Stereoselective Synthesis of *cis*- and *trans*-2,3-Disubstituted Tetrahydrofurans via Oxonium-Prins Cyclization – Access to the Cordigol Ring System

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Supporting Information — X-Ray Crystallography

Crystal data for **6c**: $C_{17}H_{16}BrNO_3$, M = 362.22, orthorhombic, *Pbca* (no. 61), a = 11.90157(8), b = 7.07893(5), c = 36.2463(2) Å, V = 3053.77(3) Å^3, Z = 8, D_c = 1.576 g cm^{-3}, μ(Cu-Kα) = 3.779 mm^{-1}, T = 173 K, colourless tablets, Oxford Diffraction Xcalibur PX Ultra diffractometer; 3021 independent measured reflections (R_{int} = 0.0246), F^2 refinement, R_1(obs) = 0.0260, wR_2(all) = 0.0671, 2917 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 145°], 205 parameters. CCDC 749262.

The bromine atom in the structure of **6c** was found to be disordered. Two partial occupancy sites separated by just *ca.* 0.55 Å were identified of *ca.* 95 and 5% occupancy, with only the major occupancy atom being refined anisotropically. The isotropic and equivalent isotropic thermal parameters of the two partial occupancy atoms were restrained to be equal, as were the two C(15)–Br distances.

Crystal data for **9**: $C_{25}H_{20}O$, M = 336.41, orthorhombic, *Pbca* (no. 61), a = 9.3602(2), b = 19.0921(5), c = 19.2655(4) Å, V = 3442.86(14) Å^3, Z = 8, D_c = 1.298 g cm^{-3}, μ(Mo-Kα) = 0.077 mm^{-1}, T = 173 K, pale yellow blocks, Oxford Diffraction Xcalibur 3 diffractometer; 4238 independent measured reflections (R_{int} = 0.0317), F^2 refinement, R_1(obs) = 0.0539, wR_2(all) = 0.1344, 2809 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 59°], 261 parameters. CCDC 749263.

Substantial disorder was found in the structure of **9**. Two orientations of *ca.* 62 and 38% occupancy were identified for the C(15) to C(20) portion of the structure (see Figs. S2, S3 and S4) with only the major occupancy non-hydrogen atoms being refined anisotropically. The equivalent 1,2- and 1,3-distances for the two orientations were restrained to be the same.

It is important to note that the disorder represents an inversion of the stereochemistry at each of the chiral carbon centres, C(15), C(19) and C(20), *i.e.* it is the enantiomer of the major occupancy orientation. Indeed, the enantiomer of the minor occupancy orientation has a very similar conformation to the major occupancy orientation (compare the figure in Scheme 3 in the paper with Fig. S6 here).

Crystal data for **10**: $C_{17}H_{16}O_2$, M = 252.30, triclinic, $P\bar{1}$ (no. 2), a = 5.2585(2), b = 10.0947(5), c = 13.0837(6) Å, α = 105.714(4), β = 94.705(4), γ = 100.581(4)°, V = 650.79(5) Å^3, Z = 2, D_c = 1.288 g cm^{-3}, μ(Cu-Kα) = 0.660 mm^{-1}, T = 173 K, colourless needles, Oxford Diffraction Xcalibur PX Ultra diffractometer; 2572 independent measured reflections (R_{int} = 0.0211), F^2 refinement, R_1(obs) = 0.0455, wR_2(all) = 0.1277, 2148 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 145°], 172 parameters. CCDC 749264.

Fig. S1 The molecular structure of **6c** (50% probability ellipsoids).

Fig. S2 The molecular structure of **9** showing the major occupancy orientation for the C(15) to C(20) moiety (50% probability ellipsoids).

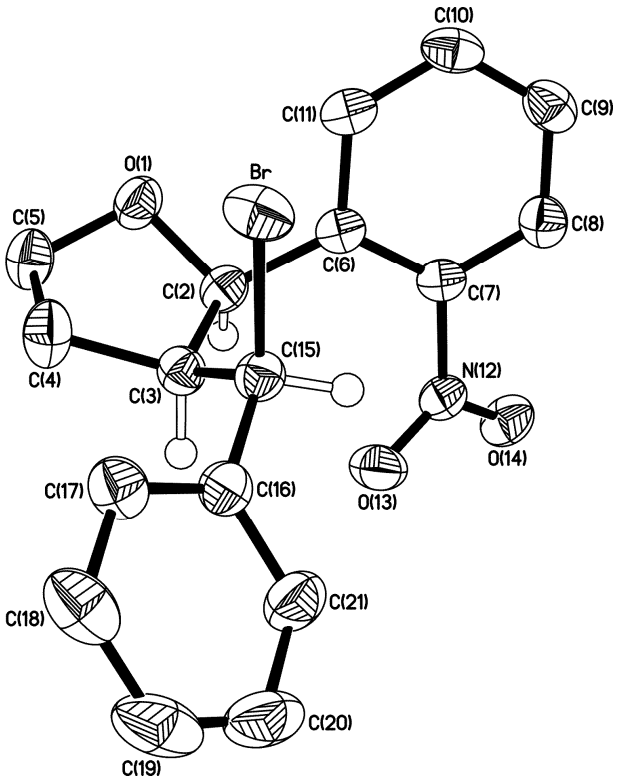
Fig. S3 The molecular structure of **9** showing the minor occupancy orientation for the C(15) to C(20) moiety.

Fig. S4 The molecular structure of **9** showing the minor occupancy orientation for the C(15) to C(20) moiety (50% probability ellipsoids).

Fig. S5 The molecular structure of **9** showing an overlay of both orientations for the C(15) to C(20) moiety (the major occupancy orientation has been drawn with solid bonds, and the minor occupancy orientation with open bonds).

Fig. S6 The molecular structure of **9** showing the enantiomer of the minor occupancy orientation for the C(15) to C(20) moiety to demonstrate its similarity to the conformation of the major occupancy orientation.

Fig. S7 The molecular structure of **10** (50% probability ellipsoids).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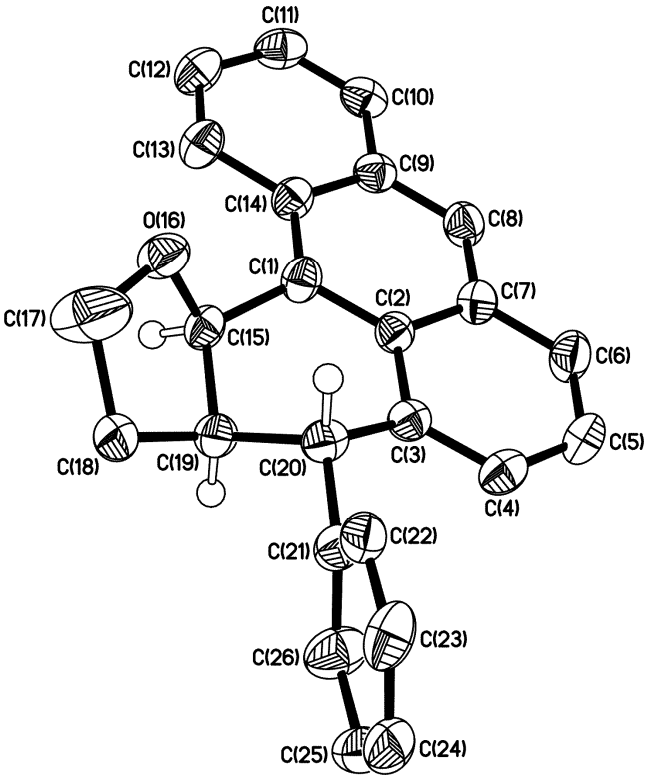
C(11)
C(9)
O(1)
Br
C(5)
C(8)
C(6)
C(2)
C(7)
C(15)
C(4)
C(3)
N(12)
O(14)
O(13)
C(17)
C(16)
C(21)
C(18)
C(20)
C(19)

Fig. S1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C(12)
C(10)
C(13)
C(9)
C(14)
C(8)
O(16)
C(1)
C(2)
C(7)
C(17)
C(15)
C(6)
C(18)
C(19)
C(20)
C(3)
C(5)
C(4)
C(21)
C(22)
C(23)
C(26)
C(25)
C(24)

Fig. S2

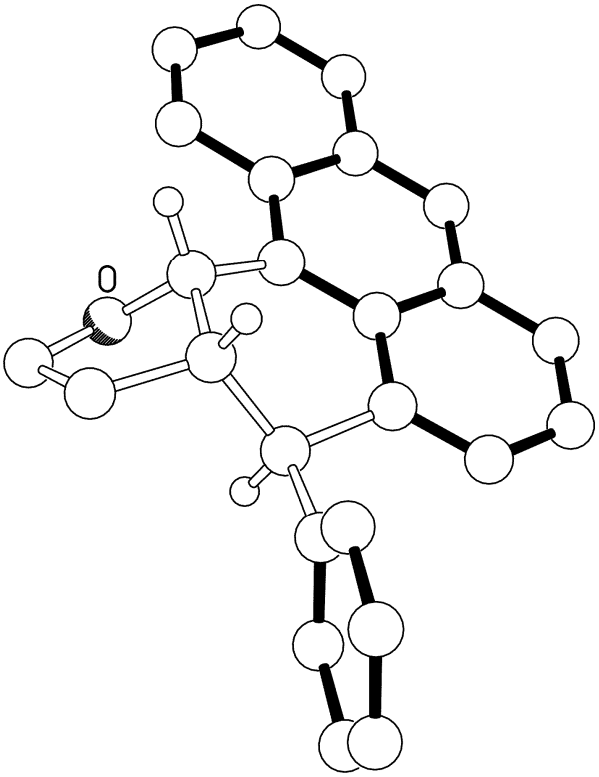
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Fig. S3

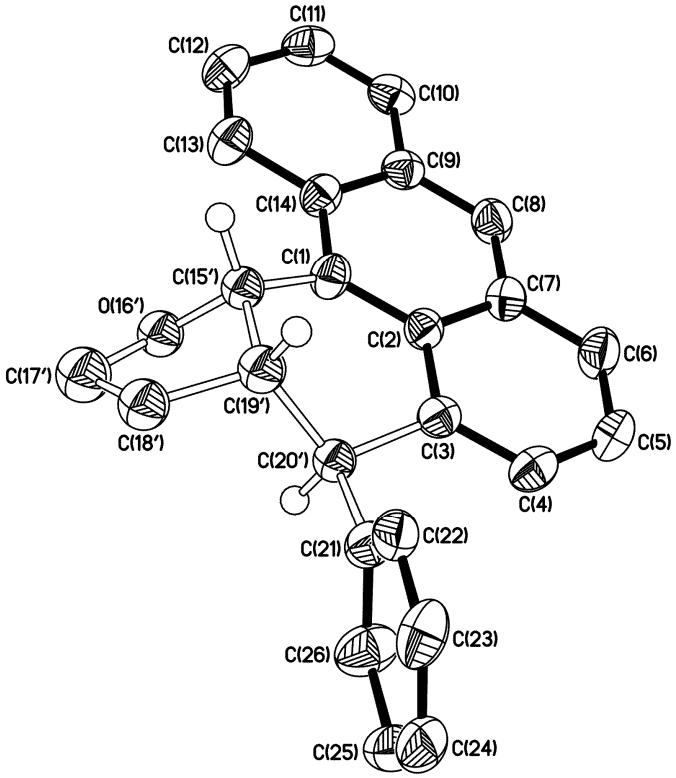
C(11)
C(12)
C(10)
C(13)
C(9)
C(14)
C(8)
C(1)
C(15')
C(7)
O(16')
C(2)
C(6)
C(17')
C(19')
C(18')
C(3)
C(5)
C(20')
C(4)
C(21)
C(22)
C(23)
C(26)
C(25)
C(24)

Fig. S4

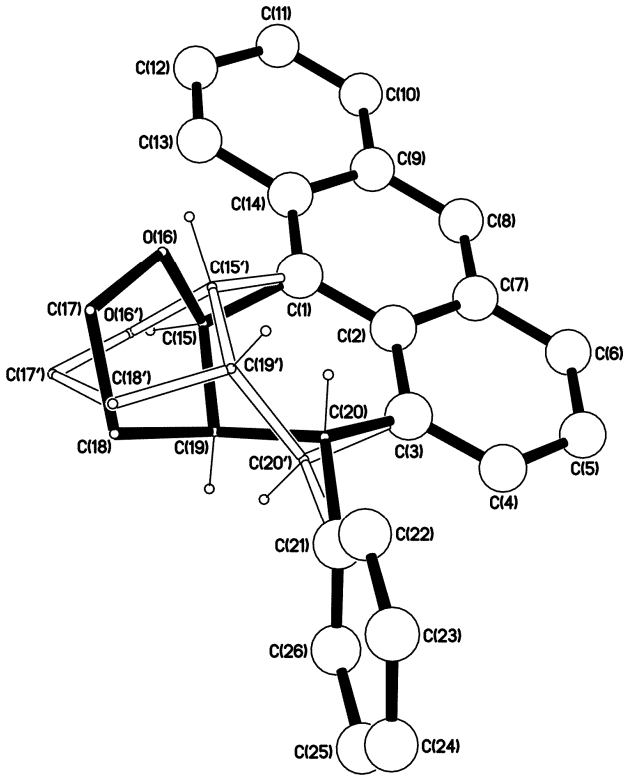
C(11)
C(12)
C(10)
C(13)
C(9)
C(14)
C(8)
O(16)
C(15')
C(7)
C(17)
O(16')
C(1)
C(15)
C(2)
C(6)
C(17')
C(18')
C(19')
C(20)
C(18)
C(19)
C(3)
C(20')
C(5)
C(4)
C(21)
C(22)
C(23)
C(26)
C(25)
C(24)

Fig. S5

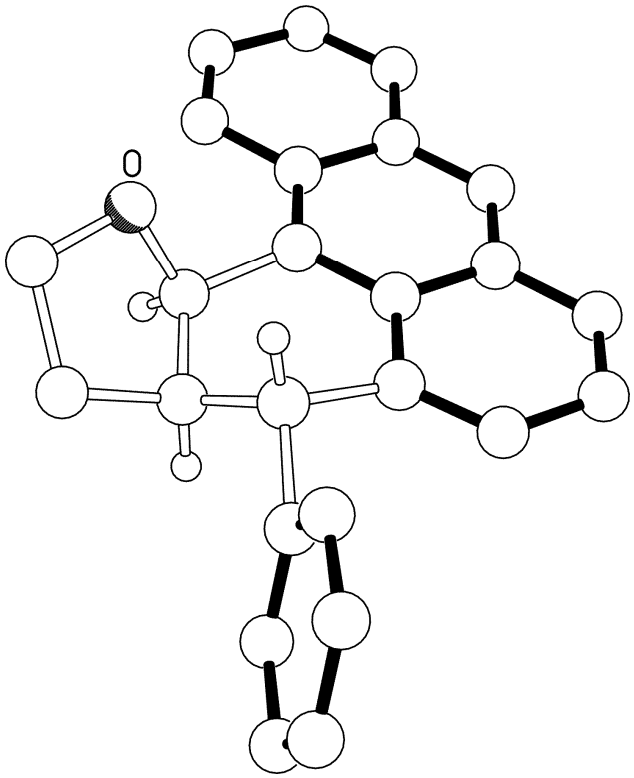
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Fig. S6

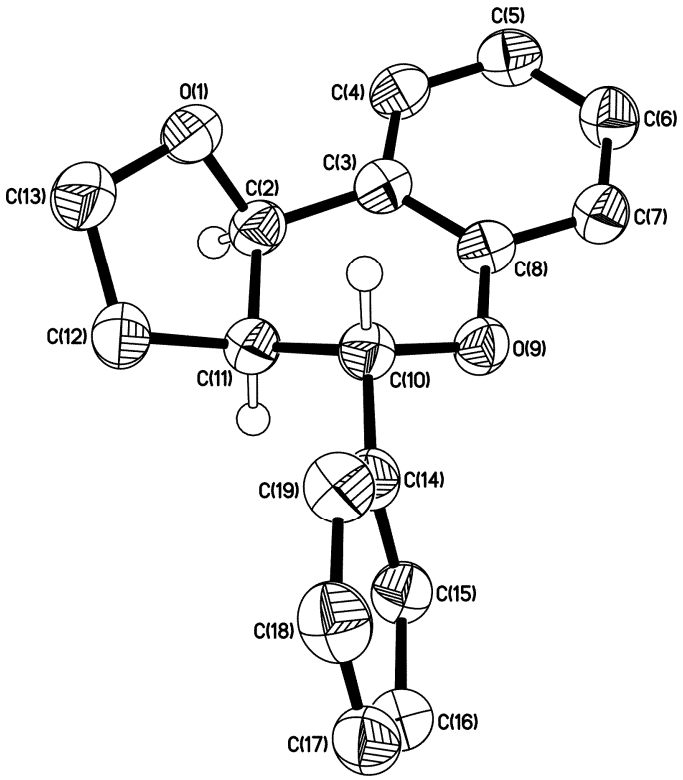

Fig. S7