SUPPLEMENTARY INFORMATION (Part 1)

Racemic Marinopyrrole B by Total Synthesis

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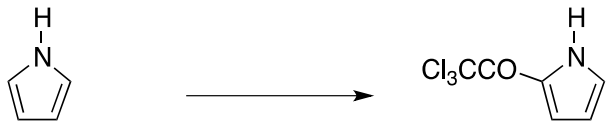
Experimental procedures for

2,2,2-Trichloro-1-(1*H*-pyrrol-2-yl)ethan-1-one (12).[16]

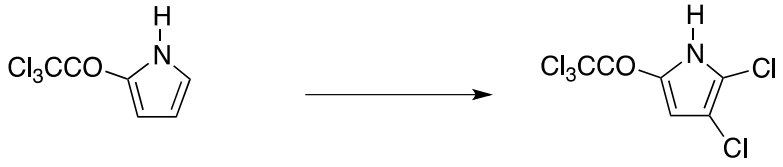


- **12**

Pyrrole (3.0 mL, 42.38 mmol) in Et_2O (19 mL) was added over 25 min at room temperature to a stirred solution of Cl_3CCOCl (4.2 mL, 37.25 mmol) in Et_2O (6 mL) in a flask equipped with a reflux condenser. The violet solution began to reflux slightly during the addition. The mixture was refluxed for an additional 3 h and then cooled to room temperature before being quenched with aqueous K_2CO_3 [K_2CO_3 (2.90 g) in water (9 mL)], which was added at a slow dropwise rate to avoid excessive bubbling. The organic phase was separated and the aqueous phase was extracted with Et_2O. The combined organic extracts were washed three times with water and brine, and dried (Na_2SO_4). The red solution was then treated with Norit (ca 250 mg) and filtered. The solvent was evaporated and the residue was recrystallized from hexanes to give **12** (6.02 g, 76%): FTIR (microscope) 3878, 3322, 3144, 3067, 2992, 2952, 1657 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 6.39 (dt, J = 4.5, 2.5 Hz, 1 H), 7.16-7.18 (m, 1 H), 7.38-7.40 (m, 1 H), 9.52 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 94.9 (s), 111.9 (d), 121.1 (d),

123.0 (s), 127.1 (d), 173.2 (s); exact mass *m*/*z* calcd for $C_6H_4Cl_3NNaO$ 233.92507, found 233.92536.

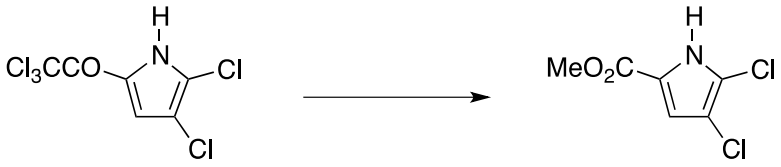
2,2,2-Trichloro-1-(4,5-dichloro-1*H*-pyrrol-2-yl)ethan-1-one (13).[17]



12 **13**

SO_2Cl_2 (2.18 mL, 26.32 mmol) was added to a stirred solution of **12** (2.54 g, 11.95 mmol) in $CHCl_3$ (6 mL). The mixture was refluxed for 30 h, cooled, poured into water (ca 10 mL) and extracted with CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (3.8 x 20 cm), using 1:100 to 3:100 Et_2O-hexanes, gave **13** (2.73 g, 81%) as a light brown solid: FTIR (microscope) 3378, 3271, 3163, 3140, 2994, 1656 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.32 (d, *J* = 3.0 Hz, 1 H), 9.93 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 94.0 (s), 113.3 (s), 120.3 (s), 120.5 (d), 123.7 (s), 172.3 (s); exact mass *m*/*z* calcd for $C_6H_2Cl_5NO$ 277.85063, found 277.85062.

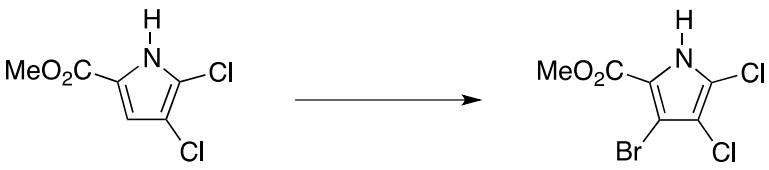
Methyl 4,5-dichloro-1*H*-pyrrole-2-carboxylate (14).[15,16]



13 **14**

A solution of **13** (1.26 g, 4.48 mmol) in MeOH (8 mL) was added to a stirred and cooled (0 °C) solution of MeONa (483.4 mg, 8.95 mmol) in MeOH (12 mL). Stirring at room temperature was continued for 13 h and most of the MeOH was then evaporated. The residue was partitioned between Et_2O and hydrochloric acid (1 M) and the aqueous phase was extracted with Et_2O. The combined organic extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (2.8 x 20 cm), using 1:20 to 1:10 EtOAc-hexanes, gave **14** (793.9 mg, 91%) as a white solid: mp 80-132 °C (sublimation); FTIR ($CDCl_3$, cast) 3252, 3127, 3013, 2960, 2899, 1702 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 3.89 (s, 3 H), 6.82 (d, J = 3.0 Hz, 1 H), 10.06 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 52.1 (q), 111.5 (s), 115.2 (d), 118.4 (s), 120.1 (s), 160.7 (s); exact mass m/z calcd for $C_6H_5{}^{35}Cl_2NO_2$ 192.96973, found 192.97013.

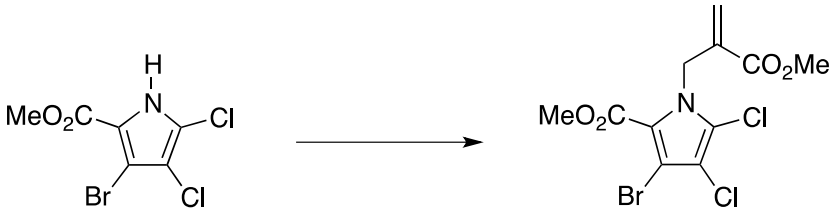
Methyl 3-bromo-4,5-dichloro-1*H*-pyrrole-2-carboxylate (7).



14 **7**

NBS (728.3 mg, 4.09 mmol) was added to a stirred solution of **14** (793.9 mg, 4.09 mmol) in MeCN (120 mL) at room temperature. The mixture was stirred for 14 h, and the solvent was then evaporated. The residue was partitioned between water and Et_2O and the aqueous phase was extracted with Et_2O. The combined organic extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (3.8 x 20 cm), using 1:10 to 3:20 EtOAc-hexanes, gave **7** (1.10 g, 98%) as a white solid: mp 130-166 °C (sublimation); FTIR ($CDCl_3$, cast) 3306, 3231, 3075, 3008, 2983, 2954, 1682, 1543, 1456 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 3.94 (s, 3 H), 9.86 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 52.3 (q), 104.0 (s), 114.0 (s), 117.9 (s), 118.8 (s), 159.7 (s); exact mass (electrospray) *m*/*z* calcd for $C_6H_3{}^{79}Br^{35}Cl_2NO_2$ (M – H) 269.873, found 269.8731.

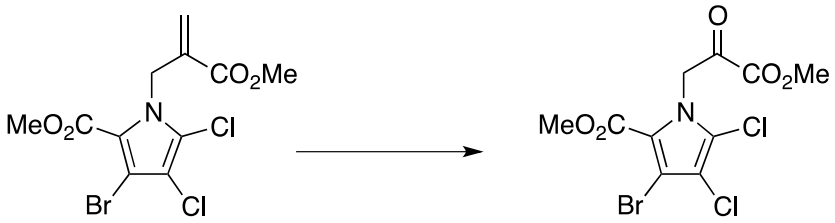
Methyl 3-bromo-4,5-dichloro-1-(3-methoxy-2-methylidene-3-oxo-propyl)-1*H*-pyrrole-2-carboxylate (16).



7 **16**

A solution of **15**[19] (321.3 mg, 1.98 mmol) in MeCN (5 mL) was added to a stirred suspension of **7** (337.3 mg, 1.24 mmol) and K_2CO_3 (690.0 mg, 4.94 mmol) in MeCN (20 mL). The mixture was refluxed for 42 h, then cooled, diluted with water and extracted with CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (2.8 x 20 cm), using 1:50 to 3:50 EtOAc-hexanes, gave **16** (436.0 mg, 95%) as a white solid: mp 108-112 °C; FTIR ($CDCl_3$, cast) 3003, 2954, 2846, 1716, 1644, 1519, 1439 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) (mixture of rotamers) δ 3.81 (s, 3 H), 3.840 and 3.844 (two s, 3 H), 4.92-4.93 (m, 1 H), 5.29-5.31 (m, 2 H), 6.24 (t, *J* = 1.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) (mixture of rotamers) δ 47.2 (t), 47.5 (t), 51.76 (q), 51.82 (q), 52.2 (q), 105.3 (s), 111.3 (s), 113.5 (s), 118.0 (s), 119.2 (s), 119.8 (s), 121.6 (s), 121.8 (s), 124.58 (t), 124.63 (t), 135.75 (s), 135.78 (s), 159.4 (s), 165.3 (s); exact mass (electrospray) *m*/*z* calcd for $C_{11}H_{10}{}^{79}Br^{35}Cl_2NNaO_4$ (M + Na) 391.9058, found 391.9062.

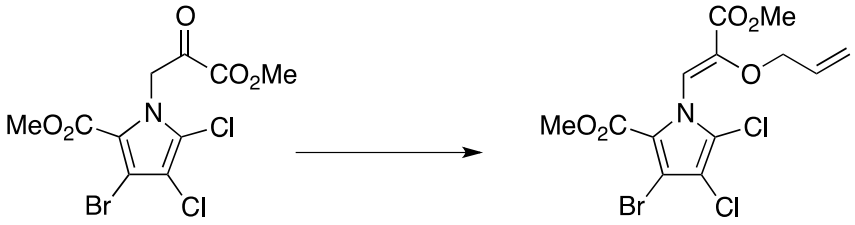
Methyl 3-bromo-4,5-dichloro-1-(3-methoxy-2,3-dioxopropyl)-1*H*-pyrrole-2-carboxylate (8).



16 **8**

A stream of ozonized oxygen was bubbled through a stirred and cooled (-78 °C) solution of **16** (1.17 g, 3.15 mmol) in CH_2Cl_2 (30 mL). After 18 min, the solution became blue. Then O_2 was allowed to bubble through the solution for 20 min to remove the excess of O_3. Me_2S (2.34 mL, 31.50 mmol) was then added, the cold bath was removed, and stirring was continued for 6.5 h. Evaporation of the solvent and flash chromatography of the residue over silica gel (3.8 x 20 cm), using 1:10 to 1:5 EtOAc-hexanes, gave **8** (1.07 g, 91%) as a white solid: mp 112-116 °C; FTIR ($CDCl_3$, cast) 3006, 2956, 2847, 1761, 1737, 1698, 1517, 1455 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 3.82-3.86 (m, 3 H), 3.96-4.00 (m, 3 H), 5.67 (s, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 52.0 (q), 53.5 (q), 53.6 (t), 105.9 (s), 113.9 (s), 119.5 (s), 122.0 (s), 159.7 (s), 160.1 (s), 185.1 (s); exact mass (electrospray) *m*/*z* calcd for $C_{10}H_8{}^{79}Br^{35}Cl_2NNaO_5$ (M + Na) 393.8858, found 393.8855.

Methyl 3-bromo-4,5-dichloro-1-[(1*E*)-3-methoxy-3-oxo-2-(prop-2-en-1-yloxy)prop-1-en-1-yl]-1*H*-pyrrole-2-carboxylate (17).

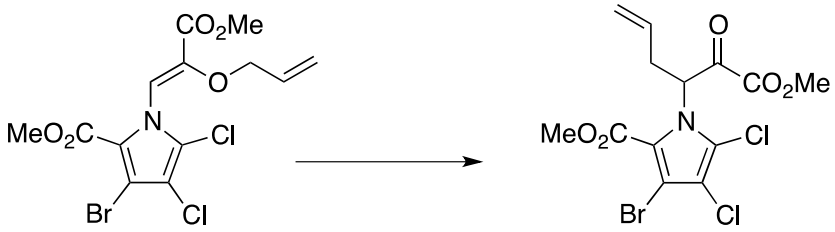


8 **17**

NaH (115.3 mg, 60% in oil, 2.88 mmol) was added to a stirred and cooled (-42 °C) solution of **8** (808.1 mg, 2.17 mmol) in DMF (20 mL). After 20 min,

allyl bromide (0.23 mL, 2.63 mmol) was added, and stirring was continued for 1.5 h, during which time the temperature was allowed to slowly reach room temperature. Stirring was continued for a further 6 h, water was then added and the mixture was extracted with Et_2O. The combined organic extracts were washed with water, dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (2.8 x 20 cm), using 1:25 to 1:10 EtOAc-hexanes, gave **17** (618.3 mg, 69%) as a white solid: mp 72-74 °C; FTIR ($CDCl_3$, cast) 3104, 3000, 2954, 1733, 1714, 1654, 1525, 1457 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 3.88 (s, 3 H), 3.90 (s, 3 H), 4.37 (ddd, J = 1.0, 1.5, 6.0 Hz, 2 H), 5.15-5.20 (m, 2 H), 5.72 (ddd, J = 6.0, 10.5, 17.0 Hz, 1 H), 7.30 (s, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 51.9 (q), 52.7 (q), 73.1 (t), 105.8 (s), 114.5 (s), 119.1 (t), 119.5 (d), 121.2 (s), 121.3 (s), 132.4 (d), 143.3 (s), 159.2 (s), 162.9 (s); exact mass (electrospray) m/z calcd for $C_{13}H_{12}{}^{79}Br^{35}Cl_2NNaO_5$ (M + Na) 433.9164, found 433.9168. A sample was crystallized from i-Pr_2O for X-ray analysis.

Methyl 3-bromo-4,5-dichloro-1-(1-methoxy-1,2-dioxohex-5-en-3-yl)-1*H*-pyrrole-2-carboxylate (9).

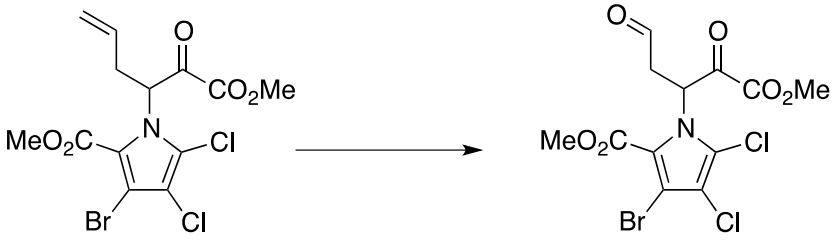


17 **9**

A solution of **17** (862.7 mg, 2.09 mmol) in PhMe (10.5 mL) was stirred and refluxed for 16 h and then cooled to room temperature. Evaporation of the solution gave **9** as a light yellow solid, which was used directly in the next step.

In an earlier experiment, the solid was purified by flash chromatography over silica gel, using 1:25 to 1:10 EtOAc-hexanes to give pure **9**: mp 104-106 °C; FTIR ($CDCl_3$, cast) 3464, 3082, 3005, 2955, 2850 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 2.63 (dt, J = 15.0, 4.0 Hz, 1 H), 3.16-3.22 (m, 1 H), 3.81 (s, 3 H), 3.90 (s, 3 H), 4.99-5.05 (m, 2 H), 5.53-5.62 (m, 1 H), 5.85 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 34.7 (t), 52.1 (q), 53.2 (q), 64.0 (d), 106.8 (s), 114.3 (s), 119.1 (s), 119.9 (s), 131.5 (d), 160.2 (s), 161.2 (s), 186.4 (s); exact mass (electrospray) *m*/*z* calcd for $C_{13}H_{12}{}^{79}Br^{35}Cl_2NNaO_5$ (M + Na) 433.9168, found 433.9161.

Methyl 3-bromo-4,5-dichloro-1-(1-methoxy-1,2,5-trioxopentan-3-yl)-1*H*-pyrrole-2-carboxylate (10).

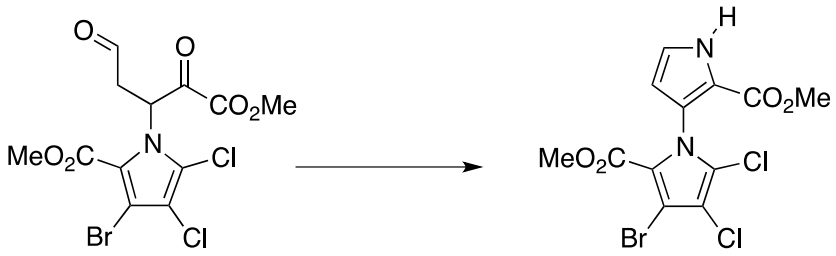


9 **10**

The above crude ketoester **9** was dissolved in MeOH (10 mL) and CH_2Cl_2 (10 mL). A stream of ozonized oxygen was bubbled through the stirred and cooled (−78 °C) solution. After 12 min, the solution became blue and O_2 was

then bubbled through the solution for 15 min to remove the excess of ozone. Ph_3P (1.11 g, 4.19 mmol) was added, the cooling bath was left in place but not recharged and stirring was continued for 14 h. Evaporation of the solution gave aldehyde **10** [^{1}H NMR ($CDCl_3$, 500 MHz) signal at δ 9.8] as a yellow residue, which was used directly in the next step.

Methyl 3-bromo-4,5-dichloro-1-[2-(methoxycarbonyl)-1*H*-pyrrol-3-yl]-1*H*-pyrrole-2-carboxylate (11).

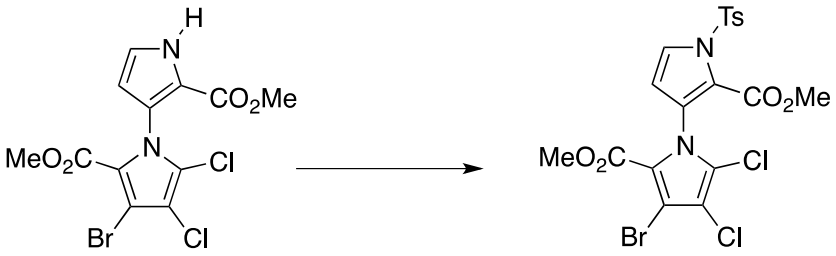


10 **11**

NH_4OAc (2.57 g, 33.3 mmol) was added to a stirred solution of the above crude ketoaldehyde **10** in AcOH (14 mL) and stirring was continued for 30 min. Saturated aqueous NH_4Cl was then added and the mixture was extracted with CH_2Cl_2. The combined organic extracts were washed with saturated aqueous $NaHCO_3$ and brine, dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (2.8 x 25 cm), using 1:10 to 3:10 EtOAc-hexanes, gave **11** (504.5 mg, 61% over three steps) as a light yellow solid: mp 188-190 °C; FTIR ($CDCl_3$, cast) 3309, 3141, 3004, 2953, 2847, 2256, 1707, 1581, 1523, 1504, 1445

cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.73 (s, 3 H), 3.77 (s, 3 H), 6.29 (d, J = 3.0 Hz, 1 H), 6.98 (d, J = 3.0 Hz, 1 H), 9.53 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 51.6 (q), 51.9 (q), 105.3 (s), 110.9 (d), 113.5 (s), 118.2 (s), 121.2 (d), 121.8 (s), 122.8 (s), 125.6 (s), 159.2 (s), 159.8 (s); exact mass (electrospray) m/z calcd for $C_{12}H_9{}^{79}Br^{35}Cl_2N_2NaO_4$ (M + Na) 416.9015, found 416.9008. A sample was crystallized from $CHCl_3$ for X-ray analysis.

Methyl 3-bromo-4,5-dichloro-1-[2-(methoxycarbonyl)-1-[(4-methyl-benzene)sulfonyl]-1*H*-pyrrol-3-yl]-1*H*-pyrrole-2-carboxylate (18).

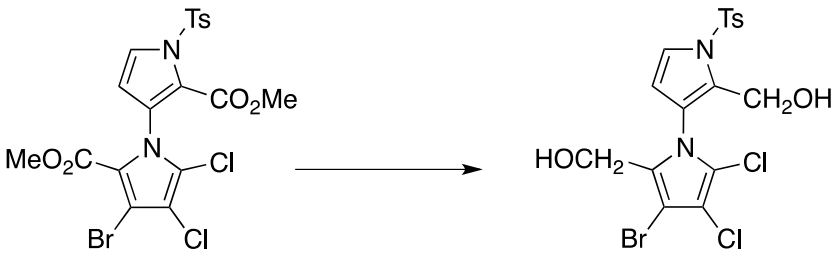


11 **18**

DMAP (286.5 mg, 2.32 mmol) and *i*-Pr_2NEt (0.41 mL, 2.35 mmol) were added to a stirred and cooled (0 °C) solution of **11** (463.8 mg, 1.16 mmol) in CH_2Cl_2 (12 mL). After 10 min, TsCl (886.5 mg, 4.65 mmol) was added. The ice bath was left in place but not recharged and stirring was continued for 24 h. The mixture was then quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (2.8 x 20 cm), using 1:10 to

1:5 EtOAc-hexanes, gave **18** (631.6 mg, 98%) as a white solid: mp 165-167 °C; FTIR ($CDCl_3$, cast) 3157, 3130, 3036, 3002, 2954, 2921, 2850, 2257, 1926, 1724, 1595, 1569, 1530, 1448, 1422 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 2.44 (s, 3 H), 3.52 (s, 3 H), 3.62 (s, 3 H), 6.35 (d, J = 3.5 Hz, 1 H), 7.34-7.37 (m, 2 H), 7.75 (d, J = 3.5 Hz, 1 H), 7.85-7.87 (m, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.8 (q), 51.6 (q), 52.2 (q), 105.8 (s), 111.4 (d), 113.9 (s), 121.2 (s), 121.7 (s), 122.4 (s), 126.3 (d), 128.0 (d), 129.6 (d), 130.9 (s), 135.6 (s), 145.5 (s), 157.8 (s), 158.5 (s); exact mass (electrospray) m/z calcd for $C_{19}H_{15}{}^{79}Br^{35}Cl_2N_2NaO_6S$ (M + Na) 570.9103, found 570.9096.

{3-Bromo-4,5-dichloro-1-[2-(hydroxymethyl)-1-[(4-methylbenzene)-sulfonyl]-1*H*-pyrrol-3-yl]-1*H*-pyrrol-2-yl}methanol (19).

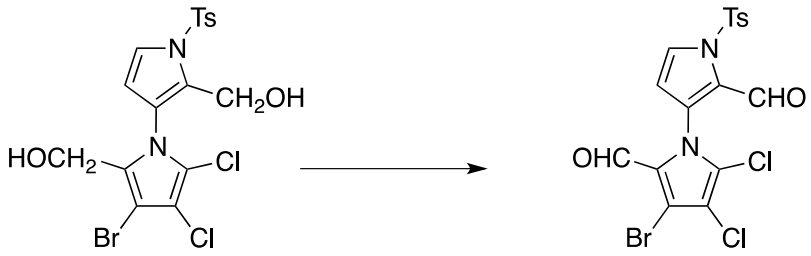


18 **19**

DIBAL-H (1.0 M in PhMe, 1.80 mL, 1.80 mmol) was added dropwise to a stirred and cooled (0 °C) solution of **18** (184.2 mg, 0.33 mmol) in CH_2Cl_2 (4 mL). The cooling bath was removed and stirring was continued for 10.5 h. MeOH (0.5 mL) and saturated aqueous Rochelle's salt (ca 10 mL) were then added

sequentially. Stirring was continued for 1 h, and the mixture was extracted with EtOAc. The combined organic extracts were washed with brine, dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (1.8 x 20 cm), using 3:10 to 2:5 EtOAc-hexanes, gave **19** (169.7 mg, 100%) as a white solid: mp 95-98 °C; FTIR (neat) 3233, 3145, 3124, 2940, 2884, 2733, 1920, 1653, 1589, 1485, 1447 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 2.44 (s, 3 H), 3.21 (br s, 1 H), 3.49 (br s, 1 H), 4.08-4.14 (m, 2 H), 4.47 (d, J = 13.5 Hz, 1 H), 4.69 (d, J = 14.0 Hz, 1 H), 6.24 (d, J = 3.5 Hz, 1 H), 7.35-7.37 (m, 3 H), 7.81-7.84 (m, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.7 (q), 52.2 (t), 54.5 (t), 98.8 (s), 111.3 (s), 111.4 (d), 116.1 (s), 122.3 (d), 123.4 (s), 127.2 (d), 130.3 (d), 131.8 (s), 131.9 (s), 135.3 (s), 146.1 (s); exact mass (electrospray) *m/z* calcd for $C_{17}H_{15}{}^{79}Br^{35}Cl_2N_2NaO_4S$ (M + Na) 514.9205, found 514.9202.

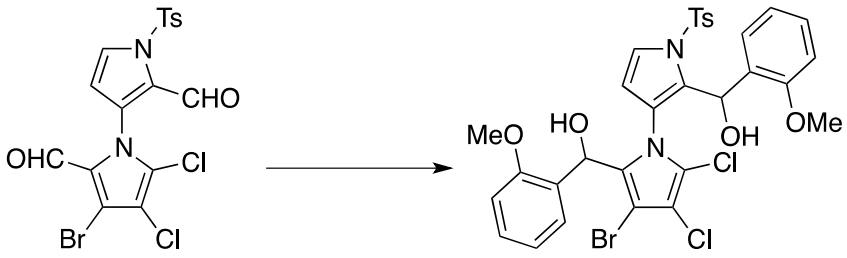
3-Bromo-4,5-dichloro-1-{2-formyl-1-[(4-methylbenzene)sulfonyl]-1*H*-pyrrol-3-yl}-1*H*-pyrrole-2-carbaldehyde (20).



19 **20**

IBX (898.8 mg, 3.21 mmol) was added to a stirred solution **19** (239.7 mg, 0.49 mmol) in DMSO (10 mL). The mixture was heated to 70 °C for 15 h and then cooled to room temperature. The resulting suspension was filtered and water was added to the filtrate. The solution was then extracted with EtOAc and the combined organic extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (2.8 x 20 cm), using 1:10 to 1:5 EtOAc-hexanes, gave **20** (332.5 mg, 87%) as a white solid: mp 140-143 °C; FTIR ($CDCl_3$, cast) 3331, 3147, 3056, 2924, 2850, 2801, 2255, 1674, 1595, 1559, 1515, 1493, 1481, 1454 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 2.44 (s, 3 H), 6.40 (dd, J = 0.5, 3.0 Hz, 1 H), 7.36-7.39 (m, 2 H), 7.63 (d, J = 3.5 Hz, 1 H), 7.76-7.79 (m, 2 H), 9.43 (s, 1 H), 9.97 (d, J = 0.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.8 (q), 111.5 (s), 112.7 (d), 114.8 (s), 125.7 (s), 126.8 (d), 127.01 (s), 127.05 (s), 127.2 (d), 130.3 (s), 130.5 (d), 134.9 (s), 146.7 (s), 176.7 (d), 178.1 (d); exact mass (electrospray) m/z calcd for $C_{17}H_{11}{}^{79}Br^{35}Cl_2N_2NaO_4S$ (M + Na) 510.8992, found 510.8890.

(3-{3-Bromo-4,5-dichloro-2-[hydroxy(2-methoxyphenyl)methyl]-1*H*-pyrrol-1-yl}-1-[(4-methylbenzene)sulfonyl]-1*H*-pyrrol-2-yl)(2-methoxy-phenyl)methanol (21).

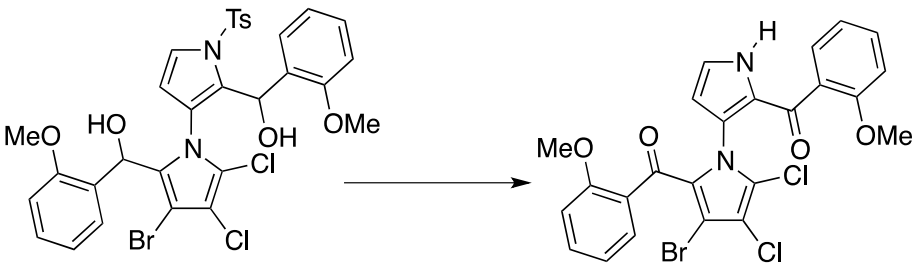


20 **21**

2-Methoxyphenylmagnesium bromide (1.0 M in THF, 3.13 mL, 3.13 mmol) was added to a stirred and cooled (0 °C) solution of **20** (153.6 mg, 0.31 mmol) in THF (3 mL), and stirring at 0 °C was continued for 4 h. The mixture was quenched with saturated aqueous Na_2SO_4 and extracted with EtOAc. The combined organic extracts were dried ($MgSO_4$) and evaporated to give **21** as a yellow residue, which was used directly in the next step.

In a subsequent attempt to oxidize the diols **21**, one isomer was recovered and had: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.45 (s, 3 H), 2.88 (d, *J* = 7.5 Hz, 1 H), 3.40 (s, 3 H), 3.60 (d, *J* = 7.5 Hz, 1 H), 3.61 (s, 3 H), 5.35 (d, *J* = 5.5 Hz, 1 H), 5.64 (d, *J* = 3.5 Hz, 1 H), 6.17 (d, *J* = 7.0 Hz, 1 H), 6.58 (d, *J* = 8.5 Hz, 1 H), 6.74-6.77 (m, 1 H), 6.84-6.90 (m, 2 H), 7.15-7.26 (m, 3 H), 7.27-7.32 (m, 3 H), 7.40-7.43 (m, 1 H), 7.62-7.66 (m, 2 H); exact mass (electrospray) *m*/*z* calcd for $C_{31}H_{27}{}^{79}Br^{35}Cl_2N_2NaO_6S$ (M + Na) 727.0042, found 727.0027. A sample was crystallized from Et_2O for X-ray analysis.

3-Bromo-4,5-dichloro-2-[(2-methoxyphenyl)carbonyl]-1-{2-[(2-methoxyphenyl)carbonyl]-1*H*-pyrrol-3-yl}-1*H*-pyrrole (22).



21 **22**

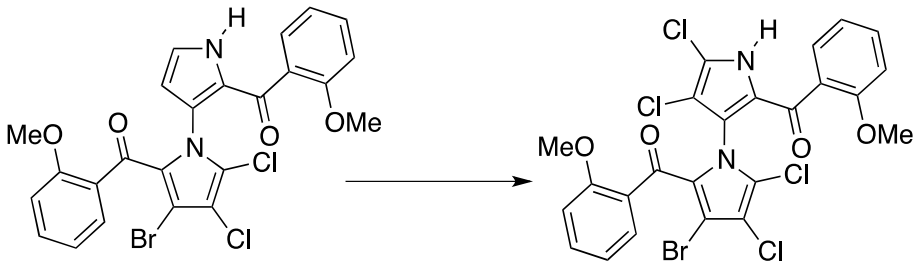
DMSO (6 mL) was added to dissolve the above crude diols **21**, and IBX (263.3 mg, 0.94 mmol) was added to the solution. The mixture was stirred at 70 °C for 29 h and then cooled, quenched with water and extracted with EtOAc. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (1.8 x 20 cm), using 1:10 to 1:5 EtOAc-hexanes, gave the intermediate ketoalcohol(s) as a yellow oil. We were unable to obtain satisfactory NMR data: exact mass (electrospray) *m/z* calcd for $C_{31}H_{25}{}^{79}Br^{35}Cl_2N_2NaO_6S$ (M + Na) 724.9886, found 724.9882.

Jones reagent (7.0 M in acetone, 0.25 mL, 1.75 mmol) was added dropwise to a stirred and cooled (0 °C) solution of the ketoalcohol(s) in acetone (2 mL) and stirring at 0 °C was continued for 4 h. The mixture was quenched with MeOH (2 mL) and stirring was continued for 30 min, by which time the mixture had become dark green. The mixture was diluted with EtOAc and washed with water and brine, dried ($MgSO_4$) and evaporated to give the diketone as a yellow

residue: exact mass (electrospray) *m*/*z* calcd for $C_{31}H_{23}{}^{79}Br^{35}Cl_2N_2NaO_6S$ (M + Na) 722.9729, found 722.9731.

MeOH (1.5 mL) and THF (1.5 mL) were then added to the diketone, followed by KOH (74.0 mg, 1.32 mmol). The mixture was stirred for 1 h at room temperature and then adjusted to pH 7.0 with hydrochloric acid (0.5 M). The neutralized mixture was extracted with EtOAc, and the combined organic extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (1.8 x 20 cm), using 1:10 to 1:2 EtOAc-hexanes, gave **22** (46.0 mg, 27% over four steps) as a yellow oil: FTIR ($CDCl_3$, cast) 3283, 3077, 3004, 2942, 2838, 2249, 1714, 1634, 1599, 1581, 1556, 1489, 1464 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 3.72 (s, 3 H), 3.78 (s, 3 H), 6.01 (t, *J* = 3.0 Hz, 1 H), 6.73 (dt, *J* = 1.0, 7.5 Hz, 1 H), 6.78 (d, *J* = 8.0 Hz, 1 H), 6.81 (d, *J* = 8.5 Hz, 1 H), 6.88 (t, *J* = 3.0 Hz, 1 H), 6.91 (dt, *J* = 1.0, 7.5 Hz, 1 H), 7.14 (dd, *J* = 1.5, 7.5 Hz, 1 H), 7.18 (dd, *J* = 2.0, 7.5 Hz, 1 H), 7.28 (ddd, *J* = 2.0, 7.5, 8.5 Hz, 1 H), 7.33 (ddd, *J* = 1.5, 7.5, 8.5 Hz, 1 H), 9.62 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 55.5 (q), 55.7 (q), 105.0 (s), 110.6 (d), 110.8 (d), 111.0 (d), 113.6 (s), 119.5 (d), 120.5 (d), 122.5 (s), 122.8 (d), 125.7 (s), 126.6 (s), 127.9 (s), 128.2 (d), 129.0 (s), 129.5 (d), 130.8 (s), 131.5 (d), 132.2 (d), 156.5 (s), 157.3 (s), 183.2 (s), 183.6 (s); exact mass (electrospray) *m*/*z* calcd for $C_{24}H_{17}{}^{79}Br^{35}Cl_2N_2NaO_4$ (M + Na) 568.9641, found 568.9636.

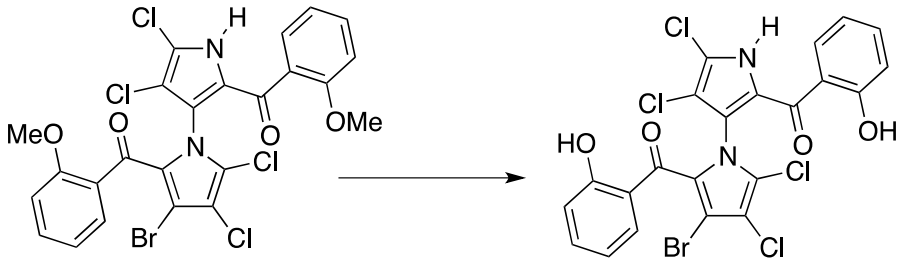
3-Bromo-4,5-dichloro-1-{4,5-dichloro-2-[(2-methoxyphenyl)carbonyl]-1*H*-pyrrol-3-yl}-2-[(2-methoxyphenyl)carbonyl]-1*H*-pyrrole (23).



22 **23**

NCS (22.7 mg, 0.17 mmol) was added to a stirred solution of **22** (45.4 mg, 0.083 mmol) in MeCN (1 mL). The mixture was heated to 35 °C for 15.5 h, cooled to room temperature, quenched with water and extracted with CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (1.8 x 20 cm), using 1:10 to 2:5 EtOAc-hexanes, gave **23** (38.8 mg, 76%) as a yellow oil: FTIR ($CDCl_3$, cast) 3200, 3004, 2943, 2838, 2250, 1726, 1634, 1599, 1581, 1558, 1489, 1463 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 3.74 (s, 3 H), 3.77 (s, 3 H), 6.74 (dt, *J* = 1.0, 7.5 Hz, 1 H), 6.79 (d, *J* = 8.5 Hz, 1 H), 6.84 (d, *J* = 8.5 Hz, 1 H), 6.92 (dt, *J* = 1.0, 7.5 Hz, 1 H), 7.16 (dd, *J* = 1.5, 7.5 Hz, 1 H), 7.18 (dd, *J* = 1.5, 7.5 Hz, 1 H), 7.29 (ddd, *J* = 2.0, 7.5, 8.5 Hz, 1 H), 7.38 (ddd, *J* = 1.5, 7.5, 8.5 Hz, 1 H), 9.88 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 55.59 (q), 55.60 (q), 106.4 (s), 110.6 (d), 110.8 (s), 111.0 (d), 114.5 (s), 119.6 (d), 119.9 (s), 120.5 (d), 122.8 (s), 123.3 (s), 125.9 (s), 126.4 (s), 128.3 (s), 128.4 (d), 129.3 (d), 130.4 (s), 132.1 (d), 132.2 (d), 156.6 (s), 157.2 (s), 182.3 (s), 183.0 (s); exact mass (electrospray) *m/z* calcd for $C_{24}H_{15}{}^{79}Br^{35}Cl_4N_2NaO_4$ (M + Na) 636.8862, found 636.8861.

2-[(3-{3-Bromo-4,5-dichloro-2-[(2-hydroxyphenyl)carbonyl]-1*H*-pyrrol-1-yl}-4,5-dichloro-1*H*-pyrrol-2-yl)carbonyl]phenol, [(±)-marinopyrrole B].



23 **(±)-marinopyrrole B**

BBr_3 (1.0 M in CH_2Cl_2, 1.04 mL, 1.04 mmol) was added to a stirred and cooled cooled (–78 °C) solution of **23** (64.1 mg, 0.104 mmol) in CH_2Cl_2 (1.5 mL). After 50 min at -78 °C, the mixture was quenched with MeOH, diluted with water and extracted with CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (1.8 x 20 cm), using 1:20 to 3:20 EtOAc-hexanes, gave (±)-marinopyrrole B (54.0 mg, 88%) as a yellow solid: FTIR ($CDCl_3$, cast) 3232, 1622, 1592, 1483, 1452 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 6.58 (t, J = 2.5 Hz, 1 H), 6.86 (t, J = 2.5 Hz, 1 H), 6.97 (dd, J = 1.0, 8.5 Hz, 1 H), 7.00 (d, J = 8.5 Hz, 1 H), 7.40-7.44 (m, 2 H), 7.48-7.54 (m, 2 H), 9.96 (br s, 1 H), 10.36 (s, 1 H), 11.10 (s, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 104.7 (s), 114.7 (s), 117.9 (d), 118.1 (d), 118.5 (s), 118.7 (d), 118.9 (s), 119.2 (d), 120.2 (s), 121.7 (s), 122.0 (s), 124.3 (s), 128.4 (s), 130.0 (d), 134.2

(d), 136.4 (d), 137.3 (d), 161.3 (s), 162.5 (s), 185.4 (s), 188.5 (s); exact mass (electrospray) *m*/*z* calcd for $C_{22}H_{10}{}^{79}Br^{35}Cl_4N_2O_4$ (M – H) 584.8584, found 584.8583. A sample was crystallized from PhMe for X-ray analysis: mp 199-201 °C.

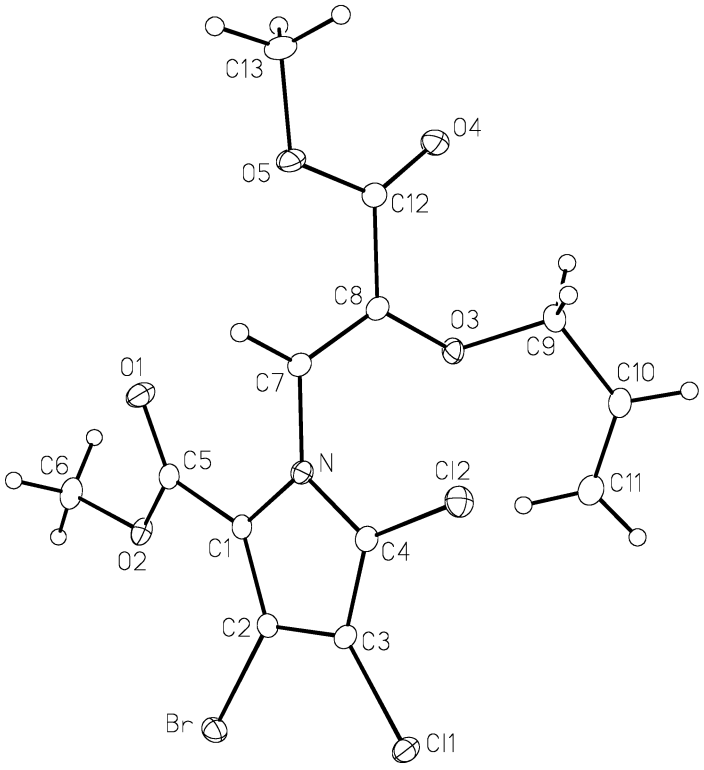


Figure 1. ORTEP diagram of **17**. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters.

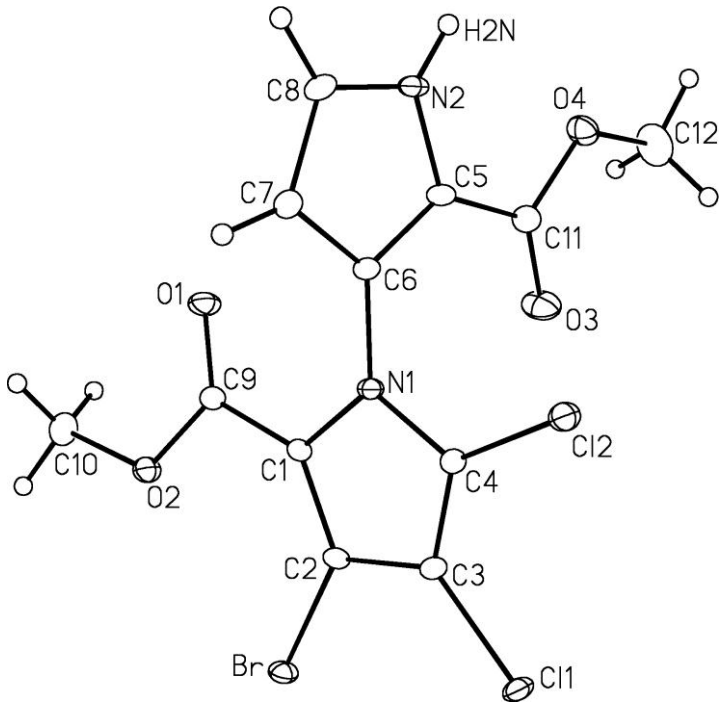


Figure 2. ORTEP diagram of **11**. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters.

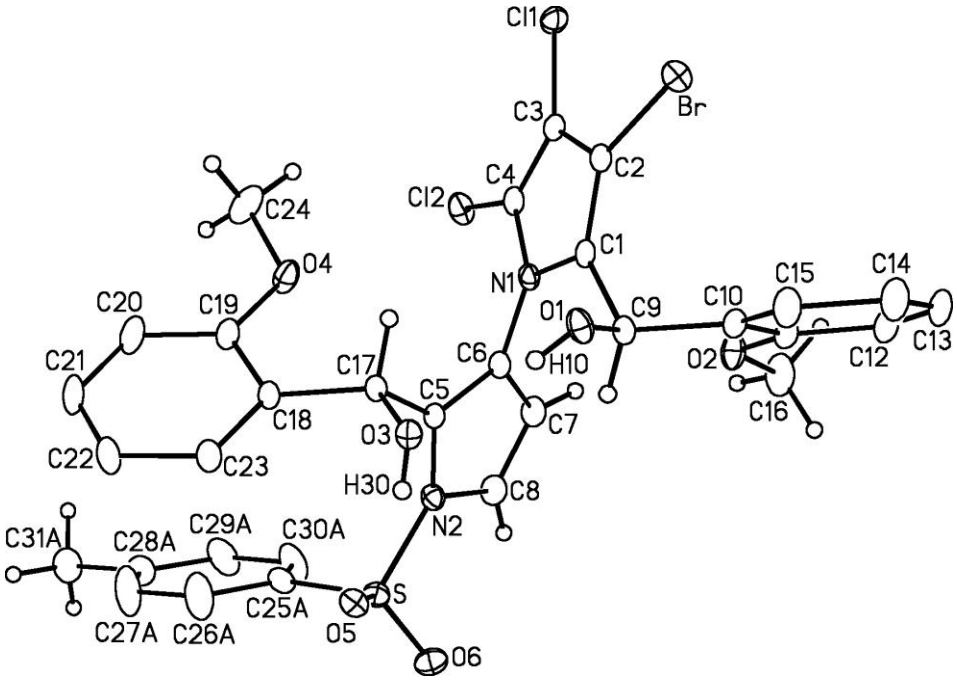


Figure 3. ORTEP diagram of one isomer of **21**. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters.

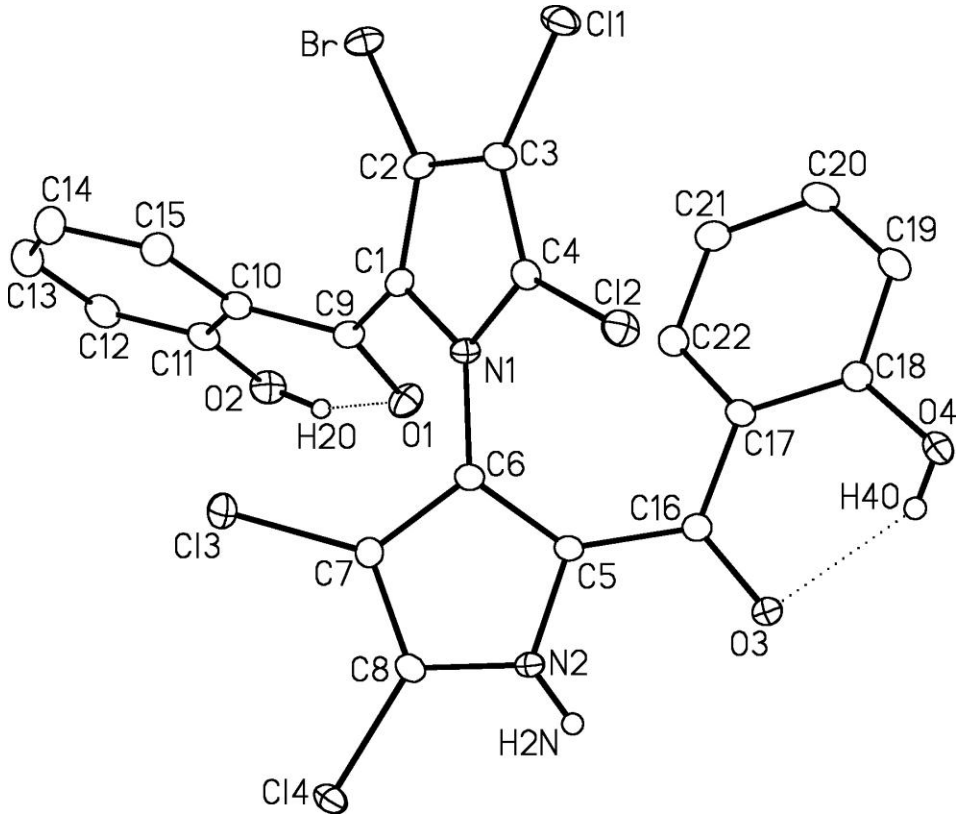
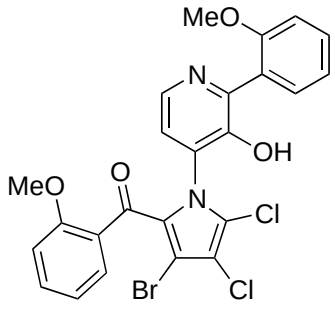


Figure 4. ORTEP diagram of (±)-Marionpyrrole B. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters.



the pyridine