Supporting Information — X-Ray Crystallography

Manuscript: Towards the Enantioselective Synthesis of (-)-Euonyminol – Preparation of a Fully Functionalised Lower-rim Model

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The X-ray crystal structure of 6

*Crystal data for **6**:* $C_{11}H_{13}N_1O_1$, M = 175.22, monoclinic, $P2_1/n$ (no. 14), a = 7.192(3), b = 14.069(4), c = 9.2117(16) Å, β = 102.365(19)°, V = 910.4(4) Å^3, Z = 4, D_c = 1.278 g cm^{-3}, μ(Mo-Kα) = 0.082 mm^{-1}, T = 123 K, colourless prism, 0.40 x 0.35 x 0.20mm, Rigaku AFC7R diffractometer; 2137 measured reflections, 1984 unique, (R_{int} = 0.0200), F^2 refinement,[1] R_1(obs) = 0.0413, wR_2(all) = 0.1203, 1664 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 53.94°], 122 parameters. CCDC 905361.

The OH hydrogen atom on O(1) was located from a ΔF map and refined freely.

The X-ray crystal structure of 17

*Crystal data for **17**:* $C_{23}H_{27}N_1O_4$, M = 381.46, monoclinic, $P2_1$ (no. 4), a = 6.2151(2), b = 16.8252(5), c = 9.7311(4) Å, β = 90.176(1)°, V = 1017.58(6) Å^3, Z = 2, D_c = 1.245 g cm^{-3}, μ(Mo-Kα) = 0.085 mm^{-1}, T = 120 K, colourless block, , 0.36 x 0.12 x 0.10mm, Nonius KappaCCD diffractometer; 12036 measured reflections, 4019 unique, (R_{int} = 0.0658), F^2 refinement,[1] R_1(obs) = 0.0518, wR_2(all) = 0.1216, 3150 independent observed [$|F_o| > 4\sigma(|F_o|)$, 99.8% complete to $2\theta_{max}$ = 52.74°], 260 parameters. CCDC 905362.

The OH hydrogen atom on O(3) was located from a ΔF map and refined freely. The absolute stereochemistry was not determined.

The X-ray crystal structure of 18c

*Crystal data for **18c**:* $C_{40}H_{47}N_1O_7$, M = 653.79, triclinic, $P\bar{1}$ (no. 2), a = 10.6749(8), b = 11.6338(9), c = 17.3660(11) Å, α = 108.132(3), β = 103.266(3), γ = 110.833(4)°, V = 1769.5(2) Å^3, Z = 2, D_c = 1.227 g cm^{-3}, μ(Mo-Kα) = 0.083 mm^{-1}, T = 273 K, colourless prism , 0.50 x 0.50 x 0.25mm, Bruker Nonius Kappa Apex 2 CCD diffractometer; 36283 measured reflections, 8417 unique, (R_{int} = 0.0248), F^2 refinement,[1] R_1(obs) = 0.0455,

wR_2(all) = 0.1277, 7356 independent observed [$|F_o| > 4\sigma(|F_o|)$, 98.6% complete to $2\theta_{max}$ = 56.00°], 439 parameters. CCDC 905363.

The X-ray crystal structure of 28a

Crystal data for **28a**: $C_{17}H_{23}NO_4 \cdot 0.5(C_4H_8O_2)$, M = 349.42, tetragonal, $P4_3$ (no. 78), a = b = 16.17422(15), c = 7.32793(11) Å, V = 1917.03(5) Å^3, Z = 4, D_c = 1.211 g cm^{-3}, μ(Cu-Kα) = 0.713 mm^{-1}, T = 173 K, colourless needles, Oxford Diffraction Xcalibur PX Ultra diffractometer; 3400 independent measured reflections (R_{int} = 0.0454), F^2 refinement,[1] R_1(obs) = 0.0374, wR_2(all) = 0.0987, 3022 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 143°], 203 parameters. The absolute structure of **28a** could not be unambiguously determined either by *R*-factor tests [R_1^+ = 0.0374, R_1^- = 0.0376] or by use of the Flack parameter [x^+ = 0.0(2), x^- = 1.2(2)], and so was assigned based on the known stereochemistries at C(2), C(3), C(8) and C(10).[2] CCDC 905364.

The included solvent in the structure of **28a** was found to be highly disordered, and the best approach to handling this electron density was found to be the SQUEEZE routine of PLATON.[3] This suggested a total of 102 electrons per unit cell, equivalent to 25.5 electrons per molecule. The crystal was grown from a mixture of ethyl acetate [$C_4H_8O_2$, 48 electrons] and hexane [C_6H_{14}, 50 electrons], and before the use of SQUEEZE the electron density distribution most resembled ethyl acetate; 0.5 ethyl acetate molecules equates to 24 electrons and so this was used as the solvent present. The atom list for the unit cell is thus low by 2 ethyl acetate molecules, *i.e.* $C_8H_{16}O_4$.

The OH hydrogen atom on O(12) was located from a ΔF map and refined freely subject to an O–H distance constraint of 0.90 Å.

The X-ray crystal structure of 31

Crystal data for **31**: $C_{19}H_{29}NO_6$, M = 367.43, monoclinic, $P2_1/c$ (no. 14), a = 10.6847(2), b = 12.1746(3), c = 14.6780(3) Å, β = 95.328(2)°, V = 1901.09(7) Å^3, Z = 4, D_c = 1.284 g cm^{-3}, μ(Cu-Kα) = 0.784 mm^{-1}, T = 173 K, colourless blocks, Oxford Diffraction Xcalibur PX Ultra diffractometer; 3756 independent measured reflections (R_{int} = 0.0297), F^2 refinement,[1] R_1(obs) = 0.0370, wR_2(all) = 0.1021, 3397 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 145°], 243 parameters. CCDC 905365.

The OH hydrogen atom on O(14) was located from a ΔF map and refined freely subject to an O–H distance constraint of 0.90 Å.

Figures:

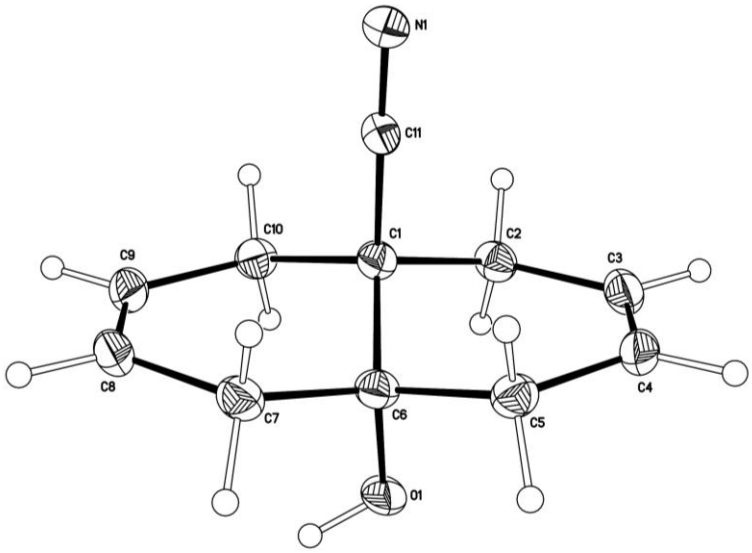

Figure 1. A view of a molecule of compound **6** crystal structure showing the numbering scheme employed. Anisotropic atomic displacement ellipsoids for the non-hydrogen atoms are shown at the 50 % probability level and hydrogen atoms are displayed as spheres of arbitrary radius.

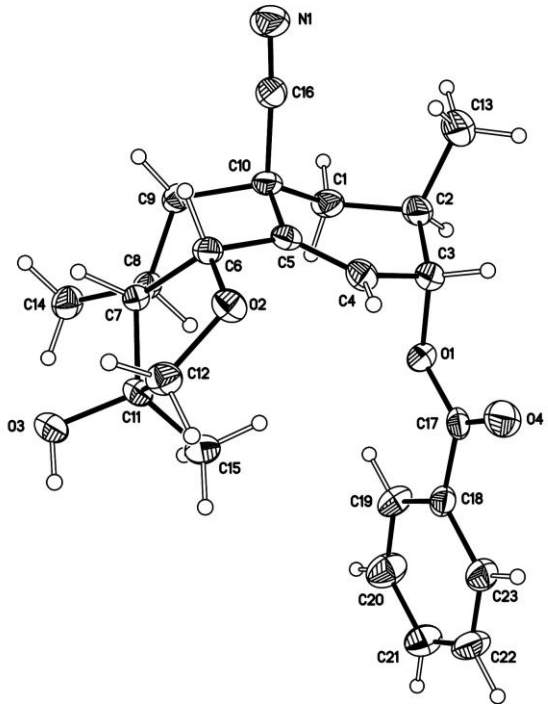

Figure 2. A view of a molecule of compound **17** crystal structure showing the numbering scheme employed. Anisotropic atomic displacement ellipsoids for the non-hydrogen atoms are shown at the 50 % probability level and hydrogen atoms are displayed as spheres of arbitrary radius.

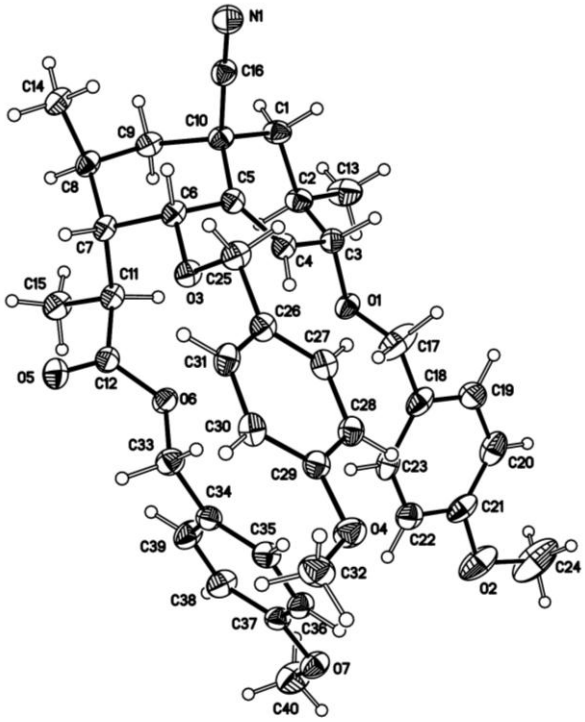

Figure 3. A view of a molecule of compound **18c** crystal structure showing the numbering scheme employed. Anisotropic atomic displacement ellipsoids for the non-hydrogen atoms are shown at the 50 % probability level and hydrogen atoms are displayed as spheres of arbitrary radius.

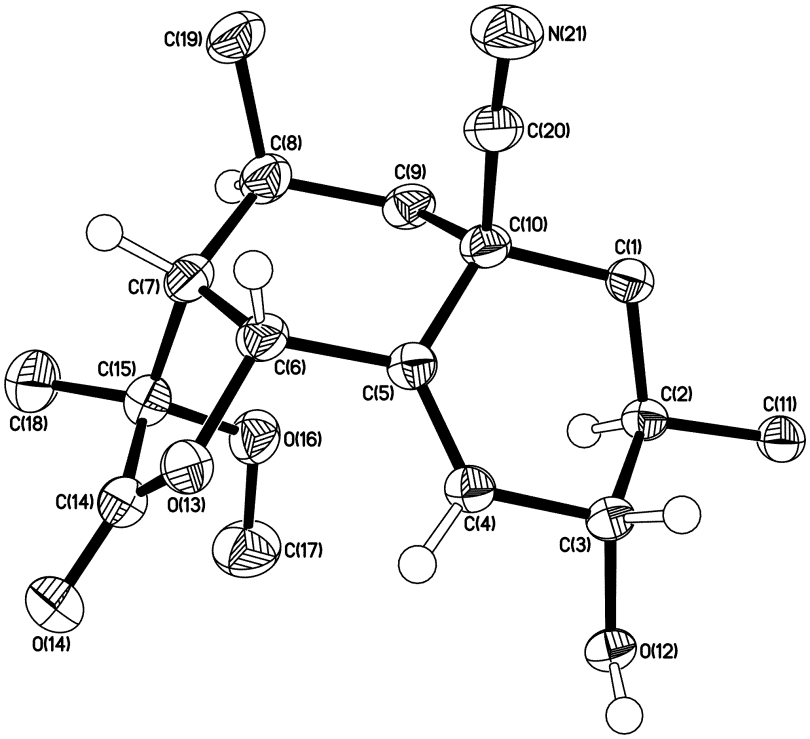

Figure 4. The crystal structure of compound **28a** (30% probability ellipsoids).

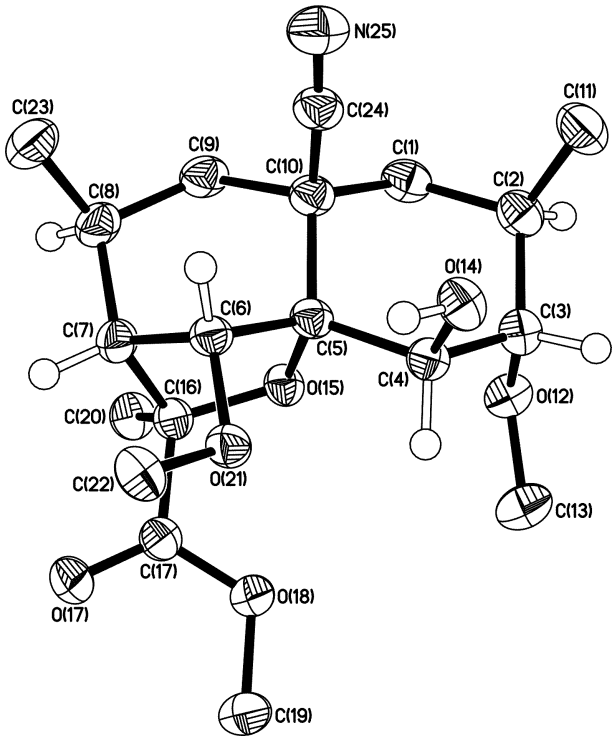

Figure 5. The crystal structure of compound **31** (50% probability ellipsoids).

References

[1] G.M. Sheldrick, *Acta Cryst.*, **2008**, *A64*, 112-122.

[2] Webber, M. J.; Weston, M.; Grainger, D. M.; Lloyd, S.; Warren, S. A.; Powell, L.; Alanine, A.; Stonehouse, J. P.; Frampton, C. S.; White, A. J. P.; Spivey, A. C. *Synlett* **2011**, *18*, 2693-2696

[3] A.L. Spek (2008) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands. See also A.L. Spek, *J. Appl. Cryst.*, 2003, **36**, 7–13.