Supplementary Material (ESI) for Chemical Communications
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Supplementary Information for

The first syntheses of enantiopure 2,2'-biindoline

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Contents

General Remarks

Dry THF and CH_2Cl_2 were obtained from a Pure Solv MD-5 solvent purification system. Anhydrous DMF and toluene were purchased and used without further purification. N_2 was dried by passage through a $CaCl_2$ tube. CuI was purified as previously described.[S1] All other reagents and solvents were purchased reagent grade and used without further purification or drying.

All reactions were performed in acetone washed and oven dried glassware with magnetic stirring under a positive pressure of N_2 unless specified that the reaction was carried out in air. Reactions performed at -40 ^{o}C used liquid N_2/CH_3CN slush baths. Thermal heating of reactions was carried out with paraffin oil baths. Microwave reactions were performed using a Discover CEM Focused Microwave Synthesis System in 10 mL closed vessels under N_2 (unless stated otherwise) with a power setting of 100 W.

Reactions heated either thermally or under microwave irradiation were cooled to RT before quenching and work-up. All organic extracts were dried with anhydrous $MgSO_4$ and gravity filtered. All solvents were evaporated under reduced pressure on a rotary evaporator and products dried under high vacuum at RT. Purification by column chromatography was performed using Flash Merck Silica Gel 60 (63-200 mesh) under a positive pressure of air. All organic solvent mixtures stated are in volume:volume proportions.

Melting points (m.p.) were determined using a Gallenkamp (Griffin) melting point apparatus. Temperatures are expressed in degrees Celsius (^{o}C) and are uncorrected. High Performance Liquid Chromatography (HPLC) was performed using a Waters 1515 pump and a Daicel Chiralcel OD-H column with a flow rate of 0.5 mL/min and a detection wavelength of 254 nm.

Proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectra were recorded at 300 and 75 MHz respectively on a Varian Mercury 300 MHz spectrometer. NMR spectra were aquired in $CDCl_3$ with chemical shifts (δ) reported in parts per million (ppm) relative to TMS (^{1}H: $\delta = 0.00$ ppm) and $CDCl_3$ (^{13}C: $\delta = 77.0$ ppm). Alternatively, where stated, spectra were aquired in $(CD_3)_2CO$ with δ values relative to $(CH_3)_2CO$ (^{1}H: $\delta = 2.05$ ppm) and $(\underline{C}D_3)_2CO$ (^{13}C: $\delta = 29.8$ ppm). Coupling constants (*J*) are reported in Hertz (Hz). *J* values listed in ^{1}H NMR spectral data refer to coupling between hydrogen nuclei. Multiplicities are reported as singlet (s), broad singlet (bs), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), pentet (p) or multiplet (m).

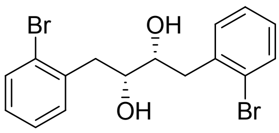
Electrospray (ES) mass spectra were obtained on a Micromass Platform LCZ spectrometer. Samples were injected as a solution in 50% CH_3CN. In some cases 1% aq. HCOOH was added to suppress dimerisation and/or aid in protonation; this is noted within by: (ES+, HCOOH). High Resolution (HR) ES mass spectrometry (MS) was performed on a Micromass QTOF2 Ultima Spectrometer. Electron Impact (EI) mass spectra were performed using a Shimadzu QP-5050 spectrometer. HR EI mass spectra were obtained using a Fison/VG Autospec-TOF spectrometer at 70 eV with a source temperature of 250 °C. Ion mass to charge (*m/z*) values of molecular ions (M), fragment peaks and adducts are stated with their relative abundances in parentheses. For compounds with more than one major isotope (eg: compounds containing bromine) all significant isotopic peaks are reported.

Infrared (IR) spectra were recorded with neat samples using a Nicolet Avatar 360 FT-IR spectrometer fitted with a Smart Omni-Sampler germanium crystal accessory. IR data is reported in nanometres (nm) with peak intensity assigned as weak (w), medium (m) or strong (s). Optical rotations were measured using a Jasco DIP-370 digital polarimeter with a 0.1 dm path length and a wavelength of 589 nm. Concentrations (*c*) are given in g/100 mL. X-ray crystallography studies were performed by Dr Anthony Willis at the Australian National University, Canberra.

Synthetic Procedures

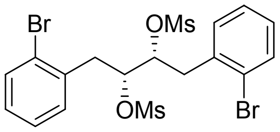
Synthesis of (2*S*,2'*S*)-2,2'-Biindoline (**1**) from (2*R*,2*R*)-2,2'-Bioxirane (**3**)

(2*R*,3*R*)-1,4-Di(2-bromophenyl)-2,3-butanediol (4)



To a solution of 2-bromoiodobenzene (854 mg, 3.02 mmol) in THF (6 mL) at -40 °C was added *i*-PrMgCl (1.82 mL, 1.66 M in THF, 3.02 mmol) and the mixture was allowed to warm to -25 °C over 2 h. The solution was cooled to -40 °C and added to a suspension of CuI (29 mg, 0.15 mmol) in THF (1 mL) at -40 °C. After 10 min, a solution of bioxirane (*R*,*R*)-**3**[S2] (98 mg, 1.14 mmol) in THF (2 mL) was added dropwise and the mixture was allowed to warm to -10 °C and maintained at this temp for 5 h. Saturated NH_4Cl (3 mL) was added slowly then the mixture was diluted with H_2O (3 mL) and EtOAc (15 mL), shaken and allowed to settle. The clear organic layer was decanted from the slurry and the process was twice repeated with EtOAc (2 x 15 mL). The combined organic layers were dried and concentrated to give a white solid (347 mg). Successive recrystallisations from EtOH (5 mL) provided two precipitate crops which were combined to give diol (*R*,*R*)-**4** (194 mg, 43%) with minor impurities. A further recrystallisation from EtOH (5 mL) provided the pure diol (*R*,*R*)-**4** (142 mg, 31%) as a white solid, m.p. 154 °C. $[\alpha]_D^{20}$ +21.1 (*c* 0.98, EtOH); ^{1}H NMR: δ 2.11 (d, *J* = 4.5 Hz, 2H, 2xOH), 2.97 (dd, *J* = 8.9, 13.7 Hz, 2H, $H1_a$, $H4_a$), 3.14 (dd, *J* = 3.8, 13.7 Hz, 2H, $H1_b$, $H4_b$), 3.86-3.94 (m, 2H, H2, H3), 7.10 (t, *J* = 8.1 Hz, 2H, 2xArH4), 7.22-7.32 (m, 4H, 2xArH5, 2xArH6), 7.55 (d, *J* = 8.1 Hz, 2H, 2xArH3); ^{13}C NMR: δ 40.6 (C1, C4), 72.8 (C2, C3), 124.8 (2xArC2), 127.5 (2xArC5), 128.3 (2xArC4), 131.8 (2xArC6), 132.9 (2xArC3), 137.7 (2xArC1); FTIR *ν* 3219 (w), 2923 (w), 1471 (w), 1440 (w), 1089 (m), 1023 (s), 917 (w), 754 (s), 739 (s); MS (ES+): 466 (45, M+Na+CH_3CN, ^{81}Br, ^{81}Br), 464 (100%, M+Na+CH_3CN, ^{81}Br, ^{79}Br), 462 (46, M+Na+CH_3CN, ^{79}Br, ^{79}Br), 425 (15, M+Na, ^{81}Br, ^{81}Br), 423 (30, M+Na, ^{81}Br, ^{79}Br), 421 (14, M+Na, ^{79}Br, ^{79}Br); HRMS (ES+) calcd for $C_{16}H_{16}{}^{81}Br^{79}BrO_2$+Na 422.9394, found 422.9398.

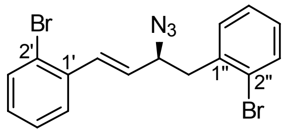
(2*R*,3*R*)-1,4-Di(2-bromophenyl)-2,3-butanediol 2,3-Dimethanesulfonate (5)



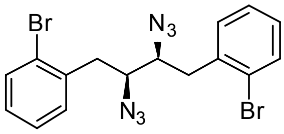
To a solution of diol (*R*,*R*)-**4** (139 mg, 0.35 mmol) and NEt_3 (88 mg, 0.87 mmol) in CH_2Cl_2 (5 mL) at 0 °C was added dropwise a solution of MsCl (88 mg, 0.77 mmol) in CH_2Cl_2 (1 mL) and the mixture was allowed to warm to RT and stirred in air for 3 h. The solution was diluted with CH_2Cl_2 (10 mL), washed with 5% $CuSO_4$ (15 mL) and saturated $NaHCO_3$ (15 mL), then dried and concentrated to give dimesylate (*R*,*R*)-**5** (162 mg, 84%) as a white solid, m.p. 172-175 °C. $[\alpha]_D^{25}$ +32.9 (*c* 4.00, CH_2Cl_2); ^{1}H NMR: δ 2.39 (s, 6H, 2xCH_3), 3.21 (dd, *J* = 10.5, 14.1 Hz, 2H, $H1_a$, $H4_a$), 3.44 (d, *J* = 14.1 Hz, 2H, $H1_b$, $H4_b$), 5.23 (d, *J* = 10.5 Hz, 2H, H2, H3), 7.18 (t, *J* = 7.8 Hz, 2H, 2xArH4), 7.26-7.39 (m, 4H, 2xArH5, 2xArH6), 7.61 (d, *J* = 7.8 Hz, 2H, 2xArH3); ^{13}C NMR: δ 36.5 (C1, C4), 37.4 (2xCH_3), 80.9 (C2, C3), 125.0 (2xArC2), 127.7 (2xArC5), 129.4 (2xArC4), 132.7 (2xArC6), 133.3 (2xArC3), 135.4 (2xArC1); FTIR *ν* 2972 (w), 1468 (w), 1356 (s), 1320 (w), 1175 (s), 1022 (m), 967 (m), 954 (m), 895 (s), 809 (m), 762 (m), 754 (m); MS (ES+, HCOOH): 622 (60, M+Na+CH_3CN, ^{81}Br, ^{81}Br), 620 (100%, M+Na+CH_3CN, ^{81}Br, ^{79}Br), 618 (52, M+Na+CH_3CN, ^{79}Br, ^{79}Br), 581 (56, M+Na, ^{81}Br, ^{81}Br), 579 (93, M+Na, ^{81}Br, ^{79}Br), 577 (52, M+Na, ^{79}Br, ^{79}Br); HRMS (ES+) calcd for $C_{18}H_{20}{}^{81}Br^{79}BrO_6S_2$+Na 578.8945, found 578.8950.

(2*S*,3*S*)-1,4-Di(2-bromophenyl)-2,3-butanediazide (6)

A mixture of dimesylate (*R*,*R*)-**5** (159 mg, 0.29 mmol) and NaN_3 (111 mg, 1.71 mmol) in DMF (1 mL) was heated at 80 °C for 264 h. H_2O (5 mL) was added and the mixture was extracted with CH_2Cl_2 (3 x 10 mL). The combined extracts were dried and concentrated giving a crude mixture of the alkene elimination product (~30 mg, ~25% conversion) and diazide (*S*,*S*)-**6** (~81 mg, ~63% conversion).

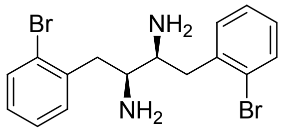


(1E,3S)-3-Azido-1,4-di(2-bromophenyl)-1-butene: ^{1}H NMR: δ 3.06-3.22 (m, 2H, H4), 4.45 (q, *J* = 7.8 Hz, 1H, H3), 6.11 (dd, *J* = 7.8, 15.6 Hz, 1H, H2), 6.90 (d, *J* = 15.6 Hz, 1H, H1), 7.09-7.18 (m, 2H, 2xArH), 7.25-7.30 (m, 3H, 3xArH), 7.48-7.58 (m, 3H, 3xArH); ^{13}C NMR: δ 41.3 (C4), 63.8 (C3), 123.7 (C2' or C2''), 124.7 (C2' or C2''), 127.3 (ArCH), 127.47 (ArCH), 127.52 (ArCH), 128.7 (ArCH), 129.2 (ArCH), 129.4 (C2), 132.0 (ArCH), 132.4 (C1), 132.9 (ArCH), 133.0 (ArCH), 136.0 (C1' or C1''), 136.4 (C1' or C1'').



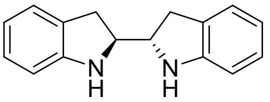
The crude mixture was dissolved in THF (3 mL), then a solution of $KMnO_4$ in H_2O (3 mL) was added and the mixture was stirred in air for 12 h. The brown slurry was diluted with CH_2Cl_2 (15 mL) and H_2O (10 mL), then 10% HCl (5 mL) and 10% Na_2SO_3 (1 mL) were added. The organic layer was separated and the aqueous solution extracted with CH_2Cl_2 (10 mL). The combined organic layers were dried, concentrated and subjected to column chromatography (1% EtOAc:hexanes) giving diazide (*S,S*)-**6** (60 mg, 47% overall) as a viscous pale yellow oil. $[\alpha]_D^{22}$ -28.5 (*c* 3.00, CH_2Cl_2); ^{1}H NMR: δ 3.06-3.22 (m, 4H, H1, H4), 3.74 (t, *J* = 6.0 Hz, 2H, H2, H3), 7.09-7.18 (m, 2H, 2xArH4), 7.25-7.30 (m, 4H, 2xArH5, 2xArH6), 7.54 (d, *J* = 8.4 Hz, 2H, 2xArH3); ^{13}C NMR: δ 38.5 (C1, C4), 63.2 (C2, C3), 124.5 (2xArC2), 127.8 (2xArC5), 129.0 (2xArC4), 131.8 (2xArC6), 133.1 (2xArC3), 136.1 (2xArC1); FTIR *v* 2105 (s), 1476 (w), 1443 (w), 1259 (w), 1024 (m), 749 (s); MS (EI+): 169 (100%).[S3]

(2*S*,3*S*)-1,4-Di(2-bromophenyl)-2,3-butanediamine (7)



A solution of diazide (*S,S*)-**6** (45.6 mg, 0.10 mmol) and PPh_3 (58 mg, 0.22 mmol) in THF (1 mL) was stirred for 2 h. H_2O (2 drops) was added from a pasteur pipette and the solution was heated at reflux for 13 h. The mixture was diluted with CH_2Cl_2 (20 mL), washed with H_2O (5 mL), dried and concentrated to give a white solid (96 mg). This was dissolved in 10% EtOAc:Et_2O (5 mL), then HCl (1 mL, 2.0 M in Et_2O) was added dropwise, forming a white precipitate. After stirring for 2 h, the suspension was vacuum filtered and the precipitate washed with Et_2O (4 x 5 mL) to give a pale yellow solid (49 mg) which was dissolved in a biphase of 15% NaOH (3 mL) and CH_2Cl_2 (3 mL). The mixture was diluted with H_2O (5 mL) and CH_2Cl_2 (15 mL), then the organic layer was separated, dried and concentrated to give diamine (*S,S*)-**7** (28.6 mg, 71%) as a viscous colourless oil.[S4] ^{1}H NMR: δ 1.83 (bs, 4H, 2xNH_2), 2.80 (dd, *J* = 8.1, 13.5 Hz, 2H, $H1_a$, $H4_a$), 3.00 (d, *J* = 13.5 Hz, 2H, $H1_b$, $H4_b$), 3.34-3.42 (m, 2H, H2, H3), 7.06 (t, *J* = 7.8 Hz, 2H, 2xArH4), 7.20-7.31 (m, 4H, 2xArH5, 2xArH6), 7.52 (d, *J* = 7.8 Hz, 2H, 2xArH3); ^{13}C NMR: δ 41.1 (C1, C4), 64.1 (C2, C3), 124.6 (2xArC2), 127.5 (2xArC5), 128.0 (2xArC4), 131.3 (2xArC6), 132.8 (2xArC3), 138.8 (2xArC1); MS (ES+, HCOOH): 401 (48, M+H, ^{81}Br, ^{81}Br), 399 (100%, M+H, ^{81}Br, ^{79}Br), 397 (47, M+H, ^{79}Br, ^{79}Br); HRMS (ES+) calcd for $C_{16}H_{19}{}^{81}Br^{79}BrN_2$ 398.9894, found 398.9889.

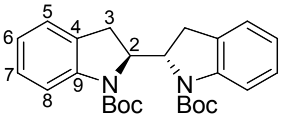
(2*S*,2'*S*)-2,2'-Biindoline (1)



A mixture of $Pd(OAc)_2$ (3.2 mg, 14.4 μmol), ±-BINAP (17.9 mg, 28.7 μmol) and toluene (0.5 mL) in a microwave vessel was stirred for 30 min to give a yellow solution. A solution of diamine (*S*,*S*)-**7** (28.6 mg, 71.8 μmol) in toluene (0.5 mL) was added, followed by NaO*t*-Bu (20.7 mg, 0.22 mmol), and the burgundy solution was heated in a microwave at 120 °C for 4 h. The mixture was diluted with toluene (15 mL) and vacuum filtered through Celite. The filtrate was concentrated and subjected to column chromatography (5% to 10% EtOAc:hexanes) giving biindoline (*S*,*S*)-**1** (9.7 mg, 57%) as a light brown solid m.p. 150-152 °C.[S5] ^{1}H NMR: δ 2.71 (dd, *J* = 8.1, 15.6 Hz, 2H, H3$_a$, H3'$_a$), 3.17 (dd, *J* = 8.7, 15.6 Hz, 2H, H3$_b$, H3'$_b$), 3.82-3.92 (m, 2H, H2, H2'), 4.20 (bs, 2H, 2xNH), 6.59 (d, *J* = 7.5 Hz, 2H, H8, H8'), 6.71 (t, *J* = 7.5 Hz, 2H, H6, H6'), 7.01 (t, *J* = 7.5 Hz, 2H, H7, H7'), 7.07 (d, *J* = 7.5 Hz, 2H, H5, H5'); ^{13}C NMR: δ 33.3 (C3, C3'), 64.9 (C2, C2'), 109.5 (C8, C8'), 119.0 (C6, C6'), 124.7 (C5, C5'), 127.4 (C7, C7'), 128.6 (C4, C4'), 150.7 (C9, C9'); FTIR *v* 3360 (w), 2843 (w), 1603 (m), 1481 (m), 1460 (m), 1238 (s), 1066 (m), 745 (s); MS (ES+, HCOOH): 237 (100%, M+H); MS (EI+): 236 (5, M$^+$), 119 (74), 118 (100%), 117 (45); HRMS (EI+) calcd for $C_{16}H_{16}N_2$ 236.1313, found 236.1312.

Preparation of the diBoc Derivative for Determination of Enantiomeric Purity

(2*S*,2'*S*)-*N*,*N'*-Di-*tert*-butoxycarbonyl-2,2'-biindoline



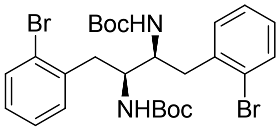
To a solution of biindoline (*S*,*S*)-**1** (6.4 mg, 27.1 μmol) and NEt_3 (6.0 mg, 59.6 μmol) in THF (0.5 mL) was added a solution of Boc_2O (12.4 mg, 56.9 μmol) in THF (0.5 mL) and the mixture was stirred in air for 144 h, during which time three additional portions of Boc_2O (3 x ~15 mg) were added (after 3, 27 and 52 h). The mixture was diluted with CH_2Cl_2 (10 mL) and H_2O (5 mL), then the organic layer was separated, dried, concentrated and subjected to column chromatography (hexanes to 4% EtOAc:hexanes) to give the diBoc derivative (9.0 mg, 76%) as a white solid, mp. 182-184 °C. $[\alpha]_D^{21}$ -91.4 (*c* 0.45, CH_2Cl_2); HPLC analysis (2.5% *i*-PrOH:hexane, retention time: 10.5 min) showed the *ee* of the biindoline derivative was >99%; ^{1}H NMR: δ 1.54 (s, 18H, 6xCH_3), 2.72 (d, *J* = 16.8 Hz, 2H, H3$_a$, H3'$_a$), 3.16 (dd, *J* = 9.6, 16.8 Hz, 2H, H3$_b$, H3'$_b$), 4.96-5.04 (m, 2H, H2, H2'), 6.91 (t, *J* = 7.5 Hz, 2H, H6, H6'), 7.01 (d, *J* = 7.5 Hz, 2H, H5, H5'), 7.16 (t, *J* = 7.5 Hz, 2H, H7, H7'), 7.70 (bs, 2H, H8, H8'); ^{13}C NMR: δ 28.4 (6xCH_3), 29.2 (C3, C3'), 60.0 (C2, C2'), 81.3 (2x<u>C</u>$(CH_3)_3$), 115.5 (C8, C8'), 122.5 (C6, C6'), 124.5 (C5, C5'), 127.3 (C7, C7'), 130.2 (C4, C4'), 143.2 (C9, C9'), 152.6 (2xC=O); FTIR *v* 2966 (w), 2919 (w), 2848 (w), 1696 (s), 1485 (m), 1390 (s), 1373 (m), 1341 (s), 1161 (m), 1021 (m), 752 (s); MS (EI+): 436 (17, M^+), 118 (100%); HRMS (EI+) calcd for $C_{26}H_{32}N_2O_4$ 436.2362, found 436.2345.

Synthesis of (2*S*,2'*S*)-2,2'-Biindoline (**1**) from (2*S*,2'*S*)-*N*,*N'*-Di-*tert*-butoxycarbonyl-2,2'-biaziridine (**8**)

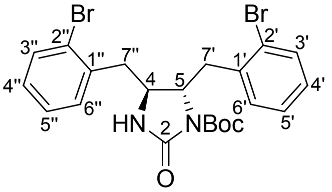
Ring Opening

(4*S*,5*S*)-4,5-Di(2-bromobenzyl)-1-*tert*-butoxycarbonyl-2-imidazolidinone (9)

(2*S*,3*S*)-1,4-Di(2-bromophenyl)-2,3-di(*N*-*tert*-butoxycarbonylamino)butane (10)



To a solution of 2-bromoiodobenzene (1.09 g, 3.86 mmol) in THF (4 mL) at -40 °C was added *i*-PrMgCl (1.61 mL, 2.0 M in THF, 3.22 mmol) and the mixture was allowed to warm to -25 °C over 2.5 h. The solution was cooled to -40 °C and added dropwise to a suspension of CuBr.SMe_2 (99 mg, 0.48 mmol) and biaziridine (*S*,*S*)-**8**[S6] (183 mg, 0.64 mmol) in THF (2 mL) at -40 °C. The solution was allowed to warm to -10 °C over 6 h, then saturated NH_4Cl (2 mL) was added slowly, followed by H_2O (5 mL) and the mixture was extracted with EtOAc (3 x 10 mL). The combined extracts were dried, concentrated and subjected to column chromatography (5% to 10% EtOAc:hexanes) affording dicarbamate (*S*,*S*)-**10** (94 mg, 24%) as a white solid, m.p. 172 °C. $[\alpha]_D^{21}$ -61.7 (*c* 1.97, CH_2Cl_2); ^{1}H NMR: δ 1.33 (s, 18H, 6xCH_3), 2.75-3.18 (m, 4H, H1, H4), 4.01-4.19 (m, 2H, H2, H3), 4.88 (bs, 2H, 2xNH), 7.02-7.14 (m, 2H, 2xArH4), 7.15-7.26 (m, 4H, 2xArH5, 2xArH6), 7.52 (d, *J* = 7.8 Hz, 2H, 2xArH3); ^{13}C NMR: δ 28.3 (6xCH_3), 39.3 (C1, C4), 54.5 (C2, C3), 79.3 (2x<u>C</u>$(CH_3)_3$), 125.2 (2xArC2), 127.3 (2xArC5), 128.1 (2xArC4), 131.4 (2xArC6), 132.7 (2xArC3), 137.7 (2xArC1), 155.9 (2xC=O); FTIR *v* 3359 (w), 2972 (w), 1681 (s), 1525 (m), 1370 (w), 1299 (w), 1250 (w), 1167 (m), 1022 (w), 752 (m); MS (ES+, HCOOH): 601 (24, M+H, ^{81}Br, ^{81}Br), 599 (45, M+H, ^{81}Br, ^{79}Br), 597 (22, M+H, ^{79}Br, ^{79}Br), 445 (48, M+H+HCOOH-2Boc, ^{81}Br, ^{81}Br), 443 (100%, M+H+HCOOH-2Boc, ^{81}Br, ^{79}Br), 441 (50, M+H+HCOOH-2Boc, ^{79}Br, ^{79}Br); HRMS (ES+) calcd for $C_{26}H_{34}{}^{79}Br_2N_2O_4$+Na 619.0783, found 619.0812.

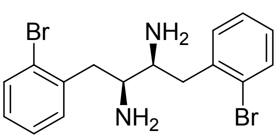


Further elution with 12% EtOAc:hexanes to 100% EtOAc yielded imidazolidinone (*S*,*S*)-**9** (141 mg, 42%) as a pale yellow syrup. $[\alpha]_D^{21}$ -33.8 (*c* 4.50, CH_2Cl_2); ^{1}H NMR: δ 1.50 (s, 9H, 3xCH_3), 2.85-2.93 (m, 3H, H7'$_a$, H7"), 3.24 (dd, *J* = 5.4, 13.2 Hz, 1H, H7'$_b$), 3.63 (t, *J* = 6.9 Hz, 1H, H4), 4.40 (dd, *J* = 5.4, 9.3 Hz, 1H, H5), 6.84 (bs, 1H, NH), 6.93-7.14 (m, 6H, H4', H4", H5', H5", H6', H6"), 7.36-7.43 (m, 2H, H3', H3"); ^{13}C NMR: δ 28.0 (3xCH_3), 38.9 (C7'), 40.9 (C7"), 52.1 (C4), 58.0 (C5), 82.4 ($\underline{C}(CH_3)_3$), 124.5 (C2' or C2"), 124.6 (C2' or C2"), 127.4 (C5' or C5"), 127.5 (C5' or C5"), 128.26 (C4' or C4"), 128.30 (C4' or C4"), 131.0 (C6' or C6"), 131.6 (C6' or C6"), 132.8 (C3' or C3"), 132.9 (C3' or C3"), 135.1 (C1' or C1"), 135.6 (C1' or C1"), 150.0 (*t*-BuOC=O), 155.6 (C2); FTIR *v* 3350 (m), 1768 (s), 1345 (m), 1242 (w), 1152 (m), 741 (s); MS (ES+, HCOOH): 527 (9, M+H, ^{81}Br, ^{81}Br), 525 (18, M+H, ^{81}Br, ^{79}Br), 523 (8, M+H, ^{79}Br, ^{79}Br), 471 (48, M+HCOOH-Boc, ^{81}Br, ^{81}Br), 469 (100%, M+HCOOH-Boc, ^{81}Br, ^{79}Br), 467 (48, M+HCOOH-Boc, ^{79}Br, ^{79}Br); HRMS (ES+) calcd for $C_{22}H_{24}{}^{79}Br_2N_2O_3$+Na 545.0051, found 545.0075.

Hydrolysis of the Imidazolidinone

(2*S*,3*S*)-1,4-Di(2-bromophenyl)-2,3-butanediamine (7)

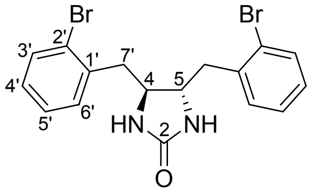
Small Scale



A suspension of imidazolidinone (*S*,*S*)-**9** (19.6 mg, 37.4 μmol) in 32% HCl (3 mL) was heated at 110 °C in a microwave under air for 12 h. The dark green suspension was vacuum filtered and the grey/brown solid was washed with H_2O (5 mL) and Et_2O (25 mL), then dissolved in a biphase of 15% NaOH (10 mL) and CH_2Cl_2 (10 mL). The acidic aqueous layer from the earlier filtration was added and alkalinity was maintained. The organic layer was separated and the aqueous solution extracted with CH_2Cl_2 (10 mL). The combined organic layers were dried and concentrated to give diamine (*S*,*S*)-**7** (13.3 mg, 89%) as a viscous brown oil spectroscopically identical to the product synthesised from the bioxirane.

Larger Scale

A suspension of imidazolidinone (*S*,*S*)-**9** (617 mg, 1.18 mmol) in EtOH (0.5 mL) and 32% HCl (3 mL) was heated at 110 °C in a microwave under air for 18 h. Et_2O (5 mL) was added to the slurry and the vessel was shaken and allowed to settle, then the supernatant liquid was decanted. This process was twice repeated with Et_2O (2 x 5 mL), then the remaining sticky solids were stirred vigorously for 1 h in 30% CH_2Cl_2:Et_2O (7 mL). The suspension was vacuum filtered and the collected solid (~300 mg) was dried in a 110 °C oven for 30 min before being dissolved in a biphase of 5 M NaOH (3 mL) and CH_2Cl_2 (3 mL). The mixture was diluted with 5 M NaOH (20 mL) and CH_2Cl_2 (30 mL), then the acidic aqueous layer from the earlier decanting was added and alkalinity was maintained. The organic layer was separated and the aqueous layer extracted with CH_2Cl_2 (15 mL). The combined organic layers were dried and concentrated to give a viscous brown oil containing diamine (*S*,*S*)-**7** (188 mg, 40% yield) and the Boc-deprotected imidazolidinone (94 mg, 19% yield).[S7]

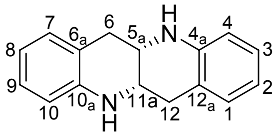


(4S,5S)-4,5-Di(2-bromobenzyl)-2-imidazolidinone: white solid, m.p. 116-117 °C. ^{1}H NMR: δ 2.90 (dd, *J* = 8.1, 13.5 Hz, 2H, 2xH7'$_a$), 3.03 (dd, *J* = 5.4, 13.5 Hz, 2H, 2xH7'$_b$), 3.85 (t, *J* = 5.4 Hz, 2H, H4, H5), 4.74 (bs, 2H, 2xNH), 7.06-7.12 (m, 2H, 2xH4'), 7.16-7.26 (m, 4H, 2xH5', 2xH6'), 7.51 (d, *J* = 8.1 Hz, 2H, 2xH3'); ^{13}C NMR: δ 41.8 (2xC7'), 57.0 (C4, C5), 124.5 (2xC2'), 127.7 (2xC5'), 128.7 (2xC4'), 131.6 (2xC6'), 133.2 (2xC3'), 136.1 (2xC1'), 161.6 (C2); FTIR *v* 3201 (w), 2925 (w), 1702 (s), 1470 (w), 1441 (w), 1025 (m), 747 (m); MS (ES+): 468 (51, M+H+CH_3CN, ^{81}Br, ^{81}Br), 466 (100%, M+H+CH_3CN, ^{81}Br, ^{79}Br), 464 (51, M+H+CH_3CN, ^{79}Br, ^{79}Br), 427 (43, M+H, ^{81}Br, ^{81}Br), 425 (86, M+H, ^{81}Br, ^{79}Br), 423 (44, M+H, ^{79}Br, ^{79}Br); HRMS (ES+) calcd for $C_{17}H_{17}{}^{81}Br^{79}BrN_2O$ 424.9687, found 424.9694.

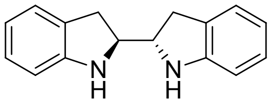
Cyclisation

(2*S*,2'*S*)-2,2'-Biindoline (1)

(5a*S*,11a*S*)-5,5a,6,11,11a,12-Hexahydrodibenzo[*b*,*g*][1,5]naphthyridine (11)



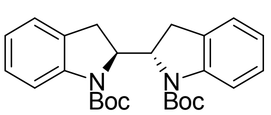
This reaction followed the cyclisation procedure described above using $Pd(OAc)_2$ (7.4 mg, 33.0 μmol), ±-BINAP (41 mg, 65.8 μmol), toluene (2 mL), a solution of diamine (*S*,*S*)-**7** (175 mg, 0.44 mmol) in toluene (2 mL), NaO*t*-Bu (190 mg, 1.98 mmol) and a 12 h reaction time. The crude mixture was subjected to column chromatography (5% to 10% EtOAc:hexanes) giving naphthyridine (*S*,*S*)-**11** (3.0 mg, 3%) as a brown solid. ^{1}H NMR: δ 2.75 (dd, *J* = 3.6, 16.8 Hz, 2H, H6$_x$, H12$_x$), 3.16 (dd, *J* = 4.2, 16.8 Hz, 2H, H6$_y$, H12$_y$), 3.51 (bs, 2H, 2xNH), 3.79 (t, *J* = 3.0 Hz, 2H, H5$_a$, H11$_a$), 6.44 (d, *J* = 7.8 Hz, 2H, H4, H10), 6.63 (t, *J* = 7.5 Hz, 2H, H2, H8), 6.93-7.00 (m, 4H, H1, H3, H7, H9); ^{13}C NMR: δ 33.5 (C6, C12), 46.8 (C5$_a$, C11$_a$), 114.5 (C4, C10), 117.2 (C6$_a$, C12$_a$), 117.3 (C2, C8), 127.1 (C3, C9), 129.9 (C1, C7), 143.6 (C4$_a$, C10$_a$); MS (ES+, HCOOH): 237 (100%, M+H); HRMS (EI+) calcd for $C_{16}H_{16}N_2$ 236.1313, found 236.1308.



Further elution provided biindoline (*S*,*S*)-**1** (82 mg, 79%) as a light brown solid, spectroscopically identical to the product synthesised from the bioxirane. $[\alpha]_D^{23}$ +10.9 (*c* 3.84, CH_2Cl_2). A sample (~15 mg) was dissolved in 50% CH_2Cl_2:MeOH (1 mL) and the solution was allowed to stand in a capped NMR tube to provide colourless crystalline needles/rods suitable for X-ray analysis.

Determination of Enantiomeric Purity

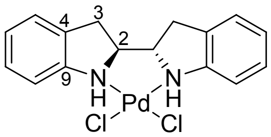
(2*S*,2'*S*)-*N*,*N'*-Di-*tert*-butoxycarbonyl-2,2'-biindoline



The diBoc derivative was prepared as described above using biindoline (*S*,*S*)-**1** (6.6 mg, 27.9 µmol), NEt_3 (6.2 mg, 61.4 µmol), THF (0.5 mL), a solution of Boc_2O (12.8 mg, 58.7 µmol) in THF (0.5 mL) and three additional portions of Boc_2O (3 x ~15 mg) affording the derivative (9.0 mg, 74%) as a white solid, spectroscopically identical to the product synthesised from the bioxirane. $[\alpha]_D^{22}$ -88.6 (*c* 0.45, CH_2Cl_2); HPLC analysis (2.5% *i*-PrOH:hexane, retention time: 11.3 min) showed the *ee* of the biindoline derivative was >99%.

Preparation of the Palladium(II) Dichloride Complex

(2*S*,2'*S*)-2,2'-Biindolinepalladium(II) Dichloride

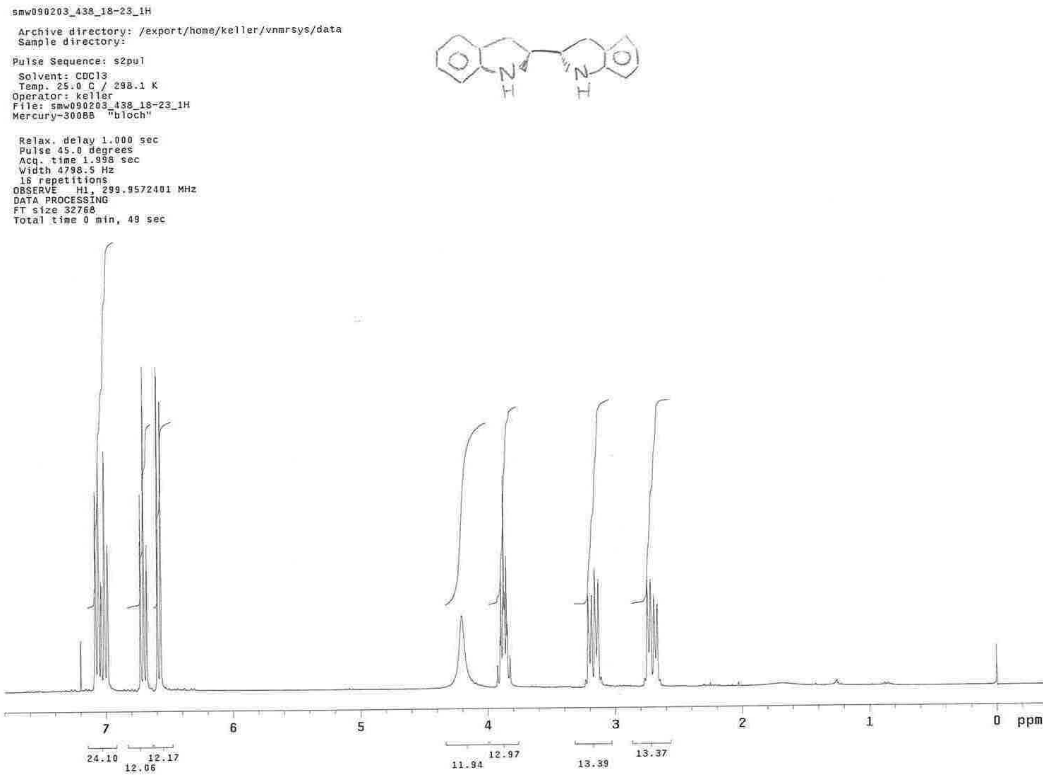


To a solution of biindoline (*S*,*S*)-**1** (9.3 mg, 39.4 µmol) in CH_2Cl_2 (1 mL) was added a solution of $Pd(CH_3CN)_2Cl_2$ (10.2 mg, 39.4 µmol) in CH_2Cl_2 (3 mL) and a yellow/orange precipitate formed. After stirring in air for 2 h, the mixture was allowed to stand in a freezer for 1 h before vacuum filtration. The precipitate was dissolved in 50% acetone:MeOH (15 mL) and gravity filtered. The filtrate was dried and concentrated to give the Pd complex (15.4 mg, 95%) as a yellow/orange powder. ^1H NMR [$(CD_3)_2CO$]: δ 3.15-3.32 (m, 4H, H3, H3'), 3.96-4.04 (m, 2H, H2, H2'), 7.24-7.30 (m, 4H, 4xArH), 7.33-7.37 (m, 2H, 2xArH), 7.46 (bs, 2H, 2xNH), 8.08-8.12 (m, 2H, 2xArH); ^{13}C NMR [$(CD_3)_2CO$]: δ 33.6 (C3, C3'), 69.3 (C2, C2'), 122.9 (2xArCH), 126.2 (2xArCH), 127.9 (2xArCH), 128.3 (2xArCH), 134.0 (2xC4), 146.4 (2xC9). A saturated solution of the complex in CH_3CN (~1 mg/mL) was allowed to stand in an uncapped NMR tube to provide orange crystals suitable for X-ray analysis.

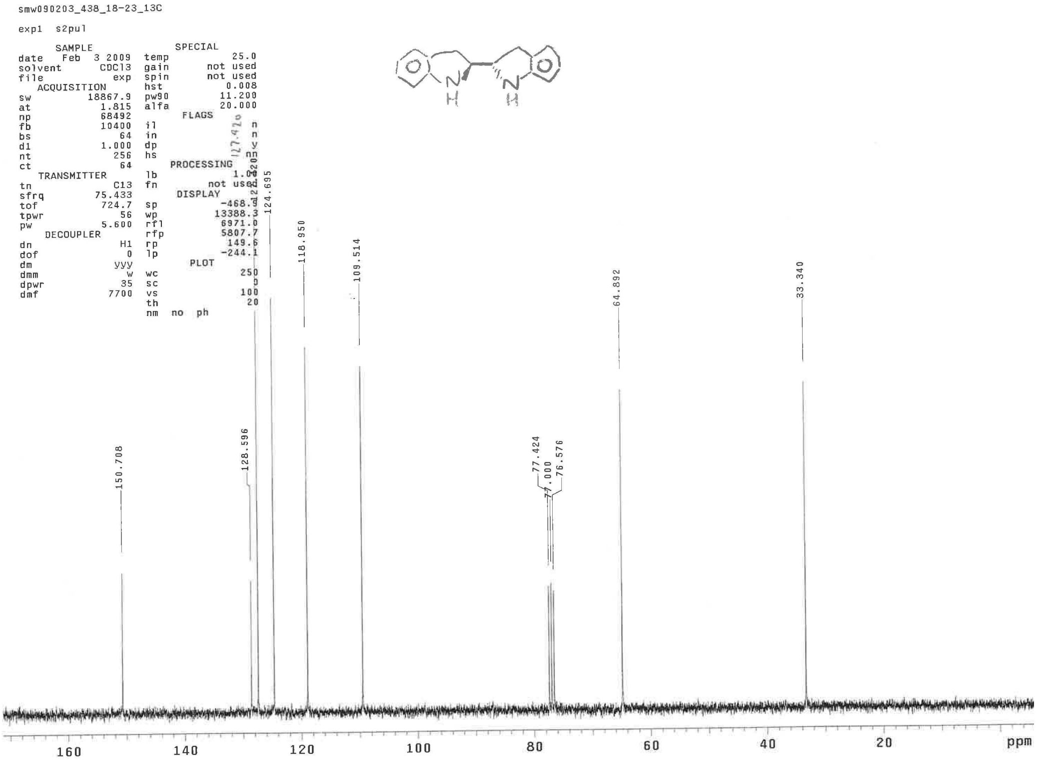
NMR Spectra of (2*S*,2'*S*)-2,2'-Biindoline (1)

These spectra were acquired using the product synthesised from the biaziridine (*S*,*S*)-**8** and are identical to the spectra of the product prepared from the bioxirane (*R*,*R*)-**3**.

^{1}H NMR (300 MHz, $CDCl_3$):



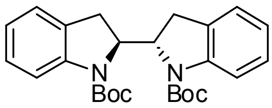
^{13}C NMR (75 MHz, $CDCl_3$):



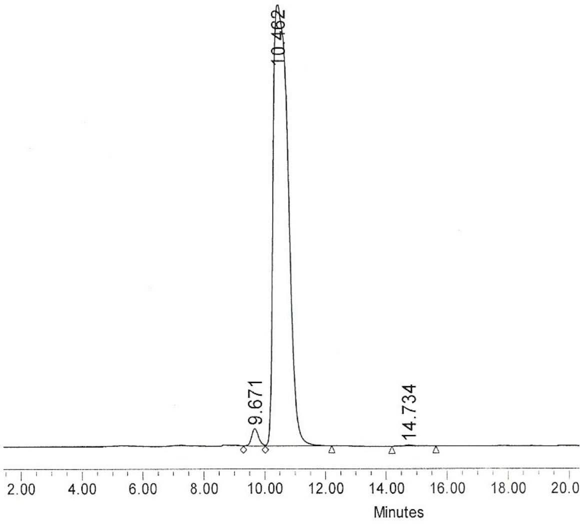
HPLC Traces

All traces were obtained using a Daicel Chiralcel OD-H column with a UV detector (254 nm) and 2.5% *i*-PrOH:hexane as the eluent with a flow rate 0.5 mL/min.

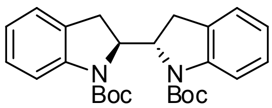
Trace **1:** DiBoc derivative of the biindoline (*S*,*S*)-**1** prepared from the bioxirane (*R*,*R*)-**3**.



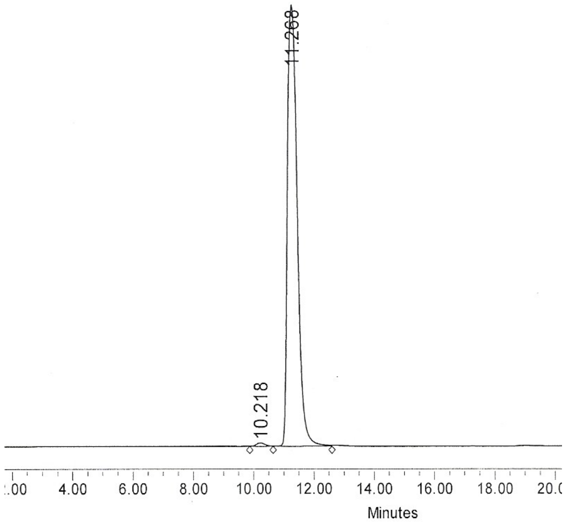
$[\alpha]_D^{21}$ **-91.4** (*c* 0.45, CH_2Cl_2)



Trace **2:** DiBoc derivative of the biindoline (*S*,*S*)-**1** prepared from the biaziridine (*S*,*S*)-**8**.



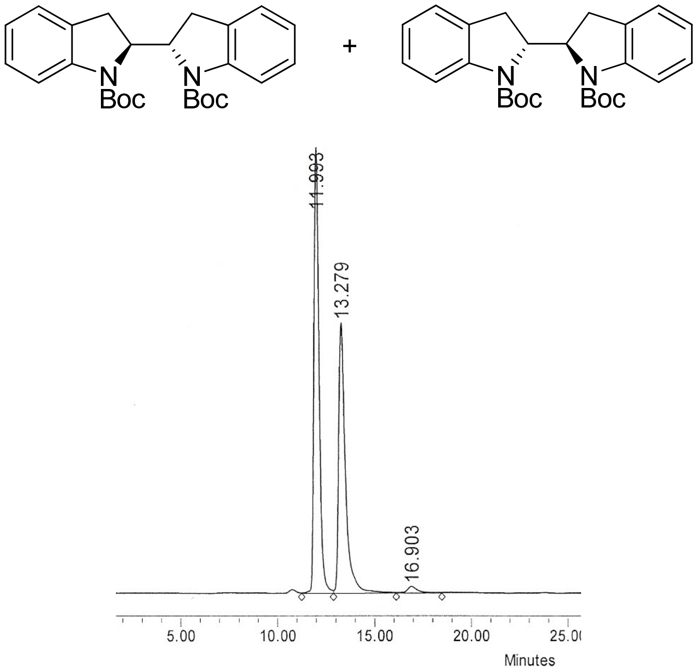
$[\alpha]_D^{22}$ **-88.6** (*c* 0.45, CH_2Cl_2)



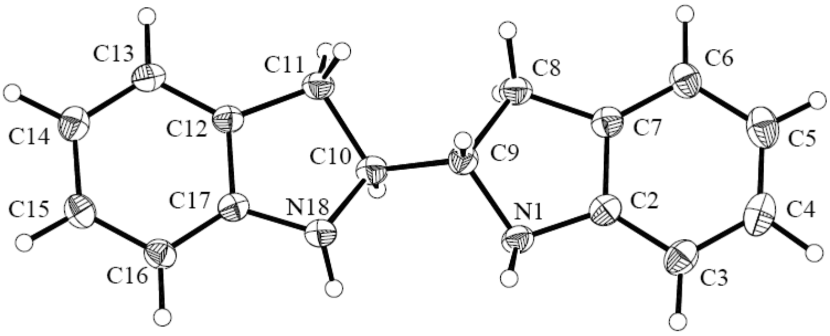
A sample of **2** spiked with **1** (to equal concentrations) gave a single peak at 10.55 min, as expected.

It should also be noted that both traces of the (*S*,*S*)-biindoline diBoc derivative (Traces **1** and **2**) showed an unidentified impurity (<2% peak area) that was eluted prior to the chiral compound at ~10 min. This was *not* the *R*,*R*-enantiomer, which eluted after the *S*,*S*-product with a retention time of ~13 min (see Trace **3** below), nor the *meso* isomer - for which the NMR data was known from previous work in our laboratory.[S8] No impurities were detected by NMR analysis of either sample (see page S11).

Trace **3:** DiBoc derivative of the biindoline (*S*,*S*)-**1** + the *R*,*R*-enantiomer (from an *R*,*R*-enriched sample).[S8]



Crystal Data for (2*S*,2'*S*)-2,2'-Biindoline



$C_{16}H_{16}N_2$

$M_r = 236.32$

Monoclinic, $P2_1$

$a = 11.6395\ (4)$ Å

$b = 7.8596\ (3)$ Å

$c = 14.2979\ (6)$ Å

$\beta = 109.257\ (3)^\circ$

$V = 1234.81\ (8)$ Å^3

$Z = 4$

$F_{000} = 504$

$D_x = 1.271$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Cell parameters from 53015 reflections

$\theta = 2.6$–27.5°

$\mu = 0.08$ mm^{-1}

$T = 200$ K

Plate, colourless

0.37 × 0.16 × 0.07 mm

Data collection

Area diffractometer

Monochromator: graphite

$T = 200$ K

φ and ω scans with CCD

Absorption correction: integration via Gaussian method (Coppens, 1970) implemented in maXus (2000)

$T_{\min} = 0.977$, $T_{\max} = 0.995$

25324 measured reflections

3033 independent reflections

2134 reflections with $I > 2.0\sigma(I)$

$R_{\text{int}} = 0.052$

$\theta_{\max} = 27.5^\circ$

$\theta_{\min} = 2.8^\circ$

$h = -15 \rightarrow 14$

$k = -10 \rightarrow 10$

$l = -18 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.040$

$wR(F^2) = 0.095$

$S = 0.87$

3033 reflections

421 parameters

Hydrogen site location: inferred from neighbouring sites

Only H-atom coordinates refined

Method = Modified Sheldrick $w = 1/[\sigma^2(F^2) + (0.05P)^2 + 0.0P]$,
where $P = (\max(F_o^2,0) + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.006$

$\Delta\rho_{\max} = 0.22$ e Å^{-3}

$\Delta\rho_{\min} = -0.25$ e Å^{-3}

Extinction correction: None

1 restraint

Primary atom site location: structure-invariant direct methods

Absolute structure: The enantiomer has been assigned by reference to an unchanging chiral centre in the synthetic procedure.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	y	z	U_{iso}*/U_{eq}
N1	0.76128 (18)	0.3973 (3)	0.28078 (16)	0.0396
C2	0.8008 (2)	0.3985 (4)	0.3862 (2)	0.0381
C3	0.7438 (3)	0.4710 (4)	0.4478 (2)	0.0474
C4	0.7988 (3)	0.4502 (5)	0.5492 (2)	0.0548
C5	0.9056 (3)	0.3599 (5)	0.5882 (2)	0.0538
C6	0.9622 (3)	0.2871 (4)	0.5251 (2)	0.0442
C7	0.9091 (2)	0.3070 (4)	0.42448 (19)	0.0389
C8	0.9453 (2)	0.2442 (4)	0.3397 (2)	0.0414
C9	0.8714 (2)	0.3560 (4)	0.25294 (19)	0.0378
C10	0.8415 (2)	0.2722 (4)	0.15361 (19)	0.0379
C11	0.9565 (2)	0.2213 (4)	0.1289 (2)	0.0390
C12	0.9160 (2)	0.2411 (3)	0.01828 (18)	0.0340
C13	0.9695 (2)	0.1901 (4)	−0.0502 (2)	0.0389
C14	0.9143 (2)	0.2313 (4)	−0.1496 (2)	0.0434
C15	0.8066 (2)	0.3249 (4)	−0.1788 (2)	0.0433
C16	0.7519 (2)	0.3782 (4)	−0.1104 (2)	0.0390
C17	0.8082 (2)	0.3363 (3)	−0.01203 (19)	0.0339
N18	0.77660 (18)	0.3844 (3)	0.07049 (16)	0.0398
N21	0.47174 (19)	0.2313 (3)	0.18044 (16)	0.0389
C22	0.4371 (2)	0.2390 (3)	0.07655 (18)	0.0335
C23	0.5007 (3)	0.1787 (4)	0.0164 (2)	0.0410
C24	0.4475 (3)	0.1996 (4)	−0.0861 (2)	0.0440
C25	0.3342 (2)	0.2739 (4)	−0.1265 (2)	0.0426
C26	0.2697 (2)	0.3283 (3)	−0.0651 (2)	0.0368
C27	0.3226 (2)	0.3124 (3)	0.03620 (18)	0.0321
C28	0.2756 (2)	0.3579 (4)	0.1194 (2)	0.0373
C29	0.3906 (2)	0.3476 (4)	0.21167 (19)	0.0352
C30	0.3643 (2)	0.2854 (4)	0.30244 (18)	0.0351
C31	0.2786 (2)	0.4049 (4)	0.33398 (19)	0.0373
C32	0.3259 (2)	0.3967 (4)	0.44522 (18)	0.0335
C33	0.2763 (3)	0.4546 (4)	0.5154 (2)	0.0423
C34	0.3447 (3)	0.4344 (4)	0.6161 (2)	0.0453
C35	0.4571 (3)	0.3584 (4)	0.6441 (2)	0.0461
C36	0.5083 (2)	0.3017 (4)	0.57421 (19)	0.0402
C37	0.4406 (2)	0.3210 (3)	0.47384 (18)	0.0340
N38	0.47369 (18)	0.2808 (3)	0.39152 (16)	0.0381
H11	0.727 (2)	0.498 (4)	0.2531 (19)	0.0465*
H31	0.664 (3)	0.534 (4)	0.418 (2)	0.0569*
H41	0.752 (3)	0.506 (4)	0.592 (2)	0.0687*
H51	0.940 (3)	0.346 (4)	0.658 (2)	0.0618*

H61	1.045 (2)	0.221 (4)	0.5518 (18)	0.0516*
H81	0.918 (2)	0.132 (4)	0.327 (2)	0.0488*
H82	1.036 (2)	0.253 (4)	0.3528 (18)	0.0490*
H91	0.922 (2)	0.460 (4)	0.2557 (18)	0.0434*
H101	0.789 (2)	0.159 (4)	0.1565 (18)	0.0435*
H111	0.982 (2)	0.111 (4)	0.154 (2)	0.0440*
H112	1.024 (2)	0.304 (3)	0.164 (2)	0.0436*
H131	1.045 (2)	0.127 (4)	−0.027 (2)	0.0464*
H141	0.953 (2)	0.189 (4)	−0.2031 (19)	0.0499*
H151	0.769 (2)	0.352 (4)	−0.252 (2)	0.0495*
H161	0.674 (2)	0.444 (4)	−0.1338 (18)	0.0438*
H181	0.699 (2)	0.401 (4)	0.0639 (19)	0.0466*
H211	0.555 (2)	0.251 (4)	0.2140 (18)	0.0455*
H231	0.583 (2)	0.117 (4)	0.047 (2)	0.0492*
H241	0.490 (2)	0.165 (4)	−0.131 (2)	0.0563*
H251	0.299 (2)	0.291 (4)	−0.201 (2)	0.0513*
H261	0.192 (2)	0.393 (4)	−0.0913 (18)	0.0427*
H281	0.215 (2)	0.275 (4)	0.1290 (18)	0.0439*
H282	0.237 (2)	0.468 (4)	0.1111 (19)	0.0440*
H291	0.431 (2)	0.468 (4)	0.2312 (18)	0.0404*
H301	0.332 (2)	0.170 (4)	0.2905 (18)	0.0389*
H311	0.186 (2)	0.375 (4)	0.3053 (18)	0.0432*
H312	0.284 (2)	0.521 (4)	0.3084 (19)	0.0424*
H331	0.197 (3)	0.509 (4)	0.494 (2)	0.0502*
H341	0.306 (2)	0.482 (4)	0.668 (2)	0.0541*
H351	0.502 (2)	0.339 (4)	0.719 (2)	0.0508*
H361	0.586 (2)	0.242 (4)	0.5911 (17)	0.0441*
H381	0.522 (2)	0.192 (4)	0.3929 (19)	0.0441*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0369 (11)	0.0403 (13)	0.0436 (13)	0.0092 (10)	0.0159 (9)	0.0058 (11)
C2	0.0374 (13)	0.0345 (15)	0.0455 (16)	−0.0058 (12)	0.0178 (11)	0.0005 (13)
C3	0.0495 (16)	0.0417 (16)	0.057 (2)	−0.0045 (14)	0.0256 (14)	−0.0072 (15)
C4	0.070 (2)	0.0498 (19)	0.056 (2)	−0.0151 (17)	0.0363 (18)	−0.0125 (16)
C5	0.0632 (19)	0.057 (2)	0.0422 (17)	−0.0186 (18)	0.0187 (14)	−0.0003 (16)
C6	0.0494 (14)	0.0437 (17)	0.0391 (16)	−0.0051 (15)	0.0140 (12)	0.0036 (15)
C7	0.0383 (12)	0.0375 (16)	0.0429 (16)	−0.0023 (12)	0.0161 (11)	0.0033 (13)
C8	0.0350 (13)	0.0456 (18)	0.0432 (15)	0.0069 (13)	0.0126 (11)	0.0064 (14)
C9	0.0374 (12)	0.0396 (16)	0.0381 (15)	0.0009 (13)	0.0145 (11)	0.0017 (13)
C10	0.0354 (12)	0.0373 (15)	0.0411 (15)	0.0026 (12)	0.0126 (10)	0.0025 (13)
C11	0.0338 (13)	0.0396 (16)	0.0411 (15)	0.0070 (12)	0.0089 (11)	0.0002 (13)
C12	0.0303 (12)	0.0304 (14)	0.0395 (14)	−0.0017 (11)	0.0090 (10)	−0.0021 (12)
C13	0.0319 (12)	0.0351 (15)	0.0492 (16)	0.0002 (12)	0.0126 (11)	−0.0043 (13)
C14	0.0468 (15)	0.0416 (17)	0.0445 (16)	−0.0070 (13)	0.0188 (12)	−0.0061 (13)
C15	0.0473 (14)	0.0407 (17)	0.0386 (15)	−0.0037 (13)	0.0098 (12)	−0.0006 (12)
C16	0.0371 (12)	0.0365 (15)	0.0400 (15)	−0.0008 (13)	0.0079 (11)	−0.0015 (13)

C17	0.0314 (11)	0.0290 (14)	0.0414 (15)	−0.0040 (11)	0.0119 (10)	−0.0039 (12)
N18	0.0342 (10)	0.0429 (13)	0.0409 (13)	0.0061 (11)	0.0105 (9)	0.0006 (12)
N21	0.0358 (11)	0.0456 (14)	0.0359 (12)	0.0044 (11)	0.0126 (9)	0.0007 (11)
C22	0.0331 (12)	0.0302 (15)	0.0398 (14)	−0.0008 (11)	0.0153 (10)	0.0006 (12)
C23	0.0416 (13)	0.0381 (16)	0.0485 (18)	−0.0005 (13)	0.0220 (13)	−0.0024 (14)
C24	0.0529 (16)	0.0412 (16)	0.0478 (17)	−0.0041 (14)	0.0299 (14)	−0.0045 (14)
C25	0.0614 (17)	0.0340 (15)	0.0347 (15)	−0.0043 (15)	0.0190 (12)	0.0003 (13)
C26	0.0383 (13)	0.0350 (16)	0.0367 (15)	−0.0025 (12)	0.0116 (11)	0.0008 (12)
C27	0.0377 (12)	0.0266 (15)	0.0356 (14)	−0.0028 (11)	0.0169 (11)	−0.0008 (11)
C28	0.0393 (13)	0.0415 (17)	0.0350 (14)	0.0044 (13)	0.0174 (11)	0.0018 (13)
C29	0.0354 (12)	0.0372 (16)	0.0343 (14)	−0.0009 (12)	0.0133 (10)	0.0007 (13)
C30	0.0385 (13)	0.0368 (15)	0.0297 (13)	−0.0024 (13)	0.0107 (10)	−0.0018 (12)
C31	0.0304 (12)	0.0462 (17)	0.0344 (14)	0.0009 (12)	0.0093 (10)	−0.0014 (13)
C32	0.0327 (11)	0.0350 (15)	0.0327 (13)	−0.0037 (11)	0.0108 (10)	0.0003 (12)
C33	0.0458 (15)	0.0425 (16)	0.0414 (17)	0.0017 (13)	0.0182 (13)	0.0005 (14)
C34	0.0591 (17)	0.0429 (18)	0.0400 (16)	−0.0050 (14)	0.0247 (14)	−0.0019 (13)
C35	0.0578 (16)	0.0429 (17)	0.0335 (15)	−0.0094 (15)	0.0095 (12)	0.0011 (13)
C36	0.0408 (13)	0.0392 (17)	0.0355 (14)	0.0034 (12)	0.0056 (11)	0.0048 (12)
C37	0.0358 (12)	0.0334 (16)	0.0328 (13)	−0.0007 (12)	0.0113 (10)	0.0023 (11)
N38	0.0356 (11)	0.0431 (13)	0.0353 (12)	0.0069 (11)	0.0114 (9)	−0.0008 (11)

Geometric parameters (Å, °)

N1—C2	1.424 (3)	N21—C22	1.406 (3)
N1—C9	1.498 (3)	N21—C29	1.485 (3)
N1—H11	0.92 (3)	N21—H211	0.94 (2)
C2—C3	1.388 (4)	C22—C23	1.391 (4)
C2—C7	1.396 (4)	C22—C27	1.391 (3)
C3—C4	1.387 (4)	C23—C24	1.400 (4)
C3—H31	1.01 (3)	C23—H231	1.04 (3)
C4—C5	1.379 (5)	C24—C25	1.382 (4)
C4—H41	1.04 (3)	C24—H241	0.96 (3)
C5—C6	1.404 (4)	C25—C26	1.397 (4)
C5—H51	0.95 (3)	C25—H251	1.02 (3)
C6—C7	1.374 (4)	C26—C27	1.380 (4)
C6—H61	1.05 (3)	C26—H261	0.99 (3)
C7—C8	1.493 (4)	C27—C28	1.507 (3)
C8—C9	1.532 (4)	C28—C29	1.541 (3)
C8—H81	0.93 (3)	C28—H281	1.00 (3)
C8—H82	1.02 (3)	C28—H282	0.96 (3)
C9—C10	1.499 (4)	C29—C30	1.510 (3)
C9—H91	1.00 (3)	C29—H291	1.05 (3)
C10—C11	1.546 (3)	C30—C31	1.541 (4)
C10—N18	1.472 (4)	C30—N38	1.475 (3)
C10—H101	1.09 (3)	C30—H301	0.97 (3)
C11—C12	1.502 (4)	C31—C32	1.503 (3)
C11—H111	0.95 (3)	C31—H311	1.04 (2)
C11—H112	1.02 (3)	C31—H312	0.99 (3)
C12—C13	1.382 (4)	C32—C33	1.390 (4)

C12—C17	1.401 (3)	C32—C37	1.394 (3)
C13—C14	1.392 (4)	C33—C34	1.406 (4)
C13—H131	0.97 (3)	C33—H331	0.97 (3)
C14—C15	1.394 (4)	C34—C35	1.372 (4)
C14—H141	1.06 (3)	C34—H341	1.05 (3)
C15—C16	1.395 (4)	C35—C36	1.395 (4)
C15—H151	1.01 (3)	C35—H351	1.04 (3)
C16—C17	1.381 (4)	C36—C37	1.399 (4)
C16—H161	1.00 (3)	C36—H361	0.98 (3)
C17—N18	1.399 (3)	C37—N38	1.390 (3)
N18—H181	0.89 (2)	N38—H381	0.89 (3)
N1···N21	3.454 (3)	N38···C3	3.331 (4)
N18···C23	3.448 (4)	N38···C34^{ii}	3.470 (4)
N18···C25^{i}	3.515 (4)	N38···C35^{ii}	3.493 (4)
N18···C26^{i}	3.527 (3)	C5···C8^{iii}	3.467 (5)
C2—N1—C9	106.05 (19)	C22—N21—C29	107.57 (19)
C2—N1—H11	113.2 (17)	C22—N21—H211	114.9 (15)
C9—N1—H11	111.3 (17)	C29—N21—H211	113.4 (17)
N1—C2—C3	128.3 (2)	N21—C22—C23	127.8 (2)
N1—C2—C7	110.3 (2)	N21—C22—C27	111.0 (2)
C3—C2—C7	121.4 (3)	C23—C22—C27	121.2 (2)
C2—C3—C4	117.5 (3)	C22—C23—C24	117.8 (3)
C2—C3—H31	120.0 (17)	C22—C23—H231	120.2 (15)
C4—C3—H31	122.5 (17)	C24—C23—H231	122.0 (15)
C3—C4—C5	121.8 (3)	C23—C24—C25	121.2 (3)
C3—C4—H41	114.5 (17)	C23—C24—H241	121.0 (17)
C5—C4—H41	123.7 (17)	C25—C24—H241	117.8 (17)
C4—C5—C6	120.1 (3)	C24—C25—C26	120.2 (3)
C4—C5—H51	119.8 (19)	C24—C25—H251	119.3 (15)
C6—C5—H51	120.1 (19)	C26—C25—H251	120.4 (15)
C5—C6—C7	118.8 (3)	C25—C26—C27	119.0 (2)
C5—C6—H61	122.6 (14)	C25—C26—H261	122.0 (15)
C7—C6—H61	118.6 (14)	C27—C26—H261	118.5 (15)
C2—C7—C6	120.3 (2)	C22—C27—C26	120.5 (2)
C2—C7—C8	108.2 (2)	C22—C27—C28	108.6 (2)
C6—C7—C8	131.5 (2)	C26—C27—C28	130.9 (2)
C7—C8—C9	103.5 (2)	C27—C28—C29	102.9 (2)
C7—C8—H81	107.6 (18)	C27—C28—H281	114.1 (16)
C9—C8—H81	108.6 (18)	C29—C28—H281	107.4 (14)
C7—C8—H82	112.6 (15)	C27—C28—H282	112.9 (16)
C9—C8—H82	112.5 (16)	C29—C28—H282	112.9 (16)
H81—C8—H82	112 (2)	H281—C28—H282	107 (2)
C8—C9—N1	102.2 (2)	C28—C29—N21	103.5 (2)
C8—C9—C10	114.1 (2)	C28—C29—C30	112.81 (19)
N1—C9—C10	113.3 (2)	N21—C29—C30	112.9 (2)
C8—C9—H91	105.8 (15)	C28—C29—H291	111.4 (14)
N1—C9—H91	110.7 (15)	N21—C29—H291	111.4 (13)
C10—C9—H91	110.3 (14)	C30—C29—H291	105.1 (14)

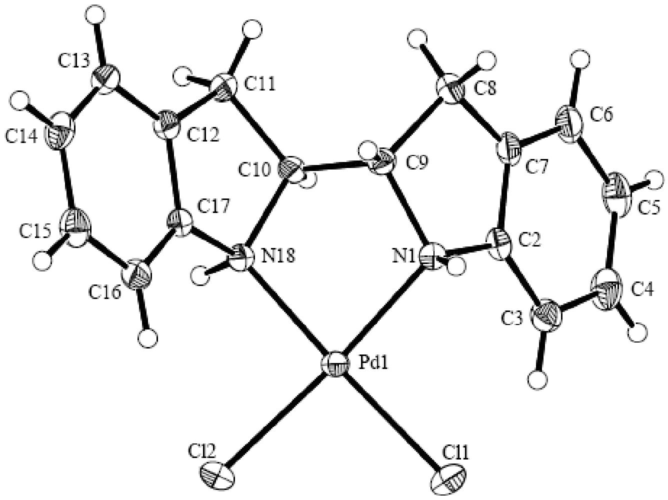
C9—C10—C11	112.4 (2)	C29—C30—C31	112.9 (2)
C9—C10—N18	113.5 (2)	C29—C30—N38	112.83 (19)
C11—C10—N18	102.9 (2)	C31—C30—N38	102.7 (2)
C9—C10—H101	106.4 (14)	C29—C30—H301	109.0 (15)
C11—C10—H101	109.6 (13)	C31—C30—H301	111.7 (15)
N18—C10—H101	112.1 (13)	N38—C30—H301	107.5 (14)
C10—C11—C12	102.6 (2)	C30—C31—C32	103.7 (2)
C10—C11—H111	109.9 (16)	C30—C31—H311	115.3 (15)
C12—C11—H111	116.2 (16)	C32—C31—H311	112.1 (14)
C10—C11—H112	107.6 (14)	C30—C31—H312	109.1 (15)
C12—C11—H112	112.4 (15)	C32—C31—H312	112.6 (15)
H111—C11—H112	108 (2)	H311—C31—H312	104 (2)
C11—C12—C13	131.1 (2)	C31—C32—C33	131.0 (2)
C11—C12—C17	108.6 (2)	C31—C32—C37	108.1 (2)
C13—C12—C17	120.2 (2)	C33—C32—C37	120.9 (2)
C12—C13—C14	119.5 (2)	C32—C33—C34	118.2 (3)
C12—C13—H131	119.0 (16)	C32—C33—H331	119.4 (17)
C14—C13—H131	121.5 (16)	C34—C33—H331	122.4 (17)
C13—C14—C15	119.7 (3)	C33—C34—C35	120.7 (3)
C13—C14—H141	120.3 (14)	C33—C34—H341	116.8 (15)
C15—C14—H141	120.0 (14)	C35—C34—H341	122.4 (15)
C14—C15—C16	121.5 (3)	C34—C35—C36	121.5 (3)
C14—C15—H151	117.4 (16)	C34—C35—H351	118.0 (15)
C16—C15—H151	121.1 (15)	C36—C35—H351	120.4 (15)
C15—C16—C17	118.0 (3)	C35—C36—C37	118.1 (2)
C15—C16—H161	119.7 (14)	C35—C36—H361	123.9 (14)
C17—C16—H161	122.3 (14)	C37—C36—H361	117.9 (14)
C12—C17—C16	121.2 (2)	C36—C37—C32	120.6 (2)
C12—C17—N18	109.9 (2)	C36—C37—N38	128.6 (2)
C16—C17—N18	128.8 (2)	C32—C37—N38	110.8 (2)
C10—N18—C17	108.2 (2)	C30—N38—C37	108.9 (2)
C10—N18—H181	114.1 (19)	C30—N38—H381	113.5 (17)
C17—N18—H181	119.6 (17)	C37—N38—H381	120.6 (18)

N1—C2—C3—C4	177.9 (3)	C10—C11—C12—C13	−168.3 (3)
N1—C2—C7—C6	−178.1 (3)	C10—C11—C12—C17	15.2 (3)
N1—C2—C7—C8	1.2 (3)	C11—C10—N18—C17	27.6 (3)
N1—C9—C8—C7	−28.9 (3)	C11—C12—C13—C14	−177.3 (3)
N1—C9—C10—N18	67.0 (3)	C11—C12—C17—C16	178.2 (2)
N1—C9—C10—C11	−176.7 (2)	C12—C13—C14—C15	0.7 (4)
N18—C10—C9—C8	−176.7 (2)	C12—C17—C16—C15	−0.9 (4)
N18—C10—C11—C12	−25.3 (3)	C13—C12—C17—C16	1.3 (4)
N18—C17—C12—C11	1.6 (3)	C13—C14—C15—C16	−0.3 (4)
N18—C17—C12—C13	−175.3 (2)	C14—C13—C12—C17	−1.2 (4)
N18—C17—C16—C15	175.1 (3)	C14—C15—C16—C17	0.4 (4)
N21—C22—C23—C24	179.5 (3)	C22—N21—C29—C28	24.6 (3)
N21—C22—C27—C26	−178.3 (2)	C22—N21—C29—C30	146.9 (2)
N21—C22—C27—C28	−0.1 (3)	C22—C23—C24—C25	−1.6 (5)
N21—C29—C28—C27	−23.6 (3)	C22—C27—C26—C25	−1.8 (4)
N21—C29—C30—N38	64.9 (3)	C22—C27—C28—C29	15.2 (3)

N21—C29—C30—C31	−179.2 (2)	C23—C22—N21—C29	166.4 (3)
N38—C30—C29—C28	−178.1 (2)	C23—C22—C27—C26	−0.5 (4)
N38—C30—C31—C32	−22.2 (3)	C23—C22—C27—C28	177.7 (3)
N38—C37—C32—C31	0.8 (3)	C23—C24—C25—C26	−0.7 (5)
N38—C37—C32—C33	−177.1 (3)	C24—C23—C22—C27	2.2 (4)
N38—C37—C36—C35	177.3 (3)	C24—C25—C26—C27	2.3 (4)
C2—N1—C9—C8	30.3 (3)	C25—C26—C27—C28	−179.5 (3)
C2—N1—C9—C10	153.5 (3)	C26—C27—C28—C29	−166.9 (3)
C2—C3—C4—C5	−0.5 (5)	C27—C22—N21—C29	−16.0 (3)
C2—C7—C6—C5	0.1 (5)	C27—C28—C29—C30	−145.9 (2)
C2—C7—C8—C9	17.9 (3)	C28—C29—C30—C31	−62.3 (3)
C3—C2—N1—C9	161.7 (3)	C29—C30—N38—C37	145.6 (2)
C3—C2—C7—C6	−0.2 (5)	C29—C30—C31—C32	−144.0 (2)
C3—C2—C7—C8	179.2 (3)	C30—N38—C37—C32	−16.2 (3)
C3—C4—C5—C6	0.5 (6)	C30—N38—C37—C36	166.9 (3)
C4—C3—C2—C7	0.4 (5)	C30—C31—C32—C33	−168.5 (3)
C4—C5—C6—C7	−0.3 (5)	C30—C31—C32—C37	13.8 (3)
C5—C6—C7—C8	−179.1 (3)	C31—C30—N38—C37	23.8 (3)
C6—C7—C8—C9	−162.9 (3)	C31—C32—C33—C34	−177.6 (3)
C7—C2—N1—C9	−20.5 (3)	C31—C32—C37—C36	178.0 (3)
C7—C8—C9—C10	−151.5 (2)	C32—C33—C34—C35	−0.4 (5)
C8—C9—C10—C11	−60.4 (3)	C32—C37—C36—C35	0.7 (4)
C9—C10—N18—C17	149.5 (2)	C33—C32—C37—C36	0.0 (4)
C9—C10—C11—C12	−147.8 (2)	C33—C34—C35—C36	1.2 (5)
C10—N18—C17—C12	−19.1 (3)	C34—C33—C32—C37	−0.2 (5)
C10—N18—C17—C16	164.6 (3)	C34—C35—C36—C37	−1.4 (5)

Symmetry codes: (i) $-x+1$, $y+1/2$, $-z$; (ii) $-x+1$, $y-1/2$, $-z+1$; (iii) $-x+2$, $y+1/2$, $-z+1$.

Crystal Data for (2*S*,2'*S*)-2,2'-Biindolinepalladium(II) Dichloride



$C_{16}H_{16}Cl_2N_2Pd{\cdot}0.225(C_2H_3N)$

$M_r = 422.86$

Orthorhombic, $P2_12_12$

$a = 21.0215\ (6)$ Å

$b = 8.2900\ (2)$ Å

$c = 9.0928\ (3)$ Å

$V = 1584.59\ (8)$ Å^3

$Z = 4$

$F_{000} = 841.073$

$D_x = 1.772$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Cell parameters from 21993 reflections

$\theta = 2.6$–$27.5°$

$\mu = 1.50$ mm^{-1}

$T = 200$ K

Needle, brown

0.36 × 0.16 × 0.07 mm

Data collection

Area
diffractometer

Monochromator: graphite

$T = 200$ K

φ & ω scans

Absorption correction: integration
via Gaussian method (Coppens, 1970) implemented in maXus (2000)

$T_{min} = 0.742$, $T_{max} = 0.902$

14560 measured reflections

3618 independent reflections

3235 reflections with $I > 2.0\sigma(I)$

$R_{int} = 0.038$

$\theta_{max} = 27.5°$

$\theta_{min} = 2.6°$

$h = -27 \rightarrow 24$

$k = -10 \rightarrow 10$

$l = -11 \rightarrow 11$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.022$

$wR(F^2) = 0.051$

$S = 0.86$

3618 reflections

225 parameters

18 restraints

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of
independent and constrained refinement

Method = Modified Sheldrick $w = 1/[\sigma^2(F^2) + (0.0P)^2 + 0.0P]$,
where $P = (\max(F_o^2,0) + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.029$

$\Delta\rho_{max} = 0.38$ e Å^{-3}

$\Delta\rho_{min} = -0.40$ e Å^{-3}

Extinction correction: None

Absolute structure: Flack (1983), 1531 Friedel-pairs

Primary atom site location: structure-invariant direct methods

Flack parameter: −0.02 (3)

Special details

Refinement. The compound is enantiometrically pure. The absolute structure of the crystal has been determined by refinement of the Flack parameter and this establishes the absolute configuration of the molecule. It is in agreement with the configuration expected on the basis of the synthetic precursors.

Away from the [($C_{16}H_{16}N_2$)$PdCl_2$] molecule there is a region of residual electron density about a crystallographic twofold axis that appears to be a solvate molecule. This has been modelled as a disordered acetonitrile molecule of crystallization. Restraints were imposed on distances, angles and displacement parameters as the atomic sites overlap with their symmetry-related counterparts. From its size it was clear that the molecule has less than full occupancy, so this has been included as a refinable parameter.

H atoms, excluding those of the acetonitrile, were all located in a difference map, but those attached to carbon atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C—H in the range 0.93–0.98, N—H in the range 0.86–0.89 Å) and with U_{iso}(H) in the range 1.2–1.5 times U_{eq} of the parent atom, after which the positions of those attached to N were refined without restraints and those attached to C were refined with riding constraints. Displacement parameters were held fixed. The acetonitrile H atoms were not located.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Pd1	0.291328 (9)	0.38821 (2)	0.50433 (2)	0.0256	
Cl1	0.34667 (4)	0.49237 (10)	0.70241 (8)	0.0379	
Cl2	0.20788 (4)	0.31574 (9)	0.65395 (8)	0.0396	
N1	0.36153 (11)	0.4479 (3)	0.3568 (3)	0.0272	
N18	0.24563 (10)	0.3017 (3)	0.3236 (3)	0.0268	
N93	−0.0061 (10)	−0.116 (3)	0.157 (2)	0.0913	0.225 (4)
C2	0.42258 (12)	0.3622 (3)	0.3541 (3)	0.0289	
C3	0.45722 (13)	0.3150 (4)	0.4750 (4)	0.0372	
C4	0.51434 (15)	0.2366 (4)	0.4491 (4)	0.0466	
C5	0.53466 (14)	0.2050 (4)	0.3069 (4)	0.0465	
C6	0.49904 (15)	0.2555 (4)	0.1870 (4)	0.0428	
C7	0.44202 (12)	0.3359 (3)	0.2106 (3)	0.0326	
C8	0.39517 (13)	0.4051 (4)	0.1040 (3)	0.0362	
C9	0.33610 (13)	0.4292 (3)	0.2010 (3)	0.0271	
C10	0.29304 (13)	0.2813 (3)	0.1997 (3)	0.0275	
C11	0.25248 (13)	0.2718 (4)	0.0589 (3)	0.0327	
C12	0.19461 (13)	0.3672 (3)	0.1027 (3)	0.0291	
C13	0.14565 (13)	0.4274 (3)	0.0178 (3)	0.0352	
C14	0.09638 (14)	0.5085 (4)	0.0856 (3)	0.0394	
C15	0.09587 (14)	0.5302 (4)	0.2372 (4)	0.0409	
C16	0.14452 (13)	0.4707 (3)	0.3236 (3)	0.0340	
C17	0.19250 (12)	0.3885 (3)	0.2546 (3)	0.0270	
C91	0.0274 (11)	0.180 (3)	0.190 (3)	0.1107	0.225 (4)
C92	0.0069 (8)	0.014 (3)	0.1676 (9)	0.0981	0.225 (4)
H11	0.3623 (15)	0.550 (4)	0.374 (4)	0.0406*	
H31	0.4429	0.3320	0.5714	0.0452*	

H41	0.5367	0.2092	0.5228	0.0565*
H51	0.5714	0.1456	0.2930	0.0563*
H61	0.5137	0.2476	0.0896	0.0508*
H81	0.4088	0.5022	0.0651	0.0447*
H82	0.3863	0.3340	0.0221	0.0438*
H91	0.3125	0.5265	0.1789	0.0319*
H101	0.3177	0.1819	0.2189	0.0319*
H111	0.2717	0.3142	−0.0257	0.0390*
H112	0.2408	0.1602	0.0364	0.0396*
H131	0.1461	0.4114	−0.0827	0.0423*
H141	0.0640	0.5513	0.0297	0.0472*
H151	0.0619	0.5809	0.2798	0.0489*
H161	0.1445	0.4885	0.4234	0.0414*
H181	0.2307 (14)	0.197 (4)	0.346 (4)	0.0398*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pd1	0.02690 (9)	0.02797 (9)	0.02207 (9)	0.00175 (8)	0.00035 (11)	0.00010 (10)
Cl1	0.0421 (4)	0.0417 (4)	0.0300 (4)	0.0070 (3)	−0.0094 (3)	−0.0067 (3)
Cl2	0.0394 (4)	0.0508 (4)	0.0288 (3)	−0.0038 (4)	0.0098 (4)	0.0021 (3)
N1	0.0266 (12)	0.0305 (12)	0.0247 (12)	−0.0012 (10)	0.0002 (10)	−0.0001 (10)
N18	0.0261 (12)	0.0300 (12)	0.0244 (12)	0.0000 (10)	0.0000 (9)	0.0002 (10)
N93	0.034 (9)	0.182 (13)	0.058 (8)	−0.012 (17)	−0.001 (8)	−0.001 (12)
C2	0.0235 (13)	0.0262 (14)	0.0370 (15)	−0.0031 (11)	0.0025 (11)	0.0000 (11)
C3	0.0318 (14)	0.0412 (15)	0.0386 (19)	0.0018 (12)	−0.0007 (13)	0.0048 (14)
C4	0.0310 (16)	0.0482 (18)	0.061 (2)	0.0037 (14)	−0.0093 (15)	0.0093 (15)
C5	0.0247 (15)	0.0424 (18)	0.072 (3)	0.0025 (13)	0.0034 (16)	−0.0050 (17)
C6	0.0277 (15)	0.0496 (18)	0.051 (2)	−0.0078 (14)	0.0060 (15)	−0.0138 (16)
C7	0.0236 (13)	0.0341 (15)	0.0403 (16)	−0.0067 (12)	0.0025 (12)	−0.0050 (13)
C8	0.0322 (15)	0.0429 (18)	0.0336 (15)	−0.0092 (14)	0.0047 (12)	−0.0022 (14)
C9	0.0281 (14)	0.0290 (14)	0.0242 (13)	0.0007 (11)	−0.0017 (11)	0.0010 (10)
C10	0.0243 (12)	0.0331 (13)	0.0250 (12)	0.0018 (12)	0.0032 (12)	−0.0020 (10)
C11	0.0289 (16)	0.0419 (17)	0.0274 (14)	−0.0039 (13)	−0.0006 (11)	−0.0070 (12)
C12	0.0277 (14)	0.0293 (14)	0.0303 (13)	−0.0046 (11)	−0.0001 (11)	0.0013 (12)
C13	0.0327 (14)	0.0428 (15)	0.0301 (16)	−0.0070 (11)	−0.0051 (13)	0.0023 (13)
C14	0.0321 (16)	0.0382 (16)	0.0478 (19)	0.0013 (14)	−0.0100 (13)	0.0037 (14)
C15	0.0285 (15)	0.0401 (17)	0.054 (2)	0.0054 (13)	0.0022 (14)	−0.0040 (15)
C16	0.0305 (15)	0.0382 (16)	0.0333 (15)	−0.0003 (12)	0.0034 (13)	−0.0043 (13)
C17	0.0227 (13)	0.0310 (13)	0.0275 (13)	−0.0029 (11)	−0.0001 (10)	0.0014 (12)
C91	0.053 (12)	0.2044 (10)	0.075 (11)	−0.014 (16)	0.010 (10)	−0.005 (14)
C92	0.035 (10)	0.194 (10)	0.066 (7)	−0.021 (18)	0.010 (9)	0.000 (13)

Geometric parameters (Å, °)

Pd1—Cl1	2.3115 (7)	C8—C9	1.536 (4)
Pd1—Cl2	2.2998 (8)	C8—H81	0.925
Pd1—N1	2.055 (2)	C8—H82	0.968
Pd1—N18	2.035 (2)	C9—C10	1.524 (4)

N1—C2	1.467 (3)	C9—H91	0.968
N1—C9	1.522 (3)	C10—C11	1.541 (4)
N1—H11	0.86 (3)	C10—H101	0.989
N18—C10	1.513 (3)	C11—C12	1.505 (4)
N18—C17	1.469 (3)	C11—H111	0.938
N18—H181	0.95 (3)	C11—H112	0.978
N93—C92	1.117 (10)	C12—C13	1.380 (4)
C2—C3	1.375 (4)	C12—C17	1.394 (4)
C2—C7	1.385 (4)	C13—C14	1.380 (4)
C3—C4	1.386 (4)	C13—H131	0.924
C3—H31	0.937	C14—C15	1.389 (4)
C4—C5	1.387 (5)	C14—H141	0.921
C4—H41	0.850	C15—C16	1.381 (4)
C5—C6	1.387 (5)	C15—H151	0.914
C5—H51	0.925	C16—C17	1.369 (4)
C6—C7	1.388 (4)	C16—H161	0.919
C6—H61	0.940	C91—C92	1.452 (10)
C7—C8	1.497 (4)		
Cl1···C91^{i}	3.22 (2)	C3···C91^{ii}	3.38 (3)
Cl1···N18^{i}	3.224 (2)	C3···C3^{v}	3.556 (6)
Cl1···C92^{i}	3.30 (2)	C4···C91^{ii}	3.36 (3)
Cl1···C17^{i}	3.408 (3)	C6···C91^{vi}	3.52 (3)
Cl1···N93^{ii}	3.50 (2)	C8···C92^{vii}	3.34 (1)
Cl1···C92^{ii}	3.57 (2)	C8···C92^{vi}	3.47 (1)
Cl2···N1^{iii}	3.382 (3)	C13···C91	3.58 (2)
Cl2···C9^{iii}	3.586 (3)	C14···C91	3.23 (3)
N93···C6^{iv}	3.31 (2)	C15···C91	3.27 (2)
N93···C8^{iv}	3.33 (2)	C15···C91^{viii}	3.56 (2)
N93···C3^{iii}	3.55 (2)		
Cl1—Pd1—Cl2	91.18 (3)	C9—C8—H82	111.4
Cl1—Pd1—N1	93.29 (7)	H81—C8—H82	107.3
Cl2—Pd1—N1	175.50 (7)	C8—C9—N1	105.3 (2)
Cl1—Pd1—N18	177.29 (7)	C8—C9—C10	111.8 (2)
Cl2—Pd1—N18	91.47 (7)	N1—C9—C10	107.3 (2)
N1—Pd1—N18	84.06 (9)	C8—C9—H91	113.8
Pd1—N1—C2	121.51 (18)	N1—C9—H91	106.8
Pd1—N1—C9	109.32 (16)	C10—C9—H91	111.4
C2—N1—C9	104.1 (2)	C9—C10—N18	107.2 (2)
Pd1—N1—H11	97 (2)	C9—C10—C11	112.1 (2)
C2—N1—H11	118 (2)	N18—C10—C11	105.1 (2)
C9—N1—H11	106 (2)	C9—C10—H101	110.9
Pd1—N18—C10	109.24 (16)	N18—C10—H101	107.9
Pd1—N18—C17	122.06 (18)	C11—C10—H101	113.2
C10—N18—C17	103.8 (2)	C10—C11—C12	101.5 (2)
Pd1—N18—H181	107.8 (20)	C10—C11—H111	115.1
C10—N18—H181	106.0 (19)	C12—C11—H111	111.6

C17—N18—H181	106.9 (19)	C10—C11—H112	111.2
N1—C2—C3	126.0 (3)	C12—C11—H112	110.4
N1—C2—C7	110.5 (2)	H111—C11—H112	107.0
C3—C2—C7	123.5 (3)	C11—C12—C13	130.2 (3)
C2—C3—C4	117.2 (3)	C11—C12—C17	110.8 (2)
C2—C3—H31	122.3	C13—C12—C17	119.0 (3)
C4—C3—H31	120.6	C12—C13—C14	119.1 (3)
C3—C4—C5	120.9 (3)	C12—C13—H131	119.6
C3—C4—H41	118.1	C14—C13—H131	121.3
C5—C4—H41	121.0	C13—C14—C15	120.8 (3)
C4—C5—C6	120.6 (3)	C13—C14—H141	119.7
C4—C5—H51	119.0	C15—C14—H141	119.5
C6—C5—H51	120.3	C14—C15—C16	120.8 (3)
C5—C6—C7	119.3 (3)	C14—C15—H151	119.1
C5—C6—H61	122.8	C16—C15—H151	120.0
C7—C6—H61	117.6	C15—C16—C17	117.6 (3)
C6—C7—C2	118.5 (3)	C15—C16—H161	120.2
C6—C7—C8	130.7 (3)	C17—C16—H161	122.2
C2—C7—C8	110.8 (2)	N18—C17—C12	109.7 (2)
C7—C8—C9	102.1 (2)	N18—C17—C16	127.5 (2)
C7—C8—H81	112.2	C12—C17—C16	122.7 (3)
C9—C8—H81	110.9	C91—C92—N93	175.3 (13)
C7—C8—H82	113.1		

Pd1—N1—C2—C3	−41.5 (4)	C2—N1—C9—C8	−25.7 (3)
Pd1—N1—C2—C7	139.4 (2)	C2—N1—C9—C10	93.6 (2)
Pd1—N1—C9—C8	−156.8 (2)	C2—C3—C4—C5	−1.2 (5)
Pd1—N1—C9—C10	−37.6 (2)	C2—C7—C6—C5	−0.3 (4)
Pd1—N18—C10—C9	−42.2 (2)	C2—C7—C8—C9	−16.8 (3)
Pd1—N18—C10—C11	−161.7 (2)	C3—C2—N1—C9	−165.0 (3)
Pd1—N18—C17—C12	144.8 (2)	C3—C2—C7—C6	1.0 (4)
Pd1—N18—C17—C16	−39.3 (4)	C3—C2—C7—C8	−178.4 (3)
Cl1—Pd1—N1—C2	71.1 (2)	C3—C4—C5—C6	1.9 (5)
Cl1—Pd1—N1—C9	−167.9 (2)	C4—C3—C2—C7	−0.3 (4)
Cl1—Pd1—N18—C10	29 (2)	C4—C5—C6—C7	−1.1 (5)
Cl1—Pd1—N18—C17	−92 (2)	C5—C6—C7—C8	178.9 (3)
Cl2—Pd1—N1—C2	−116.4 (9)	C6—C7—C8—C9	164.0 (3)
Cl2—Pd1—N1—C9	5(1)	C7—C2—N1—C9	15.8 (3)
Cl2—Pd1—N18—C10	−163.5 (2)	C7—C8—C9—C10	−90.6 (3)
Cl2—Pd1—N18—C17	75.4 (2)	C8—C9—C10—C11	−78.2 (3)
N1—Pd1—N18—C10	17.0 (2)	C9—C10—N18—C17	89.4 (2)
N1—Pd1—N18—C17	−104.0 (2)	C9—C10—C11—C12	−88.7 (3)
N1—C2—C3—C4	−179.3 (3)	C10—N18—C17—C12	21.1 (3)
N1—C2—C7—C6	−179.8 (2)	C10—N18—C17—C16	−162.9 (3)
N1—C2—C7—C8	0.8 (3)	C10—C11—C12—C13	167.2 (3)
N1—C9—C8—C7	25.6 (3)	C10—C11—C12—C17	−15.1 (3)
N1—C9—C10—N18	52.1 (3)	C11—C10—N18—C17	−30.0 (3)
N1—C9—C10—C11	166.8 (2)	C11—C12—C13—C14	178.2 (3)
N18—Pd1—N1—C2	−109.5 (2)	C11—C12—C17—C16	−179.7 (2)
N18—Pd1—N1—C9	11.6 (2)	C12—C13—C14—C15	0.2 (4)
N18—C10—C9—C8	167.0 (2)	C12—C17—C16—C15	1.7 (4)
N18—C10—C11—C12	27.4 (3)	C13—C12—C17—C16	−1.8 (4)
N18—C17—C12—C11	−3.5 (3)	C13—C14—C15—C16	−0.2 (5)
N18—C17—C12—C13	174.4 (2)	C14—C13—C12—C17	0.7 (4)
N18—C17—C16—C15	−173.7 (3)	C14—C15—C16—C17	−0.7 (4)

Symmetry codes: (i) $-x+1/2, y+1/2, -z+1$; (ii) $x+1/2, -y+1/2, -z+1$; (iii) $-x+1/2, y-1/2, -z+1$; (iv) $-x+1/2, y-1/2, -z$; (v) $-x+1, -y+1, z$; (vi) $x+1/2, -y+1/2, -z$; (vii) $-x+1/2, y+1/2, -z$; (viii) $-x, -y+1, z$.

Notes and References

S1. W. L. F. Armarego, C. L. L. Chai. *Purification of Laboratory Chemicals*, Fifth Ed. Butterworth-Heinemann, USA, 2003.

S2. M. A. Robbins, P. N. Devine and T. Oh, *Org. Synth.*, 1999, **76**, 101-109.

S3. No molecular ion was detected. Attempts to detect any characteristic ions by ES MS analysis were also unsuccessful.

S4. A small amount of the PPh_3O by-product (~8 mg) was still present after this purification process. This sample was used in the subsequent cyclisation without further purification.

S5. The quantity obtained from this synthesis was insufficient to obtain a precise optical rotation. See the specific rotation of biindoline (*S*,*S*)-**1** synthesised from biaziridine (*S*,*S*)-**8**.

S6. T. Kanger, K. Ausmees, A.-M. Muurisepp, T. Pehk and M. Lopp, *Synlett*, 2003, 1055-1057. Note that we prepared the biaziridine *via* the S_N2 cyclisation sequence. Repeated attempts to prepare the product using the alternative shorter Staudinger approach resulted in poor yields (20-25%).

S7. This mixture was used in the subsequent cyclisation without further purification of the diamine. The Boc-deprotected imidazolidinone was inert to the cyclisation conditions.

S8. M. J. Gresser, P. A. Keller and S. M. Wales, *Tetrahedron*, 2010, **66**, 6965-6976.