SUPPORTING INFORMATION

for

π-Facial Stereoselectivity in Diels-Alder Cycloadditions to 1-Oxaspiro[4.5]deca-6,9-dien-8-one. The Strong Directive Effect of Ether Oxygen in a Cross-Conjugated Ketone Setting

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Diol 5. A solution of **4** (10.0 g, 64 mmol) in dry THF (640 mL) was treated dropwise with 1.3 equiv of the Normant reagent[13] in the same solvent, allowed to react overnight at rt, and quenched with brine. The separated aqueous layer was extracted with ether (3 x 300 mL) and the combined organic solutions were dried and evaporated. The residue was purified by chromatography on silica gel (elution with ether) to give 10.7 g (77%) of **2** as a colorless oil; IR (neat, cm^{-1}) 3378, 1434, 1372, 1254; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.90 (t, *J* = 3.0 Hz, 4 H), 3.58 (t, *J* = 5.6 Hz, 2 H), 1.89-1.68 (m, 2 H), 1.65-1.51 (series of m, 10 H) (OH not observed); ^{13}C NMR (75 MHz, $CDCl_3$) δ 108.9, 69.7, 64.1, 64.0, 62.9, 39.1, 34.6 (2C), 30.4 (2C), 26.3; EI HRMS *m/z* $(M+Na)^+$ calcd 239.1254, obsd 239.1246.

Spirocyclization of 5. A solution of **5** (10.7 g, 49.5 mmol) in dry CH_2Cl_2 (580 mL) was added dry triethylamine (42.4 mL), *p*-toluenesulfonyl chloride (14.1 g, 74.1 mmol), and 0.93 g of DMAP. After 26 h of stirring at rt, the reaction mixture was quenched with brine and diluted with ether (50 mL). The organic phase was washed sequentially with brine, water, and copper sulfate solution (2 x 250 mL). The dried CH_2Cl_2 layer was freed of solvent, and the residue was chromatographed on silica gel (ether elution) to furnish **6** as colorless crystals, mp 46.5-48 °C (7.83 g, 80%); IR (neat, cm^{-1}) 1446, 1261; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.97-3.82 (m, 4 H), 3.77 (t, *J* = 6.7 Hz, 2 H), 1.89-1.78 (m, 4 H), 1.68-1.52 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 108.7, 80.7, 66.7, 64.3, 36.2, 34.1 (2C), 31.2 (2C), 25.5; ES HRMS *m/z* $(M+Na)^+$ calcd 221.1148, obsd 221.1159.

Bromination-Dehydrobromination of 6. A solution of **6** (5.00 g, 25.2 mmol) in dry ether (38 mL) was treated dropwise with bromine (2.60 mL, 6.76 g, 50.4 mmol) under gentle reflux. The reaction mixture was heated gently under N_2 for 14 h, cooled prior to the introduction of sodium ethylene glycolate solution (9 mL), and after 2 min poured into water (100 mL). The separated aqueous layer was extracted with ether (2 x 75 mL), and the combined

organic layers were dried and evaporated. The residue was taken up in a solution of KOH (8.0 g) in methanol, refluxed for 48 h, poured into water (75 mL), and extracted with ether (3 x 100 mL). The combined organic phases were dried and concentrated to leave 2.99 g (61%) of **7** as a white solid, mp 86.0-87.5 °C; IR (neat, cm^{-1}) 1416, 1176, 1035; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.92 (d, *J* = 10.1 Hz, 2 H), 5.68 (d, *J* =10.1 Hz, 2 H), 4.01-3.92 (m, 4 H), 3.88 (t, *J* = 6.6 Hz, 2 H), 2.02-1.92 (m, 2 H), 1.88-1.75 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.1, 126.0, 76.0, 68.2, 65.1, 64.7, 37.6, 26.4; EI HRMS *m/z* $(M+Na)^+$ calcd 217.0835, obsd 217.0837.

Hydrolysis of 7. A solution of **7** (1.76 g, 9.1 mmol) in 15 mL of a 2:1 THF/1M HCl was stirred at rt for 3 h, neutralized with solid $NaHCO_3$, poured into water (20 mL), and extracted with ether (3 x 20 mL). The combined organic solutions were dried and freed of solvent. Following short column chromatography on silica gel, there was isolated 1.24 g (91%) of **1** as a colorless oil; IR (neat, cm^{-1}) 1669, 1340, 1250; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.80 (dd, *J* = 10.1, 1.7 Hz, 2 H), 6.13 (dd, *J* =10.1, 1.9 Hz, 2 H), 4.08 (t, *J* = 6.5 Hz, 2 H), 2.19-2.12 (m, 3 H), 2.09-2.04 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.3, 149.9, 126.6, 77.1, 69.0, 36.6, 26.6; ES HRMS *m/z* $(M+Na)^+$ calcd 173.0573, obsd 173.0589.

Diels-Alder Cycloadditions: (a) Involving 9. A solution of **8** (359 mg, 0.679 mmol) and **1** (102 mg, 0.677 mmol) in dry diglyme was refluxed for 2 h under N_2 and freed of solvent under reduced pressure. Chromatography of the residue on silica gel afforded **10** (116 mg, 63%), **11** (17.5 mg, 10%), and **12** (10.2 mg, 6%).

For **10**: white solid, mp 140-142.5 °C; IR (neat, cm^{-1}) 1661, 1462, 1390; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37-7.35 (m, 1 H), 7.15-7.05 (m, 2 H), 7.03-6.99 (m, 1 H), 5.85 (dd, *J* = 10.3, 1.6 Hz, 1 H), 5.56 (d, *J* = 5.9 Hz, 1 H), 5.45 (d, *J* = 4.8 Hz, 1 H), 4.99 (d, *J* = 10.3 Hz, 1 H), 4.13 (dt, *J* = 8.3, 3.7 Hz, 1 H), 3.89 (dt, *J* = 8.5, 7.0 Hz, 1 H), 3.23 (dd, *J* = 9.4, 5.9 Hz, 1 H), 2.97 (ddd, *J* = 9.4, 4.8, 1.6 Hz, 1 H), 2.14-1.99 (m, 2 H), 1.86-1.69 (m, 2 H); ^{13}C NMR (75 MHz,

$CDCl_3$) δ 198.2, 151.6, 142.8, 142.7, 127.0, 124.9, 122.5, 120.3, 82.8, 82.5, 79.1, 68.4, 48.4, 47.5, 41.6, 25.3; EI HRMS *m/z* $(M+Na)^+$ calcd 291.0992, obsd 291.0991.

For **11**: white solid; IR (neat, cm^{-1}) 1666, 1043; ^1H NMR (300 MHz, $CDCl_3$) δ 7.37-7.34 (m, 1 H), 7.32-7.29 (m, 1 H), 7.23-7.19 (m, 2 H), 6.89 (dd, *J* = 10.3, 1.4 Hz, 1 H), 6.12 (d, *J* = 10.3 Hz, 1 H), 5.72 (s, 1 H), 5.42 (s, 1 H), 4.09-3.94 (m, 2 H), 2.65 (d, *J* = 7.7 Hz, 1 H), 2.12 (dd, *J* = 7.7, 1.2 Hz, 1 H), 2.06 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.1, 154.2, 143.7, 129.2, 127.1, 126.8, 119.9, 118.2, 85.3, 81.2, 79.9, 68.2, 50.0, 48.7, 41.9, 25.0; ES HRMS *m/z* $(M+Na)^+$ calcd 291.0992, obsd 291.0995.

For **12**: white solid; IR (neat, cm^{-1}) 1666, 1037; ^1H NMR (300 MHz, $CDCl_3$) δ 7.22-7.18 (m, 1 H), 7.15-7.02 (m, 3 H), 5.77 (dd, *J* = 10.1, 1.6 Hz, 1 H), 5.58 (d, *J* = 6.0 Hz, 1 H), 5.41 (d, *J* = 4.9 Hz, 1 H), 3.88-3.80 (m, 2 H), 3.45 (d, *J* = 9.0, 6.0 Hz, 1 H), 3.13 (ddd, *J* = 9.1, 4.9, 1.7 Hz, 1 H), 2.23-2.14 (m, 2 H), 2.05-1.95 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.3, 151.1, 140.7, 139.6, 128.3, 125.9, 122.4, 119.9, 83.7, 82.1, 81.0, 74.2, 67.2, 49.4, 46.9, 45.9, 32.4; ES HRMS *m/z* $(M+Na)^+$ calcd 291.0992, obsd 291.1002.

(b) Involving 13. A solution of **1** (175 mg, 1.17 mmol) and **13** (378 mg, 1.40 mmol) in dry, oxygen-free benzene was refluxed overnight under an argon atmosphere, cooled, and placed directly onto a chromatography column. There was isolated 409 mg (83%) of **14** as a white solid, mp 147-149.5 °C; IR (neat, cm^{-1}) 1666, 1447; ^1H NMR (500 MHz, $CDCl_3$) δ 7.95 (m, 4 H), 7.72 (d, *J* = 7.4 Hz, 1 H), 7.51-7.41 (m, 7 H), 7.31 (dd, *J* = 7.4, 7.4 Hz, 1 H), 7.22 (dd, *J* = 7.4, 7.4 Hz, 1 H), 6.95 (d, *J* = 7.3 Hz, 1 H), 5.86 (dd, *J* = 10.2, 1.6 Hz, 1 H), 5.09 (d, *J* = 10.3 Hz, 1 H), 3.91 (d, *J* = 9.3 Hz, 1 H), 3.68 (dd, *J* = 9.3, 1.5 Hz, 1 H), 3.62 (ddd, *J* = 8.6, 8.6, 6.7 Hz, 1 H), 3.30 (ddd, *J* = 8.1, 8.1, 2.4 Hz, 1 H), 2.08-1.85 (m, 3 H), 1.74-1.68 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.1, 151.0, 146.9, 143.7, 137.8, 136.3, 128.5, 128.5, 128.2, 128.0, 127.8, 127.4, 127.2, 124.5, 120.7, 91.1, 84.2, 79.2, 68.3, 54.1, 54.0, 42.3, 25.4; ES HRMS *m/z* $(M+Na)^+$ calcd 443.1618, obsd 443.1620.

(c) Involving 15. A solution of **1** (80 mg, 0.533 mmol) and **15** (147 g, 0.639 mmol) in dry toluene was refluxed for 48 h under N_2, cooled, and placed directly atop a column of silica gel. After elution with ethyl acetate, there was isolated 158 mg (78%) of **16** as a white solid, mp 202-204 °C; IR (neat, cm^{-1}) 1683, 1456, 1384; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29-7.16 (m, 3 H), 7.15 (dd, *J* = 6.4, 1.8 Hz, 1 H), 6.97-6.86 (m, 4 H), 6.53 (dd, *J* = 10.2, 1.9 Hz, 1 H), 5.76 (d, *J* = 10.2 Hz, 1 H), 4.78 (s, 1 H), 4.65 (s, 1 H), 3.93-3.85 (m, 2 H), 3.14 (d, *J* = 16.2 Hz, 1 H), 2.70 (m, 1 H), 2.44 (m, 1 H), 2.32-2.13 (m, 4 H), 2.06-1.85 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.5, 151.2, 146.4, 145.5, 140.6, 140.3, 127.0, 124.3, 124.1, 122.6, 122.3, 122.2, 83.4, 67.7, 55.3, 54.9, 44.1, 44.1, 35.3, 25.7, 25.7, 25.5; ES HRMS *m/z* $(M+Na)^+$ calcd 403.1668, obsd 403.1682.

(d) Involving Cyclopentadiene. A solution of **1** (99 mg, 0.66 mmol) in trifluoroethanol (5 mL) was treated with freshly distilled cyclopentadiene (43.6 mg, 0.66 mmol), stirred for 6 h at 36 °C, and concentrated. The residue was chromatographed on silica gel to give 121 mg (83%) of **17** and 10.5 mg (7%) of **18**, both as colorless oils.

For **17**: IR (neat, cm^{-1}) 1650, 1389; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.36 (dd, *J* = 10.3, 1.1 Hz, 1 H), 6.14 (dd, *J* = 5.5, 2.9 Hz, 1 H), 6.02 (dd, *J* = 5.5, 2.8 Hz, 1 H), 5.69 (d, *J* = 10.3 Hz, 1 H), 3.96 (dt, *J* = 8.1, 4.2 Hz, 1 H), 3.82 (dt, *J* = 8.2, 7.3 Hz, 1 H), 3.24 (m, 1 H), 3.01 (m, 1 H), 2.84 (dd, *J* = 8.8, 4.3 Hz, 1 H), 2.52 (ddd, *J* = 8.8, 3.5, 1.1 Hz, 1 H), 1.99-1.92 (m, 2 H), 1.80-1.69 (m, 2 H), 1.31 (dt, *J* = 3.5, 1.7 Hz, 1 H), 1.21 (d, *J* = 8.3 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.6, 153.4, 135.8, 133.8, 129.1, 79.9, 68.2, 50.7, 48.4, 47.5, 47.0, 46.0, 42.7, 24.8; ES HRMS *m/z* $(M+Na)^+$ calcd 239.1042, obsd 239.1054.

For **18**: IR (neat, cm^{-1}) 1668, 1456, 1259; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.40 (dd, *J* = 10.1, 1.3 Hz, 1 H), 5.96 (m, 2 H), 5.91 (d, *J* = 10.1 Hz, 1 H), 3.97-3.90 (m, 2 H), 3.38-3.37 (m, 1 H), 3.14-3.10 (m, 2 H), 2.83 (ddd, *J* = 8.6, 3.4, 1.4 Hz, 1 H), 2.20-2.10 (m, 3 H), 1.84-1.81 (m, 1 H), 1.49 (dt, *J* = 3.6, 1.8 Hz, 1 H), 1.42 (d, *J* = 8.4 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.1,

149.1, 135.2, 133.4, 131.0, 79.2, 66.9, 49.7, 49.3, 47.1, 46.9, 46.4, 35.5, 26.2; ES HRMS *m/z* $(M+Na)^+$ calcd 239.1042, obsd 239.1041.

(e) Involving Spiro[2.4]hepta-4,6-diene. Overnight reaction of the spirodiene (140 mg, 1.53 mmol) with **1** (229 mg, 1.53 mmol) in trifluoroethanol (5 mL) at 55 °C and workup in the predescribed manner returned 91 mg of unreacted **1** and gave 146 mg (66%) of **19** alongside 45 mg (20%) of **20**, both as colorless oils.

For **19**: IR (neat, cm^{-1}) 1665, 1387, 1246; ^1H NMR (500 MHz, $CDCl_3$) δ 6.49 (dd, *J* = 10.3, 0.9 Hz, 1 H), 6.22 (dd, *J* = 5.6, 2.8 Hz, 1 H), 5.86 (dd, *J* = 5.7, 2.8 Hz, 1 H), 5.79 (d, *J* = 10.3 Hz, 1 H), 4.01 (dt, *J* = 8.2, 4.0 Hz, 1 H), 3.89 (q, *J* = 8.3 Hz, 1 H), 3.10 (dd, *J* = 8.6, 4.4 Hz, 1 H), 2.80 (dd, *J* = 8.6, 3.3 Hz, 1 H), 2.72 (s, 1 H), 2.44 (s, 1 H), 2.07-2.03 (m, 2 H), 1.92-1.80 (m, 1 H), 0.55-0.40 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.2, 153.7, 136.2, 133.5, 129.4, 79.7, 68.1, 55.4, 52.1, 48.5, 47.0, 43.9, 42.7, 24.9, 7.8, 5.9; ES HRMS *m/z* $(M+Na)^+$ calcd 265.1199, obsd 265.1206.

For **20**: IR (neat, cm^{-1}) 1665, 1392; ^1H NMR (300 MHz, $CDCl_3$) δ 6.37 (dd, *J* = 10.2,1.4 Hz, 1 H), 6.02 (dd, *J* = 5.4, 2.8 Hz, 1 H), 5.95 (dd, *J* = 5.7, 2.8 Hz, 1 H), 5.87 (d, *J* = 10.2 Hz, 1 H), 3.93-3.80 (m, 2 H), 3.21 (dd, *J* = 8.5, 4.5 Hz, 1 H), 2.96 (ddd, *J* = 8.4, 3.5, 1.3 Hz, 1 H), 2.69-2.67 (m, 1 H), 2.39 (s, 1 H), 2.13-1.98 (m, 3 H), 1.79-1.73 (m, 1 H), 0.53-0.38 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.0, 149.5, 135.2, 133.7, 131.2, 78.8, 66.9, 54.5, 52.0, 48.2, 47.3, 44.8, 35.5, 26.1, 7.9, 6.2; ES HRMS *m/z* $(M+Na)^+$ calcd 265.1199, obsd 265.1210.

Crystallographic Results for 10. The data collection crystal was a clear, colorless rectangular chunk. Examination of the diffraction pattern on a Nonius Kappa CCD diffractometer indicated a monoclinic crystal system. All work was done at 200 K using an Oxford Cryosystems Cooler. The data collection strategy was set up to measure a quadrant of reciprocal space with a redundancy factor of 3.5, which means that 90% of the reflections were measured at least 3.5 times. A combination of phi and omega scans with a frame width of 1.0° was used. Data integration was done with Denzo,[1] and scaling and merging of the data was done with Scalepack.[1] Merging the data and averaging the symmetry equivalent reflections resulted in an Rint value of 0.031. The teXsan[2] package indicated the space group to be $P2_1/n$.

The structure was solved by direct methods in SHELXS-86.[3] Full-matrix least-squares refinements based on F^2 were performed in SHELXL-93.[4]

The hydrogen atoms were included in the model at calculated positions using a riding model with U(H) = 1.2 * Ueq(attached atom). The final refinement cycle was based on all 3006 intensities and 181 variables and resulted in agreement factors of R1(F) = 0.055 and $wR2(F^2)$ = 0.106. For the subset of data with $I > 2\sigma(I)$, the R1(F) value is 0.040 for 2362 reflections. The final difference electron density map contains maximum and minimum peak heights of 0.20 and -0.26 e/Å^3. Neutral atom scattering factors were used and include terms for anomalous dispersion.[5]

References

(1) DENZO: Otwinowski, Z. & Minor, W., Methods in Enzymology, Vol 276: Macromolecular Crystallography, part A, 307-326, (1997), Carter, Jr., C. W. & Sweet, R. M., Eds., Academic Press.

(2) teXsan: Crystal Structure Analysis Package, version 1.7-2, Molecular Structure Corporation, The Woodlands, TX (1995).

(3) SHELXS-86: Sheldrick, G. M., Acta Cryst. (1990), A46, 467-473.

(4) SHELXL-93: Sheldrick, G. M., Universitat Gottingen, Germany, 1993.

(5) International Tables for Crystallography (1992). Volume C. Dordrecht: Kluwer Academic Publishers.

Table 1. Crystallographic Details for **10**.

Empirical formula	$C_{17}H_{16}O_3$
Formula weight	268.30
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 10.1159(1) Å b = 8.0012(1) Å c = 16.4566(2) Å beta = 100.079(1) deg.
Volume	1311.43(3) $Å^3$
Z	4
Density (calculated)	1.359 Mg/m^3
Absorption coefficient	0.092 mm^{-1}
F(000)	568
Crystal size	0.12 x 0.23 x 0.23 mm
Theta range for data collection	2.51 to 27.46 deg.
Index ranges	-13<=h<=13, -10<=k<=10, -21<=l<=21
Reflections collected	22321
Independent reflections	3006 [R(int) = 0.031]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3006 / 0 / 181
Goodness-of-fit on F^2	1.071
Final R indices [I>2sigma(I)]	R1 = 0.0400, wR2 = 0.0977
R indices (all data)	R1 = 0.0548, wR2 = 0.1060
Largest diff. peak and hole	0.203 and -0.265 e/ $Å^3$

Table 2. Bond Lengths (Å) and Angles (°) for **10**.

O(1)-C(7)	1.441(2)
O(1)-C(14)	1.4580(14)
O(2)-C(9)	1.226(2)
O(3)-C(17)	1.440(2)
O(3)-C(12)	1.4506(14)
C(1)-C(2)	1.382(2)
C(1)-C(6)	1.393(2)
C(1)-C(14)	1.510(2)
C(2)-C(3)	1.396(2)
C(2)-H(2)	0.95
C(3)-C(4)	1.382(2)
C(3)-H(3)	0.95
C(4)-C(5)	1.396(2)
C(4)-H(4)	0.95
C(5)-C(6)	1.379(2)
C(5)-H(5)	0.95
C(6)-C(7)	1.511(2)
C(7)-C(8)	1.573(2)
C(7)-H(7)	1.00
C(8)-C(9)	1.507(2)
C(8)-C(13)	1.557(2)
C(8)-H(8)	1.00
C(9)-C(10)	1.461(2)
C(10)-C(11)	1.331(2)
C(10)-H(10)	0.95
C(11)-C(12)	1.502(2)
C(11)-H(11)	0.95
C(12)-C(13)	1.531(2)
C(12)-C(15)	1.551(2)
C(13)-C(14)	1.555(2)
C(13)-H(13)	1.00
C(14)-H(14)	1.00
C(15)-C(16)	1.519(2)
C(15)-H(15A)	0.99
C(15)-H(15B)	0.99
C(16)-C(17)	1.512(2)
C(16)-H(16A)	0.99
C(16)-H(16B)	0.99
C(17)-H(17A)	0.99
C(17)-H(17B)	0.99

C(7)-O(1)-C(14)	96.47(9)
C(17)-O(3)-C(12)	109.79(9)
C(2)-C(1)-C(6)	121.20(11)
C(2)-C(1)-C(14)	133.92(11)
C(6)-C(1)-C(14)	104.88(10)
C(1)-C(2)-C(3)	117.70(12)
C(1)-C(2)-H(2)	121.2
C(3)-C(2)-H(2)	121.2
C(4)-C(3)-C(2)	121.02(13)
C(4)-C(3)-H(3)	119.5
C(2)-C(3)-H(3)	119.5
C(3)-C(4)-C(5)	121.09(13)
C(3)-C(4)-H(4)	119.4
C(5)-C(4)-H(4)	119.4
C(6)-C(5)-C(4)	117.79(13)
C(6)-C(5)-H(5)	121.1
C(4)-C(5)-H(5)	121.1
C(5)-C(6)-C(1)	121.15(12)
C(5)-C(6)-C(7)	134.17(12)
C(1)-C(6)-C(7)	104.65(10)
O(1)-C(7)-C(6)	101.50(10)
O(1)-C(7)-C(8)	100.76(9)
C(6)-C(7)-C(8)	108.23(10)
O(1)-C(7)-H(7)	114.9
C(6)-C(7)-H(7)	114.9
C(8)-C(7)-H(7)	114.9
C(9)-C(8)-C(13)	117.99(10)
C(9)-C(8)-C(7)	110.41(10)
C(13)-C(8)-C(7)	100.96(9)
C(9)-C(8)-H(8)	109.0
C(13)-C(8)-H(8)	109.0
C(7)-C(8)-H(8)	109.0
O(2)-C(9)-C(10)	122.05(12)
O(2)-C(9)-C(8)	119.51(12)
C(10)-C(9)-C(8)	118.38(11)
C(11)-C(10)-C(9)	121.63(12)
C(11)-C(10)-H(10)	119.2
C(9)-C(10)-H(10)	119.2
C(10)-C(11)-C(12)	124.36(11)
C(10)-C(11)-H(11)	117.8
C(12)-C(11)-H(11)	117.8
O(3)-C(12)-C(11)	109.24(9)

O(3)-C(12)-C(13)	107.81(10)
C(11)-C(12)-C(13)	113.76(10)
O(3)-C(12)-C(15)	104.92(9)
C(11)-C(12)-C(15)	108.77(10)
C(13)-C(12)-C(15)	111.94(10)
C(12)-C(13)-C(14)	116.33(10)
C(12)-C(13)-C(8)	116.09(10)
C(14)-C(13)-C(8)	101.29(9)
C(12)-C(13)-H(13)	107.5
C(14)-C(13)-H(13)	107.5
C(8)-C(13)-H(13)	107.5
O(1)-C(14)-C(1)	101.07(9)
O(1)-C(14)-C(13)	99.77(9)
C(1)-C(14)-C(13)	110.39(10)
O(1)-C(14)-H(14)	114.6
C(1)-C(14)-H(14)	114.6
C(13)-C(14)-H(14)	114.6
C(16)-C(15)-C(12)	103.47(10)
C(16)-C(15)-H(15A)	111.1
C(12)-C(15)-H(15A)	111.1
C(16)-C(15)-H(15B)	111.1
C(12)-C(15)-H(15B)	111.1
H(15A)-C(15)-H(15B)	109.0
C(17)-C(16)-C(15)	101.24(10)
C(17)-C(16)-H(16A)	111.5
C(15)-C(16)-H(16A)	111.5
C(17)-C(16)-H(16B)	111.5
C(15)-C(16)-H(16B)	111.5
H(16A)-C(16)-H(16B)	109.3
O(3)-C(17)-C(16)	105.03(10)
O(3)-C(17)-H(17A)	1110.7
C(16)-C(17)-H(17A)	110.7
O(3)-C(17)-H(17B)	110.7
C(16)-C(17)-H(17B)	110.7
H(17A)-C(17)-H(17B)	108.8

Table 3. Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$ x 10^3) for **10.**

	x	y	z	U(eq)
O(1)	2045(1)	575(1)	3959(1)	32(1)
O(2)	266(1)	-4119(1)	2911(1)	41(1)
O(3)	5345(1)	-2602(1)	4449(1)	28(1)
C(1)	2720(1)	-1328(2)	4988(1)	24(1)
C(2)	3303(1)	-1898(2)	5761(1)	29(1)
C(3)	2489(1)	-2763(2)	6221(1)	35(1)
C(4)	1155(1)	-3077(2)	5904(1)	39(1)
C(5)	575(1)	-2521(2)	5118(1)	35(1)
C(6)	1370(1)	-1622(2)	4675(1)	27(1)
C(7)	1141(1)	-829(2)	3829(1)	30(1)
C(8)	1850(1)	-1941(2)	3244(1)	27(1)
C(9)	1393(1)	-3732(2)	3266(1)	28(1)
C(10)	2295(1)	-4938(2)	3745(1)	30(1)
C(11)	3588(1)	-4599(2)	4004(1)	29(1)
C(12)	4284(1)	-3058(2)	3773(1)	24(1)
C(13)	3354(1)	-1546(2)	3580(1)	24(1)
C(14)	3236(1)	-372(2)	4317(1)	26(1)
C(15)	5017(1)	-3486(2)	3047(1)	31(1)
C(16)	6355(1)	-2591(2)	3272(1)	35(1)
C(17)	6632(1)	-2797(2)	4200(1)	30(1)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 4. Anisotropic Displacement Parameters ($Å^2$ x 10^3) for **1 0**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	33(1)	22(1)	39(1)	3(1)	4(1)	2(1)
O(2)	32(1)	45(1)	43(1)	-7(1)	-2(1)	-9(1)
O(3)	23(1)	37(1)	24(1)	-4(1)	2(1)	0(1)
C(1)	26(1)	22(1)	27(1)	-4(1)	8(1)	-1(1)
C(2)	29(1)	30(1)	27(1)	-3(1)	6(1)	1(1)
C(3)	43(1)	37(1)	28(1)	3(1)	14(1)	7(1)
C(4)	39(1)	40(1)	42(1)	4(1)	23(1)	0(1)
C(5)	27(1)	38(1)	42(1)	-3(1)	14(1)	-2(1)
C(6)	26(1)	25(1)	30(1)	-4(1)	7(1)	2(1)
C(7)	26(1)	28(1)	34(1)	2(1)	3(1)	2(1)
C(8)	27(1)	29(1)	22(1)	3(1)	2(1)	0(1)
C(9)	28(1)	33(1)	23(1)	-5(1)	6(1)	-4(1)
C(10)	36(1)	24(1)	32(1)	-1(1)	8(1)	-6(1)
C(11)	36(1)	24(1)	26(1)	3(1)	5(1)	3(1)
C(12)	23(1)	28(1)	22(1)	0(1)	2(1)	-1(1)
C(13)	26(1)	24(1)	23(1)	3(1)	6(1)	-2(1)
C(14)	25(1)	23(1)	30(1)	0(1)	3(1)	-2(1)
C(15)	33(1)	36(1)	24(1)	-3(1)	6(1)	3(1)
C(16)	35(1)	36(1)	36(1)	0(1)	15(1)	0(1)
C(17)	23(1)	32(1)	36(1)	-5(1)	5(1)	1(1)

Table 5. Calculated Hydrogen Coordinates (x 10^4) and Isotropic Displacement Parameters (Å^2 x 10^3) for **10**.

	x	y	z	U(eq)
H(2)	4226(1)	-1709(2)	5972(1)	34
H(3)	2857(1)	-3141(2)	6760(1)	42
H(4)	625(1)	-3682(2)	6225(1)	46
H(5)	-338(1)	-2754(2)	4896(1)	41
H(7)	185(1)	-538(2)	3604(1)	35
H(8)	1611(1)	-1511(2)	2667(1)	32
H(10)	1950(1)	-5990(2)	3874(1)	36
H(11)	4105(1)	-5386(2)	4358(1)	34
H(13)	3699(1)	-862(2)	3153(1)	29
H(14)	4050(1)	324(2)	4513(1)	31
H(15A)	5146(1)	-4707(2)	3004(1)	37
H(15B)	4508(1)	-3067(2)	2517(1)	37
H(16A)	7059(1)	-3129(2)	3014(1)	42
H(16B)	6281(1)	-1398(2)	3112(1)	42
H(17A)	7012(1)	-3915(2)	4355(1)	36
H(17B)	7270(1)	-1935(2)	4461(1)	36

Crystallographic Results for 16. The data collection crystal was a clear, colorless rectangular chunk. Examination of the diffraction pattern on a Nonius Kappa CCD diffractometer indicated a monoclinic crystal system. All work was done at 200 K using an Oxford Cryosystems Cooler. The data collection strategy was set up to measure a quadrant of reciprocal space with a redundancy factor of 4.2, which means that 90% of the reflections were measured at least 4.2 times. A combination of phi and omega scans with a frame width of 1.0° was used. Data integration was done with Denzo,[1] and scaling and merging of the data was done with Scalepack.[1] Merging the data and averaging the symmetry equivalent reflections resulted in an Rint value of 0.038. The teXsan[2] package indicated the space group to be $P2_1/c$.

The structure was solved by direct methods in SHELXS-86.[3] Full-matrix least-squares refinements based on F^2 were performed in SHELXL-93.[4] Atom C(4) is disordered over two positions: C(4) and C(4A). Both atoms were kept isotropic. The occupancy factor for C(4) refined to 0.814(9) and that for C(4A) was set to 0.186(9).

The hydrogen atoms were included in the model at calculated positions using a riding model with U(H) = 1.2 * Ueq(attached atom). The final refinement cycle was based on all 3501 intensities and 262 variables and resulted in agreement factors of R1(F) = 0.060 and $wR2(F^2)$ = 0.107. For the subset of data with $I > 2\sigma(I)$, the R1(F) value is 0.041 for 2688 reflections. The final difference electron density map contains maximum and minimum peak heights of 0.22 and -0.30 e/Å^3. Neutral atom scattering factors were used and include terms for anomalous dispersion.[5]

References

(1) DENZO: Otwinowski, Z. & Minor, W., Methods in Enzymology, Vol 276: Macromolecular Crystallography, part A, 307-326, (1997), Carter, Jr., C. W. & Sweet, R. M., Eds., Academic Press.

(2) teXsan: Crystal Structure Analysis Package, version 1.7-2, Molecular Structure Corporation, The Woodlands, TX (1995).

(3) SHELXS-86: Sheldrick, G. M., Acta Cryst. (1990), A46, 467-473.

(4) SHELXL-93: Sheldrick, G. M., Universitat Gottingen, Germany, 1993.

(5) International Tables for Crystallography (1992). Volume C. Dordrecht: Kluwer Academic Publishers.

Table 6. Crystallographic Details for **16**.

Empirical formula	$C_{27}H_{24}O_2$
Formula weight	380.46
Temperature	200(2) K
Wavelength	0.71073 A
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 14.7727(2) Å b = 10.1531(1) Å c = 13.8150(2) Å beta = 106.951(1) deg.
Volume	1982.07(4) $Å^3$
Z	4
Density (calculated)	1.275 Mg/m^3
Absorption coefficient	0.079 mm^{-1}
F(000)	808
Crystal size	0.08 x 0.19 x 0.27 mm
Theta range for data collection	2.53 to 25.03 deg.
Index ranges	-17<=h<=17, -12<=k<=12, -16<=l<=16
Reflections collected	33524
Independent reflections	3501 [R(int) = 0.038]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3501 / 0 / 262
Goodness-of-fit on F^2	1.026
Final R indices [I>2sigma(I)]	R1 = 0.0413, wR2 = 0.0972
R indices (all data)	R1 = 0.0599, wR2 = 0.1072
Largest diff. peak and hole	0.222 and -0.301 e/ $Å^3$

Table 7. Bond Lengths (Å) and Angles (°) for **16**.

O(1)-C(4)	1.415(2)
O(1)-C(4A)	1.444(10)
O(1)-C(1)	1.450(2)
O(2)-C(7)	1.223(2)
C(1)-C(5)	1.498(2)
C(1)-C(13)	1.540(2)
C(1)-C(2)	1.543(2)
C(2)-C(3)	1.520(2)
C(2)-H(2A)	0.99
C(2)-H(2B)	0.99
C(3)-C(4A)	1.312(9)
C(3)-C(4)	1.525(3)
C(3)-H(3A)	0.99
C(3)-H(3B)	0.99
C(3)-H(3C)	0.99
C(3)-H(3D)	0.99
C(4)-H(4A)	0.99
C(4)-H(4B)	0.99
C(4A)-H(4C)	0.99
C(4A)-H(4D)	0.99
C(5)-C(6)	1.326(2)
C(5)-H(5)	0.95
C(6)-C(7)	1.465(2)
C(6)-H(6)	1.515(2)
C(8)-C(9)	1.530(2)
C(8)-C(13)	1.545(2)
C(8)-H(8)	1.00
C(9)-C(10)	1.502(2)
C(9)-H(9A)	0.99
C(9)-H(9B)	0.99
C(10)-C(11)	1.325(2)
C(10)-C(14)	1.531(2)
C(11)-C(12)	1.493(2)
C(11)-C(21)	1.539(2)
C(12)-C(13)	1.531(2)
C(12)-H(12A)	0.99
C(12)-H(12B)	0.99
C(13)-H(13)	1.00
C(14)-C(27)	1.526(2)
C(14)-C(15)	1.532(2)

C(14)-H(14)	1.00
C(15)-C(16)	1.379(2)
C(15)-C(20)	1.401(2)
C(16)-C(17)	1.395(2)
C(16)-H(16)	0.95
C(17)-C(18)	1.377(2)
C(17)-H(17)	0.95
C(18)-C(19)	1.390(2)
C(18)-H(18)	0.95
C(19)-C(20)	1.382(2)
C(19)-H(19)	0.95
C(20)-C(21)	1.520(2)
C(21)-C(22)	1.525(2)
C(21)-H(21)	1.00
C(22)-C(23)	1.376(2)
C(22)-C(27)	1.402(2)
C(23)-C(24)	1.393(2)
C(23)-H(23)	0.95
C(24)-C(25)	1.379(2)
C(24)-H(24)	0.95
C(25)-C(26)	1.395(2)
C(25)-H(25)	0.95
C(26)-C(27)	1.378(2)
C(26)-H(26)	0.95

C(4)-O(1)-C(1)	111.28(12)
C(4A)-O(1)-C(1)	102.9(4)
O(1)-C(1)-C(5)	106.59(12)
O(1)-C(1)-C(13)	108.47(11)
C(5)-C(1)-C(13)	111.59(12)
O(1)-C(1)-C(2)	104.73(11)
C(5)-C(1)-C(2)	111.95(12)
C(13)-C(1)-C(2)	113.02(12)
C(3)-C(2)-C(1)	103.29(12)
C(4A)-C(3)-C(2)	106.3(4)
C(2)-C(3)-C(4)	101.77(14)
O(1)-C(4)-C(3)	104.4(2)
C(3)-C(4A)-O(1)	114.9(7)
C(6)-C(5)-C(1)	124.74(14)
C(5)-C(6)-C(7)	121.90(14)
O(2)-C(7)-C(6)	121.69(14)
O(2)-C(7)-C(8)	122.73(14)

C(6)-C(7)-C(8)	115.57(13)
C(7)-C(8)-C(9)	113.01(12)
C(7)-C(8)-C(13)	109.42(11)
C(9)-C(8)-C(13)	112.29(11)
C(10)-C(9)-C(8)	111.53(12)
C(11)-C(10)-C(9)	123.84(13)
C(11)-C(10)-C(14)	113.96(13)
C(9)-C(10)-C(14)	122.20(12)
C(10)-C(11)-C(12)	124.76(13)
C(10)-C(11)-C(21)	113.87(13)
C(12)-C(11)-C(21)	121.36(12)
C(11)-C(12)-C(13)	111.21(11)
C(12)-C(13)-C(1)	112.09(11)
C(12)-C(13)-C(8)	110.60(11)
C(1)-C(13)-C(8)	111.18(11)
C(27)-C(14)-C(10)	105.57(12)
C(27)-C(14)-C(15)	105.11(11)
C(10)-C(14)-C(15)	106.55(11)
C(16)-C(15)-C(20)	119.85(14)
C(16)-C(15)-C(14)	127.91(14)
C(20)-C(15)-C(14)	112.24(13)
C(15)-C(16)-C(17)	119.6(2)
C(18)-C(17)-C(16)	120.3(2)
C(17)-C(18)-C(19)	120.7(2)
C(20)-C(19)-C(18)	119.1(2)
C(19)-C(20)-C(15)	120.49(14)
C(19)-C(20)-C(21)	126.71(14)
C(15)-C(20)-C(21)	112.79(12)
C(20)-C(21)-C(22)	105.04(11)
C(20)-C(21)-C(11)	106.16(12)
C(22)-C(21)-C(11)	105.99(11)
C(23)-C(22)-C(27)	120.56(14)
C(23)-C(22)-C(21)	126.93(13)
C(27)-C(22)-C(21)	112.50(13)
C(22)-C(23)-C(24)	119.3(2)
C(25)-C(24)-C(23)	120.4(2)
C(24)-C(25)-C(26)	120.4(2)
C(27)-C(26)-C(25)	119.4(2)
C(26)-C(27)-C(22)	119.9(2)
C(26)-C(27)-C(14)	127.60(14)
C(22)-C(27)-C(14)	112.48(12)

Table 8. Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$ x 10^3) for **16.**

	x	y	z	U(eq)
O(1)	3964(1)	2444(1)	2978(1)	38(1)
O(2)	6027(1)	1687(1)	536(1)	43(1)
C(1)	4093(1)	2872(1)	2025(1)	31(1)
C(2)	3296(1)	3885(2)	1605(1)	38(1)
C(3)	3031(1)	4318(2)	2540(1)	49(1)
C(4)	3163(2)	3047(3)	3152(2)	41(1)*
C(4A)	3515(10)	3567(14)	3284(7)	43(4)*
C(5)	3979(1)	1675(2)	1368(1)	36(1)
C(6)	4566(1)	1326(2)	848(1)	36(1)
C(7)	5397(1)	2119(2)	856(1)	31(1)
C(8)	5411(1)	3503(1)	1269(1)	28(1)
C(9)	6367(1)	4190(2)	1439(1)	31(1)
C(10)	7050(1)	3810(1)	2437(1)	28(1)
C(11)	6802(1)	3178(1)	3160(1)	28(1)
C(12)	5819(1)	2747(2)	3090(1)	29(1)
C(13)	5090(1)	3470(1)	2238(1)	28(1)
C(14)	8105(1)	4144(2)	2711(1)	32(1)
C(15)	8340(1)	4930(2)	3699(1)	33(1)
C(16)	8779(1)	6140(2)	3900(1)	39(1)
C(17)	8942(1)	6698(2)	4858(1)	47(1)
C(18)	8656(1)	6053(2)	5596(1)	46(1)
C(19)	8212(1)	4834(2)	5402(1)	38(1)
C(20)	8066(1)	4269(2)	4459(1)	32(1)
C(21)	7629(1)	2929(2)	4120(1)	30(1)
C(22)	8375(1)	2184(2)	3773(1)	31(1)
C(23)	8785(1)	998(2)	4138(1)	37(1)
C(24)	9429(1)	427(2)	3701(1)	43(1)
C(25)	9660(1)	1049(2)	2917(1)	44(1)
C(26)	9264(1)	2269(2)	2565(1)	38(1)
C(27)	8623(1)	2835(2)	2992(1)	32(1)

*Refined isotropically. Atom C(4) is disordered over two sites: C(4) and C(4A). The occupancy factor for C(4) refined to 0.814(9), and that for C(4A) is 0.186(9).

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 9. Anisotropic Displacement Parameters ($Å^2$ x 10^3) for **16**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	33(1)	38(1)	46(1)	7(1)	18(1)	4(1)
O(2)	52(1)	43(1)	39(1)	-7(1)	21(1)	1(1)
C(1)	29(1)	28(1)	35(1)	1(1)	9(1)	-1(1)
C(2)	28(1)	36(1)	45(1)	2(1)	5(1)	1(1)
C(3)	40(1)	50(1)	55(1)	-5(1)	11(1)	13(1)
C(5)	32(1)	28(1)	43(1)	-1(1)	6(1)	-5(1)
C(6)	42(1)	28(1)	36(1)	-6(1)	6(1)	-4(1)
C(7)	38(1)	32(1)	22(1)	1(1)	6(1)	1(1)
C(8)	30(1)	26(1)	27(1)	3(1)	4(1)	1(1)
C(9)	34(1)	29(1)	30(1)	1(1)	10(1)	-2(1)
C(10)	27(1)	27(1)	31(1)	-3(1)	9(1)	0(1)
C(11)	27(1)	28(1)	28(1)	-3(1)	8(1)	2(1)
C(12)	28(1)	32(1)	26(1)	-1(1)	9(1)	-1(1)
C(13)	28(1)	23(1)	31(1)	-2(1)	8(1)	-1(1)
C(14)	29(1)	34(1)	33(1)	-1(1)	12(1)	-3(1)
C(15)	24(1)	35(1)	38(1)	-4(1)	8(1)	1(1)
C(16)	31(1)	38(1)	48(1)	-4(1)	12(1)	-4(1)
C(17)	38(1)	40(1)	58(1)	-16(1)	8(1)	-7(1)
C(18)	40(1)	52(1)	42(1)	-16(1)	6(1)	-1(1)
C(19)	32(1)	47(1)	33(1)	-4(1)	5(1)	3(1)
C(20)	22(1)	37(1)	34(1)	-2(1)	5(1)	3(1)
C(21)	27(1)	35(1)	30(1)	2(1)	8(1)	1(1)
C(22)	24(1)	34(1)	33(1)	-5(1)	4(1)	-2(1)
C(23)	29(1)	38(1)	38(1)	-1(1)	2(1)	0(1)
C(24)	31(1)	39(1)	51(1)	-6(1)	3(1)	6(1)
C(25)	31(1)	47(1)	53(1)	-11(1)	12(1)	4(1)
C(26)	30(1)	44(1)	42(1)	-8(1)	13(1)	-4(1)
C(27)	24(1)	35(1)	36(1)	-6(1)	6(1)	-4(1)

Table 10. Calculated Hydrogen Coordinates (x 10^4) and Isotropic Displacement Parameters ($Å^2$ x 10^3) for **16**.

	x	y	z	U(eq)
H(2A)	3526(1)	4639(2)	1286(1)	45
H(2B)	2751(1)	3475(2)	1101(1)	45
H(3A)	2368(1)	4631(2)	2363(1)	59
H(3B)	3457(1)	5022(2)	2910(1)	59
H(3C)	3196(1)	5256(2)	2691(1)	59
H(3D)	2343(1)	4207(2)	2434(1)	59
H(4A)	3276(2)	3237(3)	3881(2)	49
H(4B)	2599(2)	2474(3)	2917(2)	49
H(4C)	3083(10)	3247(14)	3663(7)	51
H(4D)	4008(10)	4110(14)	3753(7)	51
H(5)	3447(1)	1125(2)	1320(1)	43
H(6)	4444(1)	540(2)	458(1)	44
H(8)	4931(1)	4028(1)	753(1)	34
H(9A)	6637(1)	3949(2)	886(1)	37
H(9B)	6273(1)	5156(2)	1419(1)	37
H(12A)	5688(1)	1786(2)	2963(1)	34
H(13)	5058(1)	4401(1)	2462(1)	33
H(14)	8281(1)	4617(2)	2157(1)	38
H(16)	8969(1)	6591(2)	3389(1)	47
H(17)	9251(1)	7526(2)	5003(1)	56
H(18)	8763(1)	6446(2)	6244(1)	55
H(19)	8011(1)	4395(2)	5911(1)	46
H(21)	7431(1)	2456(2)	4659(1)	36
H(23)	8630(1)	572(2)	4681(1)	44
H(24)	9712(1)	-395(2)	3945(1)	51
H(25)	10091(1)	645(2)	2616(1)	52
H(26)	9434(1)	2706(2)	2036(1)	46