SUPPORTING TEXT

General Information. Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego (1). Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Methylene chloride was distilled from calcium hydride prior to use. Chromatographic purification of products was accomplished using forced-flow chromatography on ICN 60 32-64 mesh silica gel 63 according to the method of Still *et al.* (2). TLC was performed on EM Reagents 0.25-mm Silica Gel 60-F plates. Visualization of the developed chromatogram was performed by fluorescence quenching or anisaldehyde stain.

^{1}H and ^{13}C NMR spectra were recorded on Varian Mercury 300 (300 MHz and 75 MHz, respectively) at room temperature or an elevated temperature, as noted, and are internally referenced to residual protio solvent signals. Data for ^{1}H are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, coupling constant (Hz), and assignment. Data for ^{13}C NMR are reported in terms of chemical shift. IR spectra were recorded on a Perkin-Elmer Paragon 1000 spectrometer and are reported in terms of frequency of absorption (cm^{-1}). Mass spectra were obtained from the UC Irvine Mass Spectral facility. HPLC was performed on Hewlett-Packard 1100 Series chromatographs using Chiralcel AD column (1.6 x 25 cm) and AD guard (1.6 x 5 cm), Chiralcel OD–H (1.6 x 25 cm) and OD guard (1.6 x 5 cm), or Chiralcel AS (1.6 x 25 cm) and AS guard (1.6 x 5 cm), as noted.

General Procedure. An amber 2-dram vial equipped with a magnetic stir bar, containing (2*S*, 5*S*)-5-benzyl-2-*tert*-butyl-3-methyl-imidazolidin-4-one (catalyst **1**) or (2*S*, 5*S*)-2-*tert*-butyl-5-(1*H*-indol-3-ylmethyl)3-methyl-imidazolidin-4-one (catalyst **8a**) acid salt and tryptamine or tryptophol substrate was charged with methylene chloride and water, then placed in a bath of the appropriate temperature. The solution was stirred for 5 min before addition of the α,β-unsaturated aldehyde. The resulting suspension was stirred at constant temperature until complete consumption of the indole was observed as determined by TLC. To the reaction mixture was then added pH 7.0 buffer and extracted with diethyl ether and concentrated *in vacuo*. The resulting residue was purified by silica gel chromatography (solvents noted) to afford the title compounds. The enantioselectivity was determined by subjecting approximately 10 mg of the title compound to an excess of sodium borohydride and 1 ml of absolute ethanol. After 15 min, the remaining sodium borohydride was quenched with saturated aqueous $NaHCO_3$, and the

mixture was extracted with CH_2Cl_2. The organic layer was separated, filtered through a silica gel plug, and subjected to HPLC analysis.

(2*R*,3*R*)-8-Allyl-3a-(3-oxo-propyl)-3,3a,8,8a-tetrahydro-2*H*-pyrrolo[2,3-*b*]indole-1-carboxylic acid *tert*-butyl ester (Table 2, entry 1). Prepared according to the general procedure from acrolein (153 μl, 2.43 mmol), *N*-10-BOC-1-allyltryptamine (166 mg, 0.608 mmol), and (2*R*, 5*R*)-catalyst **8a** TFA salt (48 mg, 0.122 mmol) in CH_2Cl_2 (1.63 ml) and water (0.290 ml) at –80°C for 25 h to provide the title compound as a colorless oil (178 mg, 89% yield, 89% ee) after silica gel chromatography in 25% EtOAc/hexanes. IR (film) 2971, 2932, 2873, 2727, 1725, 1695, 1606, 1491, 1394, 1366, 1220, 1158, 1105, 1080, 936, 888, 743 cm^{-1}; ^1H NMR (300 MHz, VT = 90°C, C_7D_8) δ 9.18 (s, 1H, CHO), 6.96 (d, *J* = 2.8 Hz, 1H, 4-ArH), 6.68 (d, *J* = 7.1 Hz, 1H, 6-ArH), 6.67 (t, *J* = 7.0 Hz, 1H, 5-ArH), 6.29 (d, *J* = 7.7 Hz, 1H, 7-ArH), 5.79 (ddd, *J* = 5, 11, 17 Hz, 1H, $CH_2C\mathbf{H}CH_2$), 5.27 (s, 1H, NCHN), 5.16 (dd, *J* = 1.1, 17 Hz, 1H, $CH_2CHC\mathbf{H}_2$), 5.00 (d, *J* = 1.1, 10 Hz, 1H $CH_2CHC\mathbf{H}_2$), 4.00 (d, *J* = 5 Hz, 2H, $NC\mathbf{H}_2CH$), 3.65 (t, *J* = 8.8 Hz, 1H, $CH_2C\mathbf{H}HN$); 2.83 (dt, *J* = 6.0, 15.4 Hz, 1H, $CH_2CH\mathbf{H}N$); 2.08 (app q, *J* = 2.2 Hz, 1H, $CH_2CH\mathbf{H}CHO$), 1.93-1.46 (m, 5H, $C\mathbf{H}_2CH_2N$, $C\mathbf{H}_2CH\mathbf{H}CHO$), 1.49 (s, 9H, $C(C\mathbf{H}_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.6, 155.0 [153.9], 150.5, 134.5, 130.9, 128.9, 122.9, [117.7] 117.4, 116.0, 106.2, [84.6] 84.1, [80.7] 80.0, [56.9] 55.5, 48.6, 45.6 [45.0], 40.4, 39.0 [38.5], [31.7] 31.3, 28.7; HRMS (CI) exact mass calcd for ($C_{21}H_{28}N_2O_3$) requires *m/z* 356.2100, found *m/z* 356.2112. $[\alpha]_D$ = 449.1 (*c* = 1.0, $CHCl_3$). The enantiomeric ratio was determined by HPLC analysis of the alcohol, obtained by $NaBH_4$ reduction of the aldehyde, using a Chiracel OD–H and OD guard column (4% ethanol/hexanes, 1 ml/min); *R* isomer t_r = 10.7 min and *S* isomer t_r = 12.3 min. The minor counterparts of doubled signals due to Boc rotamers are shown in [ ].

(2*R*,3*R*)-8-Allyl-3a-(3-oxo-propyl)-3,3a,8,8a-tetrahydro-2*H*-pyrrolo[2,3-*b*]indole-1-carboxylic acid ethyl ester (Table 2, entry 2). Prepared according to the general procedure from acrolein (153 μl, 2.43 mmol), *N*-10-ethylcarbamate-1-allyltryptamine (166 mg, 0.608 mmol), and (2*R*, 5*R*)-catalyst **8a** TFA salt (48 mg, 0.122 mmol) in CH_2Cl_2 (1.63 ml) and water (0.290 ml) at –80°C for 26 h to provide the title compound as a colorless oil (178 mg, 89% yield, 89% ee) after silica gel chromatography in 15-25% EtOAc/hexanes. IR (film) 3053, 2979, 2933, 2723, 1698, 1606, 1491, 1464, 1417, 1381, 1343, 1311, 1212, 1165, 1106, 1082, 1031, 936, 891,

744 cm^{-1}; ^1H NMR (300 MHz, VT = 80°C, C_7D_8) δ 9.17 (s, 1H, CHO), 7.01 (d, *J* = 1.2 Hz, 1H, 4-ArH), 6.68 (d, *J* = 7.61 Hz, 1H, 6-ArH), 6.60 (t, *J* = 7.3 Hz, 1H, 5-ArH), 6.31 (d, *J* = 7.9 Hz, 1H, 7-ArH), 5.79 (ddd, *J* = 5.5, 10.7, 22.3 Hz, 1H, $CH_2C\mathbf{H}CH_2$), 5.29 (s, 1H, NCHN), 5.18 (d, *J* = 17 Hz, 1H, $CH_2CHC\mathbf{H}_2$), 5.02 (d, *J* = 1.2, 10 Hz, 1H $CH_2CHC\mathbf{H}_2$), 4.04 (m, 4H, $NC\mathbf{H}_2CH$, $CH_3C\mathbf{H}_2O$), 3.67 (t, *J* = 8.2 Hz, 1H, $CH_2C\mathbf{H}HN$); 2.86 (dt, *J* = 5.8, 16.8 Hz, 1H, $CH_2CH\mathbf{H}N$); 2.10 (app. q, *J* = 2.4 Hz, 1H, $CH_2CH\mathbf{H}CHO$), 1.97-1.46 (m, 5H, $C\mathbf{H}_2CH_2N$, $C\mathbf{H}_2CH\mathbf{H}CHO$), 1.09 (t, *J* = 7.0 Hz, 3H, $CH_2C\mathbf{H}_3$); ^{13}C NMR (75 MHz, C_7D_8) δ 199.0, 157.4, 150.4, 134.8, 131.0, 128.8, 122.6, 117.7, 115.9, 106.5, 84.5, 61.1, 48.6, 45.3, 40.1, 38.7, 38.1, 31.2, 14.9; HRMS (CI) exact mass calcd for ($C_{19}H_{24}N_2O_3$) requires *m/z* 328.1787, found *m/z* 328.1792. $[\alpha]_D$ = 308.2 (*c* = 1.0, $CHCl_3$). The enantiomeric ratio was determined by HPLC analysis of the alcohol, obtained by $NaBH_4$ reduction of the aldehyde, using a Chiracel AD and AD guard column (6% ethanol/hexanes, 1 ml/min); *R* isomer t_r = 11.5 min and *S* isomer t_r = 13.6 min.

(2*R*,3*R*)-8-Prenyl-3a-(3-oxo-propyl)-3,3a,8,8a-tetrahydro-2*H*-pyrrolo[2,3-*b*]indole-1-carboxylic acid ethyl ester (Table 2, entry 3). Prepared according to the general procedure from acrolein (131 µl, 2.08 mmol), *N*-10-ethylcarbamate-1-prenyltryptamine (171 mg, 0.521 mmol), and (2*R*, 5*R*)-catalyst **8a** TFA salt (41 mg, 0.104 mmol) in CH_2Cl_2 (1.43 ml) and water (0.253 ml) at –80°C for 24 h to provide the title compound as a colorless oil (179 mg, 89% yield, 89% ee) after silica gel chromatography in 15% EtOAc/hexanes. IR (film) 2959, 2927, 2703, 1716, 1695, 1604, 1487, 1444, 1412, 1380, 1348, 1311, 1209, 1161, 1108, 1081, 1017, 932, 895, 772, 745 cm^{-1}; ^1H NMR (300 MHz, VT = 90°C, C_7D_8) δ 9.29 (t, *J* = 1.6 Hz, 1H, CHO), 7.09 (d, *J* = 1.6 Hz, 1H, 4-ArH), 6.78 (dd, *J* = 1.6, 7.7 Hz, 1H, 6-ArH), 6.70 (t, *J* = 8.2 Hz, 1H, 5-ArH), 6.43 (d, *J* = 8.2 Hz, 1H, 7-ArH), 5.39 (m, 2H, $CH_2C\mathbf{H}C(CH_3)_2$, NCHN), 4.29 (dd, *J* = 6.0, 15.9 Hz, 1H, $CH_3CH\mathbf{H}O$), 4.16 (dd, *J* = 7.1, 14.3 Hz, 2H, $NC\mathbf{H}_2CH$,), 4.05 (dd, *J* = 5.5, 16.5 Hz, 1H, $CH_3C\mathbf{H}HO$), 3.76 (t, *J* = 8.7 Hz, 1H, $CH_2C\mathbf{H}HN$); 2.95 (dt, *J* = 6.0, 14.8 Hz, 1H, $CH_2CH\mathbf{H}N$); 2.17 (app q, *J* = 2.2 Hz, 1H, $CH_2CH\mathbf{H}CHO$), 2.09-1.56 (m, 5H, $C\mathbf{H}_2CH_2N$, $C\mathbf{H}_2CH\mathbf{H}CHO$), 1.77 (s, 3H, $C(C\mathbf{H}_3)_2$), 1.70 (s, 3H, $C(C\mathbf{H}_3)_2$), 1.18 (t, *J* = 7.1 Hz, 3H, $CH_2C\mathbf{H}_3$); ^{13}C NMR (75 MHz, C_7D_8) δ 198.5, 158.4, 150.9, 133.6, 131.5, 128.8, 122.6, 122.1, 117.6, 106.6, 84.8, 60.9, 45.4, 44.2, 43.4, 40.1, 38.5, 31.4, 25.4, 17.9, 14.7; HRMS (CI) exact mass calcd for ($C_{21}H_{28}N_2O_3$) requires *m/z* 356.2100, found *m/z* 356.2093. $[\alpha]_D$ = 265.7 (*c* = 1.0, $CHCl_3$). The enantiomeric ratio was determined by HPLC analysis of the alcohol, obtained by $NaBH_4$

reduction of the aldehyde, using a Chiracel AD and AD guard column (2% ethanol/hexanes, 1 ml/min); *R* isomer t_r = 38.1 min and *S* isomer t_r = 42.6 min.

(2*R*,3*R*)-8-Benzyl-3a-(3-oxo-propyl)-3,3a,8,8a-tetrahydro-2*H*-pyrrolo[2,3-*b*]indole-1-carboxylic acid allyl ester (Table 2, entry 4). Prepared according to the general procedure from acrolein (133 μl, 2.13 mmol), *N*-10-allylcarbamate-1-benzyltryptamine (170 mg, 0.532 mmol), and (2*R*, 5*R*)-catalyst **8a** TFA salt (42 mg, 0.106 mmol) in CH_2Cl_2 (1.43 ml) and water (0.253 ml) at −80°C for 24 h to provide the title compound as a colorless oil (166 mg, 83% yield, 89% ee) after silica gel chromatography in 15% EtOAc/hexanes. IR (film) 3063, 3033, 2946, 2887, 2711, 1701, 1603, 1491, 1452, 1408, 1364, 1354, 1330, 1213, 1159, 1105, 1083, 1032, 978, 939, 882, 743, 700 cm^{-1}; ^1H NMR (300 MHz, VT = 90°C, C_7D_8) δ 9.20 (s, 1H, CHO), 7.35 (d, *J* = 7.1 Hz, 1H, BnH), 7.22-6.99 (m, 5H, BnH, 4-ArH), 6.76 (d, *J* = 7.2 Hz, 1H, 6-ArH), 6.67 (t, *J* = 7.1 Hz, 1H, 5-ArH), 6.33 (d, *J* = 8.2 Hz, 1H, 7-ArH), 5.82 (ddd, *J* = 6.0, 11.0, 22.0 Hz, 1H, $CH_2C\mathbf{H}CH_2$), 5.42 (s, 1H, NCHN), 5.16 (d, *J* = 17 Hz, 1H, $CH_2CHC\mathbf{H}_2$), 5.04 (d, *J* = 10.4 Hz, 1H $CH_2CHC\mathbf{H}_2$), 4.74-4.50 (m, 4H, $CH_2C\mathbf{H_2}O$, $NC\mathbf{H_2}Ar$), 3.78 (t, *J* = 8.7 Hz, 1H, $CH_2C\mathbf{H}HN$); 3.00 (dt, *J* = 6.0, 17.0 Hz, 1H, $CH_2CH\mathbf{H}N$); 2.21-2.16 (m, 2H, $CH_2C\mathbf{H_2}CHO$), 1.86-1.77 (m, 2H, $C\mathbf{H_2}CH_2N$), 1.66-1.57 (m, 2H, $C\mathbf{H}_2CH_2CHO$); ^{13}C NMR (75 MHz, C_7D_8) δ 201, 155.5 [154.4], 150.7, 139.2, 133.1 [132.9], 129.3, [128.8] 128.6, 127.6, 127.2 [126.8], 123.1, [118.8] 118.2, 117.9 [117.7], 106.6, 84.3, [66.6] 66.2, [57.0] 55.6, 45.4, 40.2, 39.2 [38.5], [31.7] 31.4; HRMS (CI) exact mass calcd for ($C_{24}H_{26}N_2O_3$) requires *m/z* 390.1943, found *m/z* 390.1945. $[\alpha]_D$ = 247.8 (*c* = 1.0, $CHCl_3$). The enantiomeric ratio was determined by HPLC analysis of the alcohol, obtained by $NaBH_4$ reduction of the aldehyde, using a Chiracel AD and AD guard column (6% isopropyl alcohol/hexanes, 1 ml/min); *R* isomer t_r = 31.0 min and *S* isomer t_r = 39.7 min. The minor counterparts of doubled signals due to Boc rotamers are shown in [ ].

(2*S*,3*S*)-8-Benzyl-3a-(3-oxo-propyl)-3,3a,8,8a-tetrahydro-2*H*-pyrrolo[2,3-*b*]indole-1-carboxylic acid *tert*-butyl ester (Table 2, entry 5). Prepared according to the general procedure from acrolein (0.54 ml, 8.0 mmol), *N*-10-BOC-1-benzyltryptamine (700 mg, 2.0 mmol), and (2*S*, 5*S*)-catalyst **8a** TFA (114 mg, 0.40 mmol), and trifluoroacetic acid (31 μl, 0.40 mmol) in CH_2Cl_2 (5.0 ml) and H_2O (1. 0 ml) at −80°C was added acrolein. After stirring for 24 h

at this temperature, the reaction mixture was purified by column chromatography (silica, 10% EtOAc in hexanes) to provide the title compound (670 mg, 82%) as a colorless, viscous oil; 90% ee; IR (thin film) 2974, 2930, 2719, 1123, 1692, 1604, 1493, 1393, 1365, 1158 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.60 (d, *J* = 22.5 Hz, 1H), 7.18-7.34 (m, 5H), 6.95-7.06 (m, 2H), 6.67 (approx d, *J* = 6.6 Hz, 1H), 6.25 (br dd, *J* = 7.2, 31.5 Hz, 1H), 5.40 (d, *J* = 47.4 Hz, 1H), 4.65 (approx s, 2H), 3.86 (br td, *J* = 9.9, 61.8 Hz, 1H), 3.08 (td, *J* = 6.0, 11.4 Hz, 1H), 1.90-2.40 (m, 6H), 1.32 (d, *J* = 29.7 Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.5, 154.8, 153.8, 150.8, 130.9, 128.9, 128.8, 128.5, 127.3, 126.9, 126.3, 123.0, 118.0, 117.6, 106.4, 85.3, 84.2, 80.8, 80.1, 57.2, 55.6, 50.8, 50.3, 45.7, 45.2, 40.5, 39.3, 38.4, 32.0, 31.6, 28.7, 28.5; HRMS (CI) exact mass calcd for ($C_{25}H_{30}N_2O_3^+$) requires *m/z* 406.2256, found *m/z*; $[\alpha]_D^{25}$ = –270.1 (*c* = 1.0, $CHCl_3$). The enantiomeric purity was determined by HPLC analysis of the alcohol, obtained by $NaBH_4$ reduction of the aldehyde, using a by HPLC with a Chiralcel ODH column and ODH guard column (4% EtOH/hexanes, 1 ml/min flow); *R* isomer t_r = 10.5 min and *S* isomer t_r = 12.0 min.

(2*S*,3*R*,3a*R*)-8-Allyl-3a-(1-benzoyl-3-oxo-propyl)-3,3a,8,8a-tetrahydro-2*H*-pyrrolo[2,3-*b*]indole-1-carboxylic acid *tert*-butyl ester (Table 3, entry 1). Prepared according to the general procedure from methyl 4-oxo-4-phenyl-but-2-enal (131 mg, 0.816 mmol), *N*-10-BOC-1-allyltryptamine (61 mg, 0.204 mmol), and (2*S*, 5*S*)-catalyst **1** TFA salt (14.7 mg, 0.0408 mmol) in CH_2Cl_2 (410 μl) at –40°C for 64 h to provide the title compound as a yellow oil (91.9 mg, 92% yield, 94% ee, 12.7:1 dr) after silica gel chromatography in 25% EtOAc/hexanes. IR (film) 3053, 2968, 2882, 2825, 1717, 1693, 1602, 1493, 1445, 1388, 1369, 1221, 1150, 1097, 973, 935, 883, 773, 745, 692 cm^{-1}; ^1H NMR (300 MHz, VT = 90°C, C_7D_8) δ 8.94 (s, 1H, CHO), 7.95 (d, *J* = 8.2 Hz, 2H, COAr *o*-H), 7.13-6.94 (m, 4H, 4-ArH, COAr *m*-H, COAr *p*-H), 6.77 (d, *J* = 7.7 Hz, 1H, 6-ArH), 6.54 (t, *J* = 7.1 Hz, 1H, 5-ArH), 6.31 (d, *J* = 7.7 Hz, 1H, 7-ArH), 5.96 (s, 1H, NCHN), 5.85 (ddd, *J* = 4.5, 10.4, 22.5 Hz, 1H, $CH_2C\mathbf{H}CH_2$), 5.19 (d, *J* = 17 Hz, 1H, $CH_2CHC\mathbf{H}_2$), 5.02 (d, *J* = 10.4 Hz, 1H $CH_2CHC\mathbf{H}_2$), 4.36 (dd, *J* = 2.7, 9.9 Hz, 2H, $NC\mathbf{H}_2CH$), 3.98 (m, 1H, $CH_2C\mathbf{H}HN$), 3.59 (m, 1H, C**H**COPh), 2.86 (dd, *J* = 9.9, 18.7 Hz, 1H, $CH_2CH\mathbf{H}N$), 2.67 (m, 1H, CHCH**H**CHO), 2.12 (m, 1H, $CH_2CH\mathbf{H}CHO$), 1.76 (m, 2H, $C\mathbf{H_2}CH_2N$), 1.45 (s, 9H, $C(C\mathbf{H}_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.6, 197.6, 150.5, 135.0, 132.5, 130.6, 129.1, 128.9, 128.3, 128.1, 125.3, 124.6, 123.0, 117.5, 115.5, 106.4, 81.9, 79.4, 48.4, 45.0, 44.9, 44.5, 36.5, 28.4, HRMS (CI) exact mass calcd for ($C_{28}H_{33}N_2O_4$) requires *m/z* 461.5738, found *m/z*

461.2440 $[\alpha]_D$ = –247.1 (*c* = 1.0, $CHCl_3$). The enantiomeric ratio was determined by HPLC analysis of the alcohol, obtained by $NaBH_4$ reduction of the aldehyde, using a Chiracel OD-H and OD guard column (5% ethanol/hexanes, 1 ml/min); *Major* isomer t_r = 18.9 min and *Minor* isomer t_r = 26.3 min. The diastereomeric ratio was determined by HPLC analysis of the alcohol, obtained by $NaBH_4$ reduction of the aldehyde, using a Chiracel Sil-Rx and (4% ethanol/hexanes, 1 ml/min); *Major* isomer t_r = 10.4 min and *Minor* isomer t_r = 11.3 min.

(2*S*,3*R*,3a*R*)-8-Allyl-3a-(1-benzoyloxymethyl-3-oxo-propyl)-3,3a,8,8a-tetrahydro-2*H*-pyrrolo[2,3-*b*]indole-1-carboxylic acid *tert*-butyl ester (Table 3, entry 2). Prepared according to the general procedure from 4-benzyloxy-but-2-enal (155 mg, 0.816 mmol), *N*-10-BOC-1-allyltryptamine (61 mg, 0.204 mmol), and (2*S*, 5*S*)-catalyst **1** TFA salt (14.7 mg, 0.0408 mmol) in CH_2Cl_2 (410 μl) at –40°C for 44 h to provide the title compound as a colorless oil (65.5 mg, 66% yield, 91% ee, 22.4:1 dr) after silica gel chromatography in 20% EtOAc/hexanes. IR (film) 2980, 2872, 1734, 1724, 1689, 1606, 1493, 1389 1365, 1316, 1272, 1218, 1154, 1105, 1065, 1026, 942, 888, 770, 716 cm^{-1}; ^1H NMR (300 MHz, VT = 90°C, C_7D_8) δ 9.37 (s, 1H, CHO), 8.02 (d, *J* = 6.6 Hz, 2H, COAr *o*-H), 7.24-7.03 (m, 4H, 4-ArH, COAr *m*-H, COAr *p*-H), 6.82 (d, *J* = 7.1 Hz, 1H, 6-ArH), 6.66 (t, *J* = 7.1 Hz, 1H, 5-ArH), 6.38 (d, *J* = 8.2 Hz, 1H, 7-ArH), 5.94-5.85 (m, 1H, $CH_2C\mathbf{H}CH_2$), 5.73 (s, 1H, NCHN), 5.27 (d, *J* = 17 Hz, 1H, $CH_2CHC\mathbf{H}_2$), 5.11 (d, *J* = 10.4 Hz, 1H $CH_2CHC\mathbf{H}_2$), 4.52 (dd, *J* = 4.4, 11.5 Hz, 2H, $NC\mathbf{H}_2CH$), 4.11 (m, 1H, CHC**H**HO), 3.96 (dd, *J* = 6.5, 11.5 Hz, 1H, CHCH**H**O), 3.78 (m, 1H, $CH_2C\mathbf{H}HN$), 2.90-2.80 (m, 1H, CHCH**H**CHO), 2.67-2.59 (m, 1H, CHC**H**HCHO), 2.41-2.16 (m, 3H, $CH_2CH\mathbf{H}N$, C**H**HCH_2N, C**H**CH_2O), 1.81-1.71 (m, 1H, CH**H**CH_2N), 1.50 (s, 9H, $C(C\mathbf{H}_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.5, 193.5, 166.5, 150.8, 142.8, 134.5, 133.4, 129.4, 128.7, 125.7, 123.6, 119.3, 117.5, 116.1, 109.8, 106.7, 88.7, 65.7, 59.5, 48.6, 45.6, 43.9, 40.3, 37.2, 28.7, HRMS (CI) exact mass calcd for ($C_{29}H_{35}N_2O_5$) requires *m/z* 491.5998, found *m/z* 491.2546 $[\alpha]_D$ = –148 (*c* = 1.0, $CHCl_3$). The enantiomeric ratio was determined by HPLC analysis of the alcohol, obtained by $NaBH_4$ reduction of the aldehyde, using a Chiracel AD and AD guard column (5% ethanol/hexanes, 1 ml/min); *Major* isomer t_r = 11.7 min and *Minor* isomer t_r = 14.8 min. The diastereomeric ratio was determined by HPLC analysis of the alcohol, obtained by $NaBH_4$ reduction of the aldehyde, using a Chiracel Sil and (5% ethanol/hexanes, 1 ml/min); *Minor* isomer t_r = 12.1 min and *Major* isomer t_r = 13.7 min.

(2*S*,3*R*,3a*R*)-8-Allyl-3a-(1-methoxycarbonyl-3-oxo-propyl)-3,3a,8,8a-tetrahydro-2*H*-pyrrolo[2,3-*b*]indole-1-carboxylic acid *tert*-butyl ester (Table 3, entry 3). Prepared according to the general procedure from methyl 4-oxo-butenoate (165 mg, 1.45 mmol), *N*-10-BOC-1-allyltryptamine (109 mg, 0.362 mmol), and (2*S*, 5*S*)-catalyst **1** TFA salt (26.1 mg, 0.0724 mmol) in CH_2Cl_2 (700 μl) at −60°C for 29 h to provide the title compound as a colorless oil (140 mg, 93% yield, 91% ee, 44:1 dr) after silica gel chromatography in 10-20% EtOAc/hexanes. IR (film) 2973, 2904, 2736, 1730, 1696, 1607, 1493, 1389, 1365, 1217, 1152, 1098, 935, 890, 742 cm^{-1}; ^1H NMR (300 MHz, VT = 90°C, C_7D_8) δ 9.15 (s, 1H, CHO), 7.06 (obs, 1H, 4-ArH), 6.71 (d, *J* = 7.1 Hz, 1H, 6-ArH), 6.64 (t, *J* = 6.6 Hz, 1H, 5-ArH), 6.38 (d, *J* = 7.7 Hz, 1H, 7-ArH), 5.96 (s, 1H, NCHN), 5.96-5.80 (m, 1H, $CH_2C\mathbf{H}CH_2$), 5.28 (d, *J* = 17 Hz, 1H, $CH_2CHC\mathbf{H}_2$), 5.11 (d, *J* = 9.9 Hz, 1H $CH_2CHC\mathbf{H}_2$), 4.08 (s, 2H, $NC\mathbf{H}_2CH$), 3.80 (m, 1H, $CH_2C\mathbf{H}HN$), 3.42 (s, 3H, $CO_2C\mathbf{H_3}$), 3.28 (d, *J* = 11.0 Hz, 1H, $C\mathbf{H}CO_2CH_3$), 2.85 (dd, *J* = 9.9, 16.5 Hz, 1H, $CH_2CH\mathbf{H}N$), 2.70 (dd, *J* = 11.0, 18.1 Hz, 1H, $CH_2CH\mathbf{H}CHO$), 2.20 (m, 1H, $CHCH\mathbf{H}CHO$), 2.11 (t, *J* = 18.2 Hz, 2H, $C\mathbf{H_2}CH_2N$), 1.52 (s, 9H, $C(C\mathbf{H}_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.1, 172.2, 150.6, 135.0, 130.0, 129.0, 125.4, 122.8, 117.7, 115.6, 106.5, 82.4, 79.5, 59.2, 47.4, 45.9, 44.9, 43.6, 38.3, 37.0, 28.5, HRMS (CI) exact mass calcd for ($C_{23}H_{31}N_2O_5$) requires *m/z* 415.2233, found *m/z* 415.2253 $[\alpha]_D = -189.9$ (*c* = 1.0, $CHCl_3$). The enantiomeric ratio was determined by HPLC analysis of the alcohol, obtained by $NaBH_4$ reduction of the aldehyde, using a Chiracel AD and AD guard column (5% ethanol/hexanes, 1 ml/min); *Major* isomer t_r = 10.0 min and *Minor* isomer t_r = 14.8 min. The diastereomeric ratio was determined by HPLC analysis of the alcohol, obtained by $NaBH_4$ reduction of the aldehyde, using a Chiracel Sil-Rx and (5% ethanol/hexanes, 1 ml/min); *Minor* isomer t_r = 9.2 min and *Major* isomer t_r = 10.5 min.

(2*S*,3*R*,3a*R*)-8-Allyl-3a-(1-methoxycarbonyl-3-oxo-propyl)-5-methyl-3,3a,8,8a-tetrahydro-2*H*-pyrrolo[2,3-*b*]indole-1-carboxylic acid *tert*-butyl ester (Table 3, entry 4). Prepared according to the general procedure from methyl 4-oxo-butenoate (160 mg, 1.4 mmol), *N*-10-BOC-1-allyl-5-methyltryptamine (110 mg, 0.35 mmol), and (2*S*, 5*S*)-catalyst **1** TFA salt (25.2 mg, 0.07 mmol) in CH_2Cl_2 (700 μl) at −60°C for 18 h to provide the title compound as a colorless oil (141 mg, 94% yield, 92% ee, >50:1 dr) after silica gel chromatography in 10-20% EtOAc/hexanes. IR (film) 2966, 2871, 2729, 1730, 1694, 1616, 1501, 1395, 1363, 1221, 1154,

1095, 949, 917, 893, 800, 772 cm^{-1}; ^1H NMR (300 MHz, VT = 90°C, C_7D_8) δ 9.15 (s, 1H, CHO), 7.06 (obs, 1H, 4-ArH), 6.62 (s, 1H, 6-ArH), 6.33 (d, *J* = 7.7 Hz, 1H, 7-ArH), 5.95 (s, 1H, NCHN), 5.99-5.90 (m, 1H, $CH_2C\mathbf{H}CH_2$), 5.29 (d, *J* = 17 Hz, 1H, $CH_2CHC\mathbf{H}_2$), 5.13 (d, *J* = 9.9 Hz, 1H $CH_2CHC\mathbf{H}_2$), 4.08 (s, 2H, $NC\mathbf{H}_2CH$), 3.81 (m, 1H, $CH_2C\mathbf{H}HN$), 3.44 (s, 3H, $CO_2C\mathbf{H_3}$), 3.30 (dd, *J* = 10.4, 3.3 Hz, 1H, $C\mathbf{H}CO_2CH_3$), 2.90 (td, *J* = 6.6, 10.4 Hz, 1H, $CH_2CH\mathbf{H}N$), 2.72 (dd, *J* = 10.4, 18.1 Hz, 1H, $CHCH\mathbf{H}CHO$), 2.21 (s, 3H, $ArC\mathbf{H_3}$), 2.26-2.08 (m, 2H, $C\mathbf{H_2}CH_2N$), 1.84 (dd, *J* = 6.0, 12.0, 1H, $CH_2CH\mathbf{H}CHO$), 1.52 (s, 9H, $C(C\mathbf{H}_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.1, 172.2, 148.6, 135.2, 130.4, 129.7, 126.6, 125.4, 123.4, 115.5, 106.5, 82.6, 79.4, 51.2, 48.9, 45.9, 44.9, 43.7, 36.9, 28.5, 20.6 HRMS (CI) exact mass calcd for ($C_{24}H_{32}N_2O_5$) requires *m/z* 428.2311, found *m/z* 428.2327 $[\alpha]_D = -164.5$ (*c* = 1.0, $CHCl_3$). The enantiomeric ratio was determined by HPLC analysis of the alcohol, obtained by $NaBH_4$ reduction of the aldehyde, using a Chiracel AS and AS guard column (2% ethanol/hexanes, 1 ml/min); *Major* isomer t_r = 10.6 min and *Minor* isomer t_r = 12.8 min. The diastereomeric ratio was determined by HPLC analysis of the alcohol, obtained by $NaBH_4$ reduction of the aldehyde, using a Chiracel AS and AS guard column (7% ethanol/hexanes, 1 ml/min); *Major* isomer t_r = 5.8, 6.2 min and *Minor* isomer t_r = 6.9, 7.3 min.

(2*S*,3*R*,3a*R*)-8-Allyl-3a-(1-methoxycarbonyl-3-oxo-propyl)-5-methoxy-3,3a,8,8a-tetrahydro-2*H*-pyrrolo[2,3-*b*]indole-1-carboxylic acid *tert*-butyl ester (Table 3, entry 5). Prepared according to the general procedure from methyl 4-oxo-butenoate (102 mg, 0.9 mmol), *N*-10-BOC-1-allyl-5-methoxytryptamine (74 mg, 0.23 mmol), and (2*S*, 5*S*)-catalyst **1** TFA salt (16.0 mg, 0.045 mmol) in CH_2Cl_2 (460 μl) at −60°C for 20 h to provide the title compound as a colorless oil (141 mg, 99% yield, 90% ee, 10:1 dr) after silica gel chromatography in 10-20% EtOAc/hexanes. IR (film) 2976, 2927, 2839, 2721, 1730, 1691, 1496, 1437, 1393, 1364, 1222, 1149, 1041, 987, 943, 909, 889, 806, 772 cm^{-1}; ^1H NMR (300 MHz, VT = 90°C, C_7D_8) δ 9.05 (s, 1H, CHO), 6.55 (dd, *J* = 2.2, 8.2 Hz, 1H, 4-ArH), 6.45 (d, *J* = 1.6 Hz, 1H, 6-ArH), 6.22 (d, *J* = 8.8 Hz, 1H, 7-ArH), 5.82 (s, 1H, NCHN), 5.86 (ddd, *J* = 4.5, 10.4, 22.5 Hz, 1H, $CH_2C\mathbf{H}CH_2$), 5.20 (dd, *J* = 1.6, 17.0 Hz, 1H, $CH_2CHC\mathbf{H}_2$), 5.02 (dd, *J* = 1.6, 11 Hz, 1H $CH_2CHC\mathbf{H}_2$), 3.97 (d, *J* = 4.4 Hz, 2H, $NC\mathbf{H}_2CH$), 3.70 (m, 1H, $CH_2C\mathbf{H}HN$), 3.41 (s, 3H, $CO_2C\mathbf{H_3}$), 3.30 (s, 3H, $ArOC\mathbf{H_3}$), 3.18 (dd, *J* = 10.4, 3.3 Hz, 1H, $C\mathbf{H}CO_2CH_3$), 2.81 (td, *J* = 6.6, 10.4 Hz, 1H, $CH_2CH\mathbf{H}N$), 2.62 (dd, *J* = 10.4, 18.1 Hz, 1H, $CHCH\mathbf{H}CHO$), 2.10-1.90 (m, 2H, $C\mathbf{H_2}CH_2N$),

1.72 (dd, J = 6.6, 12.6, 1H, $CH_2CH\mathbf{H}CHO$), 1.42 (s, 9H, $C(C\mathbf{H}_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.0, 171.4, 150.1, 135.4, 128.9, 115.4, 114.2, 110.6, 106.9, 83.0, 79.3, 55.7, 51.0, 49.4, 45.7, 44.9, 43.6, 36.7, 28.4 HRMS (CI) exact mass calcd for ($C_{24}H_{32}N_2O_6$) requires *m/z* 444.2260, found *m/z* 444.2258 $[\alpha]_D$ = –162.5 (*c* = 1.0, $CHCl_3$). The enantiomeric ratio was determined by HPLC analysis of the alcohol, obtained by $NaBH_4$ reduction of the aldehyde, using a Chiracel AS and AS guard column (5% ethanol/hexanes, 1 ml/min); *Major* isomer t_r = 8.6 min and *Minor* isomer t_r = 10.4 min. The diastereomeric ratio was determined by HPLC analysis of the alcohol, obtained by $NaBH_4$ reduction of the aldehyde, using a Chiracel Sil-Rx column (5% ethanol/hexanes, 1 ml/min); *Minor* isomer t_r = 20.5 min and *Major* isomer t_r = 22.1 min.

(2*S*,3*R*,3a*R*)-6-Bromo-3a-(1-methoxycarbonyl-3-oxo-propyl)-8-(3-methyl-but-2-enyl)-3,3a,8,8a-tetrahydro-2*H*-pyrrolo[2,3-*b*]indole-1-carboxylic acid *tert*-butyl ester (Table 3, entry 6). Prepared according to the general procedure from methyl 4-oxo-butenoate (597 mg, 5.22 mmol), *N*-10-BOC-1-Prenyl-6-Bromotryptamine (710 mg, 1.74 mmol), and (2*S*, 5*S*)-catalyst **1** (86 mg, 0.35 mmol), and trifluoroacetic acid (27 μl, 0.35 mmol) in CH_2Cl_2 (43.5 ml) at –40°C for 24 h to provide the title compound as a colorless oil (778 mg, 86% yield, 97% ee, 31:1 dr) after silica gel chromatography in 20% EtOAc/hexanes as a colorless, viscous oil. IR (thin film) 2971, 2928, 2716, 1728, 1696, 1600, 1490, 1396, 1364, 1158 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.56 (s, 1H), 6.73 (d, J = 7.5 Hz, 1H), 6.68 (d, J = 7.5 Hz, 1H), 6.37 (s, 1H), 5.71 (br s, 1H), 5.09 (br s, 1H), 3.80-4.09 (m, 3H), 3.62 (s, 3H), 3.21 (dd, J = 2.7, 11.1 Hz, 1H), 2.80-3.01 (m, 2H), 2.33 (br d, J = 17.7 Hz, 1H), 1.91-2.07 (m, 2H), 1.71 (s, 3H), 1.68 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.4, 172.8, 172.5, 154.3, 15.7, 151.6, 134.4, 128.7, 125.6, 124.1, 123.3, 121.3, 120.8, 120.1, 119.8, 109.1, 81.9, 80.9, 80.1, 58.2, 56.9, 52.4, 45.4, 44.7, 43.6, 43.5, 36.6, 36.4, 28.7, 26.0, 18.5; HRMS (CI) exact mass calcd for ($C_{25}H_{33}BrN_2O_5^+$) requires *m/z* 520.1573, found *m/z* 520.1582; $[\alpha]_D^{25}$ = –196.3 (*c* = 1.0, $CHCl_3$). The enantiomeric ratio was determined by HPLC analysis of the alcohol, obtained by $NaBH_4$ reduction of the aldehyde, using a Chiracel OD-H and OD guard column (6% ethanol/hexanes, 1 ml/min); *Major* isomer t_r = 8.4 min and *Minor* isomer t_r = 11.1 min. The diastereomeric ratio was determined by HPLC analysis of the alcohol, obtained by $NaBH_4$ reduction of the aldehyde, using a Chiracel Sil-Rx column (3% ethanol/hexanes, 1 ml/min); *Minor* isomer t_r = 18.1 min and *Major* isomer t_r = 19.5 min.

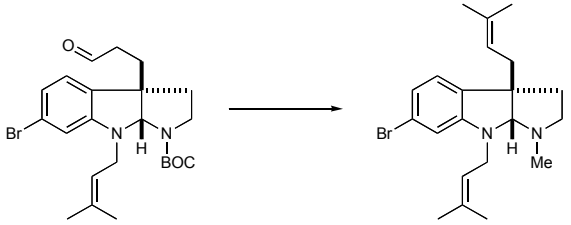
(2*S*,3*R*,3a*R*)-8-Allyl-3a-(1-methoxycarbonyl-3-oxo-propyl)-7-methyl-3,3a,8,8a-tetrahydro-2*H*-pyrrolo[2,3-*b*]indole-1-carboxylic acid *tert*-butyl ester (Table 3, entry 7). Prepared according to the general procedure from methyl 4-oxo-butenoate (160 mg, 1.4 mmol), *N*-10-BOC-1-allyl-7-methyltryptamine (110 mg, 0.35 mmol), and (2*S*, 5*S*)-catalyst **1** TFA salt (25.2 mg, 0.07 mmol) in CH_2Cl_2 (700 μl) at –60°C for 30 h to provide the title compound as a colorless oil (146 mg, 97% yield, 99% ee, 17:1 dr) after silica gel chromatography in 10-20% EtOAc/hexanes. IR (film) 2976, 2880, 2725, 1738, 1727, 1694, 1601, 1591, 1468, 1402, 1365, 1335, 1250, 1221, 1166, 1136, 937, 911, 881 cm^{-1}; ^1H NMR (300 MHz, VT = 90°C, C_7D_8) δ 9.21 (d, *J* = 4.4 Hz, 1H, CHO), 7.06 (obs, 1H, 4-ArH), 6.83 (d, *J* = 6.6 Hz, 1H, 6-ArH), 6.33 (obs, 1H, 5-ArH), 5.83 (s, 1H, NCHN), 6.05 - 5.87 (m, 1H, $CH_2C\mathbf{H}CH_2$), 5.31 (d, *J* = 17 Hz, 1H, $CH_2CHC\mathbf{H}_2$), 5.11 (d, *J* = 10.4 Hz, 1H $CH_2CHC\mathbf{H}_2$), 4.28 (s, 2H, $NC\mathbf{H}_2CH$), 3.77 (m, 1H, $CH_2C\mathbf{H}HN$), 3.44 (s, 3H, $CO_2C\mathbf{H_3}$), 3.33 (dd, *J* = 7.7, 3.3 Hz, 1H, $C\mathbf{H}CO_2CH_3$), 2.92 (dd, *J* = 10.4, 17.0 Hz, 1H, CHCH**H**CHO), 2.72 (dd, *J* = 10.4, 17.6 Hz, 1H, $CH_2CH\mathbf{H}N$), 2.27 (s, 3H, $ArC\mathbf{H_3}$), 2.26-2.10 (m, 2H, $C\mathbf{H_2}CH_2N$), 1.89 (m, 1H, $CH_2CH\mathbf{H}CHO$), 1.54 (s, 9H, $C(C\mathbf{H}_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.0, 172.3, 148.7, 136.8, 132.4, 128.9, 128.1, 125.3, 120.7, 119.1, 115.5, 83.6, 79.3, 51.3, 51.1, 45.8, 44.5, 44.2, 37.2, 28.4, 21.0, 19.0 HRMS (CI) exact mass calcd for ($C_{24}H_{32}N_2O_5$) requires *m/z* 428.2311, found *m/z* 428.2324 $[\alpha]_D$ = –176.7 (*c* = 1.0, $CHCl_3$). The enantiomeric ratio was determined by HPLC analysis of the alcohol, obtained by $NaBH_4$ reduction of the aldehyde, using a Chiracel AD and AD guard column (5% ethanol/hexanes, 1 ml/min); *Major* isomer t_r = 14.0 min and *Minor* isomer t_r = 16.6 min. The diastereomeric ratio was determined by HPLC analysis of the alcohol, obtained by $NaBH_4$ reduction of the aldehyde, using a Chiracel Sil-Rx column (5% ethanol/hexanes, 1 ml/min); *Major* isomer t_r = 10.0 min and *Minor* isomer t_r = 10.7 min.

(2*S*,3*R*,3a*R*)-2-(8-Benzyl-2,3,8,8a-tetrahydro-furo[2,3-*b*]indole-3a-yl)-4-oxo-butyric acid *tert*-butyl ester (Scheme 6). Prepared according to the general procedure from *t*-butyl 4-oxo-butenoate (622 mg, 4 mmol), *N*-Benzyltryptophol (334 mg, 1.33 mmol), and (2*S*, 5*S*)-catalyst **1** TFA salt (96 mg, 0.266 mmol) in CH_2Cl_2 (4.80 ml) and IPA (500 μl) at –60°C for 40 h to provide the title compound as a colorless oil (325 mg, 80% yield, 93% ee, 12:1 dr) after silica gel chromatography in 15% EtOAc/hexanes. IR (film) 2729, 1721, 1601, 1601, 1407, 1446, 1363,

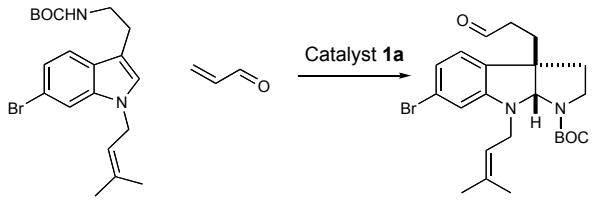
1254, 1217, 1150, 1026, 948, 772 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.57 (s, 1H, CHO), 7.38-7.23 (m, 5H, CH_2ArH), 7.06 (d, *J* = 7.8 Hz, 1H, 4-ArH), 7.02 (d, *J* = 7.2 Hz, 1H, 6-ArH), 6.67 (t, *J* = 7.5 Hz, 1H, 5-ArH), 6.34 (d, *J* = 7.8 Hz, 1H, 7-ArH), 5.64 (s, 1H, NCHO), 4.50 (Abq, *J* =15.9 Hz, Δυ = 18.3, 2H, NCH_2Ar), 3.94 (dd, *J* = 7.2, 8.1 Hz, 1H $CH_2CH\mathbf{H}O$), 3.52-3.44 (m, 1H), 3.25 (dd, *J* = 3.3, 11.7 Hz, 1H), 2.78 (dd, *J* = 11.7, 18.6 Hz, 1H), 2.42-2.25 (m, 2H), 2.14-2.0 (m, 1H), 1.38 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.4, 171, 150., 138.1, 130.0, 128.9, 128.4, 127.4, 127.1, 123.1, 117.8, 105.7, 98.3, 81.7, 66.5, 57.6, 48.9, 46.1, 43.4, 38.5, 28.0, HRMS (CI) exact mass calcd for ($C_{25}H_{28}NO_4$) requires *m/z* 406.2018, found *m/z* 406.2027 $[\alpha]_D$ = –94 (*c* = 1.25, $CHCl_3$). The enantiomeric ratio was determined by HPLC analysis of the alcohol, obtained by $NaBH_4$ reduction of the aldehyde, using a Chiracel AS and AS guard column (2% isopropyl alcohol/hexanes, 1 ml/min); *Minor* isomer t_r = 20.7 min and *Major* isomer t_r = 23.5 min. The diastereomeric ratio was determined by NMR analysis.

Determination of Absolute Stereochemistry

1. Determination of the absolute stereochemistry of (*S*)-6-Bromo-8-(3-methyl-but-2-enyl)-3a-(3-oxo-propyl)-3,3a,8,8a-tetrahydro-2*H*-pyrrolo[2,3-*b*]indole-1-carboxylic acid *tert*-butyl ester by correlation to (*S*)-flustramine B.



(*S*)-6-Bromo-8-(3-methyl-but-2-enyl)-3a-(3-oxo-propyl)-3,3a,8,8a-tetrahydro-2*H*-pyrrolo[2,3-*b*]indole-1-carboxylic acid *tert*-butyl ester.



Prepared according to the general procedure from acrolein (0.17 ml, 2.56 mmol), *N*-10-BOC-1-Prenyl-6-Bromotryptamine (258 mg, 0.64 mmol), and (2*S*, 5*S*)-catalyst **1** (31 mg, 0.13 mmol), and trifluoroacetic acid (9.8 µl, 0.13 mmol) in CH_2Cl_2 (4.2 ml) at –84°C for 72 h to

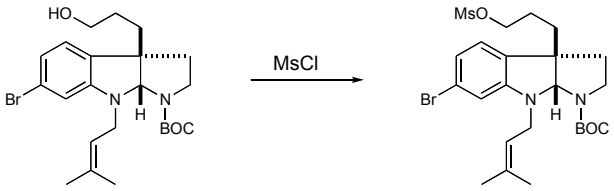
provide the title compound as a colorless oil (231 mg, 78% yield, 80% ee) after silica gel chromatography in 10% EtOAc/hexanes as a colorless, viscous oil**.** IR (thin film) 2971, 2929, 2717, 1723, 1695, 1601, 1490, 1447, 1394, 1366, 1250, 1219, 1158 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.63 (s, 1H), 6.75 (d, *J* = 7.8 Hz, 1H), 6.69 (d, *J* = 7.8 Hz, 1H), 6.38 (s, 1H), 5.25 (d, *J* = 41.1 Hz, 1H), 5.08 (br s, 1H), 3.65-4.09 (m, 3H), 2.94 (br s, 1H), 1.89-2.43 (m, 6H), 1.76 (s, 3H), 1.71 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.2, 154.7, 153.8, 151.8, 134.7, 134.4, 130.3, 123.9, 122.7, 121.5, 120.8, 120.0, 119.7, 109.0, 84.7, 84.1, 80.9, 80.2, 56.5, 55.2, 45.7, 45.2, 43.8, 40.3, 39.0, 38.3, 31.2, 28.7, 26.1, 18.5; HRMS (CI) exact mass calcd for ($C_{23}H_{31}BrN_2O_3$+Na+CH_3OH^+) requires *m/z* 517.1678, found *m/z* 517.1674; $[\alpha]_D^{20}$ = –218.9 (*c* = 1.0, $CHCl_3$).

The enantiomeric purity was determined after conversion to alcohol.

(*S*)-6-Bromo-3a-(3-hydoxypropyl)-8-(3-methyl-but-2-enyl)-3,3a,8,8a-tetrahydro-2*H*-pyrrolo[2,3-*b*]indole-1-carboxylic acid *tert*-butyl ester. To a solution of the previous compound (496 mg, 1.07 mmol) in MeOH (5.0 ml) at 0°C was added sodium borohydride (243 mg, 6.42 mmol). After stirring for 15 min at this temperature, the reaction mixture was quenched with 0.5 N HCl solution and extracted with EtOAc. The combined extract was washed with brine, dried over sodium sulfate, concentrated, and purified by column chromatography (silica, 30% EtOAc in hexanes) to provide the title compound (450 mg, 90%) as a colorless, viscous oil; 80% ee; IR (thin film) 3207, 2965, 2934, 1690, 1600, 1577, 1491, 1444, 1390, 1366, 1253, 1222, 1155, 1077, 1058 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.77 (d, *J* = 7.8 Hz, 1H), 6.70 (d, *J* = 7.8 Hz, 1H), 6.37 (s, 1H), 5.30 (d, *J* = 43.5 Hz, 1H), 5.09 (br s, 1H), 3.62-4.08 (m, 3H), 3.54 (br s, 2H), 2.96 (br s, 1H), 1.21-2.02 (m, 6H), 1.73 (s, 3H), 1.70 (s, 3H), 1.47 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.8, 153.9, 151.8, 151.7, 134.4, 134.2, 131.6, 123.9, 122.2, 121.8, 121.1, 119.7, 119.4, 108.8, 85.1, 84.5, 80.8, 80.1, 63.1, 57.0, 55.8, 45.7, 45.2, 44.0, 38.9, 38.2, 35.8, 35.7, 28.8, 26.1, 26.0, 18.4; HRMS (CI) exact mass calcd for ($C_{23}H_{33}BrN_2O_3$+Na^+) requires *m/z* 487.1572, found *m/z* 487.1582. $[\alpha]_D^{26}$ = –204.1 (*c* = 1.0, $CHCl_3$).

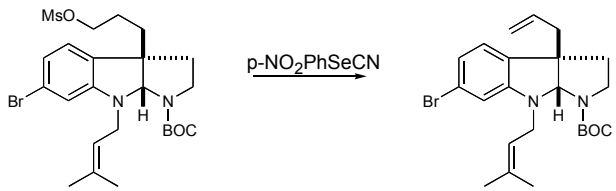
The enantiomeric purity was determined by HPLC with a Chiralcel ODH column and ODH guard column (4% EtOH/hexanes, 1 ml/min flow); t_r = 11.4 min and 14.1 min.

(*S*)-6-Bromo-3a-(3-Methanesulfonyloxypropyl)-8-(3-methyl-but-2-enyl)-3,3a,8,8a-tetrahydro-2*H*-pyrrolo[2,3-*b*]indole-1-carboxylic acid *tert*-butyl ester. To a solution of the



previous compound (115 mg, 0.25 mmol) and triethylamine (45 μl, 0.33 mmol) in CH_2Cl_2 (2.5 mL) at 0°C was added dropwise methanesulfonyl chloride (23 μl, 0.30 mmol). After stirring for 10 min at this temperature, the mixture was allowed to warm up to room temperature and stirred for 10 min. The reaction was quenched with saturated NH_4Cl solution and extracted with CH_2Cl_2. The combined extract was washed with brine, dried over sodium sulfate, concentrated, and purified by column chromatography (silica, 20–30% EtOAc in hexanes) to provide the title compound (133 mg, 99%) as a colorless, viscous oil; IR (thin film) 2940, 2820, 2730, 2635, 1457, 1437, 1343, 1280, 1234, 1198, 1167, 1107, 1089 cm^{-1};. ^1H NMR (300 MHz, $CDCl_3$) δ 6.78 (d, J = 7.8 Hz, 1H), 6.73 (d, J = 7.8 Hz, 1H), 6.40 (s, 1H), 5.30 (d, J = 46.2 Hz, 1H), 5.10 (br s, 1H), 3.69-4.18 (m, 5H), 2.97 (s, 3H), 2.95 (br s, 1H), 1.65-2.06 (m, 6H), 1.73 (s, 3H), 1.70 (s, 3H), 1.46 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.7, 153.9, 151.8, 151.7, 134.6, 134.4, 130.8, 123.9, 122.5, 121.6, 120.9, 119.9, 119.6, 118.9, 84.9, 84.2, 80.9, 80.1, 70.1, 56.8, 55.5, 45.7, 45.2, 43.9, 39.0, 38.2, 37.6, 35.4, 28.7, 26.1, 25.4, 18.5; HRMS (CI) exact mass calcd for ($C_{24}H_{35}BrN_2O_5S$+Na^+) requires m/z 565.1348, found m/z 565.1337. $[\alpha]_D^{22}$ = –204.3 (c = 1.0, $CHCl_3$).

(*S*)-3a-Allyl-6-bromo-8-(3-methyl-but-2-enyl)-3,3a,8,8a-tetrahydro-2*H*-pyrrolo[2,3-*b*]indole-1-carboxylic acid *tert*-butyl ester. To a slurry of 2-nitrophenyl selenocyanate (409

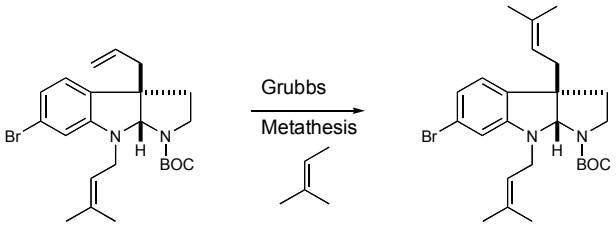


mg, 1.80 mmol) in EtOH (6.0 ml) at 0°C was added sodium borohydride (75 mg, 1.98 mmol) and stirred for 30 min. The reaction mixture was allowed to warm up to room temperature and added dropwise a solution of the previous compound (490 mg, 0.90 mmol) in EtOH (7.0 ml). After stirring for 3 h. at this temperature, the reaction mixture was diluted with CH_2Cl_2 and washed with water and dried over sodium sulfate, and the solvent was removed *in vacuo*. The product was used directly in the next reaction without further purification. ^1H NMR (300 MHz,

$CDCl_3$) δ 8.26 (dd, *J* = 1.5, 8.1 Hz, 1H), 7.44-7.49 (m, 1H), 7.23-7.34 (m, 2H), 6.76 (d, *J* = 7.8 Hz, 1H), 6.70 (d, *J* = 7.8 Hz, 1H), 6.37 (s, 1H), 5.30 (d, *J* = 46.2 Hz, 1H), 5.07 (br s, 1H), 3.67-4.08 (m, 3H), 2.95 (br s, 1H), 2.83 (t, *J* = 6.6 Hz, 1H), 1.78-2.05 (m, 6H), 1.75 (s, 3H), 1.71 (s, 3H), 1.46 (s, 9H)

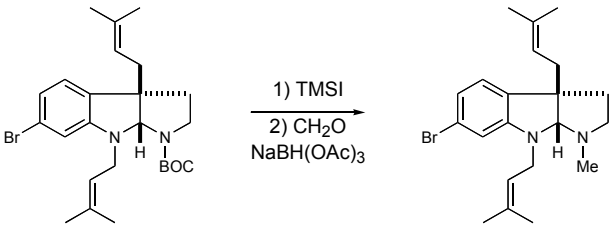
To a solution of selenide from the reaction above in THF (13 ml) at 0°C was added dropwise 30% H_2O_2 (0.46 ml, 4.5 mmol) and allowed to warm up to room temperature. After stirring for 20 min at this temperature, the reaction mixture was stirred for 2 h at 50°C and quenched with 10% $Na_2S_2O_4$ solution, and extracted with CH_2Cl_2. The combined extract was washed with brine, dried over sodium sulfate, concentrated, and purified by column chromatography (silica, 3–5% EtOAc in hexanes) to provide the title compound (364 mg, 90%) as a pale yellow oil; IR (thin film) 2965, 2926, 1700, 1601, 1490, 1395, 1366, 1245, 1162 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.80 (d, *J* = 7.8 Hz, 1H), 6.71 (dd, *J* = 7.8 Hz, 1H), 6.39 (s, 1H), 5.62 (dt, 1H, *J* = 7.2, 24.6 Hz), 5.32 (d, *J* = 31.5 Hz, 1H), 5.00-5.14 (m, 3H), 3.66-4.11 (m, 3H), 3.00 (dd, *J* = 6.0, 15.3 Hz, 1H), 2.49 (dd, *J* = 6.0, 13.8Hz, 1H), 2.37 (dd, *J* = 7.8, 13.8Hz, 1H), 1.98 (t, *J* = 5.1 Hz, 2H), 1.72 (s, 3H), 1.69 (s, 3H), 1.47 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.7, 153.9, 151.8, 151.5, 134.2, 133.8, 131.7, 124.1, 122.3, 121.7, 121.2, 119.7, 119.4, 118.7, 108.9, 84.9, 84.4, 80.6, 79.9, 56.8, 55.7, 45.8, 45.3, 44.1, 43.5, 37.9, 37.4, 28.8, 26.1, 18.5; HRMS (CI) exact mass calcd for ($C_{23}H_{31}BrN_2O_2$+Na^+) requires *m/z* 469.1466, found *m/z* 469.1471.; $[\alpha]_D^{24}$ = –159.5 (*c* = 1.0, $CHCl_3$).

(*S*)-6-Bromo-3a,8-bis-(3-methyl-but-2-enyl)-3,3a,8,8a-tetrahydro-2*H*-pyrrolo[2,3-*b*]indole-1-carboxylic acid *tert*-butyl ester. To a solution of Grubbs' catalyst (20 mg, 0.02 mmol) in CH_2Cl_2 (3.0 ml) were simultaneously added via syringe 3.1 ml of 2-methyl-2-butene and a solution of the previous compound (350 mg, 0.78 mmol) in CH_2Cl_2 (3.8 ml) at room temperature. The reaction mixture was warmed up at 40 °C and stirred for 1 h. The solvent and remained 2-methyl-2-butene were removed *in vacuo*. The crude material was purified by column chromatography (silica, 3% EtOAc in hexanes) to provide the title compound (350 mg, 94%) as a pale yellow oil; IR (thin film) 2973, 2927, 1700, 1601, 1490, 1447, 1394, 1365, 1249, 1217, 1158 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$)



δ 6.79 (d, *J* = 6.9 Hz, 1H), 6.70 (d, *J* = 6.6 Hz, 1H), 6.40 (s, 1H), 5.30 (d, *J* = 27.6 Hz, 1H), 5.10 (br s, 1H), 5.00 (br t, *J* = 7.2 Hz, 1H), 3.62-4.05 (m, 3H), 3.00 (br s, 1H), 2.36 (d, *J* = 7.2 Hz, 2H), 1.94-2.03 (m, 2H), 1.72 (s, 3H), 1.69 (s, 3H), 1.67 (s, 3H), 1.54 (s, 3H), 1.46 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.8, 154.0, 151.6, 151.3, 135.0, 134.2, 132.4, 123.9, 122.1, 121.6, 121.2, 119.7, 119.4, 109.0, 84.9, 84.6, 80.5, 79.8, 57.2, 56.1, 46.0, 45.3, 44.2, 43.9, 37.6, 37.4, 37.1, 28.8, 26.3, 26.1, 26.0, 18.4; HRMS (CI) exact mass calcd for ($C_{25}H_{35}BrN_2O_2$+Na $^+$) requires *m/z* 497.1779, found *m/z* 497.1796.; $[\alpha]_D^{29}$ = –169.5 (*c* = 1.0, $CHCl_3$).

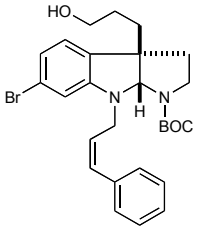
(*S*)-6-bromo-1-methyl-3a,8-bis-(3-methyl-but-2-enyl)-(3ar,8ac)-1,2,3,3a,8,8a-hexahydro-pyrrolo[2,3-*b*]indole, flustramine B. To a solution of the previous compound (55 mg, 0.11 mmol) in CH_3CN (1.32 ml) at 0^{o}C was added dropwise trimethylsilyl iodide (33 μl, 0.23 mmol). After stirring for 15 min. at this temperature, the reaction mixture was quenched with sat. $NaHCO_3$ solution, and extracted with CH_2Cl_2. The combined extract was washed with brine and dried over sodium sulfate, and the solvent was removed *in vacuo*. The product was used directly in the next reaction without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.81 (d, *J* = 7.5 Hz, 1H), 6.68 (dd, *J* = 1.8, 7.8 Hz, 1H), 6.40 (d, *J* = 1.8 Hz, 1H), 5.17 (br t, 1H, *J* = 7.2 Hz), 5.02 (br t, 1H, *J* = 7.8 Hz), 4.65 (s, 1H), 3.82 (dd, *J* = 7.2, 15.9 Hz, 1H), 3.74 (dd, *J* = 6.6, 15.3 Hz, 1H), 3.01 (ddd, 1H, *J* = 1.5, 6.6, 10.5 Hz), 2.68 (ddd, 1H, *J* = 6.0, 10.8, 17.1 Hz), 2.40 (d, *J* = 6.9 Hz, 2H), 1.84-1.96 (m, 2H), 1.73 (s, 6H), 1.70 (s, 3H), 1.57 (s, 3H)



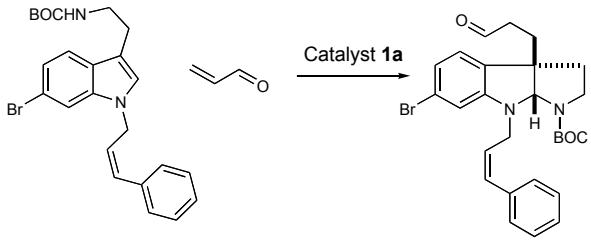
To a solution of amine from the reaction above in THF (1.2 ml) at –10^{o}C was added 37% formaldehyde (43 μl, 0.7 mmol) and sodium triacetoxyborohydride (148 mg, 0.7 mmol). The reaction mixture was warmed to room temperature, stirred for 30 min, quenched with water, and extracted with EtOAc. The combined extract was washed with 0.5 N KOH solution and brine, dried over sodium sulfate, concentrated, and purified by column chromatography (silica, 40–50% EtOAc in hexanes) to provide the title compound (38 mg, 89%) as a colorless oil; IR (thin film) 2963, 2927, 2854, 2789, 1560, 1485, 1444, 1345, 1250, 1124 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.79 (d, *J* = 8.4 Hz, 1H), 6.73 (dd, *J* = 1.8, 7.8 Hz, 1H), 6.49 (d, *J* = 1.8 Hz, 1H), 5.12 (br t, *J* = 6.3 Hz, 1H), 4.93 (br t, *J* = 7.8 Hz, 1H), 4.26 (s, 1H), 3.87 (dd, *J* = 6.0, 16.5 Hz, 1H), 3.79 (dd, *J* = 7.2, 16.2 Hz, 1H), 2.66 (ddd, 1H, *J* = 3.3, 6.6, 9.6 Hz), 2.55 (ddd, 1H, *J* = 6.0, 9.3,

15.0 Hz), 2.47 (s, 3H), 2.38 (d, *J* = 6.6 Hz, 2H), 1.82-2.07 (m, 2H), 1.71 (s, 6H), 1.65 (s, 3H), 1.56 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.2, 135.0, 134.9, 134.0, 124.2, 121.5, 120.5, 120.8, 120.5, 120.1, 110.2, 91.8, 57.1, 53.1, 46.6, 39.3, 38.6, 38.5, 26.3, 26.1, 18.5; HRMS (CI) exact mass calcd for ($C_{21}H_{29}BrN_2^+$) requires *m/z* 388.1514, found *m/z* 388.1519.; $[\alpha]_D^{22}$ = –93.9 (*c* = 1.6, $CHCl_3$). $[\alpha]_D^{23}$ = –93.5 (*c* = 1.5, EtOH). Lit. (3) $[\alpha]_D^{20}$ = –511 (*c* = 0.0039, EtOH).

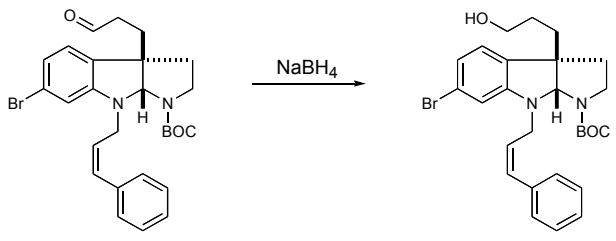
2. Determination of the absolute stereochemistry of (*S*)-6-bromo-3a-(3-hydoxy-propyl)-8-(3-phenyl-allyl)-3,3a,8,8a-tetrahydro-2*H*-pyrrolo[2,3-*b*]indole-1-carboxylic acid *tert*-butyl ester by x-ray crystallography.



(*S*)-6-Bromo-3a-(3-hydoxy-propyl)-8-(3-phenyl-allyl)-3,3a,8,8a-tetrahydro-2*H*-pyrrolo[2,3-*b*]indole-1-carboxylic acid *tert*-butyl ester. To a solution of compound *N*-10-BOC-1-(3-phenyl-allyl)-6-bromotryptamine (50 mg, 0.11 mmol), (*S,S*)-catalyst **1** (5.4 mg, 0.022 mmol), and trifluoroacetic acid (1.7 μl, 0.022 mmol) in CH_2Cl_2 (0.2 ml) at –60^{o}C was added acrolein (30 μl, 0.44 mmol). After stirring for 36 h at this temperature, the reaction mixture was quenched with saturated $NaHCO_3$ solution, and extracted with CH_2Cl_2. The combined extract was washed with brine, dried over sodium sulfate, and concentrated. The product was used directly in the next reaction without further purification.

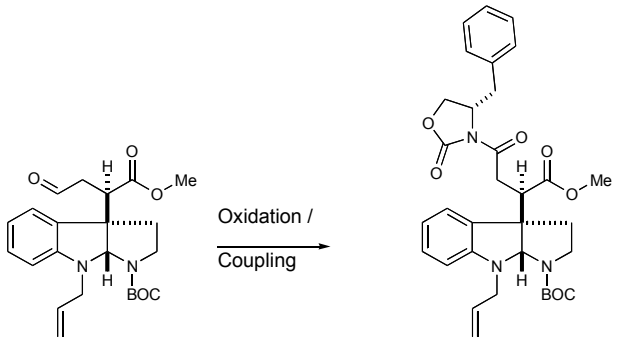


To a solution of amine from the reaction above in MeOH (0.2 ml) at 0^{o}C was added sodium borohydride (25 mg, 0.66 mmol). After stirring for 15 min at this temperature, the reaction mixture was quenched with 0.5 N HCl solution and extracted with EtOAc. The combined extract was washed with brine, dried over sodium sulfate, concentrated, and purified by column chromatography



(silica, 30% EtOAc/hexanes) to provide the title compound (33 mg, 58%) as a colorless, solid; 82% ee; IR (thin film) 3437, 2928, 1690, 1601, 1490, 1398, 1366, 1218, 1156, 1058 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.20-7.34 (m, 5H), 6.82 (d, *J* = 7.5 Hz, 1H), 6.75 (d, *J* = 7.5 Hz, 1H), 6.53 (d, *J* = 17.1 Hz, 1H), 6.50 (s, 1H), 6.11-6.22 (m, 1H), 5.37 (d, *J* = 46.5 Hz, 1H), 5.09 (br s, 1H), 3.70-4.23 (m, 3H), 3.54 (br d, *J* = 6.6 Hz, 2H), 2.97-3.11 (m, 1H), 1.21-2.09 (m, 6H), 1.45 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.8, 153.7, 151.7, 1374.2, 131.5, 131.2, 128.8, 128.6, 127.7, 127.5, 126.5, 125.8, 124.1, 122.4, 120.3, 119.9, 109.1, 108.9, 84.9, 84.6, 80.9, 80.2, 63.1, 57.3, 56.0, 45.7, 45.1, 39.0, 38.4, 36.2, 35.9, 28.9, 28.7; HRMS (CI) exact mass calcd for ($C_{27}H_{33}BrN_2O_3$ + H) requires *m/z* 513.1750, found *m/z* 513.1750. $[\alpha]_D^{26}$ = –116.2 (*c* = 3.3, $CHCl_3$). The enantiomeric purity was determined by HPLC with a Chiralcel ODH column and ODH guard column (4% EtOH/hexanes, 1 ml/min flow); t_r = 20.5 min and 22.2 min. This compound was crystallized from evaporation of deuterated chloroform. Coordinates and report are appended as JFA01.

3.Determination of the absolute stereochemistry of (2*S*,3*R*,3a*R*)-8-allyl-3a-(1-methoxycarbonyl-3-oxo-propyl)-3,3a,8,8a-tetrahydro-2*H*-pyrrolo[2,3-*b*]indole-1-carboxylic acid *tert*-butyl ester by derivatization to (2*S*,3*R*,3a*R*)-8-allyl-3a-[3-(4-(*S*)-benzyl-2-oxo-oxazolidin-3-yl)-1-methoxycarbonyl-3-oxo-propyl]-3,3a,8,8a-tetrahydro-2*H*-pyrrolo[2,3-*b*]indole-1-carboxylic acid *tert*-butyl ester and subsequent x-ray crystallography.



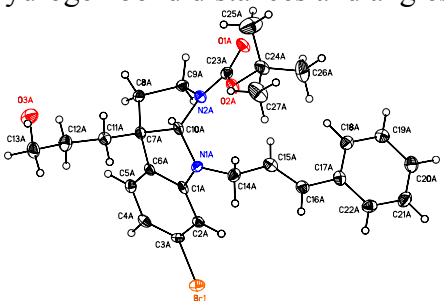
(2*S*,3*R*,3a*R*)-8-Allyl-3a-[3-(4-(*S*)-benzyl-2-oxo-oxazolidin-3-yl)-1-methoxycarbonyl-3-oxo-propyl]-3,3a,8,8a-tetrahydro-2*H*-pyrrolo[2,3-b]indole-1-carboxylic acid *tert*-butyl ester. (2*S*,3*R*,3a*R*)-8-Allyl-3a-(1-methoxycarbonyl-3-oxo-propyl)-3,3a,8,8a-tetrahydro-2H-pyrrolo[2,3-b]indole-1-carboxylic acid *tert*-butyl ester was dissolved in *tert*-butyl alcohol (4.5 ml) and 2-methyl-2-butene (1.2 ml) and subsequently was stirred for 10 min. To this solution was added an

aqueous solution (1.8 ml) of $NaClO_2$ (90.4 mg, 2.23 mmol) and NaH_2PO_4 (138 mg, 1.56 mmol) in one portion. The reaction mixture was stirred at room temperature for 2 h. The organics were removed by concentrating *in vacuo*. The residue was diluted with 5 ml of H_2O, and adjusted to a neutral pH with 1 M HCl. Extraction with EtOAc (3 x 10 ml), drying over Na_2SO_4, and concentration in vacuo provided (2*S*,3*R*,3a*R*)-2-(8-allyl-1-*tert*-butoxycarbonyl-2,3,8,8a-tetrahydro-1*H*-pyrrolo[2,3-*b*]indol-3a-yl)-succinic acid 1-methyl ester. This isolated residue was dissolved in THF (2 ml), TEA (65 µl, 0.468 mmol), and PivCl (27.5 µl, 0.223 mmol) and allowed to stir at room temperature for 15 min. To this solution was added LiCl (9.4 mg, 0.223 mmol) and (*S*)-4-benzyl-oxazolidin-2-one, which was stirred for an additional 8 h. The solution was diluted with 10 ml of H_2O, and adjusted to a neutral pH with 1 M HCl. Extraction with Et_2O (3 x 10 ml), drying over Na_2SO_4, and concentration *in vacuo* provided (2*S*,3*R*,3a*R*)-8-allyl-3a-[3-(4-(*S*)-benzyl-2-oxo-oxazolidin-3-yl)-1-methoxycarbonyl-3-oxo-propyl]-3,3a,8,8a-tetrahydro-2*H*-pyrrolo[2,3-b]indole-1-carboxylic acid tert-butyl ester. The resulting solid was crystallized from benzene/hexanes. Coordinates and report are appended as JFA03.

1. Perrin, D. D. & Armarego, W. L. F. (1988) *Purification of Laboratory Chemicals (*Pregamon Press, Oxford), 3rd Ed.
2. Still, W. C., Kahn, M. & Mitra, A. J. (1978) *J. Org. Chem.* **43,** 2923-2925.
3. Holst, P. B., Anthoni, U., Christophersen, C. & Nielsen, P. H. (1994) *J. Nat. Prod.* **57**, 997-1000.

Appendix 1

Contents



JFA01

Note: CCDC 197024 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. Structure factors are available from the authors via e-mail:xray@caltech.edu

Table 4. Crystal data and structure refinement for JFA01 (CCDC 197024)

Empirical formula	$C_{27}H_{33}BrN_2O_3$
Formula weight	513.46
Crystallization solvent	Hexanes/Dichloromethane
Crystal habit	Block
Crystal size	0.17 x 0.22 x 0.22 mm^3
Crystal color	Colorless

Data collection

Preliminary photos	Rotation
Type of diffractometer	Bruker smart 1000
Wavelength	0.71073 Å MoKα
Data collection temperature	98(2) K
θ range for 18,881 reflections used in lattice determination	2.45 to 28.05°
Unit cell dimensions	a = 8.8345(4) Å b = 15.4918(7) Å β= 97.229 (1)° c = 18.3034(9) Å
Volume	2485.1(2) $Å^3$
Z	4
Crystal system	Monoclinic
Space group	$P2_1$
Density (calculated)	1.372 g/cm^3
F(000)	1072
Data collection program	Bruker smart v5.054
θ range for data collection	1.73 to 28.37°
Completeness to θ = 28.37°	95.2 %
Index ranges	$-11 \le h \le 11$, $-20 \le k \le 20$, $-24 \le l \le 24$
Data collection scan type	ω scans at 7 ϕ settings
Data reduction program	Bruker saint v6.022
Reflections collected	51,296
Independent reflections	11,520 [R_{int}= 0.0576]
Absorption coefficient	1.685 mm^{-1}
Absorption correction	None

Table 4 (cont.)

Structure solution and refinement

Structure solution program	shelxs-97
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	shelxl-97
Refinement method	Full matrix least-squares on F^2
Data/restraints/parameters	11,520/1/603
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.255
Final R indices [I>2σ(I), 9,294 reflections]	$R^1 = 0.0330$, $wR^2 = 0.0561$
R indices (all data)	$R^1 = 0.0461$, $wR^2 = 0.0579$
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Maximum shift/error	0.002
Average shift/error	0.000
Largest difference peak and hole	0.984 and -0.316 e.Å^{-3}

Special Refinement Details

There are two molecules in the asymmetric unit. The conformation of each is very similar, with the exception of the propyl alcohol side group bonded to C7 (see Fig. 7 and Table 6). Hydrogen bonds are formed between the hydroxyl group of this side group and the carbonyl oxygen of the group bonded to N2. All hydrogen atoms were restrained to ride on the atom to which they are bonded and the temperature factor set to 1.2 times the U_{eq} (1.5 times for methyl hydrogens) of the bonded atom. Hydroxyl hydrogens were allowed to rotate about the C-O bond and methyl hydrogens to rotate about the C-C to optimize the fit to electron density.

Refinement of F^2 against ALL reflections. The weighted R factor (wR) and goodness of fit (S) are based on F^2, conventional R factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R factors(gt) etc. and is not relevant to the choice of reflections for refinement.

All estimated standard deviations (esds) (except the esd in the dihedral angle between two least squares (l.s.) planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles, and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

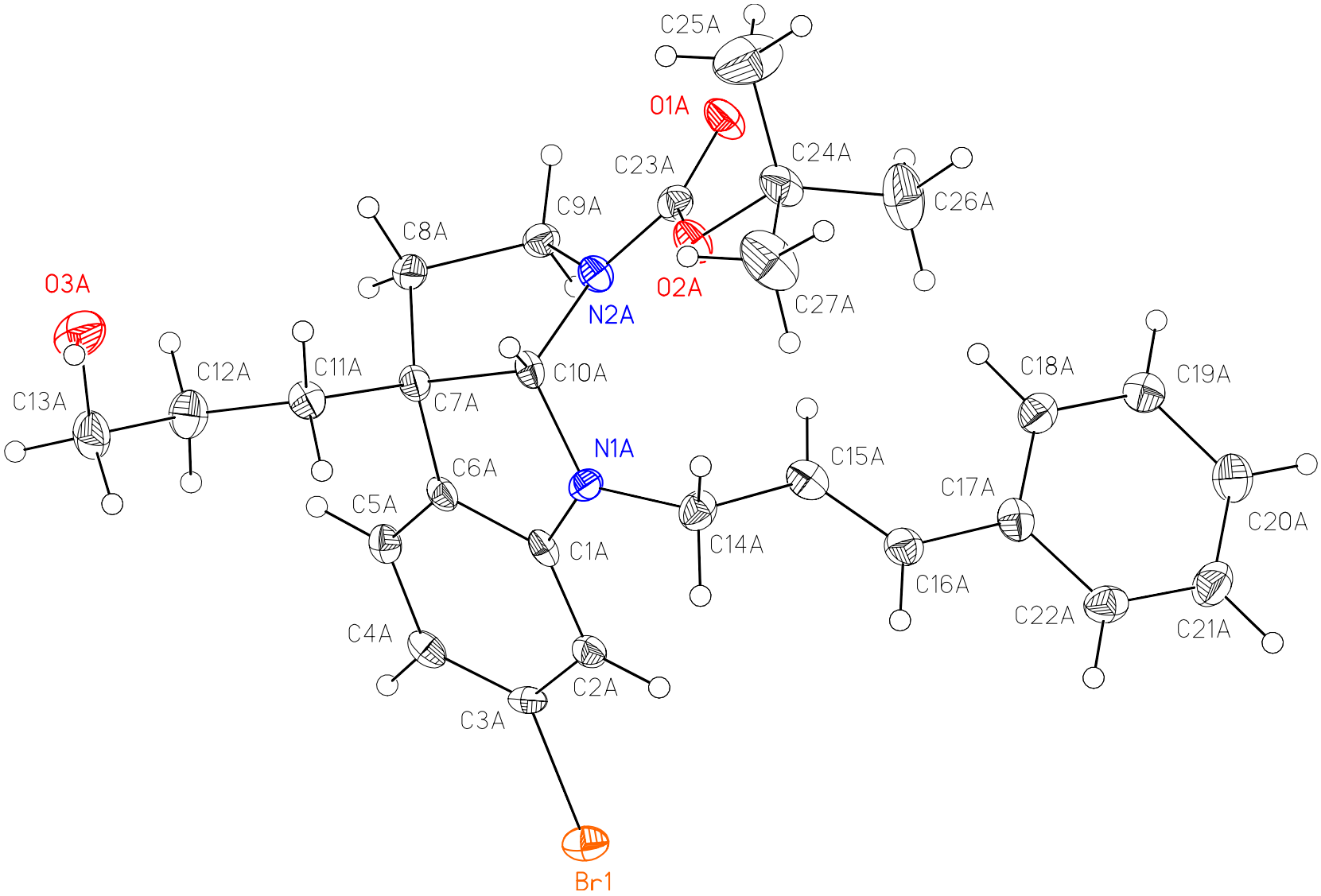


Figure 5. Molecule A of JFA01 with labels. Nonhydrogen atoms are shown with 50% probability ellipsoids.

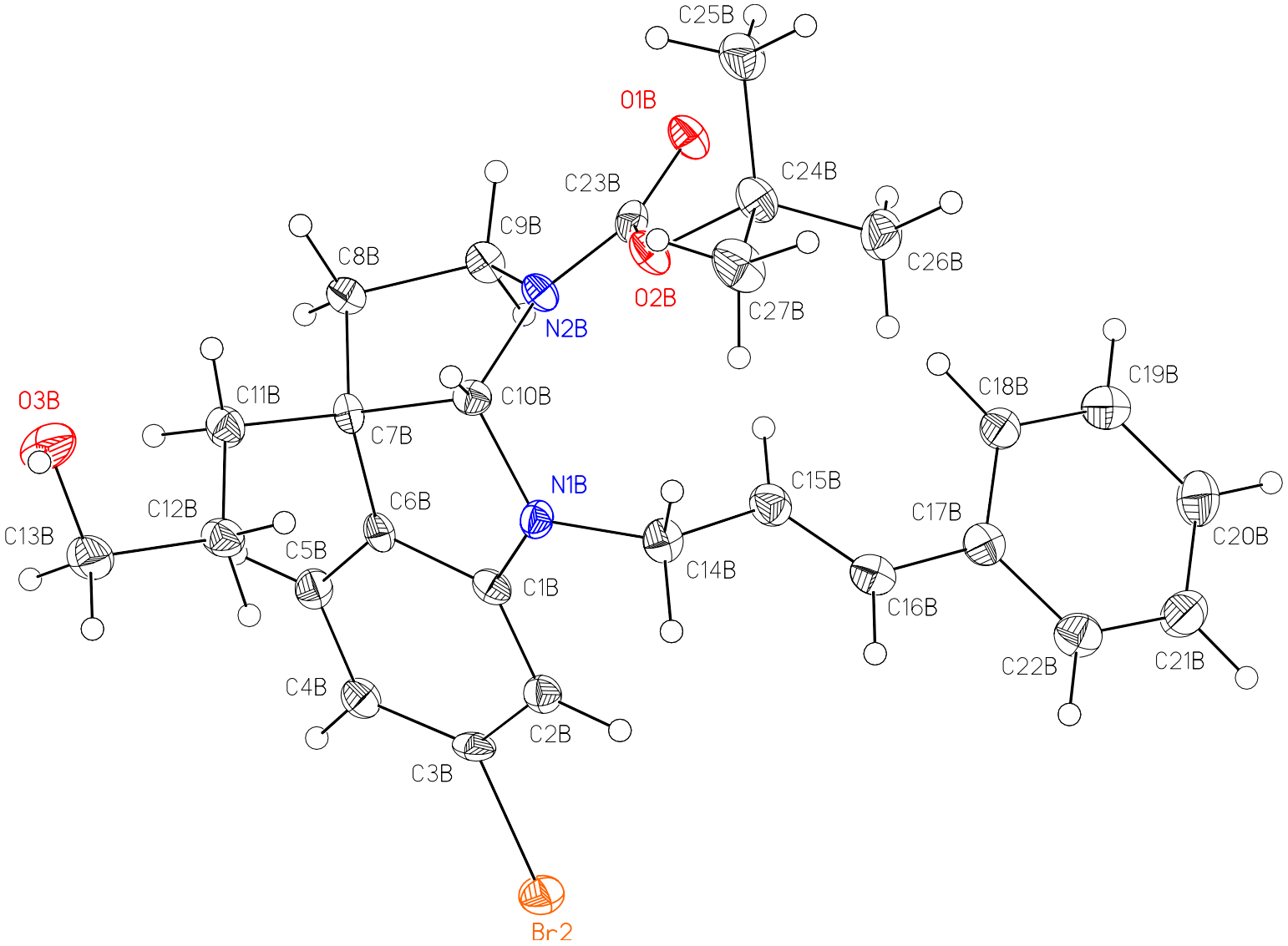


Figure 6. Molecule B of JFA01 with labels. Nonhydrogen atoms are shown with 50% probability ellipsoids.

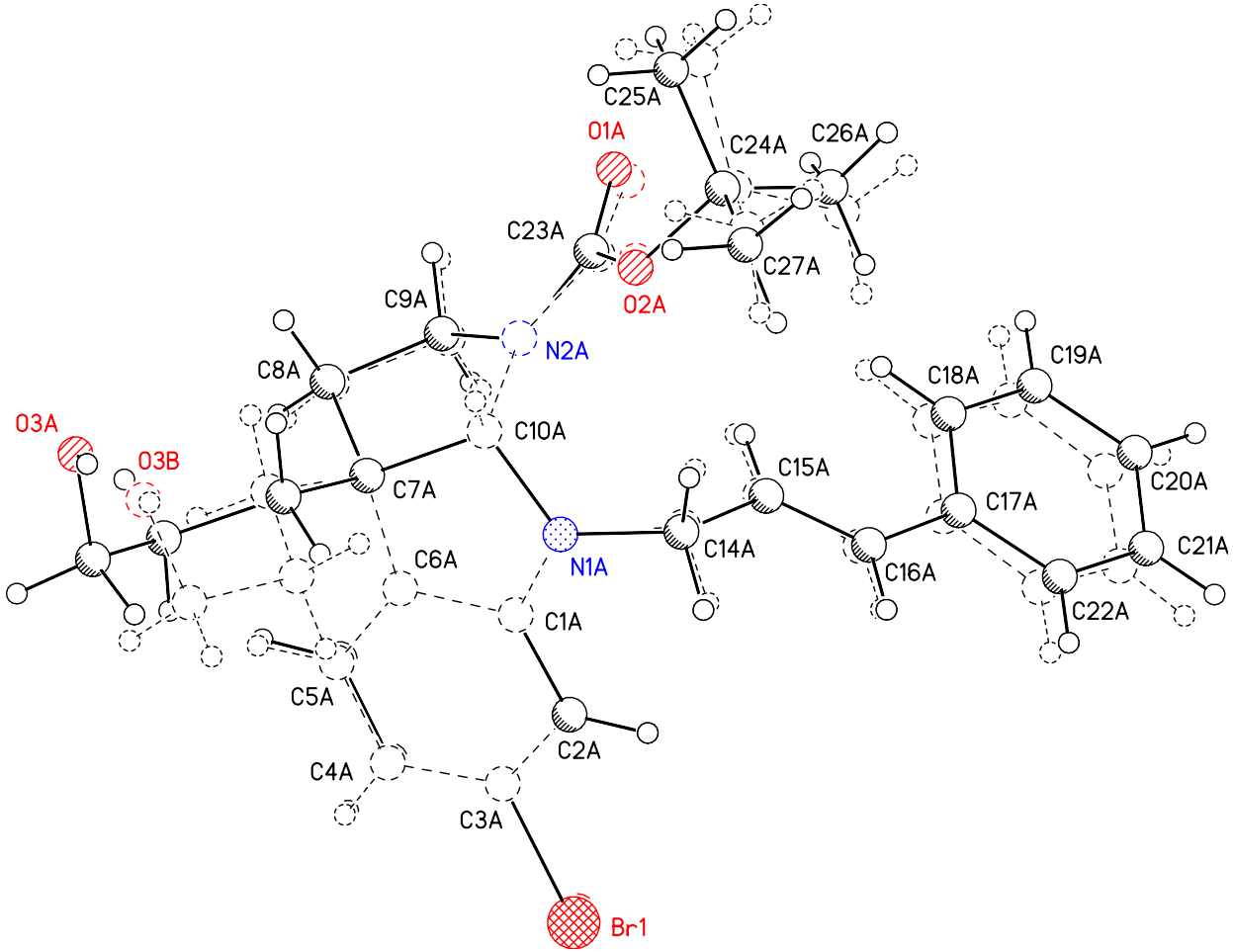


Figure 7. Molecule A and Molecule B of JFA01 superimposed on each other. Atoms N1, N2, and C1 through C10 (of both molecules) were used to define the overlap. Minor perturbations of the side groups bonded to N1 and N2 are evident. The largest difference can be seen in the torsion angles around the propyl alcohol side group bonded to C7 and terminated by the hydroxyl group at O3 (see Table 9).

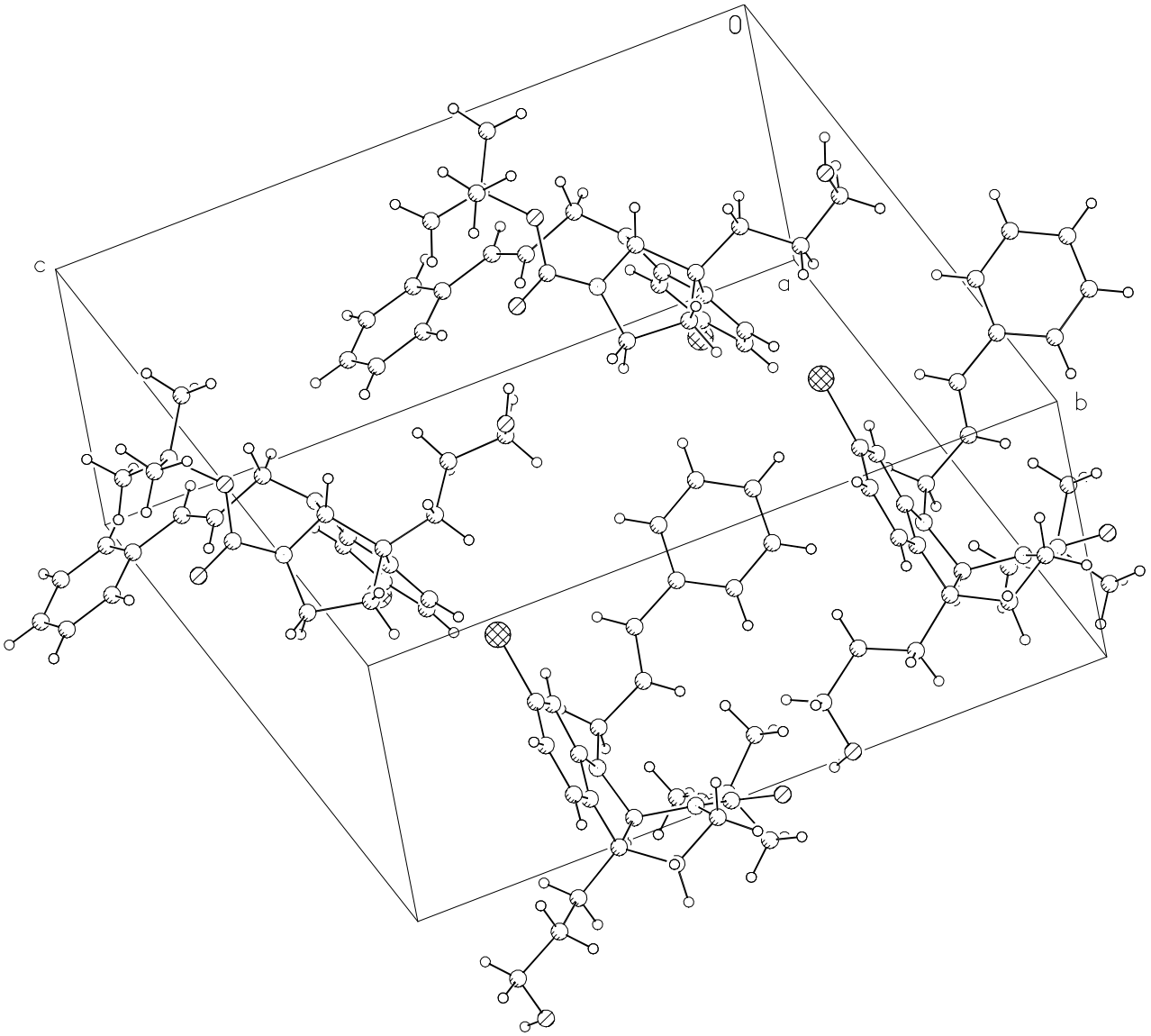


Figure 8. Unit cell contents of JFA01.

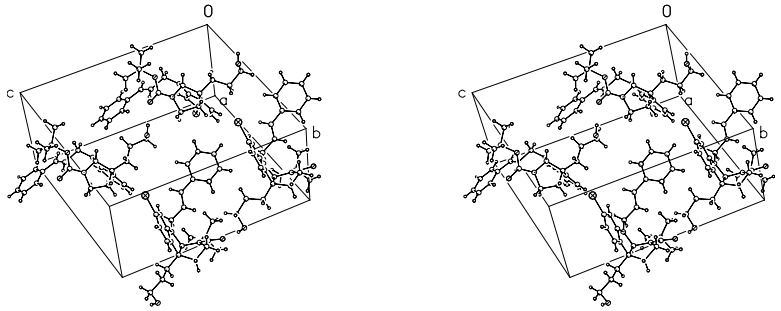


Figure 9. Stereo view of unit cell contents of JFA01.

Table 5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for JFA01 (CCDC 197024). U^{eq} is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U^{eq}
Br(1)	4290(1)	8079(1)	7556(1)	21(1)
O(1A)	11045(2)	9700(1)	4643(1)	23(1)
O(2A)	12094(2)	8675(1)	5443(1)	20(1)
O(3A)	13729(2)	10844(1)	8792(1)	32(1)
N(1A)	9773(2)	8481(1)	6688(1)	16(1)
N(2A)	10437(2)	9596(1)	5813(1)	16(1)
C(1A)	8489(3)	8759(2)	6989(1)	15(1)
C(2A)	7183(2)	8289(2)	7069(1)	16(1)
C(3A)	6082(3)	8706(2)	7418(1)	15(1)
C(4A)	6223(3)	9549(2)	7667(1)	17(1)
C(5A)	7542(3)	10004(2)	7562(1)	16(1)
C(6A)	8670(3)	9613(2)	7230(1)	15(1)
C(7A)	10220(3)	9943(2)	7069(1)	16(1)
C(8A)	10099(3)	10756(2)	6595(1)	18(1)
C(9A)	9604(3)	10422(2)	5808(1)	17(1)
C(10A)	10714(3)	9218(2)	6558(1)	15(1)
C(11A)	11392(3)	9998(2)	7770(1)	18(1)
C(12A)	11093(3)	10666(2)	8325(1)	25(1)
C(13A)	12299(3)	10626(2)	8997(1)	26(1)
C(14A)	9856(3)	7662(2)	6307(1)	20(1)
C(15A)	8885(3)	7614(2)	5563(1)	21(1)
C(16A)	8085(3)	6926(2)	5321(2)	20(1)
C(17A)	7203(3)	6809(2)	4593(1)	19(1)
C(18A)	7148(3)	7419(2)	4028(1)	21(1)
C(19A)	6281(3)	7286(2)	3356(1)	22(1)
C(20A)	5473(3)	6519(2)	3228(2)	27(1)
C(21A)	5522(3)	5906(2)	3783(2)	27(1)
C(22A)	6362(3)	6051(2)	4450(2)	22(1)
C(23A)	11184(3)	9358(2)	5245(1)	18(1)
C(24A)	12987(3)	8233(2)	4918(1)	23(1)
C(25A)	14125(4)	8850(2)	4664(2)	49(1)
C(26A)	11917(3)	7875(2)	4285(2)	41(1)
C(27A)	13755(4)	7523(2)	5389(2)	40(1)
Br(2)	10555(1)	3102(1)	7477(1)	22(1)
O(1B)	4125(2)	4801(1)	10400(1)	21(1)
O(2B)	2696(2)	3987(1)	9543(1)	19(1)
O(3B)	1307(2)	5642(1)	6120(1)	31(1)
N(1B)	5063(2)	3729(1)	8287(1)	16(1)
N(2B)	4519(2)	4817(1)	9198(1)	15(1)
C(1B)	6405(3)	3947(2)	8011(1)	15(1)
C(2B)	7642(3)	3425(2)	7927(1)	17(1)
C(3B)	8815(3)	3802(2)	7598(1)	16(1)
C(4B)	8803(3)	4646(2)	7356(1)	18(1)
C(5B)	7540(3)	5154(2)	7458(1)	18(1)
C(6B)	6367(3)	4815(2)	7792(1)	15(1)
C(7B)	4898(3)	5235(2)	7972(1)	16(1)

C(8B)	5227(3)	5985(2)	8516(1)	18(1)
C(9B)	5587(3)	5549(2)	9264(1)	18(1)
C(10B)	4212(3)	4506(2)	8432(1)	16(1)
C(11B)	3862(3)	5520(2)	7275(1)	19(1)
C(12B)	3430(3)	4809(2)	6728(1)	20(1)
C(13B)	2621(3)	5166(2)	6001(1)	26(1)
C(14B)	4911(3)	2923(2)	8674(1)	19(1)
C(15B)	5941(3)	2840(2)	9403(1)	21(1)
C(16B)	6704(3)	2133(2)	9618(1)	19(1)
C(17B)	7655(3)	1981(2)	10327(2)	19(1)
C(18B)	7799(3)	2574(2)	10910(1)	19(1)
C(19B)	8752(3)	2399(2)	11555(2)	23(1)
C(20B)	9544(3)	1636(2)	11644(2)	29(1)
C(21B)	9411(3)	1040(2)	11073(2)	28(1)
C(22B)	8478(3)	1217(2)	10427(2)	23(1)
C(23B)	3815(3)	4549(2)	9767(1)	17(1)
C(24B)	1873(3)	3506(2)	10079(1)	21(1)
C(25B)	975(3)	4129(2)	10506(2)	26(1)
C(26B)	2967(3)	2965(2)	10581(1)	29(1)
C(27B)	795(3)	2950(2)	9569(1)	30(1)

Table 6. Bond lengths [Å] and angles [°] for JFA01 (CCDC 197024)

Br(1)-C(3A)	1.901(2)	C(19A)-H(19A)	0.9500
O(1A)-C(23A)	1.215(3)	C(20A)-C(21A)	1.386(4)
O(2A)-C(23A)	1.351(3)	C(20A)-H(20A)	0.9500
O(2A)-C(24A)	1.484(3)	C(21A)-C(22A)	1.365(4)
O(3A)-C(13A)	1.404(3)	C(21A)-H(21A)	0.9500
O(3A)-H(3A)	0.8400	C(22A)-H(22A)	0.9500
N(1A)-C(1A)	1.390(3)	C(24A)-C(25A)	1.502(4)
N(1A)-C(10A)	1.450(3)	C(24A)-C(26A)	1.506(4)
N(1A)-C(14A)	1.455(3)	C(24A)-C(27A)	1.506(4)
N(2A)-C(23A)	1.351(3)	C(25A)-H(25A)	0.9800
N(2A)-C(10A)	1.475(3)	C(25A)-H(25B)	0.9800
N(2A)-C(9A)	1.476(3)	C(25A)-H(25C)	0.9800
C(1A)-C(2A)	1.388(3)	C(26A)-H(26A)	0.9800
C(1A)-C(6A)	1.397(3)	C(26A)-H(26B)	0.9800
C(2A)-C(3A)	1.388(3)	C(26A)-H(26C)	0.9800
C(2A)-H(2A)	0.9500	C(27A)-H(27A)	0.9800
C(3A)-C(4A)	1.384(3)	C(27A)-H(27B)	0.9800
C(4A)-C(5A)	1.395(3)	C(27A)-H(27C)	0.9800
C(4A)-H(4A)	0.9500	Br(2)-C(3B)	1.916(2)
C(5A)-C(6A)	1.372(3)	O(1B)-C(23B)	1.221(3)
C(5A)-H(5A)	0.9500	O(2B)-C(23B)	1.342(3)
C(6A)-C(7A)	1.525(3)	O(2B)-C(24B)	1.491(3)
C(7A)-C(8A)	1.526(3)	O(3B)-C(13B)	1.415(3)
C(7A)-C(11A)	1.547(3)	O(3B)-H(3B)	0.8400
C(7A)-C(10A)	1.558(3)	N(1B)-C(1B)	1.388(3)
C(8A)-C(9A)	1.540(3)	N(1B)-C(14B)	1.451(3)
C(8A)-H(8A1)	0.9900	N(1B)-C(10B)	1.461(3)
C(8A)-H(8A2)	0.9900	N(2B)-C(23B)	1.343(3)
C(9A)-H(9A1)	0.9900	N(2B)-C(9B)	1.470(3)
C(9A)-H(9A2)	0.9900	N(2B)-C(10B)	1.475(3)
C(10A)-H(10A)	1.0000	C(1B)-C(2B)	1.384(3)
C(11A)-C(12A)	1.497(3)	C(1B)-C(6B)	1.402(3)
C(11A)-H(11A)	0.9900	C(2B)-C(3B)	1.390(3)
C(11A)-H(11B)	0.9900	C(2B)-H(2B)	0.9500
C(12A)-C(13A)	1.523(3)	C(3B)-C(4B)	1.381(3)
C(12A)-H(12A)	0.9900	C(4B)-C(5B)	1.397(3)
C(12A)-H(12B)	0.9900	C(4B)-H(4B)	0.9500
C(13A)-H(13A)	0.9900	C(5B)-C(6B)	1.372(3)
C(13A)-H(13B)	0.9900	C(5B)-H(5B)	0.9500
C(14A)-C(15A)	1.517(3)	C(6B)-C(7B)	1.525(3)
C(14A)-H(14A)	0.9900	C(7B)-C(8B)	1.533(3)
C(14A)-H(14B)	0.9900	C(7B)-C(11B)	1.538(3)
C(15A)-C(16A)	1.323(3)	C(7B)-C(10B)	1.575(3)
C(15A)-H(15A)	0.9500	C(8B)-C(9B)	1.524(3)
C(16A)-C(17A)	1.467(4)	C(8B)-H(8B1)	0.9900
C(16A)-H(16A)	0.9500	C(8B)-H(8B2)	0.9900
C(17A)-C(18A)	1.398(3)	C(9B)-H(9B1)	0.9900
C(17A)-C(22A)	1.396(3)	C(9B)-H(9B2)	0.9900
C(18A)-C(19A)	1.381(3)	C(10B)-H(10B)	1.0000
C(18A)-H(18A)	0.9500	C(11B)-C(12B)	1.505(3)
C(19A)-C(20A)	1.391(4)	C(11B)-H(11C)	0.9900

C(11B)-H(11D)	0.9900	C(3A)-C(4A)-C(5A)	118.3(2)
C(12B)-C(13B)	1.533(3)	C(3A)-C(4A)-H(4A)	120.9
C(12B)-H(12C)	0.9900	C(5A)-C(4A)-H(4A)	120.9
C(12B)-H(12D)	0.9900	C(6A)-C(5A)-C(4A)	120.2(2)
C(13B)-H(13C)	0.9900	C(6A)-C(5A)-H(5A)	119.9
C(13B)-H(13D)	0.9900	C(4A)-C(5A)-H(5A)	119.9
C(14B)-C(15B)	1.521(3)	C(5A)-C(6A)-C(1A)	119.9(2)
C(14B)-H(14C)	0.9900	C(5A)-C(6A)-C(7A)	131.1(2)
C(14B)-H(14D)	0.9900	C(1A)-C(6A)-C(7A)	109.0(2)
C(15B)-C(16B)	1.321(3)	C(6A)-C(7A)-C(8A)	112.8(2)
C(15B)-H(15B)	0.9500	C(6A)-C(7A)-C(11A)	112.4(2)
C(16B)-C(17B)	1.473(4)	C(8A)-C(7A)-C(11A)	114.7(2)
C(16B)-H(16B)	0.9500	C(6A)-C(7A)-C(10A)	101.64(19)
C(17B)-C(22B)	1.388(3)	C(8A)-C(7A)-C(10A)	104.99(19)
C(17B)-C(18B)	1.402(3)	C(11A)-C(7A)-C(10A)	109.2(2)
C(18B)-C(19B)	1.388(3)	C(7A)-C(8A)-C(9A)	104.16(19)
C(18B)-H(18B)	0.9500	C(7A)-C(8A)-H(8A1)	110.9
C(19B)-C(20B)	1.374(4)	C(9A)-C(8A)-H(8A1)	110.9
C(19B)-H(19B)	0.9500	C(7A)-C(8A)-H(8A2)	110.9
C(20B)-C(21B)	1.389(4)	C(9A)-C(8A)-H(8A2)	110.9
C(20B)-H(20B)	0.9500	H(8A1)-C(8A)-H(8A2)	108.9
C(21B)-C(22B)	1.381(4)	N(2A)-C(9A)-C(8A)	101.73(19)
C(21B)-H(21B)	0.9500	N(2A)-C(9A)-H(9A1)	111.4
C(22B)-H(22B)	0.9500	C(8A)-C(9A)-H(9A1)	111.4
C(24B)-C(26B)	1.502(3)	N(2A)-C(9A)-H(9A2)	111.4
C(24B)-C(27B)	1.516(3)	C(8A)-C(9A)-H(9A2)	111.4
C(24B)-C(25B)	1.525(3)	H(9A1)-C(9A)-H(9A2)	109.3
C(25B)-H(25D)	0.9800	N(1A)-C(10A)-N(2A)	115.61(19)
C(25B)-H(25E)	0.9800	N(1A)-C(10A)-C(7A)	104.97(18)
C(25B)-H(25F)	0.9800	N(2A)-C(10A)-C(7A)	104.02(19)
C(26B)-H(26D)	0.9800	N(1A)-C(10A)-H(10A)	110.6
C(26B)-H(26E)	0.9800	N(2A)-C(10A)-H(10A)	110.6
C(26B)-H(26F)	0.9800	C(7A)-C(10A)-H(10A)	110.6
C(27B)-H(27D)	0.9800	C(12A)-C(11A)-C(7A)	116.4(2)
C(27B)-H(27E)	0.9800	C(12A)-C(11A)-H(11A)	108.2
C(27B)-H(27F)	0.9800	C(7A)-C(11A)-H(11A)	108.2
		C(12A)-C(11A)-H(11B)	108.2
C(23A)-O(2A)-C(24A)	122.26(19)	C(7A)-C(11A)-H(11B)	108.2
C(13A)-O(3A)-H(3A)	109.5	H(11A)-C(11A)-H(11B)	107.3
C(1A)-N(1A)-C(10A)	109.57(19)	C(11A)-C(12A)-C(13A)	110.8(2)
C(1A)-N(1A)-C(14A)	123.6(2)	C(11A)-C(12A)-H(12A)	109.5
C(10A)-N(1A)-C(14A)	122.91(19)	C(13A)-C(12A)-H(12A)	109.5
C(23A)-N(2A)-C(10A)	124.2(2)	C(11A)-C(12A)-H(12B)	109.5
C(23A)-N(2A)-C(9A)	121.6(2)	C(13A)-C(12A)-H(12B)	109.5
C(10A)-N(2A)-C(9A)	111.96(18)	H(12A)-C(12A)-H(12B)	108.1
C(2A)-C(1A)-N(1A)	127.6(2)	O(3A)-C(13A)-C(12A)	109.7(2)
C(2A)-C(1A)-C(6A)	121.8(2)	O(3A)-C(13A)-H(13A)	109.7
N(1A)-C(1A)-C(6A)	110.6(2)	C(12A)-C(13A)-H(13A)	109.7
C(1A)-C(2A)-C(3A)	116.4(2)	O(3A)-C(13A)-H(13B)	109.7
C(1A)-C(2A)-H(2A)	121.8	C(12A)-C(13A)-H(13B)	109.7
C(3A)-C(2A)-H(2A)	121.8	H(13A)-C(13A)-H(13B)	108.2
C(4A)-C(3A)-C(2A)	123.4(2)	N(1A)-C(14A)-C(15A)	114.6(2)
C(4A)-C(3A)-Br(1)	118.72(18)	N(1A)-C(14A)-H(14A)	108.6
C(2A)-C(3A)-Br(1)	117.85(18)	C(15A)-C(14A)-H(14A)	108.6

N(1A)-C(14A)-H(14B)	108.6	C(23B)-O(2B)-C(24B)	121.67(19)
C(15A)-C(14A)-H(14B)	108.6	C(13B)-O(3B)-H(3B)	109.5
H(14A)-C(14A)-H(14B)	107.6	C(1B)-N(1B)-C(14B)	121.5(2)
C(16A)-C(15A)-C(14A)	123.9(3)	C(1B)-N(1B)-C(10B)	110.43(19)
C(16A)-C(15A)-H(15A)	118.0	C(14B)-N(1B)-C(10B)	122.60(18)
C(14A)-C(15A)-H(15A)	118.0	C(23B)-N(2B)-C(9B)	122.0(2)
C(15A)-C(16A)-C(17A)	127.2(3)	C(23B)-N(2B)-C(10B)	126.0(2)
C(15A)-C(16A)-H(16A)	116.4	C(9B)-N(2B)-C(10B)	111.62(18)
C(17A)-C(16A)-H(16A)	116.4	C(2B)-C(1B)-N(1B)	128.5(2)
C(18A)-C(17A)-C(22A)	117.5(2)	C(2B)-C(1B)-C(6B)	121.3(2)
C(18A)-C(17A)-C(16A)	123.5(2)	N(1B)-C(1B)-C(6B)	110.2(2)
C(22A)-C(17A)-C(16A)	119.0(2)	C(1B)-C(2B)-C(3B)	116.4(2)
C(19A)-C(18A)-C(17A)	121.5(2)	C(1B)-C(2B)-H(2B)	121.8
C(19A)-C(18A)-H(18A)	119.2	C(3B)-C(2B)-H(2B)	121.8
C(17A)-C(18A)-H(18A)	119.2	C(4B)-C(3B)-C(2B)	124.1(2)
C(18A)-C(19A)-C(20A)	119.4(3)	C(4B)-C(3B)-Br(2)	118.21(18)
C(18A)-C(19A)-H(19A)	120.3	C(2B)-C(3B)-Br(2)	117.67(18)
C(20A)-C(19A)-H(19A)	120.3	C(3B)-C(4B)-C(5B)	117.6(2)
C(21A)-C(20A)-C(19A)	119.7(3)	C(3B)-C(4B)-H(4B)	121.2
C(21A)-C(20A)-H(20A)	120.2	C(5B)-C(4B)-H(4B)	121.2
C(19A)-C(20A)-H(20A)	120.2	C(6B)-C(5B)-C(4B)	120.3(2)
C(22A)-C(21A)-C(20A)	120.4(3)	C(6B)-C(5B)-H(5B)	119.8
C(22A)-C(21A)-H(21A)	119.8	C(4B)-C(5B)-H(5B)	119.8
C(20A)-C(21A)-H(21A)	119.8	C(5B)-C(6B)-C(1B)	120.1(2)
C(21A)-C(22A)-C(17A)	121.5(3)	C(5B)-C(6B)-C(7B)	130.1(2)
C(21A)-C(22A)-H(22A)	119.2	C(1B)-C(6B)-C(7B)	109.8(2)
C(17A)-C(22A)-H(22A)	119.2	C(6B)-C(7B)-C(8B)	111.5(2)
O(1A)-C(23A)-O(2A)	125.0(2)	C(6B)-C(7B)-C(11B)	112.1(2)
O(1A)-C(23A)-N(2A)	125.2(2)	C(8B)-C(7B)-C(11B)	111.46(19)
O(2A)-C(23A)-N(2A)	109.8(2)	C(6B)-C(7B)-C(10B)	101.80(19)
O(2A)-C(24A)-C(25A)	109.8(2)	C(8B)-C(7B)-C(10B)	104.52(19)
O(2A)-C(24A)-C(26A)	109.6(2)	C(11B)-C(7B)-C(10B)	114.8(2)
C(25A)-C(24A)-C(26A)	112.0(2)	C(9B)-C(8B)-C(7B)	104.4(2)
O(2A)-C(24A)-C(27A)	101.76(19)	C(9B)-C(8B)-H(8B1)	110.9
C(25A)-C(24A)-C(27A)	111.8(2)	C(7B)-C(8B)-H(8B1)	110.9
C(26A)-C(24A)-C(27A)	111.4(3)	C(9B)-C(8B)-H(8B2)	110.9
C(24A)-C(25A)-H(25A)	109.5	C(7B)-C(8B)-H(8B2)	110.9
C(24A)-C(25A)-H(25B)	109.5	H(8B1)-C(8B)-H(8B2)	108.9
H(25A)-C(25A)-H(25B)	109.5	N(2B)-C(9B)-C(8B)	102.1(2)
C(24A)-C(25A)-H(25C)	109.5	N(2B)-C(9B)-H(9B1)	111.3
H(25A)-C(25A)-H(25C)	109.5	C(8B)-C(9B)-H(9B1)	111.3
H(25B)-C(25A)-H(25C)	109.5	N(2B)-C(9B)-H(9B2)	111.3
C(24A)-C(26A)-H(26A)	109.5	C(8B)-C(9B)-H(9B2)	111.3
C(24A)-C(26A)-H(26B)	109.5	H(9B1)-C(9B)-H(9B2)	109.2
H(26A)-C(26A)-H(26B)	109.5	N(1B)-C(10B)-N(2B)	113.86(19)
C(24A)-C(26A)-H(26C)	109.5	N(1B)-C(10B)-C(7B)	104.60(18)
H(26A)-C(26A)-H(26C)	109.5	N(2B)-C(10B)-C(7B)	103.70(19)
H(26B)-C(26A)-H(26C)	109.5	N(1B)-C(10B)-H(10B)	111.4
C(24A)-C(27A)-H(27A)	109.5	N(2B)-C(10B)-H(10B)	111.4
C(24A)-C(27A)-H(27B)	109.5	C(7B)-C(10B)-H(10B)	111.4
H(27A)-C(27A)-H(27B)	109.5	C(12B)-C(11B)-C(7B)	114.7(2)
C(24A)-C(27A)-H(27C)	109.5	C(12B)-C(11B)-H(11C)	108.6
H(27A)-C(27A)-H(27C)	109.5	C(7B)-C(11B)-H(11C)	108.6
H(27B)-C(27A)-H(27C)	109.5	C(12B)-C(11B)-H(11D)	108.6

C(7B)-C(11B)-H(11D)	108.6	C(19B)-C(20B)-H(20B)	120.3
H(11C)-C(11B)-H(11D)	107.6	C(21B)-C(20B)-H(20B)	120.3
C(11B)-C(12B)-C(13B)	111.4(2)	C(22B)-C(21B)-C(20B)	119.8(3)
C(11B)-C(12B)-H(12C)	109.3	C(22B)-C(21B)-H(21B)	120.1
C(13B)-C(12B)-H(12C)	109.3	C(20B)-C(21B)-H(21B)	120.1
C(11B)-C(12B)-H(12D)	109.3	C(21B)-C(22B)-C(17B)	121.9(3)
C(13B)-C(12B)-H(12D)	109.3	C(21B)-C(22B)-H(22B)	119.1
H(12C)-C(12B)-H(12D)	108.0	C(17B)-C(22B)-H(22B)	119.1
O(3B)-C(13B)-C(12B)	110.9(2)	O(1B)-C(23B)-O(2B)	124.4(2)
O(3B)-C(13B)-H(13C)	109.5	O(1B)-C(23B)-N(2B)	124.5(2)
C(12B)-C(13B)-H(13C)	109.5	O(2B)-C(23B)-N(2B)	111.1(2)
O(3B)-C(13B)-H(13D)	109.5	O(2B)-C(24B)-C(26B)	110.5(2)
C(12B)-C(13B)-H(13D)	109.5	O(2B)-C(24B)-C(27B)	101.47(19)
H(13C)-C(13B)-H(13D)	108.1	C(26B)-C(24B)-C(27B)	111.4(2)
N(1B)-C(14B)-C(15B)	114.8(2)	O(2B)-C(24B)-C(25B)	110.5(2)
N(1B)-C(14B)-H(14C)	108.6	C(26B)-C(24B)-C(25B)	112.1(2)
C(15B)-C(14B)-H(14C)	108.6	C(27B)-C(24B)-C(25B)	110.4(2)
N(1B)-C(14B)-H(14D)	108.6	C(24B)-C(25B)-H(25D)	109.5
C(15B)-C(14B)-H(14D)	108.6	C(24B)-C(25B)-H(25E)	109.5
H(14C)-C(14B)-H(14D)	107.5	H(25D)-C(25B)-H(25E)	109.5
C(16B)-C(15B)-C(14B)	123.9(2)	C(24B)-C(25B)-H(25F)	109.5
C(16B)-C(15B)-H(15B)	118.0	H(25D)-C(25B)-H(25F)	109.5
C(14B)-C(15B)-H(15B)	118.0	H(25E)-C(25B)-H(25F)	109.5
C(15B)-C(16B)-C(17B)	127.5(3)	C(24B)-C(26B)-H(26D)	109.5
C(15B)-C(16B)-H(16B)	116.3	C(24B)-C(26B)-H(26E)	109.5
C(17B)-C(16B)-H(16B)	116.3	H(26D)-C(26B)-H(26E)	109.5
C(22B)-C(17B)-C(18B)	117.6(2)	C(24B)-C(26B)-H(26F)	109.5
C(22B)-C(17B)-C(16B)	118.9(2)	H(26D)-C(26B)-H(26F)	109.5
C(18B)-C(17B)-C(16B)	123.5(2)	H(26E)-C(26B)-H(26F)	109.5
C(19B)-C(18B)-C(17B)	120.4(2)	C(24B)-C(27B)-H(27D)	109.5
C(19B)-C(18B)-H(18B)	119.8	C(24B)-C(27B)-H(27E)	109.5
C(17B)-C(18B)-H(18B)	119.8	H(27D)-C(27B)-H(27E)	109.5
C(20B)-C(19B)-C(18B)	120.9(3)	C(24B)-C(27B)-H(27F)	109.5
C(20B)-C(19B)-H(19B)	119.5	H(27D)-C(27B)-H(27F)	109.5
C(18B)-C(19B)-H(19B)	119.5	H(27E)-C(27B)-H(27F)	109.5
C(19B)-C(20B)-C(21B)	119.3(3)		

Table 7. Anisotropic displacement parameters ($Å^2$ x 10^4) for JFA01 (CCDC 197024). The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$h^2 a^{*2} U^{11}$ + ... + 2 *h k a* b* U*^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	168(1)	227(1)	246(1)	57(2)	36(1)	-14(2)
O(1A)	318(11)	258(11)	131(10)	24(8)	46(8)	36(8)
O(2A)	210(10)	238(11)	159(10)	-13(8)	45(8)	79(8)
O(3A)	258(11)	334(13)	326(12)	73(9)	-82(9)	-69(9)
N(1A)	170(11)	142(11)	181(12)	-19(9)	51(10)	-32(9)
N(2A)	168(11)	182(11)	135(11)	9(9)	8(9)	19(9)
C(1A)	194(13)	174(14)	84(13)	-3(10)	12(11)	44(11)
C(2A)	199(12)	159(16)	123(12)	21(10)	18(10)	2(10)
C(3A)	134(13)	176(13)	151(14)	52(11)	28(10)	-17(10)
C(4A)	148(13)	237(14)	111(13)	39(11)	-3(10)	56(11)
C(5A)	194(14)	152(13)	135(14)	5(11)	-20(11)	38(11)
C(6A)	142(13)	211(14)	90(13)	-2(11)	-1(10)	-1(11)
C(7A)	162(13)	195(14)	134(13)	-27(11)	17(11)	-12(11)
C(8A)	208(14)	151(14)	184(14)	-21(11)	54(11)	-15(11)
C(9A)	183(14)	150(13)	185(14)	8(11)	34(11)	-7(11)
C(10A)	149(13)	190(14)	109(13)	-24(10)	-3(10)	14(11)
C(11A)	142(13)	215(15)	173(14)	-7(11)	18(11)	16(11)
C(12A)	232(15)	256(16)	247(16)	-36(12)	-21(12)	12(12)
C(13A)	279(16)	295(17)	181(15)	-22(12)	-49(12)	-2(13)
C(14A)	202(14)	163(14)	243(15)	-32(12)	46(12)	6(11)
C(15A)	209(14)	236(16)	192(14)	22(12)	39(11)	41(12)
C(16A)	211(15)	195(15)	208(15)	-13(11)	70(12)	13(11)
C(17A)	132(13)	249(15)	199(15)	-47(12)	32(11)	34(11)
C(18A)	188(14)	184(14)	260(16)	-35(12)	60(12)	9(11)
C(19A)	191(14)	232(15)	226(15)	9(12)	29(12)	11(12)
C(20A)	250(16)	329(18)	209(16)	-10(13)	-55(13)	-23(13)
C(21A)	228(15)	260(16)	306(17)	-52(13)	17(13)	-65(12)
C(22A)	234(15)	177(14)	272(16)	17(12)	84(12)	14(12)
C(23A)	146(13)	191(15)	194(15)	-20(11)	25(11)	-28(11)
C(24A)	278(14)	220(20)	224(13)	-16(13)	130(11)	78(13)
C(25A)	450(20)	311(19)	780(30)	-43(18)	390(20)	15(16)
C(26A)	522(19)	380(20)	311(17)	-136(14)	13(15)	97(15)
C(27A)	490(20)	385(19)	354(19)	4(15)	159(16)	246(16)
Br(2)	191(1)	237(1)	232(1)	-8(2)	51(1)	40(2)
O(1B)	242(10)	259(11)	126(10)	-9(8)	11(8)	-36(8)
O(2B)	198(10)	243(10)	140(9)	7(8)	45(8)	-73(8)
O(3B)	261(11)	318(12)	305(12)	-85(9)	-108(9)	109(9)
N(1B)	169(11)	129(11)	168(12)	26(9)	27(9)	-1(9)
N(2B)	146(11)	184(12)	107(11)	-12(9)	1(9)	-33(9)
C(1B)	146(13)	195(14)	110(13)	-31(10)	-7(10)	-22(11)
C(2B)	191(13)	164(13)	148(13)	-14(10)	7(11)	-16(11)
C(3B)	114(13)	229(15)	145(14)	-49(11)	25(10)	43(11)
C(4B)	172(13)	202(15)	168(14)	2(11)	37(11)	-30(11)
C(5B)	208(14)	156(14)	166(14)	-2(11)	11(11)	-24(11)
C(6B)	164(13)	179(14)	97(13)	14(10)	-14(10)	-9(10)
C(7B)	170(13)	169(14)	124(13)	37(10)	11(11)	-4(10)

C(8B)	189(14)	197(14)	160(14)	-2(11)	45(11)	3(11)
C(9B)	174(13)	192(14)	163(14)	0(11)	16(11)	-34(11)
C(10B)	131(13)	175(14)	160(14)	-10(11)	19(11)	3(11)
C(11B)	207(14)	204(15)	158(14)	-2(11)	-4(11)	-1(12)
C(12B)	185(14)	259(15)	166(14)	-21(11)	11(11)	30(12)
C(13B)	269(16)	305(17)	174(15)	-39(12)	-35(12)	38(13)
C(14B)	189(12)	182(17)	201(13)	5(11)	13(10)	-50(11)
C(15B)	237(14)	205(16)	200(14)	3(10)	56(11)	-31(11)
C(16B)	166(14)	218(15)	205(15)	-28(12)	46(11)	-54(12)
C(17B)	157(14)	194(15)	234(15)	18(11)	73(11)	-46(11)
C(18B)	168(14)	203(15)	221(15)	25(12)	66(11)	-5(11)
C(19B)	216(15)	223(15)	270(16)	-31(12)	64(12)	-42(12)
C(20B)	273(17)	327(18)	251(17)	61(13)	-42(13)	35(14)
C(21B)	300(17)	234(16)	302(17)	0(13)	20(14)	48(13)
C(22B)	242(15)	224(16)	231(15)	-41(12)	14(12)	-35(12)
C(23B)	149(13)	167(14)	188(15)	49(11)	4(11)	26(11)
C(24B)	192(13)	256(15)	188(14)	22(12)	46(11)	-50(12)
C(25B)	292(16)	256(16)	259(16)	25(12)	110(13)	-48(13)
C(26B)	313(14)	256(19)	308(15)	102(14)	128(12)	26(14)
C(27B)	339(15)	297(19)	292(14)	-4(14)	125(12)	-160(14)

Table 8. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for JFA01 (CCDC 197024).

	x	*y*	*z*	U^{iso}
H(3A)	14390	10496	8988	47
H(2A)	7051	7713	6895	19
H(4A)	5442	9811	7903	20
H(5A)	7659	10587	7722	20
H(8A1)	11095	11056	6625	21
H(8A2)	9331	11159	6751	21
H(9A1)	8486	10332	5717	21
H(9A2)	9916	10823	5433	21
H(10A)	11820	9078	6689	18
H(11A)	11441	9426	8014	21
H(11B)	12409	10112	7617	21
H(12A)	10072	10568	8479	30
H(12B)	11099	11246	8099	30
H(13A)	12031	11032	9378	31
H(13B)	12337	10036	9207	31
H(14A)	9535	7196	6624	24
H(14B)	10932	7553	6237	24
H(15A)	8850	8106	5252	25
H(16A)	8081	6458	5655	24
H(18A)	7720	7937	4109	25
H(19A)	6237	7716	2983	26
H(20A)	4891	6416	2764	32
H(21A)	4968	5383	3698	32
H(22A)	6376	5626	4825	27
H(25A)	13584	9311	4372	73
H(25B)	14786	8540	4361	73
H(25C)	14747	9100	5093	73
H(26A)	11243	7447	4469	61
H(26B)	12510	7601	3930	61
H(26C)	11304	8345	4042	61
H(27A)	14380	7775	5816	60
H(27B)	14406	7186	5100	60
H(27C)	12979	7146	5557	60
H(3B)	527	5394	5908	46
H(2B)	7688	2841	8085	20
H(4B)	9624	4874	7127	21
H(5B)	7493	5737	7296	21
H(8B1)	6106	6330	8397	22
H(8B2)	4327	6367	8507	22
H(9B1)	6660	5349	9347	21
H(9B2)	5393	5941	9669	21
H(10B)	3093	4431	8277	19
H(11C)	2917	5771	7424	23
H(11D)	4388	5980	7030	23
H(12C)	2749	4395	6938	25
H(12D)	4361	4494	6632	25
H(13C)	3330	5544	5770	31

H(13D)	2323	4683	5659	31
H(14C)	5137	2441	8350	23
H(14D)	3838	2861	8769	23
H(15B)	6040	3326	9721	25
H(16B)	6631	1668	9277	23
H(18B)	7242	3100	10862	23
H(19B)	8857	2814	11941	28
H(20B)	10175	1516	12092	35
H(21B)	9962	512	11126	34
H(22B)	8396	805	10040	28
H(25D)	1686	4480	10836	39
H(25E)	315	3800	10797	39
H(25F)	348	4506	10160	39
H(26D)	3505	2567	10286	43
H(26E)	2403	2634	10914	43
H(26F)	3709	3341	10870	43
H(27D)	86	3321	9256	45
H(27E)	218	2571	9862	45
H(27F)	1383	2599	9259	45

Table 9. Selected torsion angles [°] for JFA01 (CCDC 197024)

C(6A)-C(7A)-C(11A)-C(12A)	-68.1(3)
C(7A)-C(11A)-C(12A)-C(13A)	177.9(2)
C(11A)-C(12A)-C(13A)-O(3A)	64.7(3)
C(6B)-C(7B)-C(11B)-C(12B)	56.7(3)
C(7B)-C(11B)-C(12B)-C(13B)	-170.8(2)
C(11B)-C(12B)-C(13B)-O(3B)	-57.3(3)

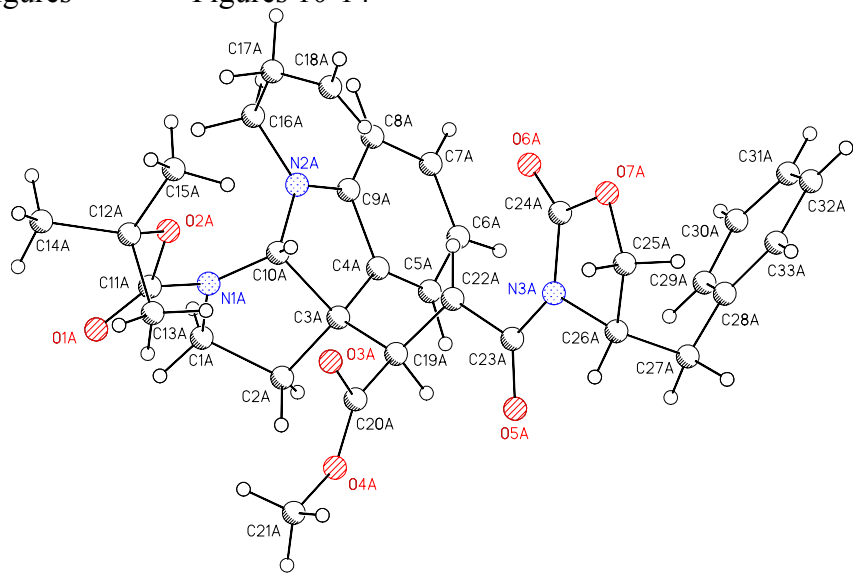
Table 10. Hydrogen bonds for JFA01 (CCDC 197024) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(3A)-H(3A)...O(1B)#1	0.84	1.94	2.772(2)	169.9
O(3B)-H(3B)...O(1A)#2	0.84	1.94	2.769(3)	170.8

Symmetry transformations used to generate equivalent atoms:
#1 -*x*+2,*y*+1/2,-*z*+2
#2 -*x*+1,*y*-1/2,-*z*+1

Appendix 2

Table 11. Crystal data
Figures Figures 10-14



JFA03

Note: CCDC 234570 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. Structure factors are available from the authors via e-mail:xray@caltech.edu

Table 12. Crystal data and structure refinement for JFA03 (CCDC 234570)

Empirical formula	$C_{33}H_{39}N_3O_7$
Formula weight	589.67
Crystallization solvent	Benzene/Hexane
Crystal habit	Blade
Crystal size	0.30 x 0.08 x 0.04 mm^3
Crystal color	Colorless

Data collection

Preliminary photos	Rotation
Type of diffractometer	Bruker smart 1000
Wavelength	0.71073 Å MoKα
Data collection temperature	100(2) K
θ range for 1808 reflections used in lattice determination	2.31 to 29.95°
Unit cell dimensions	a = 8.911(3) Å b = 35.439(11) Å β= 92.251(6)° c = 9.979(3) Å
Volume	3149.0(17) $Å^3$
Z	4
Crystal system	Monoclinic
Space group	$P2_1$
Density (calculated)	1.244 g/cm^3
F(000)	1,256
Data collection program	Bruker smart v5.054
θ range for data collection	2.04 to 28.40°
Completeness to θ = 28.40°	89.8 %
Index ranges	$-11 < h < 11$, $-31 < k < 45$, $-12 < l < 13$
Data collection scan type	ω scans at 3 ϕ settings
Data reduction program	Bruker saint v6.45
Reflections collected	19,204
Independent reflections	9,952 [R_{int}= 0.2073]
Absorption coefficient	0.088 mm^{-1}
Absorption correction	None
Maximum and minimum transmission	0.9965 and 0.9742

Table 12 (cont.)

Structure solution and refinement

Structure solution program	shelxs-97
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	shelxl -97
Refinement method	Full matrix least-squares on F^2
Data/restraints/parameters	9,952/1/353
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.511
Final *R* indices [I>2σ(I), 3250 reflections]	$R^1 = 0.1539$, $wR^2 = 0.2733$
R indices (all data)	$R^1 = 0.3072$, $wR^2 = 0.2968$
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Maximum shift/error	0.004
Average shift/error	0.000
Largest difference peak and hole	0.821 and -0.567 e.Å^{-3}

Special Refinement Details

The crystals were of low quality and diffracted poorly. As shown in Table 12, the measured intensities represent only 90% of the possible measurements and less than one-third of those were stronger than two times their sigma. Consequently, it was not possible to obtain a satisfactory refinement of the structure. The results of this structure determination are useful only for the verification of relative stereochemistry.

Refinement of F^2 against ALL reflections. The weighted *R* factor (*wR*) and goodness of fit (S) are based on F^2, conventional *R* factors (*R*) are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating *R* factors(gt) etc. and is not relevant to the choice of reflections for refinement.

All estimated standard deviations (esds) (except the esd in the dihedral angle between two least squares (l.s.) planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles, and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

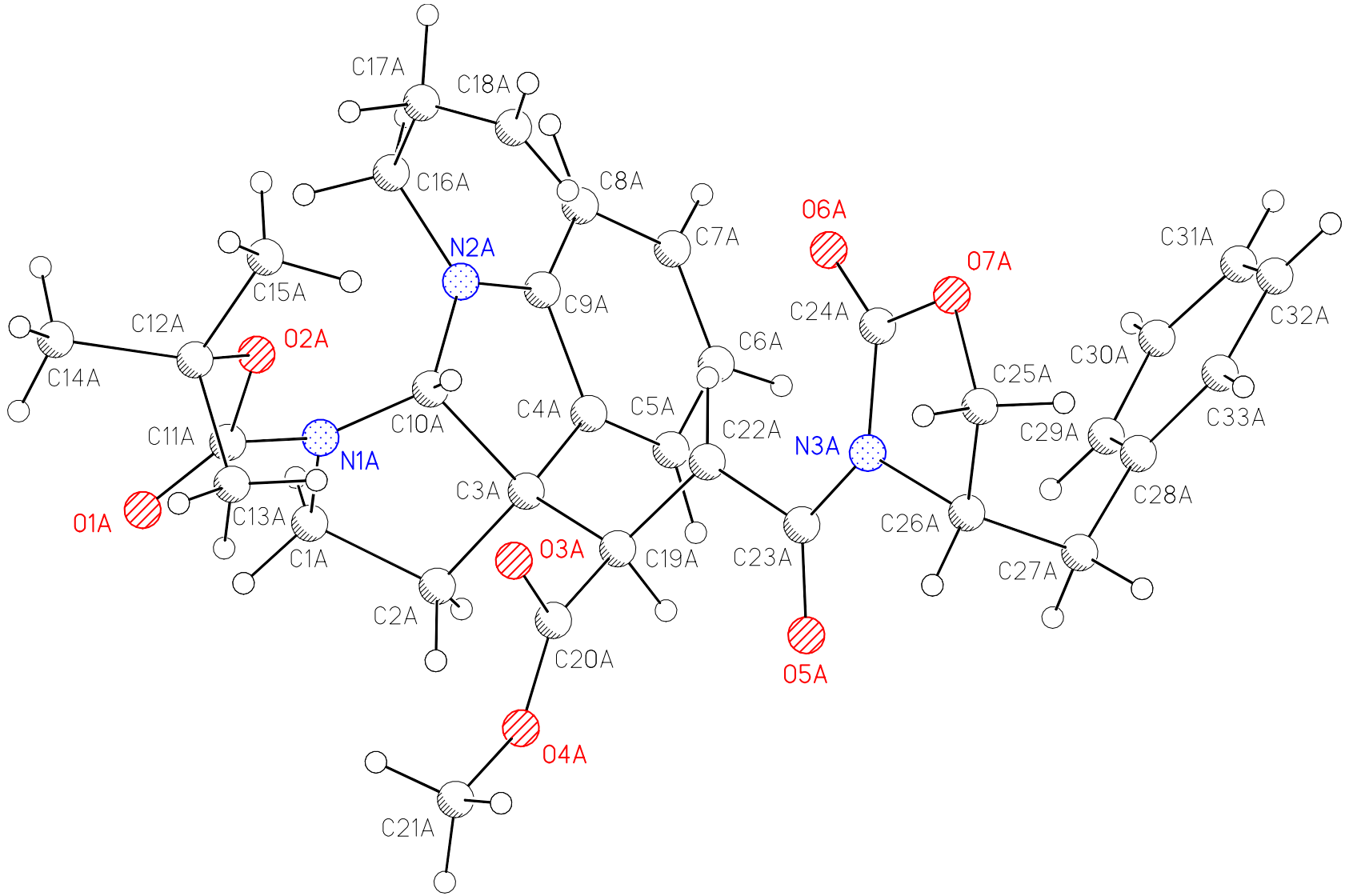


Figure 10. Molecule A of JFA03 with labels.

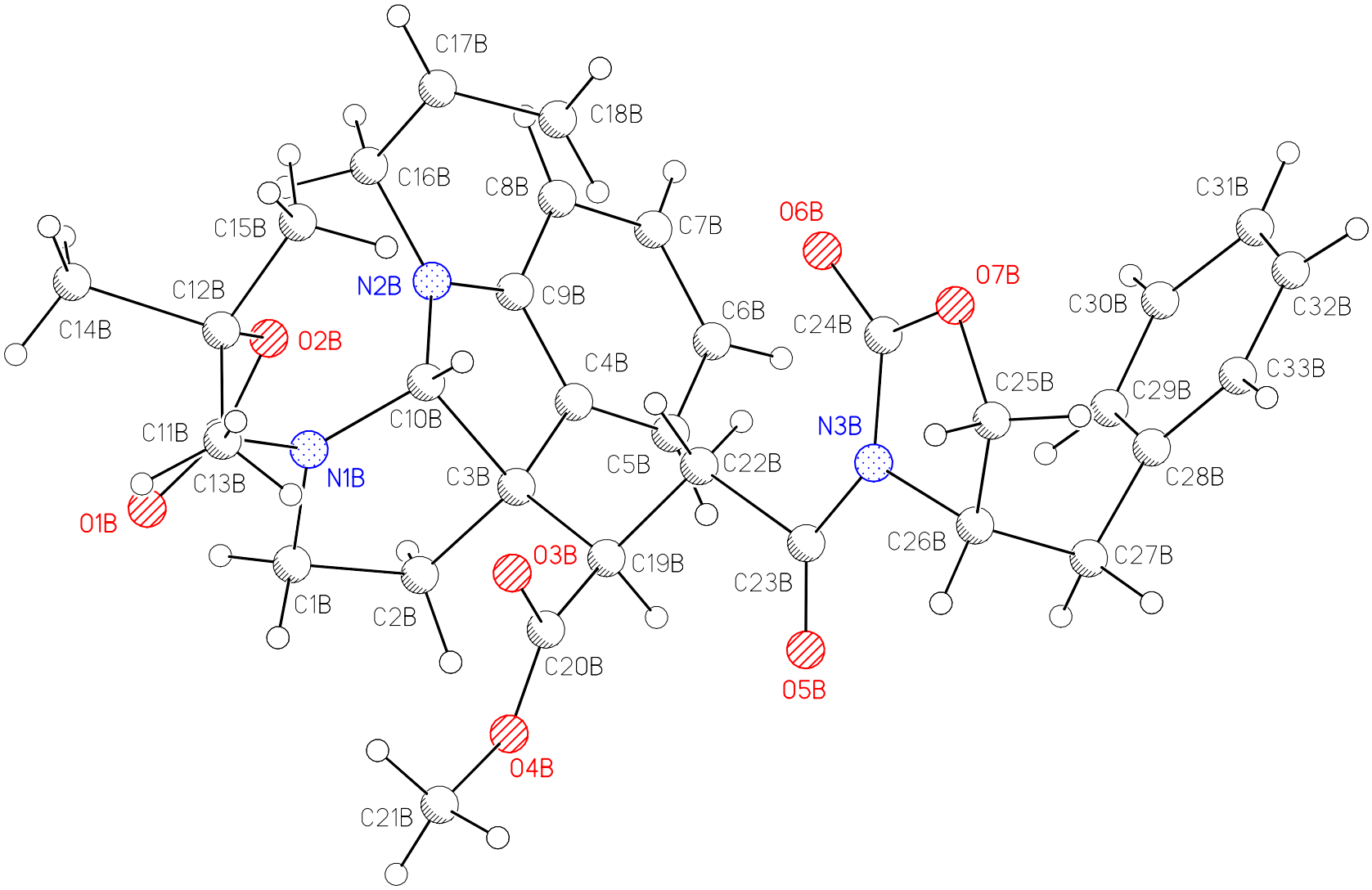


Figure 11. Molecule B of JFA03 with labels.

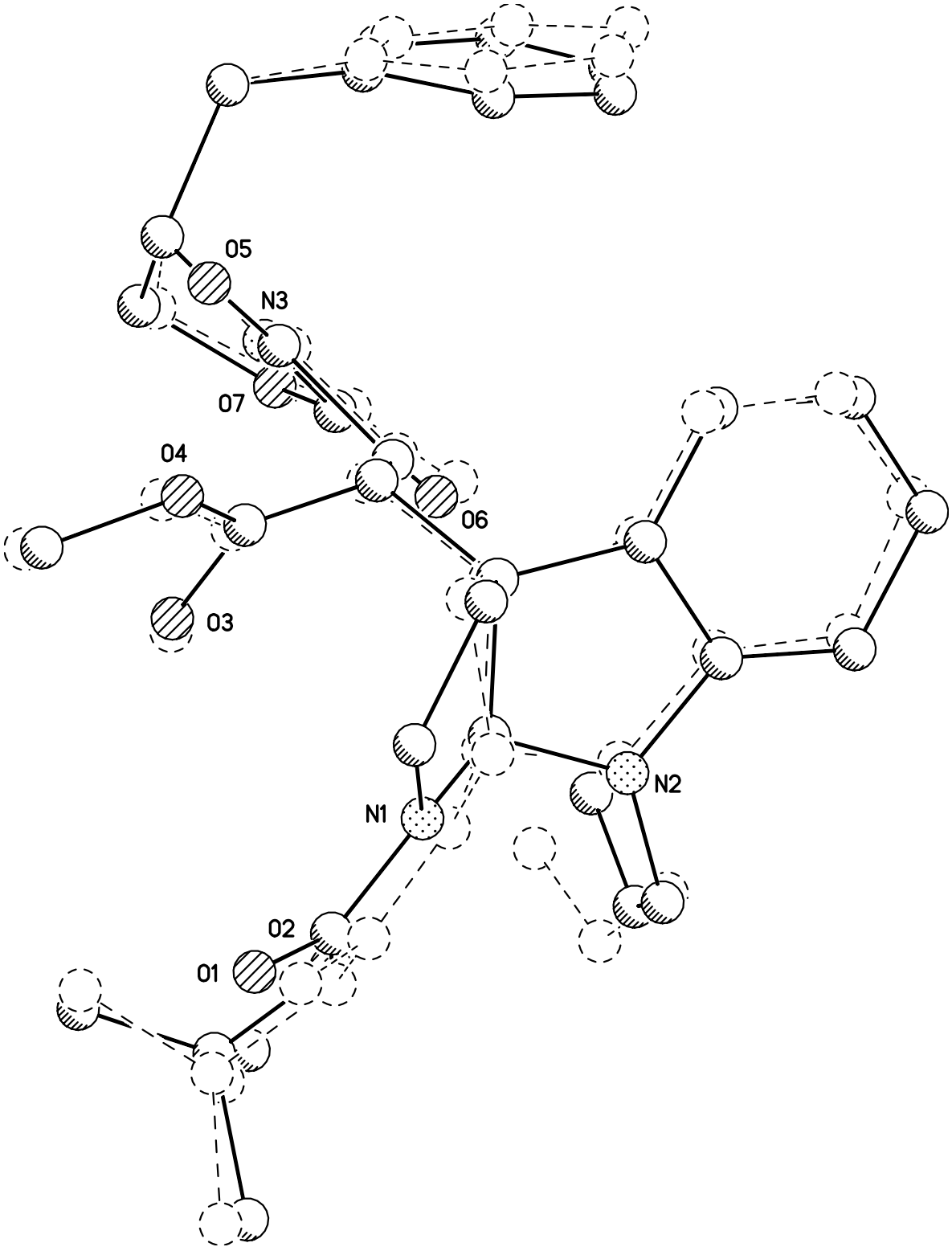


Figure 12. Superposition of molecules A and B of JFA03.

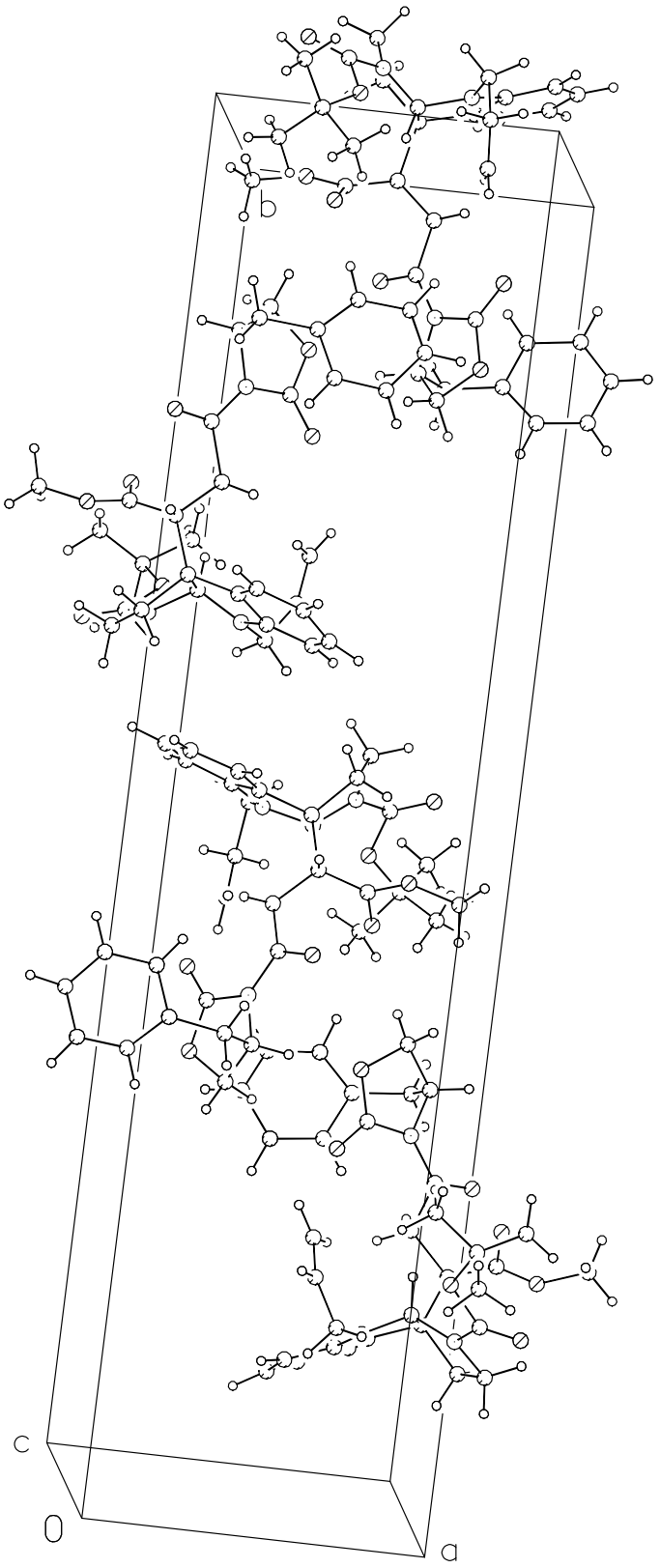


Figure 13. Unit cell contents of JFA03.

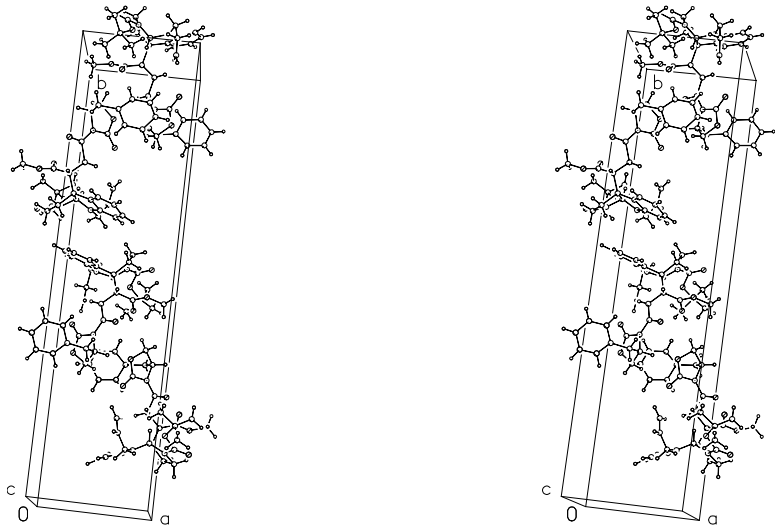


Figure 14. Stereo view of unit cell contents of JFA03.