*** Supplementary Material ***

A Domino Ring-opening / Epoxidation of 1,2-Dioxines

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General Experimental

^1H NMR and ^{13}C NMR were recorded in CDCl_3 solution using a 200 MHz, 300 MHz or 600 MHz instrument, with TMS (0 ppm, ^1H) and CDCl_3 (77.0 ppm, ^{13}C) as internal standard. Thin-layer chromatography was performed using aluminium sheets silica gel 60 F₂₅₄. THF was distilled from benzophenone ketyl.

Acetylation of 3c and 4c. To a 70:30 mixture of **3c** and **4c** (102 mg, 0.39 mmol) in pyridine (1 ml) was added acetic anhydride (1 ml). The mixture was stirred for 16 hours then the volatiles removed *in vacuo* (0.1 mm). The products were separated by flash chromatography (90:10 hexane/ethyl acetate) to give **5c** and **6c** as colorless oils (114 mg, 96%). **5c**; R_f 0.48 (80:20 hexane/ethyl acetate); IR (neat) 2929, 2854, 1736, 1693, 1598, 1450, 1371, 1232, 1024, 705 cm^{-1} ; ^1H NMR (CDCl_3 , 300) δ 1.14-1.26 (m, 5H), 1.75-1.84 (m, 6H), 2.10 (s, 3H); 3.20 (dd, J = 6.3, 1.8 Hz, 1H), 4.34 (d, J = 1.8 Hz, 1H), 4.62 (dd, J = 6.3, 6.3 Hz, 1H), 7.48-7.53 (m, 2H), 7.60-7.63 (m, 1H), 8.01-8.05 (m, 2H); ^{13}C NMR (75) δ 20.7, 25.7, 25.8, 26.1, 27.7, 28.5, 40.4, 55.3, 58.0, 76.1, 128.3, 128.8, 133.9, 135.3, 170.5, 193.5; EIMS m/z (%) 260 ($\text{M}^+ - \text{COCH}_3$, 20), 242 (10), 219 (20), 137 (55), 105 (100). **6c**; R_f 0.40 (80:20 hexane/ethyl acetate); IR (neat) 2927, 2854, 1738, 1693, 1598, 1451, 1371, 1230 cm^{-1} ; ^1H NMR (CDCl_3 , 300) δ 1.11-1.25 (m, 5H), 1.66-1.82 (m, 6H), 2.15 (s, 3H), 3.34 (dd, J = 5.1, 2.1 Hz, 1H), 4.08 (d, J = 2.1 Hz, 1H), 4.81 (dd, J = 7.2, 5.1 Hz, 1H), 7.48-7.53 (m, 2H), 7.60-7.66 (m, 1H), 7.99-8.03 (m, 2H); ^{13}C NMR (75) δ 20.8, 25.6, 25.7, 26.0, 28.7, 28.7, 40.1, 55.3, 58.7, 75.4, 128.4, 128.8, 134.0, 135.2, 170.5, 193.6; EIMS m/z (%) 303 (MH^+ , 15), 260 (260, 30), 105 (100); HRMS calcd for (ESI, $\text{M} + \text{Na}$) $\text{C}_{18}\text{H}_{22}\text{O}_4\text{Na}_1$: 325.1415; found: 325.1414.

Details of crystal structure determination of for C₁₆H₁₄O₃.

Crystal data for C₁₆H₁₄O₃: $M = 254.27$, $T = 223(2)$ K, monoclinic, $P2_1/c$, $a = 14.5102(13)$, $b = 11.6817(10)$, $c = 7.7251(7)$ Å, $\beta = 103.101(2)^\circ$, $V = 1275.4(2)$ Å³, $Z = 4$, $D_x = 1.324$, $F(000) = 536$, $\mu = 0.091$ mm⁻¹, no. of unique data (Bruker AXS SMART CCD using Mo K α radiation so that $\theta_{\max} = 30.1^\circ$) = 3721, no. of parameters = 172, R (all data) = 0.067, wR (all data) = 0.157, $\rho = 0.39$ e Å⁻³. The structure was solved by direct-methods (SIR92) and refined (anisotropic displacement parameters, H atoms in the riding model approximation and a weighting scheme $w = 1/[\sigma^2(F_o^2) + 0.0821P^2 + 0.2198P]$ where $P = (F_o^2 + 2F_c^2)/3$) with SHELXL-97 on F^2 using all reflections.

Figure S(1) Molecular structure and crystallographic numbering scheme for **C₁₆H₁₄O₃**.

Figure S(2) Molecular aggregation in C₁₆H₁₄O₃.

Symmetry related molecules are linked into a chain, propagated by glide symmetry along the c-direction, *via* hydrogen-bonding interactions so that O31-H...O1ⁱ is 2.01 Å, O31...O1ⁱ is 2.8399(14) Å and the angle at H is 178° for symmetry operation *i*: $x, 3/2 - y, -1/2 + z$.

Pulse Sequence: s2pul

13C OBSERVE
Pulse Sequence: s2pul

Table S(1) Hard copy of Crystallographic Information File (CIF) for C₁₆H₁₄O₃.

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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. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

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