29)-C(40)-C(41)	-73.33(15)	C(30)-C(29)-C(40)-C(41)	58.41(16)
C(27)-C(29)-C(40)-C(45)	107.08(12)	C(30)-C(29)-C(40)-C(45)	-121.18(12)
C(45)-C(40)-C(41)-C(42)	1.24(17)	C(29)-C(40)-C(41)-C(42)	-178.35(11)
C(40)-C(41)-C(42)-C(43)	-0.15(19)	C(46)-O(18)-C(43)-C(42)	5.3(2)
C(46)-O(18)-C(43)-C(44)	-174.61(13)	C(41)-C(42)-C(43)-O(18)	179.11(12)
C(41)-C(42)-C(43)-C(44)	-1.01(19)	O(18)-C(43)-C(44)-C(45)	-179.06(12)
C(42)-C(43)-C(44)-C(45)	1.05(19)	C(43)-C(44)-C(45)-C(40)	0.08(19)
C(41)-C(40)-C(45)-C(44)	-1.20(18)	C(29)-C(40)-C(45)-C(44)	178.42(11)
C(32)-C(31)-C(47)-C(48)	131.14(15)	C(30)-C(31)-C(47)-C(48)	-105.96(16)
C(50)-O(19)-C(49)-O(20)	49.53(17)	C(50)-O(19)-C(49)-C(60)	165.09(13)
C(50)-O(19)-C(49)-C(61)	-71.43(16)	C(52)-O(20)-C(49)-O(19)	-48.55(16)
C(52)-O(20)-C(49)-C(60)	-163.35(11)	C(52)-O(20)-C(49)-C(61)	73.22(14)
C(49)-O(19)-C(50)-O(21)	155.82(13)	C(49)-O(19)-C(50)-C(51)	-27.40(18)
O(21)-C(50)-C(51)-C(52)	179.00(12)	O(19)-C(50)-C(51)-C(52)	2.41(15)

O(21)-C(50)-C(51)-C(56)	-55.01(15)	O(19)-C(50)-C(51)-C(56)	128.40(11)
O(21)-C(50)-C(51)-C(53)	58.61(16)	O(19)-C(50)-C(51)-C(53)	-117.98(12)
C(49)-O(20)-C(52)-O(22)	-156.49(12)	C(49)-O(20)-C(52)-C(51)	26.60(17)
C(50)-C(51)-C(52)-O(22)	-179.11(12)	C(56)-C(51)-C(52)-O(22)	55.42(16)
C(53)-C(51)-C(52)-O(22)	-55.27(15)	C(50)-C(51)-C(52)-O(20)	-2.31(16)
C(56)-C(51)-C(52)-O(20)	-127.78(12)	C(53)-C(51)-C(52)-O(20)	121.53(12)
C(50)-C(51)-C(53)-C(64)	42.57(13)	C(52)-C(51)-C(53)-C(64)	-82.53(12)
C(56)-C(51)-C(53)-C(64)	160.81(10)	C(50)-C(51)-C(53)-C(54)	-94.59(11)
C(52)-C(51)-C(53)-C(54)	140.30(10)	C(56)-C(51)-C(53)-C(54)	23.64(12)
C(64)-C(53)-C(54)-C(57)	-15.25(16)	C(51)-C(53)-C(54)-C(57)	118.69(11)
C(64)-C(53)-C(54)-C(59)	111.55(11)	C(51)-C(53)-C(54)-C(59)	-114.51(10)
C(64)-C(53)-C(54)-C(55)	-132.75(11)	C(51)-C(53)-C(54)-C(55)	1.19(12)
C(57)-C(54)-C(55)-C(71)	82.52(13)	C(59)-C(54)-C(55)-C(71)	-39.10(15)
C(53)-C(54)-C(55)-C(71)	-152.56(11)	C(57)-C(54)-C(55)-C(56)	-150.95(10)
C(59)-C(54)-C(55)-C(56)	87.44(11)	C(53)-C(54)-C(55)-C(56)	-26.02(12)
C(71)-C(55)-C(56)-C(51)	169.74(12)	C(54)-C(55)-C(56)-C(51)	42.09(13)
C(50)-C(51)-C(56)-C(55)	79.09(12)	C(52)-C(51)-C(56)-C(55)	-153.27(11)
C(53)-C(51)-C(56)-C(55)	-40.50(12)	C(58)-O(23)-C(57)-O(25)	167.64(10)
C(58)-O(23)-C(57)-C(54)	-17.68(15)	C(59)-C(54)-C(57)-O(25)	162.13(11)
C(55)-C(54)-C(57)-O(25)	42.30(15)	C(53)-C(54)-C(57)-O(25)	-74.02(15)
C(59)-C(54)-C(57)-O(23)	-12.20(15)	C(55)-C(54)-C(57)-O(23)	-132.03(10)
C(53)-C(54)-C(57)-O(23)	111.65(12)	C(59)-O(24)-C(58)-O(23)	-44.09(14)
C(59)-O(24)-C(58)-C(63)	-158.67(11)	C(59)-O(24)-C(58)-C(62)	77.46(14)
C(57)-O(23)-C(58)-O(24)	45.10(14)	C(57)-O(23)-C(58)-C(63)	159.40(10)
C(57)-O(23)-C(58)-C(62)	-77.76(12)	C(58)-O(24)-C(59)-O(26)	-166.41(12)
C(58)-O(24)-C(59)-C(54)	16.03(16)	C(57)-C(54)-C(59)-O(26)	-164.44(12)
C(55)-C(54)-C(59)-O(26)	-46.42(16)	C(53)-C(54)-C(59)-O(26)	65.67(15)
C(57)-C(54)-C(59)-O(24)	13.02(15)	C(55)-C(54)-C(59)-O(24)	131.04(11)
C(53)-C(54)-C(59)-O(24)	-116.87(11)	C(51)-C(53)-C(64)-C(65)	-74.40(14)
C(54)-C(53)-C(64)-C(65)	55.94(16)	C(51)-C(53)-C(64)-C(69)	104.87(12)
C(54)-C(53)-C(64)-C(69)	-124.79(12)	C(69)-C(64)-C(65)-C(66)	1.37(18)
C(53)-C(64)-C(65)-C(66)	-179.36(11)	C(64)-C(65)-C(66)-C(67)	-0.17(18)

C(70)-O(27)-C(67)-C(66)	2.9(2)	C(70)-O(27)-C(67)-C(68)	-177.33(13)
C(65)-C(66)-C(67)-O(27)	178.72(12)	C(65)-C(66)-C(67)-C(68)	-1.06(19)
O(27)-C(67)-C(68)-C(69)	-178.76(12)	C(66)-C(67)-C(68)-C(69)	1.03(19)
C(67)-C(68)-C(69)-C(64)	0.22(19)	C(65)-C(64)-C(69)-C(68)	-1.40(18)
C(53)-C(64)-C(69)-C(68)	179.28(11)	C(56)-C(55)-C(71)-C(72)	123.01(15)
C(54)-C(55)-C(71)-C(72)	-115.60(15)		

Appendix B – Crystal Structure of compound 15

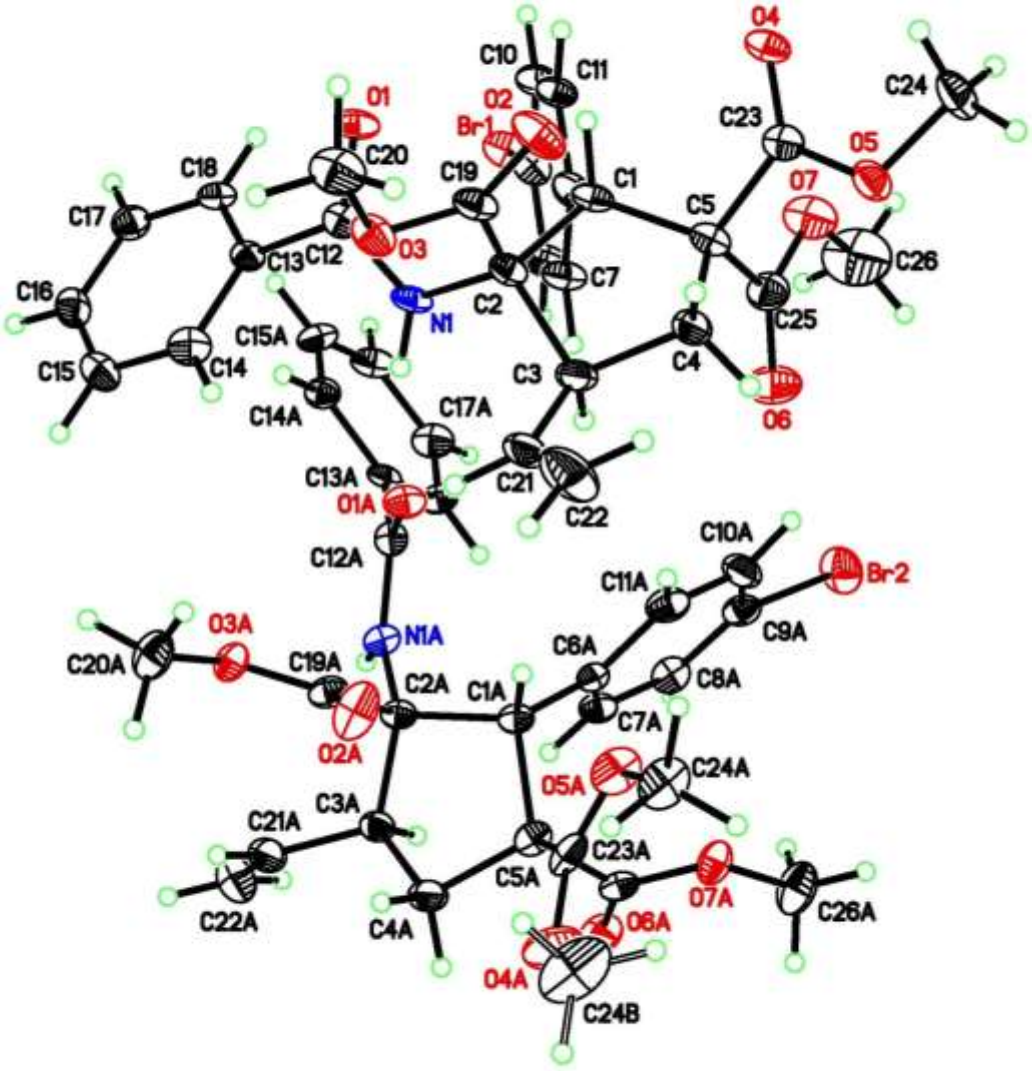
The compound crystallizes as colorless block-like crystals from a solvent mixture of chloroform, ethyl acetate, diethyl ether, benzene and pentane. There are two crystallographically independent, yet chemically identical, molecules of the compound in the asymmetric unit of the primitive, acentric, orthorhombic space group $P2_12_12_1$.

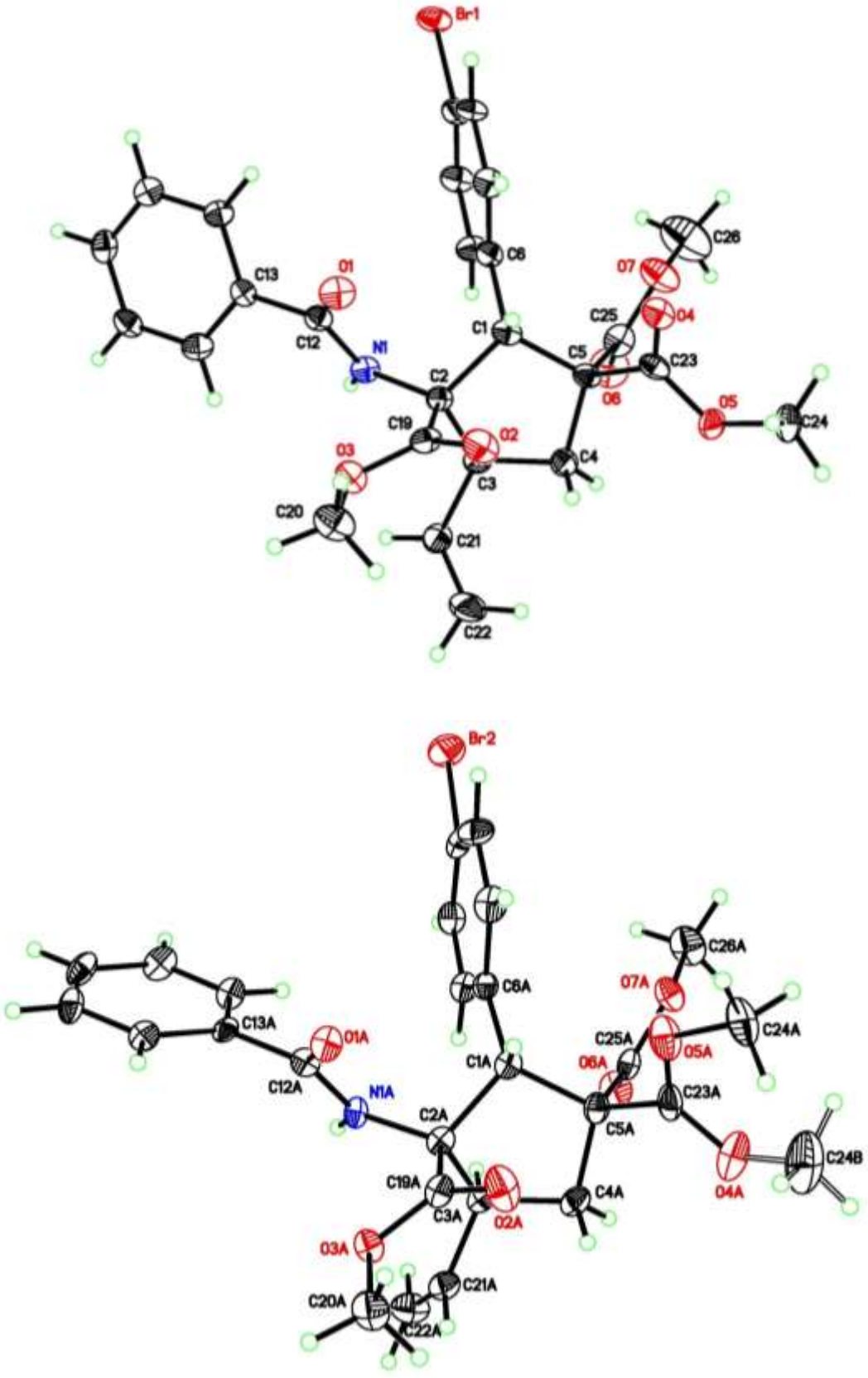
Two methods of determining the absolute stereochemistry were applied to the data. The comparison of intensities of Friedel pairs of reflections gave an absolute structure parameter (Flack parameter) of 0.002(6). A value of zero indicates the correct enantiomorph of the space group; a value of one the inverted absolute stereochemistry. The second analysis is the Hooft analysis (see additional article for further information). The Hooft *y* parameter was measured to be: 0.009(6) (a value of zero indicates the correct stereochemistry) and the P2(true) and P3(true) values (measures of racemic twin components) were both 1.000, indicating no racemic twinning within the sample. The correct absolute stereochemistry is depicted in the Figures.

The structure of each of the two molecules is essentially identical and only differs in that one of the two molecules has some disorder present in one of the acetyl groups (C24A/C24B). The other differences are changes in torsional angles. They are otherwise identical in connectivity and stereochemistry. Significant differences are the orientation of the vinyl group and the orientation of the major component of the disordered acetyl with respect to the ordered molecule.

The structure of the molecules is as expected. The two independent amide moieties form H-bonds to nearby acceptor atoms. N1 forms an H-bond to the amide oxygen, O1A, of a neighboring molecule while the second molecule (N1A) forms an H-bond to an acetyl oxygen (O4) of a symmetry related "first" molecule. This results in a one-dimensional chain of molecules that run through the lattice parallel to the *c*-axis.

The disorder was refined with the two components having an occupancy summed to unity, giving an approximately 0.64:0.36 occupancy ratio. This disorder does have some effect on the C-O bond distances of the acetyl group, resulting in an average of the single and double-bond character.


O4
C10
C11
C24
O1
O2
Br1
C23
O5
C18
C19
C1
C5
O7
C17
C20
C13
C12
O3
C7
C26
C16
N1
C2
C25
C15A
C15
C14
C3
C4
O6
C14A
C17A
C13A
C21
O1A
C22
C12A
C10A
Br2
C11A
C9A
O3A
N1A
C6A
C20A
C19A
C2A
C1A
C8A
C7A
O2A
C24A
O5A
C3A
C21A
C23A
C5A
O7A
C26A
C22A
C4A
O6A
O4A
C24B


Br1
C6
C26
O7
O1
C13
C25
O4
C1
C12
N1
C5
C23
C2
O6
O5
C24
C19
O2
O3
C4
C3
C20
C21
C22
Br2
C6A
C26A
O7A
C13A
O1A
C25A
C24A
O5A
C1A
O6A
C12A
N1A
C23A
C2A
C5A
C24B
C19A
C4A
O4A
C3A
O2A
O3A
C21A
C20A
C22A

CRYSTAL SUMMARY

Crystal data for $C_{26}H_{26}BrNO_7$; M_r = 544.39; Orthorhombic; space group $P2_12_12_1$; *a* = 11.9755(7) Å; *b* = 19.1059(12) Å; *c* = 22.4599(14) Å; α = 90°; β = 90°; γ = 90°; V = 5138.9(5) $Å^3$; Z = 8; T = 120(2) K; λ(Mo-Kα) = 0.71073 Å; μ(Mo-Kα) = 1.644 mm^{-1}; d_{calc} = 1.407g.cm^{-3}; 67562 reflections collected; 10488 unique (R_{int} = 0.0817); giving R_1 = 0.0392, wR_2 = 0.0749 for 8071 data with [I>2σ(I)] and R_1 = 0.0671, wR_2 = 0.0900 for all 10488 data. Residual electron density ($e^-.Å^{-3}$) max/min: 0.410/-0.428.

An arbitrary sphere of data were collected on a colorless block-like crystal, having approximate dimensions of 0.38 × 0.19 × 0.12 mm, on a Bruker Kappa X8-APEX-II diffractometer using a combination of ω- and φ-scans of 0.5°. Data were corrected for absorption and polarization effects and analyzed for space group determination. The structure was solved by direct methods and expanded routinely. The model was refined by full-matrix least-squares analysis of F^2 against all reflections. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Thermal parameters for the hydrogens were tied to the isotropic thermal parameter of the atom to which they are bonded (1.5 × for methyl, 1.2 × for all others).

Table 1. Crystal data and structure refinement for su038.

Identification code	su038
Empirical formula	C26 H26 Br N O7
Formula weight	544.39
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 11.9755(7) Å α = 90°
	b = 19.1059(12) Å β = 90°
	c = 22.4599(14) Å γ = 90°
Volume	5138.9(5) $Å^3$
Z	8
Density (calculated)	1.407 $g.cm^{-3}$
Absorption coefficient (μ)	1.644 mm^{-1}
F(000)	2240
Crystal size	0.38 × 0.19 × 0.12 mm^3
θ range for data collection	1.40 to 26.39°
Index ranges	$-14 \leq h \leq 13$, $-23 \leq k \leq 23$, $-28 \leq l \leq 27$
Reflections collected	67562

Independent reflections	10488 [R_{int} = 0.0817]
Completeness to θ = 26.39°	99.8 %
Absorption correction	empirical
Max. and min. transmission	0.9427 and 0.7836
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10488 / 0 / 648
Goodness-of-fit on F^2	1.026
Final R indices [I>2σ(I)]	R_1 = 0.0392, wR_2 = 0.0749
R indices (all data)	R_1 = 0.0671, wR_2 = 0.0900
Absolute structure parameter	0.002(6)
Largest diff. peak and hole	0.410 and -0.428 $e^{-}.Å^{-3}$

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for su038. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Br(1)	0.35400(3)	0.05798(2)	0.05995(2)	0.028(1)
O(1)	0.7724(2)	0.14114(13)	-0.09452(10)	0.024(1)
O(2)	0.9329(2)	0.01860(14)	-0.16764(11)	0.030(1)
O(3)	1.0094(2)	0.10654(13)	-0.11610(11)	0.024(1)
O(4)	0.7202(2)	-0.10988(13)	-0.17290(11)	0.023(1)
O(5)	0.8538(2)	-0.18739(12)	-0.14783(10)	0.025(1)
O(6)	0.8119(3)	-0.15552(15)	0.01488(12)	0.039(1)
O(7)	0.6652(2)	-0.16036(14)	-0.04703(12)	0.034(1)
N(1)	0.8734(3)	0.08528(14)	-0.02395(12)	0.019(1)
C(1)	0.7842(3)	-0.01754(18)	-0.07883(15)	0.019(1)
C(2)	0.8919(3)	0.02596(18)	-0.06300(16)	0.018(1)
C(3)	0.9712(3)	-0.02905(19)	-0.03324(17)	0.022(1)
C(4)	0.9497(3)	-0.09462(19)	-0.07007(17)	0.023(1)
C(5)	0.8233(3)	-0.09653(19)	-0.08031(15)	0.019(1)
C(6)	0.6813(3)	-0.00094(19)	-0.04260(16)	0.020(1)
C(7)	0.6764(3)	-0.0053(2)	0.01958(16)	0.024(1)

C(8)	0.5788(3)	0.0114(2)	0.04987(17)	0.026(1)
C(9)	0.4862(3)	0.03370(19)	0.01880(17)	0.023(1)
C(10)	0.4886(3)	0.03916(19)	-0.04309(16)	0.022(1)
C(11)	0.5862(3)	0.02142(19)	-0.07210(16)	0.021(1)
C(12)	0.8127(3)	0.14041(18)	-0.04437(16)	0.019(1)
C(13)	0.7987(3)	0.20074(18)	-0.00297(15)	0.016(1)
C(14)	0.8875(3)	0.2258(2)	0.03067(16)	0.023(1)
C(15)	0.8744(3)	0.28546(18)	0.06587(17)	0.024(1)
C(16)	0.7719(3)	0.31890(19)	0.06753(16)	0.024(1)
C(17)	0.6831(3)	0.29324(19)	0.03528(16)	0.023(1)
C(18)	0.6962(3)	0.23441(19)	0.00006(15)	0.020(1)
C(19)	0.9439(3)	0.05019(19)	-0.12165(16)	0.021(1)
C(20)	1.0607(4)	0.1289(2)	-0.17136(17)	0.032(1)
C(21)	1.0918(3)	-0.0073(2)	-0.02852(18)	0.028(1)
C(22)	1.1756(3)	-0.0374(2)	-0.0549(2)	0.043(1)
C(23)	0.7916(3)	-0.13034(19)	-0.13923(16)	0.020(1)
C(24)	0.8309(4)	-0.2276(2)	-0.20145(17)	0.032(1)
C(25)	0.7681(4)	-0.14058(19)	-0.03118(17)	0.026(1)
C(26)	0.6032(4)	-0.1987(3)	-0.0021(2)	0.061(2)
Br(2)	0.64198(4)	-0.23606(2)	0.21692(2)	0.036(1)
O(1A)	0.8903(2)	0.07177(12)	0.11314(10)	0.021(1)

O(2A)	1.1681(2)	0.07169(13)	0.14012(12)	0.033(1)
O(3A)	1.0691(2)	0.16320(12)	0.17143(11)	0.019(1)
O(4A)	1.3347(2)	-0.07974(15)	0.20077(13)	0.037(1)
O(5A)	1.2056(2)	-0.09853(14)	0.12960(12)	0.030(1)
O(6A)	1.0962(2)	-0.11088(13)	0.31737(11)	0.027(1)
O(7A)	1.1130(2)	-0.17520(12)	0.23394(11)	0.024(1)
N(1A)	0.9076(2)	0.07396(14)	0.21340(13)	0.016(1)
C(1A)	1.0359(3)	-0.02809(18)	0.19091(15)	0.016(1)
C(2A)	1.0227(3)	0.05060(18)	0.21125(15)	0.016(1)
C(3A)	1.0791(3)	0.05214(18)	0.27365(15)	0.019(1)
C(4A)	1.1845(3)	0.00784(19)	0.26348(17)	0.023(1)
C(5A)	1.1449(3)	-0.05395(17)	0.22442(14)	0.019(1)
C(6A)	0.9344(3)	-0.07371(18)	0.19862(16)	0.017(1)
C(7A)	0.8748(3)	-0.08114(18)	0.25156(15)	0.020(1)
C(8A)	0.7875(3)	-0.12802(19)	0.25743(17)	0.023(1)
C(9A)	0.7581(3)	-0.16845(19)	0.20943(17)	0.022(1)
C(10A)	0.8105(3)	-0.1611(2)	0.15483(18)	0.026(1)
C(11A)	0.8992(3)	-0.1145(2)	0.14978(17)	0.025(1)
C(12A)	0.8464(3)	0.07987(17)	0.16298(15)	0.017(1)
C(13A)	0.7258(3)	0.09647(18)	0.17109(15)	0.017(1)
C(14A)	0.6777(3)	0.14972(19)	0.13734(16)	0.020(1)

C(15A)	0.5659(3)	0.1655(2)	0.14353(17)	0.023(1)
C(16A)	0.4999(3)	0.1272(2)	0.18293(16)	0.025(1)
C(17A)	0.5466(3)	0.0736(2)	0.21597(17)	0.026(1)
C(18A)	0.6601(3)	0.05866(19)	0.21075(15)	0.020(1)
C(19A)	1.0923(3)	0.09548(19)	0.16859(16)	0.019(1)
C(20A)	1.1450(4)	0.20774(19)	0.13873(17)	0.029(1)
C(21A)	1.1041(3)	0.1228(2)	0.30011(17)	0.024(1)
C(22A)	1.0603(4)	0.1457(2)	0.35017(19)	0.034(1)
C(23A)	1.2364(3)	-0.07848(19)	0.18198(18)	0.024(1)
C(24A)	1.2865(5)	-0.1278(3)	0.0901(3)	0.030(2)
C(24B)	1.4237(12)	-0.0948(8)	0.1635(6)	0.051(5)
C(25A)	1.1165(3)	-0.11604(19)	0.26482(17)	0.020(1)
C(26A)	1.0687(4)	-0.2350(2)	0.26584(19)	0.035(1)
H(1B)	0.9011	0.0856	0.0124	0.022
H(1A)	0.7652	-0.0051	-0.1209	0.023
H(3A)	0.9431	-0.0380	0.0080	0.027
H(4A)	0.9745	-0.1369	-0.0483	0.027
H(4B)	0.9900	-0.0922	-0.1085	0.027
H(7A)	0.7404	-0.0198	0.0413	0.029
H(8A)	0.5760	0.0075	0.0920	0.031
H(10A)	0.4250	0.0546	-0.0647	0.026

H(11A)	0.5882	0.0247	-0.1143	0.025
H(14A)	0.9574	0.2023	0.0297	0.028
H(15A)	0.9354	0.3030	0.0885	0.029
H(16A)	0.7627	0.3598	0.0911	0.028
H(17A)	0.6126	0.3160	0.0372	0.027
H(18A)	0.6347	0.2170	-0.0222	0.024
H(20A)	1.1040	0.1717	-0.1644	0.048
H(20B)	1.0026	0.1381	-0.2010	0.048
H(20C)	1.1104	0.0919	-0.1860	0.048
H(21A)	1.1080	0.0320	-0.0041	0.034
H(22A)	1.1634	-0.0768	-0.0798	0.051
H(22B)	1.2491	-0.0199	-0.0493	0.051
H(24A)	0.8881	-0.2638	-0.2063	0.048
H(24B)	0.8319	-0.1964	-0.2361	0.048
H(24C)	0.7573	-0.2497	-0.1981	0.048
H(26A)	0.5352	-0.2182	-0.0198	0.091
H(26B)	0.5829	-0.1670	0.0305	0.091
H(26C)	0.6495	-0.2368	0.0135	0.091
H(1AB)	0.8771	0.0844	0.2479	0.019
H(1AA)	1.0538	-0.0274	0.1474	0.019
H(3AA)	1.0298	0.0263	0.3021	0.022

H(4AA)	1.2151	-0.0092	0.3018	0.027
H(4AB)	1.2427	0.0354	0.2427	0.027
H(7AA)	0.8948	-0.0530	0.2848	0.024
H(8AA)	0.7485	-0.1322	0.2941	0.027
H(10B)	0.7863	-0.1875	0.1214	0.032
H(11B)	0.9367	-0.1100	0.1127	0.030
H(14B)	0.7222	0.1753	0.1099	0.024
H(15B)	0.5339	0.2025	0.1210	0.028
H(16B)	0.4228	0.1378	0.1871	0.030
H(17B)	0.5013	0.0470	0.2423	0.031
H(18B)	0.6926	0.0227	0.2343	0.024
H(20D)	1.1144	0.2553	0.1368	0.044
H(20E)	1.1545	0.1894	0.0983	0.044
H(20F)	1.2175	0.2088	0.1589	0.044
H(21B)	1.1545	0.1526	0.2795	0.029
H(22C)	1.0097	0.1171	0.3718	0.041
H(22D)	1.0793	0.1909	0.3647	0.041
H(24D)	1.2572	-0.1274	0.0494	0.045
H(24E)	1.3026	-0.1762	0.1020	0.045
H(24F)	1.3553	-0.1001	0.0919	0.045
H(24G)	1.4929	-0.0962	0.1868	0.076

H(24H)	1.4297	-0.0585	0.1328	0.076
H(24I)	1.4116	-0.1404	0.1445	0.076
H(26D)	1.0725	-0.2766	0.2404	0.052
H(26E)	0.9908	-0.2259	0.2768	0.052
H(26F)	1.1128	-0.2429	0.3020	0.052

Table 3. Anisotropic displacement parameters ($Å^2$) for su038.

The anisotropic displacement factor exponent takes the form:

$-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br(1)	0.0173(2)	0.0443(2)	0.0223(2)	-0.0059(2)	0.0044(2)	0.0006(2)
O(1)	0.0282(16)	0.0363(16)	0.0083(13)	-0.0016(11)	-0.0024(12)	0.0025(13)
O(2)	0.0273(17)	0.0449(17)	0.0187(15)	-0.0134(13)	0.0046(13)	-0.0069(13)
O(3)	0.0269(16)	0.0300(15)	0.0139(13)	-0.0043(11)	0.0041(12)	-0.0055(12)
O(4)	0.0238(15)	0.0322(15)	0.0130(14)	-0.0015(11)	-0.0020(12)	-0.0025(12)
O(5)	0.0253(14)	0.0250(13)	0.0236(14)	-0.0091(10)	-0.0034(14)	0.0018(13)
O(6)	0.050(2)	0.0500(19)	0.0184(16)	0.0084(13)	-0.0055(15)	0.0014(15)
O(7)	0.0293(18)	0.0485(18)	0.0243(16)	0.0096(12)	0.0036(14)	-0.0136(14)
N(1)	0.0195(18)	0.0273(16)	0.0091(14)	-0.0040(12)	-0.0035(14)	0.0020(14)
C(1)	0.017(2)	0.028(2)	0.0109(19)	-0.0012(15)	-0.0022(16)	-0.0007(16)
C(2)	0.0166(19)	0.0228(18)	0.0143(18)	-0.0041(15)	-0.0006(17)	0.0004(15)
C(3)	0.022(2)	0.026(2)	0.018(2)	-0.0023(16)	-0.0062(18)	0.0033(17)
C(4)	0.021(2)	0.024(2)	0.022(2)	-0.0034(16)	-0.0049(18)	0.0008(16)
C(5)	0.015(2)	0.027(2)	0.0158(19)	-0.0036(15)	-0.0009(15)	-0.0008(16)
C(6)	0.018(2)	0.026(2)	0.017(2)	-0.0043(15)	0.0019(16)	-0.0022(16)

C(7)	0.021(2)	0.035(2)	0.016(2)	-0.0032(16)	-0.0039(17)	0.0050(17)
C(8)	0.022(2)	0.041(2)	0.015(2)	-0.0035(17)	0.0016(18)	-0.0004(18)
C(9)	0.019(2)	0.030(2)	0.021(2)	-0.0054(17)	0.0054(18)	-0.0027(17)
C(10)	0.013(2)	0.031(2)	0.020(2)	0.0007(16)	-0.0018(16)	0.0005(16)
C(11)	0.024(2)	0.029(2)	0.0101(19)	-0.0013(15)	-0.0003(17)	-0.0009(17)
C(12)	0.018(2)	0.023(2)	0.016(2)	-0.0005(15)	0.0033(16)	-0.0010(16)
C(13)	0.020(2)	0.0204(19)	0.0090(18)	0.0012(14)	0.0009(16)	-0.0032(16)
C(14)	0.022(2)	0.031(2)	0.017(2)	-0.0005(16)	0.0048(17)	0.0019(17)
C(15)	0.022(2)	0.030(2)	0.021(2)	-0.0035(16)	0.0010(19)	-0.0065(17)
C(16)	0.033(2)	0.022(2)	0.016(2)	-0.0041(16)	0.0039(19)	-0.0023(18)
C(17)	0.025(2)	0.025(2)	0.0184(19)	0.0018(16)	0.0007(17)	0.0014(17)
C(18)	0.020(2)	0.0250(19)	0.0145(19)	0.0018(16)	-0.0041(16)	0.0027(17)
C(19)	0.018(2)	0.029(2)	0.0149(19)	-0.0059(17)	-0.0025(16)	0.0043(17)
C(20)	0.031(3)	0.045(3)	0.020(2)	0.0019(19)	0.005(2)	-0.007(2)
C(21)	0.022(2)	0.029(2)	0.033(2)	-0.0088(18)	-0.014(2)	0.0052(18)
C(22)	0.021(2)	0.054(3)	0.054(3)	-0.018(2)	-0.006(2)	-0.004(2)
C(23)	0.016(2)	0.025(2)	0.017(2)	0.0041(16)	0.0024(18)	-0.0054(17)
C(24)	0.037(3)	0.030(2)	0.029(2)	-0.0152(18)	-0.0028(19)	-0.0023(19)
C(25)	0.033(3)	0.028(2)	0.017(2)	0.0019(17)	0.001(2)	0.0016(19)
C(26)	0.055(4)	0.082(4)	0.046(3)	0.024(3)	0.009(3)	-0.026(3)
Br(2)	0.0248(2)	0.0356(2)	0.0465(3)	-0.0009(2)	0.0028(2)	-0.0098(2)

O(1A)	0.0226(15)	0.0296(14)	0.0109(12)	0.0006(10)	0.0029(11)	0.0035(11)
O(2A)	0.0298(18)	0.0283(15)	0.0412(17)	0.0082(12)	0.0212(14)	0.0048(13)
O(3A)	0.0224(15)	0.0178(14)	0.0179(14)	0.0042(10)	0.0057(12)	0.0011(11)
O(4A)	0.0233(18)	0.0528(19)	0.0353(17)	0.0106(14)	0.0034(14)	0.0105(14)
O(5A)	0.0348(18)	0.0355(16)	0.0201(15)	-0.0014(12)	0.0093(13)	0.0124(13)
O(6A)	0.0352(17)	0.0293(15)	0.0174(15)	0.0066(11)	0.0028(13)	0.0026(13)
O(7A)	0.0293(17)	0.0183(13)	0.0233(14)	0.0041(10)	0.0073(12)	0.0025(11)
N(1A)	0.0143(15)	0.0221(16)	0.0115(15)	0.0005(12)	0.0051(13)	0.0048(12)
C(1A)	0.017(2)	0.0212(19)	0.0095(18)	0.0027(14)	0.0020(15)	0.0001(15)
C(2A)	0.0172(19)	0.0219(19)	0.0099(17)	0.0023(16)	0.0011(16)	-0.0004(15)
C(3A)	0.0159(19)	0.0218(19)	0.0184(19)	0.0019(16)	-0.0014(16)	-0.0020(16)
C(4A)	0.019(2)	0.027(2)	0.023(2)	0.0037(16)	-0.0046(17)	-0.0013(16)
C(5A)	0.0169(17)	0.0213(17)	0.0191(18)	0.0027(15)	0.0031(18)	0.0028(18)
C(6A)	0.019(2)	0.017(2)	0.0163(19)	0.0028(14)	-0.0022(16)	0.0012(15)
C(7A)	0.021(2)	0.026(2)	0.0122(18)	0.0016(14)	0.0007(16)	0.0027(16)
C(8A)	0.021(2)	0.027(2)	0.020(2)	0.0027(16)	0.0062(18)	0.0027(17)
C(9A)	0.014(2)	0.026(2)	0.025(2)	0.0053(17)	-0.0014(18)	0.0007(16)
C(10A)	0.029(2)	0.029(2)	0.020(2)	-0.0011(17)	-0.0066(18)	-0.0059(18)
C(11A)	0.029(2)	0.031(2)	0.014(2)	0.0064(17)	0.0012(17)	0.0028(18)
C(12A)	0.019(2)	0.0192(18)	0.0140(18)	0.0005(13)	0.0043(18)	-0.0010(16)
C(13A)	0.0162(19)	0.0222(19)	0.0116(18)	-0.0038(15)	-0.0048(16)	0.0016(16)

C(14A)	0.021(2)	0.024(2)	0.0151(19)	0.0013(15)	0.0000(16)	-0.0005(16)
C(15A)	0.023(2)	0.029(2)	0.018(2)	0.0038(17)	-0.0029(18)	0.0080(18)
C(16A)	0.015(2)	0.042(2)	0.017(2)	-0.0034(18)	0.0001(17)	0.0044(18)
C(17A)	0.022(2)	0.037(2)	0.018(2)	0.0043(18)	0.0038(18)	-0.0023(18)
C(18A)	0.020(2)	0.0264(19)	0.0123(17)	0.0051(16)	0.0027(17)	0.0009(17)
C(19A)	0.018(2)	0.024(2)	0.015(2)	0.0051(15)	0.0008(17)	0.0014(17)
C(20A)	0.029(2)	0.026(2)	0.033(2)	0.0097(16)	0.009(2)	-0.002(2)
C(21A)	0.023(2)	0.027(2)	0.023(2)	-0.0003(16)	-0.0034(18)	-0.0021(17)
C(22A)	0.037(3)	0.032(2)	0.033(3)	-0.0057(19)	0.000(2)	-0.007(2)
C(23A)	0.020(2)	0.018(2)	0.034(2)	0.0091(17)	0.0049(19)	0.0050(16)
C(24A)	0.037(4)	0.035(4)	0.018(3)	-0.004(3)	0.014(3)	0.015(3)
C(24B)	0.037(9)	0.063(10)	0.053(10)	0.022(7)	0.026(7)	0.015(7)
C(25A)	0.016(2)	0.024(2)	0.021(2)	0.0032(15)	-0.0025(16)	0.0049(16)
C(26A)	0.040(3)	0.024(2)	0.041(3)	0.0114(19)	0.011(2)	-0.002(2)

Table 4. Bond lengths [Å] for su038.

atom-atom	distance	atom-atom	distance
Br(1)-C(9)	1.891(4)	O(1)-C(12)	1.226(4)
O(2)-C(19)	1.204(4)	O(3)-C(19)	1.338(4)
O(3)-C(20)	1.450(4)	O(4)-C(23)	1.207(4)
O(5)-C(23)	1.334(4)	O(5)-C(24)	1.454(4)
O(6)-C(25)	1.194(5)	O(7)-C(25)	1.337(5)
O(7)-C(26)	1.452(5)	N(1)-C(12)	1.360(4)
N(1)-C(2)	1.450(4)	C(1)-C(6)	1.510(5)
C(1)-C(2)	1.576(5)	C(1)-C(5)	1.580(5)
C(2)-C(19)	1.529(5)	C(2)-C(3)	1.566(5)
C(3)-C(21)	1.506(5)	C(3)-C(4)	1.523(5)
C(4)-C(5)	1.532(5)	C(5)-C(23)	1.521(5)
C(5)-C(25)	1.537(5)	C(6)-C(11)	1.386(5)
C(6)-C(7)	1.400(5)	C(7)-C(8)	1.390(5)
C(8)-C(9)	1.378(5)	C(9)-C(10)	1.394(5)
C(10)-C(11)	1.380(5)	C(12)-C(13)	1.490(5)
C(13)-C(18)	1.388(5)	C(13)-C(14)	1.390(5)
C(14)-C(15)	1.396(5)	C(15)-C(16)	1.385(5)
C(16)-C(17)	1.377(5)	C(17)-C(18)	1.384(5)
C(21)-C(22)	1.300(5)	Br(2)-C(9A)	1.906(4)
O(1A)-C(12A)	1.246(4)	O(2A)-C(19A)	1.200(4)
O(3A)-C(19A)	1.325(4)	O(3A)-C(20A)	1.445(4)
O(4A)-C(23A)	1.252(5)	O(4A)-C(24B)	1.386(13)
O(5A)-C(23A)	1.291(5)	O(5A)-C(24A)	1.428(6)
O(6A)-C(25A)	1.209(4)	O(7A)-C(25A)	1.327(4)
O(7A)-C(26A)	1.449(4)	N(1A)-C(12A)	1.353(4)
N(1A)-C(2A)	1.450(4)	C(1A)-C(6A)	1.506(5)

C(1A)-C(2A)	1.579(5)	C(1A)-C(5A)	1.585(5)
C(2A)-C(19A)	1.532(5)	C(2A)-C(3A)	1.556(5)
C(3A)-C(21A)	1.506(5)	C(3A)-C(4A)	1.537(5)
C(4A)-C(5A)	1.546(5)	C(5A)-C(23A)	1.526(5)
C(5A)-C(25A)	1.532(5)	C(6A)-C(7A)	1.394(5)
C(6A)-C(11A)	1.410(5)	C(7A)-C(8A)	1.383(5)
C(8A)-C(9A)	1.372(5)	C(9A)-C(10A)	1.385(5)
C(10A)-C(11A)	1.391(5)	C(12A)-C(13A)	1.490(5)
C(13A)-C(18A)	1.391(5)	C(13A)-C(14A)	1.393(5)
C(14A)-C(15A)	1.380(5)	C(15A)-C(16A)	1.394(5)
C(16A)-C(17A)	1.382(5)	C(17A)-C(18A)	1.394(5)
C(21A)-C(22A)	1.316(5)	N(1)-H(1B)	0.8800
C(1)-H(1A)	1.0000	C(3)-H(3A)	1.0000
C(4)-H(4A)	0.9900	C(4)-H(4B)	0.9900
C(7)-H(7A)	0.9500	C(8)-H(8A)	0.9500
C(10)-H(10A)	0.9500	C(11)-H(11A)	0.9500
C(14)-H(14A)	0.9500	C(15)-H(15A)	0.9500
C(16)-H(16A)	0.9500	C(17)-H(17A)	0.9500
C(18)-H(18A)	0.9500	C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800	C(20)-H(20C)	0.9800
C(21)-H(21A)	0.9500	C(22)-H(22A)	0.9500
C(22)-H(22B)	0.9500	C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800	C(24)-H(24C)	0.9800
C(26)-H(26A)	0.9800	C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800	N(1A)-H(1AB)	0.8800
C(1A)-H(1AA)	1.0000	C(3A)-H(3AA)	1.0000
C(4A)-H(4AA)	0.9900	C(4A)-H(4AB)	0.9900
C(7A)-H(7AA)	0.9500	C(8A)-H(8AA)	0.9500
C(10A)-H(10B)	0.9500	C(11A)-H(11B)	0.9500
C(14A)-H(14B)	0.9500	C(15A)-H(15B)	0.9500
C(16A)-H(16B)	0.9500	C(17A)-H(17B)	0.9500
C(18A)-H(18B)	0.9500	C(20A)-H(20D)	0.9800

C(20A)-H(20E)	0.9800	C(20A)-H(20F)	0.9800
C(21A)-H(21B)	0.9500	C(22A)-H(22C)	0.9500
C(22A)-H(22D)	0.9500	C(24A)-H(24D)	0.9800
C(24A)-H(24E)	0.9800	C(24A)-H(24F)	0.9800
C(24B)-H(24G)	0.9800	C(24B)-H(24H)	0.9800
C(24B)-H(24I)	0.9800	C(26A)-H(26D)	0.9800
C(26A)-H(26E)	0.9800	C(26A)-H(26F)	0.9800

Symmetry transformations used to generate equivalent atoms:

Table 5. Bond angles [°] for su038.

atom-atom-atom	angle	atom-atom-atom	angle
C(19)-O(3)-C(20)	113.9(3)	C(23)-O(5)-C(24)	116.5(3)
C(25)-O(7)-C(26)	115.4(3)	C(12)-N(1)-C(2)	118.9(3)
C(6)-C(1)-C(2)	115.8(3)	C(6)-C(1)-C(5)	117.0(3)
C(2)-C(1)-C(5)	105.4(3)	N(1)-C(2)-C(19)	110.3(3)
N(1)-C(2)-C(3)	111.0(3)	C(19)-C(2)-C(3)	108.9(3)
N(1)-C(2)-C(1)	115.1(3)	C(19)-C(2)-C(1)	107.4(3)
C(3)-C(2)-C(1)	103.8(3)	C(21)-C(3)-C(4)	115.3(3)
C(21)-C(3)-C(2)	115.2(3)	C(4)-C(3)-C(2)	102.6(3)
C(3)-C(4)-C(5)	105.6(3)	C(23)-C(5)-C(4)	112.8(3)
C(23)-C(5)-C(25)	106.6(3)	C(4)-C(5)-C(25)	109.3(3)
C(23)-C(5)-C(1)	110.5(3)	C(4)-C(5)-C(1)	105.5(3)
C(25)-C(5)-C(1)	112.4(3)	C(11)-C(6)-C(7)	117.4(3)
C(11)-C(6)-C(1)	118.5(3)	C(7)-C(6)-C(1)	124.0(3)
C(8)-C(7)-C(6)	120.7(3)	C(9)-C(8)-C(7)	120.0(3)
C(8)-C(9)-C(10)	120.7(4)	C(8)-C(9)-Br(1)	120.1(3)
C(10)-C(9)-Br(1)	119.1(3)	C(11)-C(10)-C(9)	118.0(3)
C(10)-C(11)-C(6)	123.1(3)	O(1)-C(12)-N(1)	122.0(3)
O(1)-C(12)-C(13)	121.4(3)	N(1)-C(12)-C(13)	116.7(3)
C(18)-C(13)-C(14)	119.4(3)	C(18)-C(13)-C(12)	119.3(3)
C(14)-C(13)-C(12)	121.3(3)	C(13)-C(14)-C(15)	120.2(4)
C(16)-C(15)-C(14)	119.4(4)	C(17)-C(16)-C(15)	120.4(3)
C(16)-C(17)-C(18)	120.2(4)	C(17)-C(18)-C(13)	120.3(3)
O(2)-C(19)-O(3)	123.2(3)	O(2)-C(19)-C(2)	122.9(3)
O(3)-C(19)-C(2)	113.7(3)	C(22)-C(21)-C(3)	125.9(4)
O(4)-C(23)-O(5)	124.7(3)	O(4)-C(23)-C(5)	125.8(3)
O(5)-C(23)-C(5)	109.5(3)	O(6)-C(25)-O(7)	124.6(4)

O(6)-C(25)-C(5)	124.3(4)	O(7)-C(25)-C(5)	111.1(3)
C(19A)-O(3A)-C(20A)	114.7(3)	C(23A)-O(4A)-C(24B)	121.6(7)
C(23A)-O(5A)-C(24A)	119.2(4)	C(25A)-O(7A)-C(26A)	115.1(3)
C(12A)-N(1A)-C(2A)	120.8(3)	C(6A)-C(1A)-C(2A)	115.9(3)
C(6A)-C(1A)-C(5A)	115.4(3)	C(2A)-C(1A)-C(5A)	104.0(3)
N(1A)-C(2A)-C(19A)	111.5(3)	N(1A)-C(2A)-C(3A)	112.2(3)
C(19A)-C(2A)-C(3A)	108.4(3)	N(1A)-C(2A)-C(1A)	113.5(3)
C(19A)-C(2A)-C(1A)	107.3(3)	C(3A)-C(2A)-C(1A)	103.6(3)
C(21A)-C(3A)-C(4A)	112.9(3)	C(21A)-C(3A)-C(2A)	117.3(3)
C(4A)-C(3A)-C(2A)	102.3(3)	C(3A)-C(4A)-C(5A)	104.6(3)
C(23A)-C(5A)-C(25A)	107.0(3)	C(23A)-C(5A)-C(4A)	111.6(3)
C(25A)-C(5A)-C(4A)	108.9(3)	C(23A)-C(5A)-C(1A)	113.0(3)
C(25A)-C(5A)-C(1A)	109.9(3)	C(4A)-C(5A)-C(1A)	106.5(3)
C(7A)-C(6A)-C(11A)	117.0(3)	C(7A)-C(6A)-C(1A)	124.8(3)
C(11A)-C(6A)-C(1A)	118.2(3)	C(8A)-C(7A)-C(6A)	122.3(3)
C(9A)-C(8A)-C(7A)	118.9(3)	C(8A)-C(9A)-C(10A)	121.5(3)
C(8A)-C(9A)-Br(2)	120.0(3)	C(10A)-C(9A)-Br(2)	118.5(3)
C(9A)-C(10A)-C(11A)	118.9(4)	C(10A)-C(11A)-C(6A)	121.3(4)
O(1A)-C(12A)-N(1A)	120.9(3)	O(1A)-C(12A)-C(13A)	123.0(3)
N(1A)-C(12A)-C(13A)	116.1(3)	C(18A)-C(13A)-C(14A)	119.6(3)
C(18A)-C(13A)-C(12A)	121.0(3)	C(14A)-C(13A)-C(12A)	119.3(3)
C(15A)-C(14A)-C(13A)	120.4(4)	C(14A)-C(15A)-C(16A)	119.9(4)
C(17A)-C(16A)-C(15A)	120.0(4)	C(16A)-C(17A)-C(18A)	120.1(4)
C(13A)-C(18A)-C(17A)	119.9(3)	O(2A)-C(19A)-O(3A)	123.7(3)
O(2A)-C(19A)-C(2A)	122.2(3)	O(3A)-C(19A)-C(2A)	113.7(3)
C(22A)-C(21A)-C(3A)	123.8(4)	O(4A)-C(23A)-O(5A)	124.8(4)
O(4A)-C(23A)-C(5A)	118.1(4)	O(5A)-C(23A)-C(5A)	117.1(3)
O(6A)-C(25A)-O(7A)	125.0(3)	O(6A)-C(25A)-C(5A)	124.0(3)
O(7A)-C(25A)-C(5A)	110.9(3)	C(12)-N(1)-H(1B)	120.6
C(2)-N(1)-H(1B)	120.6	C(6)-C(1)-H(1A)	105.9
C(2)-C(1)-H(1A)	105.9	C(5)-C(1)-H(1A)	105.9
C(21)-C(3)-H(3A)	107.8	C(4)-C(3)-H(3A)	107.8

C(2)-C(3)-H(3A)	107.8	C(3)-C(4)-H(4A)	110.6
C(5)-C(4)-H(4A)	110.6	C(3)-C(4)-H(4B)	110.6
C(5)-C(4)-H(4B)	110.6	H(4A)-C(4)-H(4B)	108.8
C(8)-C(7)-H(7A)	119.7	C(6)-C(7)-H(7A)	119.7
C(9)-C(8)-H(8A)	120.0	C(7)-C(8)-H(8A)	120.0
C(11)-C(10)-H(10A)	121.0	C(9)-C(10)-H(10A)	121.0
C(10)-C(11)-H(11A)	118.4	C(6)-C(11)-H(11A)	118.4
C(13)-C(14)-H(14A)	119.9	C(15)-C(14)-H(14A)	119.9
C(16)-C(15)-H(15A)	120.3	C(14)-C(15)-H(15A)	120.3
C(17)-C(16)-H(16A)	119.8	C(15)-C(16)-H(16A)	119.8
C(16)-C(17)-H(17A)	119.9	C(18)-C(17)-H(17A)	119.9
C(17)-C(18)-H(18A)	119.8	C(13)-C(18)-H(18A)	119.8
O(3)-C(20)-H(20A)	109.5	O(3)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5	O(3)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5	H(20B)-C(20)-H(20C)	109.5
C(22)-C(21)-H(21A)	117.1	C(3)-C(21)-H(21A)	117.1
C(21)-C(22)-H(22A)	120.0	C(21)-C(22)-H(22B)	120.0
H(22A)-C(22)-H(22B)	120.0	O(5)-C(24)-H(24A)	109.5
O(5)-C(24)-H(24B)	109.5	H(24A)-C(24)-H(24B)	109.5
O(5)-C(24)-H(24C)	109.5	H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5	O(7)-C(26)-H(26A)	109.5
O(7)-C(26)-H(26B)	109.5	H(26A)-C(26)-H(26B)	109.5
O(7)-C(26)-H(26C)	109.5	H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5	C(12A)-N(1A)-H(1AB)	119.6
C(2A)-N(1A)-H(1AB)	119.6	C(6A)-C(1A)-H(1AA)	107.0
C(2A)-C(1A)-H(1AA)	107.0	C(5A)-C(1A)-H(1AA)	107.0
C(21A)-C(3A)-H(3AA)	108.0	C(4A)-C(3A)-H(3AA)	108.0
C(2A)-C(3A)-H(3AA)	108.0	C(3A)-C(4A)-H(4AA)	110.8
C(5A)-C(4A)-H(4AA)	110.8	C(3A)-C(4A)-H(4AB)	110.8
C(5A)-C(4A)-H(4AB)	110.8	H(4AA)-C(4A)-H(4AB)	108.9
C(8A)-C(7A)-H(7AA)	118.8	C(6A)-C(7A)-H(7AA)	118.8
C(9A)-C(8A)-H(8AA)	120.5	C(7A)-C(8A)-H(8AA)	120.5

C(9A)-C(10A)-H(10B)	120.6	C(11A)-C(10A)-H(10B)	120.6
C(10A)-C(11A)-H(11B)	119.4	C(6A)-C(11A)-H(11B)	119.4
C(15A)-C(14A)-H(14B)	119.8	C(13A)-C(14A)-H(14B)	119.8
C(14A)-C(15A)-H(15B)	120.0	C(16A)-C(15A)-H(15B)	120.0
C(17A)-C(16A)-H(16B)	120.0	C(15A)-C(16A)-H(16B)	120.0
C(16A)-C(17A)-H(17B)	120.0	C(18A)-C(17A)-H(17B)	120.0
C(13A)-C(18A)-H(18B)	120.0	C(17A)-C(18A)-H(18B)	120.0
O(3A)-C(20A)-H(20D)	109.5	O(3A)-C(20A)-H(20E)	109.5
H(20D)-C(20A)-H(20E)	109.5	O(3A)-C(20A)-H(20F)	109.5
H(20D)-C(20A)-H(20F)	109.5	H(20E)-C(20A)-H(20F)	109.5
C(22A)-C(21A)-H(21B)	118.1	C(3A)-C(21A)-H(21B)	118.1
C(21A)-C(22A)-H(22C)	120.0	C(21A)-C(22A)-H(22D)	120.0
H(22C)-C(22A)-H(22D)	120.0	O(5A)-C(24A)-H(24D)	109.5
O(5A)-C(24A)-H(24E)	109.5	O(5A)-C(24A)-H(24F)	109.5
O(4A)-C(24B)-H(24G)	109.5	O(4A)-C(24B)-H(24H)	109.5
H(24G)-C(24B)-H(24H)	109.5	O(4A)-C(24B)-H(24I)	109.5
H(24G)-C(24B)-H(24I)	109.5	H(24H)-C(24B)-H(24I)	109.5
O(7A)-C(26A)-H(26D)	109.5	O(7A)-C(26A)-H(26E)	109.5
H(26D)-C(26A)-H(26E)	109.5	O(7A)-C(26A)-H(26F)	109.5
H(26D)-C(26A)-H(26F)	109.5	H(26E)-C(26A)-H(26F)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 6. Torsion angles [°] for su038.

atom-atom-atom-atom	angle	atom-atom-atom-atom	angle
C(12)-N(1)-C(2)-C(19)	54.7(4)	C(12)-N(1)-C(2)-C(3)	175.5(3)
C(12)-N(1)-C(2)-C(1)	-67.0(4)	C(6)-C(1)-C(2)-N(1)	-11.4(4)
C(5)-C(1)-C(2)-N(1)	-142.4(3)	C(6)-C(1)-C(2)-C(19)	-134.6(3)
C(5)-C(1)-C(2)-C(19)	94.4(3)	C(6)-C(1)-C(2)-C(3)	110.2(3)
C(5)-C(1)-C(2)-C(3)	-20.8(3)	N(1)-C(2)-C(3)-C(21)	-71.7(4)
C(19)-C(2)-C(3)-C(21)	49.9(4)	C(1)-C(2)-C(3)-C(21)	164.1(3)
N(1)-C(2)-C(3)-C(4)	162.2(3)	C(19)-C(2)-C(3)-C(4)	-76.2(3)
C(1)-C(2)-C(3)-C(4)	38.0(4)	C(21)-C(3)-C(4)-C(5)	-167.4(3)
C(2)-C(3)-C(4)-C(5)	-41.3(4)	C(3)-C(4)-C(5)-C(23)	148.9(3)
C(3)-C(4)-C(5)-C(25)	-92.8(3)	C(3)-C(4)-C(5)-C(1)	28.2(4)
C(6)-C(1)-C(5)-C(23)	103.6(4)	C(2)-C(1)-C(5)-C(23)	-126.1(3)
C(6)-C(1)-C(5)-C(4)	-134.2(3)	C(2)-C(1)-C(5)-C(4)	-3.9(4)
C(6)-C(1)-C(5)-C(25)	-15.3(4)	C(2)-C(1)-C(5)-C(25)	115.1(3)
C(2)-C(1)-C(6)-C(11)	121.3(4)	C(5)-C(1)-C(6)-C(11)	-113.4(4)
C(2)-C(1)-C(6)-C(7)	-57.3(5)	C(5)-C(1)-C(6)-C(7)	68.0(5)
C(11)-C(6)-C(7)-C(8)	0.9(6)	C(1)-C(6)-C(7)-C(8)	179.5(4)
C(6)-C(7)-C(8)-C(9)	-1.1(6)	C(7)-C(8)-C(9)-C(10)	0.6(6)
C(7)-C(8)-C(9)-Br(1)	-179.0(3)	C(8)-C(9)-C(10)-C(11)	0.2(6)
Br(1)-C(9)-C(10)-C(11)	179.7(3)	C(9)-C(10)-C(11)-C(6)	-0.4(6)
C(7)-C(6)-C(11)-C(10)	-0.1(6)	C(1)-C(6)-C(11)-C(10)	-178.8(3)
C(2)-N(1)-C(12)-O(1)	0.7(5)	C(2)-N(1)-C(12)-C(13)	-178.5(3)
O(1)-C(12)-C(13)-C(18)	40.9(5)	N(1)-C(12)-C(13)-C(18)	-139.9(3)
O(1)-C(12)-C(13)-C(14)	-136.2(4)	N(1)-C(12)-C(13)-C(14)	42.9(5)
C(18)-C(13)-C(14)-C(15)	-1.8(5)	C(12)-C(13)-C(14)-C(15)	175.4(3)
C(13)-C(14)-C(15)-C(16)	0.8(5)	C(14)-C(15)-C(16)-C(17)	0.7(6)
C(15)-C(16)-C(17)-C(18)	-1.1(6)	C(16)-C(17)-C(18)-C(13)	0.1(5)

C(14)-C(13)-C(18)-C(17)	1.3(5)	C(12)-C(13)-C(18)-C(17)	-175.9(3)
C(20)-O(3)-C(19)-O(2)	3.6(5)	C(20)-O(3)-C(19)-C(2)	178.8(3)
N(1)-C(2)-C(19)-O(2)	-153.7(3)	C(3)-C(2)-C(19)-O(2)	84.2(4)
C(1)-C(2)-C(19)-O(2)	-27.6(5)	N(1)-C(2)-C(19)-O(3)	31.1(4)
C(3)-C(2)-C(19)-O(3)	-91.0(3)	C(1)-C(2)-C(19)-O(3)	157.2(3)
C(4)-C(3)-C(21)-C(22)	3.3(6)	C(2)-C(3)-C(21)-C(22)	-116.0(5)
C(24)-O(5)-C(23)-O(4)	-1.1(5)	C(24)-O(5)-C(23)-C(5)	177.8(3)
C(4)-C(5)-C(23)-O(4)	-138.5(4)	C(25)-C(5)-C(23)-O(4)	101.6(4)
C(1)-C(5)-C(23)-O(4)	-20.8(5)	C(4)-C(5)-C(23)-O(5)	42.6(4)
C(25)-C(5)-C(23)-O(5)	-77.3(4)	C(1)-C(5)-C(23)-O(5)	160.4(3)
C(26)-O(7)-C(25)-O(6)	4.1(6)	C(26)-O(7)-C(25)-C(5)	-176.4(4)
C(23)-C(5)-C(25)-O(6)	139.4(4)	C(4)-C(5)-C(25)-O(6)	17.3(5)
C(1)-C(5)-C(25)-O(6)	-99.4(4)	C(23)-C(5)-C(25)-O(7)	-40.1(4)
C(4)-C(5)-C(25)-O(7)	-162.2(3)	C(1)-C(5)-C(25)-O(7)	81.0(4)
C(12A)-N(1A)-C(2A)-C(19A)	54.6(4)	C(12A)-N(1A)-C(2A)-C(3A)	176.4(3)
C(12A)-N(1A)-C(2A)-C(1A)	-66.6(4)	C(6A)-C(1A)-C(2A)-N(1A)	-21.6(4)
C(5A)-C(1A)-C(2A)-N(1A)	-149.4(3)	C(6A)-C(1A)-C(2A)-C(19A)	-145.2(3)
C(5A)-C(1A)-C(2A)-C(19A)	87.0(3)	C(6A)-C(1A)-C(2A)-C(3A)	100.2(3)
C(5A)-C(1A)-C(2A)-C(3A)	-27.6(3)	N(1A)-C(2A)-C(3A)-C(21A)	-70.6(4)
C(19A)-C(2A)-C(3A)-C(21A)	52.9(4)	C(1A)-C(2A)-C(3A)-C(21A)	166.7(3)
N(1A)-C(2A)-C(3A)-C(4A)	165.3(3)	C(19A)-C(2A)-C(3A)-C(4A)	-71.2(3)
C(1A)-C(2A)-C(3A)-C(4A)	42.6(3)	C(21A)-C(3A)-C(4A)-C(5A)	-168.1(3)
C(2A)-C(3A)-C(4A)-C(5A)	-41.1(3)	C(3A)-C(4A)-C(5A)-C(23A)	147.5(3)
C(3A)-C(4A)-C(5A)-C(25A)	-94.7(3)	C(3A)-C(4A)-C(5A)-C(1A)	23.8(3)
C(6A)-C(1A)-C(5A)-C(23A)	111.6(3)	C(2A)-C(1A)-C(5A)-C(23A)	-120.3(3)
C(6A)-C(1A)-C(5A)-C(25A)	-7.7(4)	C(2A)-C(1A)-C(5A)-C(25A)	120.4(3)
C(6A)-C(1A)-C(5A)-C(4A)	-125.5(3)	C(2A)-C(1A)-C(5A)-C(4A)	2.6(3)
C(2A)-C(1A)-C(6A)-C(7A)	-52.5(5)	C(5A)-C(1A)-C(6A)-C(7A)	69.5(4)
C(2A)-C(1A)-C(6A)-C(11A)	130.5(3)	C(5A)-C(1A)-C(6A)-C(11A)	-107.6(4)
C(11A)-C(6A)-C(7A)-C(8A)	2.4(5)	C(1A)-C(6A)-C(7A)-C(8A)	-174.7(3)
C(6A)-C(7A)-C(8A)-C(9A)	-0.3(6)	C(7A)-C(8A)-C(9A)-C(10A)	-2.9(6)
C(7A)-C(8A)-C(9A)-Br(2)	177.6(3)	C(8A)-C(9A)-C(10A)-C(11A)	3.7(6)

Br(2)-C(9A)-C(10A)-C(11A)	-176.7(3)	C(9A)-C(10A)-C(11A)-C(6A)	-1.5(6)
C(7A)-C(6A)-C(11A)-C(10A)	-1.5(6)	C(1A)-C(6A)-C(11A)-C(10A)	175.8(3)
C(2A)-N(1A)-C(12A)-O(1A)	-6.8(5)	C(2A)-N(1A)-C(12A)-C(13A)	173.3(3)
O(1A)-C(12A)-C(13A)-C(18A)	130.7(4)	N(1A)-C(12A)-C(13A)-C(18A)	-49.4(4)
O(1A)-C(12A)-C(13A)-C(14A)	-47.9(5)	N(1A)-C(12A)-C(13A)-C(14A)	132.0(3)
C(18A)-C(13A)-C(14A)-C(15A)	0.7(5)	C(12A)-C(13A)-C(14A)-C(15A)	179.2(3)
C(13A)-C(14A)-C(15A)-C(16A)	-1.2(6)	C(14A)-C(15A)-C(16A)-C(17A)	0.3(6)
C(15A)-C(16A)-C(17A)-C(18A)	1.1(6)	C(14A)-C(13A)-C(18A)-C(17A)	0.8(5)
C(12A)-C(13A)-C(18A)-C(17A)	-177.8(3)	C(16A)-C(17A)-C(18A)-C(13A)	-1.7(6)
C(20A)-O(3A)-C(19A)-O(2A)	-1.9(5)	C(20A)-O(3A)-C(19A)-C(2A)	170.8(3)
N(1A)-C(2A)-C(19A)-O(2A)	-146.8(4)	C(3A)-C(2A)-C(19A)-O(2A)	89.3(4)
C(1A)-C(2A)-C(19A)-O(2A)	-22.0(5)	N(1A)-C(2A)-C(19A)-O(3A)	40.4(4)
C(3A)-C(2A)-C(19A)-O(3A)	-83.5(4)	C(1A)-C(2A)-C(19A)-O(3A)	165.2(3)
C(4A)-C(3A)-C(21A)-C(22A)	-123.4(4)	C(2A)-C(3A)-C(21A)-C(22A)	118.1(4)
C(24B)-O(4A)-C(23A)-O(5A)	8.6(9)	C(24B)-O(4A)-C(23A)-C(5A)	-173.7(7)
C(24A)-O(5A)-C(23A)-O(4A)	3.3(6)	C(24A)-O(5A)-C(23A)-C(5A)	-174.4(4)
C(25A)-C(5A)-C(23A)-O(4A)	-80.2(4)	C(4A)-C(5A)-C(23A)-O(4A)	38.8(4)
C(1A)-C(5A)-C(23A)-O(4A)	158.8(3)	C(25A)-C(5A)-C(23A)-O(5A)	97.7(4)
C(4A)-C(5A)-C(23A)-O(5A)	-143.3(3)	C(1A)-C(5A)-C(23A)-O(5A)	-23.3(4)
C(26A)-O(7A)-C(25A)-O(6A)	7.5(5)	C(26A)-O(7A)-C(25A)-C(5A)	-170.1(3)
C(23A)-C(5A)-C(25A)-O(6A)	141.0(4)	C(4A)-C(5A)-C(25A)-O(6A)	20.2(5)
C(1A)-C(5A)-C(25A)-O(6A)	-96.1(4)	C(23A)-C(5A)-C(25A)-O(7A)	-41.4(4)
C(4A)-C(5A)-C(25A)-O(7A)	-162.2(3)	C(1A)-C(5A)-C(25A)-O(7A)	81.5(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for su038 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1B)...O(1A)	0.88	2.28	3.096(4)	153.7
N(1A)-H(1AB)...O(4)#1	0.88	2.18	3.055(4)	172.2

Symmetry transformations used to generate equivalent atoms:

#1 -x+3/2,-y,z+1/2

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