High 1,4-*syn* stereoinduction in boron-mediated aldol reactions of methyl ketones.

Luiz C. Dias,^{*a} Rosana Z. Baú, Márcio A. de Sousa and J. Zukerman-Schpector^b

^a *Instituto de Química, Universidade Estadual de Campinas, UNICAMP*

C.P. 6154, 13083-970, Campinas, SP, Brazil

^b *Departamento de Química, UFSCar, C.P. 676, 13565-905, São Carlos, SP, Brazil*

Supporting Information

General Information: ¹H NMR spectra were recorded on either a Varian Gemini-300 (300 MHz) or a Varian Inova-500 (500 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl₃ at 7.26 ppm) unless otherwise indicated. Data are reported as (ap = apparent, s = singlet, d = doublet, t = triplet, q = quartet, qt = quintet, apt = apparent triplet, m = multiplet, brs = broad singlet, bd = broad doublet, dd = doublet of doublets, coupling constant(s) in Hz; integration. Proton-decoupled ¹³C NMR spectra were recorded on either a Varian Gemini-300 (75 MHz), a Bruker AC 300/P (75 MHz) or a Varian Inova-500 (125 MHz) spectrometers and are recorded in ppm using solvent as an internal standard (CDCl₃ at 77.0 ppm) unless otherwise indicated.

MP: 57.0-59.0 °C; $[\alpha]_D^{20} +28.15$ (c 1.07, CHCl_3); IR. (film, cm^{-1}) 3508, 2980, 2921, 1779, 1698, 1455, 1386, 1291, 1210, 1109, 986, 905, 763, 746, 703; ^1H NMR (300 MHz, CDCl_3) 7.20-7.40 (m, 5H), 5.14 (brd, J 0.7 Hz, 1H), 5.00 (dd, J 1.5, 2.9 Hz, 1H), 4.72 (ddd, J 3.3, 6.5, 12.9 Hz, 1H); 4.44 (brs, 1H); 4.18-4.28 (m, 2H); 3.97 (ddd, J 3.3, 7.0, 14.0 Hz, 1H), 3.29 (dd, J 3.3, 13.6 Hz, 1H), 2.83 (dd, J 9.5, 13.2 Hz, 1H), 2.70-3.00 (brs, 1H); 1.75 (s, 3H); 1.21 (d, J 7.0 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) 176.8 (C=O), 152.8 (C=O), 143.6 (C_0), 134.9 (C_0), 129.3 (CH), 128.8 (CH), 127.3 (CH), 111.7 (CH_2), 73.9 (CH), 66.2 (CH_2), 55.2 (CH), 40.1 (CH), 37.8 (CH_2), 19.5 (CH_3), 10.1 (CH_3); TLC (30% EtOAc/Hexanes) R_f 0.17; HRMS Calcd: 303.1470; found: 303.1472.

MP: 76.0-78.0 °C; $[\alpha]_D^{20} -11.57$ (c 1.29, CHCl_3); IR (film, cm^{-1}) 3361, 3088, 2980, 2939, 1764, 1629, 1465, 1383, 1316, 1192, 1058, 1031, 984, 928, 907, 651, 567, 549, 466; ^1H NMR (300 MHz, CDCl_3) 5.15 (brs, 1H), 4.96 (brs, 1H), 4.32 (brs, 1H), 4.02 (brs, 1H), 3.72 (s, 3H), 3.21 (s, 3H), 3.08 (m, 1H), 1.71 (t, J 0.7 Hz, 3H), 1.10 (d, J 7.0 Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) 178.0 (C=O), 143.1 (C_0), 111.8 (CH_2), 74.0 (CH), 61.5 (CH_3), 36.4 (CH), 31.9 (CH_3), 19.5 (CH_3), 9.9 (CH_3); TLC (40% EtOAc/hexanes) R_f 0.18; HRMS Calcd: 187.1208; found: 187.1276.

IR (film, cm^{-1}) 2957, 2934, 2856, 1740, 1661, 1613, 1586, 1513, 1463, 1412, 1384, 1301, 1249, 1173, 1083, 1042, 996, 939, 870, 836, 792, 776, 671; ^1H NMR (300 MHz, CDCl_3) 7.24 (d, J 8.4 Hz, 2H), 6.87 (d, J 8.8 Hz, 2H), 4.37 (d, J 11.5 Hz, 1H), 4.41 (d, J 11.5 Hz, 1H), 3.94 (dd, J 2.9, 8.4 Hz, 1H), 3.81 (s, 3H), 3.58 (s, 3H), 3.57 (m, 1H), 3.16 (m, 1H), 3.12 (s, 3H), 1.91 (m, 1H), 1.12 (d, J 7.0 Hz, 3H), 1.01 (d, J 7.0 Hz, 3H), 0.91 (s, 9H), 0.08 (s, 6H); TLC (40% EtOAc/Hexanes) R_f 0.45.

[α]_D²⁰ +19.5 (*c* 1.03, CHCl₃); IR (film, cm⁻¹) 2956, 2931, 2856, 1711, 1670, 1613, 1586, 1513, 1463, 1360, 1302, 1249, 1173, 1091, 1042, 1006, 953, 863, 837, 775, 674, 579, 515; ¹H NMR (300 MHz, CDCl₃) 7.25 (d, *J* 8.4 Hz, 2H), 6.88 (d, *J* 8.4 Hz, 2H), 4.37 (d, *J* 11.3 Hz, 1H), 4.42 (d, *J* 11.3 Hz, 1H), 4.04 (t, *J* 5.2 Hz), 3.82 (s, 3H), 3.49 (dd, *J* 5.9, 9.1 Hz, 1H), 3.21 (dd, *J* 6.2, 9.2 Hz, 1H), 2.78 (m, 1H), 2.12 (s, 3H), 1.91 (m, 1H), 1.09 (d, *J* 7.0 Hz, 3H), 0.96 (d, *J* 7.0 Hz, 3H), 0.89 (s, 9H), 0.06 (s, 3H), 0.02 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) 211.3 (C=O), 158.8 (C₀), 130.5 (C₀), 129.0 (CH), 113.6 (CH), 74.1 (CH), 72.6 (CH₂), 71.8 (CH₂), 55.2 (CH₃), 50.3 (CH), 38.9 (CH), 29.3 (CH₃), 26.1 (CH₃), 18.4 (C₀), 14.6 (CH₃), 12.9 (CH₃), -3.9 (CH₃), -4.2 (CH₃); TLC (10% EtOAc/hexanes) *R*_f 0.30; HRMS Calcd: 365.2148; found: 365.4241.

IR (film, cm⁻¹) 2963, 2835, 2243, 1661, 1615, 1518, 1461, 1387, 1303, 1250, 1171, 1115, 1079, 1033, 995, 915, 830, 733, 627; ¹H NMR (300MHz, CDCl₃) 7.41 (d, *J* 8.8 Hz, 2H), 6.88 (d, *J* 8.8 Hz, 2H), 5.48 (s, 1H), 4.05 (dd, *J* 4.6, 11.17 Hz, 1H), 3.80 (s, 3H), 3.72 (s, 3H), 3.53 (t, *J* 11.2 Hz, 1H), 3.20 (s, 3H), 3.18 (m, 2H), 1.98 (m, 1H), 1.28 (d, *J* 7.0 Hz, 3H), 0.77 (d, *J* 7.0 Hz, 3H); TLC (60% EtOAc/Hexanes) *R*_f 0.37.

MP: 67.0-69.0°C; [α]_D²⁰ +50.0 (*c* 1.0, CHCl₃); IR (KBr, cm⁻¹) 2964, 2927, 2859, 1702, 1615, 1516, 1396, 1375, 1343, 1301, 1247, 1181, 1170, 1113, 1074, 1036, 1019, 982, 968, 822, 807, 736, 637, 493; ¹H NMR (300 MHz, CDCl₃) 7.35 (d, *J* 8.8 Hz, 2H), 6.87 (d, *J* 8.8 Hz, 2H), 5.45 (s, 1H), 4.13 (dd, *J* 4.8, 11.1 Hz, 1H), 3.95 (dd, *J* 2.9, 10.1 Hz, 1H), 3.80 (s, 3H), 3.56 (t, *J* 11.0 Hz, 1H), 2.70 (qd, *J* 2.9, 7.1 Hz, 1H), 2.23 (s, 3H), 2.06 (m, 1H), 1.25 (d, *J* 7.0 Hz, 3H), 0.81 (d, *J* 7.0 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) 210.2 (C=O), 159.6 (C₀), 130.7 (C₀), 127.0 (CH), 113.3 (CH), 100.7 (CH), 83.0 (CH), 72.8 (CH₂), 55.2 (CH₃), 48.6 (CH), 31.0 (CH), 28.4 (CH₃), 12.1 (CH₃), 9.5 (CH₃); TLC (40% EtOAc/Hexanes) *R*_f 0.35; HRMS Calcd: 278.1518; found: 278.1497.

MP: 56.9-57.2 °C; IR (KBr, cm^{-1}) 3071, 3037, 2912, 2815, 2728, 1734, 1693, 1596, 1487, 1441, 1328, 1258, 1150, 1041, 990, 870, 796, 732, 682, 653, 470; ^1H NMR (300 MHz, CDCl_3) 9.98 (s, 1H), 7.25-7.50 (m, 9H), 5.14 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3) 192.0 (C=O), 159.3 (C_0), 137.8 (C_0), 136.3 (C_0), 130.1 (CH), 128.6 (CH), 128.2 (CH), 127.5 (CH), 123.6 (CH), 122.1 (CH), 113.3 (CH), 70.2 (CH_2); TLC (25% EtOAc/hexanes) *R_f* 0.56; HRMS Calcd: 212.0837; found: 212.0843.

Representative Procedure for Methyl Ketone Aldol Reaction: To a stirred solution of (c-Hex) $_2$ BCl (1.5 eq) in anhydrous Et_2O (8 mL) at 0 °C was added Et_3N (1.7 eq). A solution of methyl ketone **7** (1.5 eq) in anhydrous Et_2O (2 mL) was added, leading to the precipitation of $\text{Et}_3\text{N} \cdot \text{HCl}$. The resulting white heterogeneous reaction mixture was stirred at 0 °C (15 min) before cooling to -78 °C, at which point freshly distilled aldehyde (2 eq) was added (aldehyde **2e** was added as a 1.0 M solution in Et_2O). After 4 h at -78 °C and 10 h at -20 °C, the reaction mixture was quenched by addition of 7 mL of a pH 7 buffer/MeOH solution (1/6, v/v), and 2 mL of a 30% H_2O_2 /MeOH (1/2, v/v) solution. The ice bath was removed and the reaction was allowed to warm to room temperature and stirred for 1 h. The solution was diluted with Et_2O and water, the layers were separated and the aqueous layer extracted with Et_2O . The combined organic extracts were washed with water and brine, dried (MgSO_4) and concentrated *in vacuo*. Purification by silica gel chromatography gave the aldol adducts.

MP: 73.5-75.0 °C; $[\alpha]_{\text{D}}^{20} +70.0$ (*c* 1.0, CH_2Cl_2); IR (film, cm^{-1}) 3446, 2965, 2938, 2854, 1706, 1616, 1519, 1462, 1399, 1367, 1250, 1171, 1118, 1072, 1039, 828; ^1H NMR (300 MHz, CDCl_3) 7.31 (d, *J* 8.8 Hz, 2H), 6.84 (d, *J* 8.8 Hz, 2H), 5.42 (s, 1H), 4.19 (m, 1H), 4.11 (dd, *J*, 11.2, 4.6 Hz, 1H), 3.94 (dd, *J* 10.1, 3.1 Hz, 1H), 3.78 (s, 3H); 3.54 (t, *J* 11.2 Hz, 1H); 3.18 (brd, *J* 2.2 Hz, 1H); 2.73 (m, 1H); 2.68 (dd, *J* 8.2, 3.1 Hz, 1H); 2.60 (dd, *J* 17.5, 8.4 Hz, 1H); 2.13 (m, 1H); 1.22 (d, *J* 6.9 Hz, 3H); 1.15 (d, *J* 6.6 Hz, 3H); 0.79 (d, *J* 6.6 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) 213.4 (C=O), 159.7 (C_0), 130.5 (C_0), 127.0 (CH), 113.4 (CH), 100.8 (CH), 82.8 (CH), 72.7 (CH_2), 63.9 (CH), 55.2 (CH_3), 48.65 (CH),

48.6 (CH₂), 30.9 (CH), 22.3 (CH₃), 12.1 (CH₃), 9.1 (CH₃); TLC (40% EtOAc/Hexanes) *R_f* 0.14; HRMS Calcd: 322.1780; found: 322.1750.

[α]_D²⁰ +53.7 (*c* 1.9, CH₂Cl₂); IR (film, cm⁻¹) 3457, 2959, 2875, 1706, 1616, 1519, 1462, 1393, 1303, 1250, 1171, 1124, 1034, 832; ¹H NMR (500 MHz, CDCl₃) 7.33 (d, *J* 8.8 Hz, 2H), 6.85 (d, *J* 8.8 Hz, 2H), 5.43 (s, 1H), 4.12 (dd, *J* 11.3, 4.9 Hz, 1H), 3.92 (dd, *J* 10.1, 3.0 Hz, 1H), 3.80 (m, 1H), 3.78 (s, 3H); 3.54 (t, *J* 11.1 Hz, 1H); 3.08 (brs, 1H); 2.72 (m, 2H); 2.58 (dd, *J* 17.5, 9.6 Hz, 1H); 2.04 (m, 1H); 1.64 (m, 1H), 1.24 (d, *J* 7.3 Hz, 3H); 0.89 (d, *J* 6.7 Hz, 3H); 0.86 (d, *J* 7.0 Hz, 3H), 0.79 (d, *J* 6.7 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) 214.4 (C=O), 159.8 (C₀), 130.7 (C₀), 127.1 (CH), 113.4 (CH), 100.8 (CH), 83.0 (CH), 72.7 (CH₂), 72.1 (CH), 55.2 (CH₃), 48.7 (CH), 44.1 (CH₂), 32.9 (CH), 30.9 (CH), 18.3 (CH₃), 17.8 (CH₃), 12.0 (CH₃), 9.2 (CH₃); TLC (40% EtOAc/Hexanes) *R_f* 0.35; HRMS Calcd: 350.2093; found: 350.2030.

MP: 59.2-60.1 °C; [α]_D²⁰ +46.4 (*c* 1.4, CH₂Cl₂); IR (film, cm⁻¹) 3512, 2962, 2925, 2856, 1713, 1614, 1516, 1458, 1399, 1236, 1115, 1075, 825; ¹H NMR (300 MHz, CDCl₃) 7.33 (d, *J* 8.8 Hz, 2H), 6.84 (d, *J* 8.8 Hz, 2H), 5.43 (s, 1H), 4.97 brs, 1H), 4.82 (brs, 1H), 4.46 (brdd, *J* 3.1, 8.2 Hz, 1H), 4.12 (dd, *J* 4.8, 11.3 Hz, 1H), 3.94 (dd, *J* 3.1, 10.1 Hz, 1H), 3.78 (s, 3H); 3.54 (t, *J* 11.0 Hz, 1H); 3.15 (brs, 1H); 2.66-2.83 (m, 3H); 2.05 (m, 1H); 1.67 (s, 3H), 1.24 (d, *J* 6.9 Hz, 3H); 0.80 (d, *J* 6.6 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) 213.2 (C=O), 159.7 (C₀), 145.6 (C₀), 130.6 (C₀), 127.1 (CH), 113.4 (CH), 110.9 (CH₂), 100.9 (CH), 83.0 (CH), 72.8 (CH₂), 70.9 (CH), 55.3 (CH₃), 48.7 (CH), 46.0 (CH₂), 30.9 (CH), 18.5 (CH₃), 12.1 (CH₃), 9.2 (CH₃); TLC (30% EtOAc/Hexanes) *R_f* 0.17; HRMS Calcd: 348.1937; found: 348.1931.

[α]_D²⁰ +72.7 (*c* 1.1, CH₂Cl₂); IR (film, cm⁻¹) 3488, 2963, 2931, 2845, 1707, 1614, 1522, 1458, 1390, 1306, 1249, 1173, 1081, 1034, 825; ¹H NMR (300 MHz, CDCl₃) 7.32 (d, *J* 8.8 Hz, 2H), 7.19-7.30 (m, 5H), 6.85 (d, *J* 8.8 Hz, 2H), 5.40 (s, 1H), 5.06 (brd, *J* 6.9 Hz, 1H), 4.11 (dd, *J* 4.6, 11.2 Hz, 1H), 3.90 (dd, *J* 2.9, 9.9 Hz, 1H), 3.78 (s, 3H), 3.58 (brd, *J* 2.2 Hz, 1H), 3.51 (t, *J* 11.0 Hz, 1H), 2.80-2.96 (m, 2H), 2.69 (ddd, *J* 3.1, 6.9, 14.1 Hz, 1H), 2.03 (m, 1H), 1.21 (d, *J* 6.9 Hz, 3H), 0.76 (d, *J* 6.9 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) 213.2 (C=O), 159.7 (C₀), 142.7 (C₀), 130.6 (C₀), 128.2 (CH), 127.3 (CH), 127.1 (CH), 125.4 (CH), 113.4 (CH), 100.9 (CH), 83.0 (CH), 72.7 (CH₂), 69.8 (CH), 55.2 (CH₃), 49.5 (CH₂), 48.6 (CH), 30.8 (CH), 11.9 (CH₃), 9.0 (CH₃); TLC (30% EtOAc/Hexanes) *R*_f 0.17; HRMS Calcd: 384.1937; found: 384.1867.

[α]_D²⁰ +79.9 (*c* 1.0, CHCl₃); IR (film, cm⁻¹) 3483, 2959, 2840, 1703, 1613, 1587, 1518, 1487, 1454, 1385, 1303, 1250, 1171, 1117, 1076, 1032, 830, 784, 737, 699; ¹H NMR (300 MHz, CDCl₃) 7.34-7.48 (m, 7H), 7.20-7.28 (m, 1H), 7.02 (t, *J* 1.8 Hz, 1H), 6.81-6.92 (m, 4H), 5.45 (s, 1H), 5.10 (dd, *J* 4.2, 7.9 Hz, 1H), 5.05 (s, 2H), 4.14 (dd, *J* 4.5, 11.2 Hz, 1H), 3.95 (dd, *J* 4.6, 11.2 Hz, 1H), 3.77 (s, 3H), 3.55 (t, *J* 11.4 Hz, 1H), 2.87 (m, 2H), 2.74 (qd, *J* 2.9, 7.0 Hz, 1H), 2.07 (m, 1H), 1.25 (d, *J* 7.3 Hz, 3H), 0.81 (d, *J* 6.6 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) 213.2 (C=O), 159.7 (C₀), 158.7 (C₀), 144.4 (C₀), 136.8 (C₀), 130.5 (C₀), 129.3 (CH), 128.4 (CH), 127.7 (CH), 127.3 (CH), 127.1 (CH), 118.0 (CH), 113.7 (CH), 113.4 (CH), 112.0 (CH), 100.8 (CH), 83.0 (CH), 72.7 (CH₂), 69.9 (CH₂), 69.6 (CH₃), 55.1 (CH₃), 49.4 (CH₂), 48.6 (CH₃), 30.8 (CH), 12.0 (CH₃), 9.0 (CH₃); TLC (20% EtOAc/Hexanes) *R*_f 0.16; HRMS Calcd: 490.2355; found: 490.2353.

Crystallographic data for compound 10a

Table 1. Crystal data and structure refinement.

Empirical formula	C ₁₈ H ₂₆ O ₅
Formula weight	322.39
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, P2 ₁
Unit cell dimensions	a = 5.3464(9) Å b = 10.571(2) Å c = 15.713(4) Å (= 97.759(10)°
Volume	879.9(3) Å ³
Z, Calculated density	2, 1.217 Mg/m ³
Absorption coefficient	0.088 mm ⁻¹
F(000)	348
Crystal size	0.20 x 0.10 x 0.05 mm
Theta range for data collection	1.31 to 25.45 deg.
Limiting indices	-6 ≤ h ≤ 0, -12 ≤ k ≤ 0, -18 ≤ l ≤ 19
Reflections collected / unique	1884 / 1698
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1698 / 1 / 213
Goodness-of-fit on F ²	1.027
Final R indices [I > 2σ(I)]	R ₁ = 0.0793, wR ₂ = 0.1909
R indices (all data)	R ₁ = 0.1482, wR ₂ = 0.2192
Extinction coefficient	0.19(3)
Largest diff. peak and hole	0.327 and -0.229 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$). $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
O(1)	9538(7)	777(4)	7835(2)	51(1)
O(2)	8938(9)	2794(5)	7259(3)	75(2)
O(3)	10281(10)	-1833(5)	9042(4)	90(2)
O(4)	11690(30)	-3576(12)	7947(13)	290(11)
O(5)	971(11)	-469(8)	4834(4)	108(2)
C(1)	12110(11)	211(7)	9131(4)	54(2)
C(2)	11889(13)	-1160(6)	8813(4)	62(2)
C(3)	13662(16)	-1623(7)	8243(6)	82(2)
C(4)	13940(20)	-3029(9)	8160(8)	112(3)
C(5)	11882(10)	1114(6)	8358(4)	52(2)
C(6)	11823(13)	2521(6)	8589(5)	62(2)
C(7)	11225(14)	3246(7)	7747(5)	74(2)
C(8)	9255(11)	1485(7)	7065(4)	56(2)
C(9)	6956(13)	1039(7)	6483(4)	64(2)
C(10)	5448(14)	1849(8)	5964(4)	74(2)
C(11)	3450(16)	1385(12)	5378(5)	90(3)
C(12)	2924(15)	107(9)	5363(5)	79(2)
C(13)	4409(18)	-705(10)	5872(5)	92(3)
C(14)	6420(15)	-237(8)	6436(5)	78(2)
C(15)	10287(15)	483(7)	9777(4)	73(2)
C(16)	15650(20)	-3480(13)	7578(9)	152(6)
C(17)	14328(12)	2970(8)	9045(5)	79(2)
C(18)	-590(20)	330(15)	4260(6)	126(4)

Table 3. Bond lengths [Å] and angles [deg].

O(1)-C(8)	1.414(7)
O(1)-C(5)	1.448(7)
O(2)-C(8)	1.431(9)
O(2)-C(7)	1.434(8)
O(3)-C(2)	1.208(8)
O(4)-C(4)	1.339(14)
O(5)-C(12)	1.385(10)
O(5)-C(18)	1.421(13)
C(1)-C(15)	1.527(9)
C(1)-C(2)	1.533(10)
C(1)-C(5)	1.538(9)
C(2)-C(3)	1.473(10)
C(3)-C(4)	1.502(12)
C(4)-C(16)	1.456(14)
C(5)-C(6)	1.532(10)
C(6)-C(17)	1.508(9)
C(6)-C(7)	1.524(10)
C(8)-C(9)	1.505(9)
C(9)-C(10)	1.369(10)
C(9)-C(14)	1.379(12)
C(10)-C(11)	1.401(12)
C(11)-C(12)	1.380(15)
C(12)-C(13)	1.355(12)
C(13)-C(14)	1.389(11)
C(8)-O(1)-C(5)	109.8(4)
C(8)-O(2)-C(7)	108.6(5)
C(12)-O(5)-C(18)	116.7(9)
C(15)-C(1)-C(2)	111.6(6)
C(15)-C(1)-C(5)	114.8(5)
C(2)-C(1)-C(5)	109.6(5)
O(3)-C(2)-C(3)	121.9(7)

O(3)-C(2)-C(1)	119.1(6)
C(3)-C(2)-C(1)	119.0(6)
C(2)-C(3)-C(4)	117.5(8)
O(4)-C(4)-C(16)	108.7(11)
O(4)-C(4)-C(3)	110.6(9)
C(16)-C(4)-C(3)	117.2(11)
O(1)-C(5)-C(6)	109.3(5)
O(1)-C(5)-C(1)	105.4(4)
C(6)-C(5)-C(1)	114.7(5)
C(17)-C(6)-C(7)	108.8(6)
C(17)-C(6)-C(5)	111.9(6)
C(7)-C(6)-C(5)	106.9(6)
O(2)-C(7)-C(6)	111.1(6)
O(1)-C(8)-O(2)	109.4(5)
O(1)-C(8)-C(9)	109.7(5)
O(2)-C(8)-C(9)	108.8(5)
C(10)-C(9)-C(14)	118.6(7)
C(10)-C(9)-C(8)	122.2(7)
C(14)-C(9)-C(8)	119.1(7)
C(9)-C(10)-C(11)	120.6(9)
C(12)-C(11)-C(10)	119.3(8)
C(13)-C(12)-C(11)	120.6(7)
C(13)-C(12)-O(5)	114.2(8)
C(11)-C(12)-O(5)	125.2(9)
C(12)-C(13)-C(14)	119.5(9)
C(9)-C(14)-C(13)	121.3(9)

Table 4. Anisotropic displacement parameters ($A^2 \times 10^3$).

The anisotropic displacement factor exponent takes the form:

$$-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$$

	U11	U22	U33	U23	U13	U12
O(1)	49(2)	49(2)	52(2)	1(2)	1(2)	-6(2)
O(2)	88(3)	51(3)	78(3)	8(3)	-13(2)	-2(2)
O(3)	88(3)	63(3)	122(4)	11(3)	30(3)	-15(3)
O(4)	231(13)	139(10)	540(30)	-151(16)	190(16)	-86(10)
O(5)	97(4)	130(6)	91(4)	-28(4)	-12(3)	-9(4)
C(1)	46(3)	62(4)	50(3)	-4(3)	-8(3)	-1(3)
C(2)	66(4)	50(4)	66(4)	9(3)	-2(3)	2(3)
C(3)	99(6)	43(4)	105(6)	-8(4)	21(5)	-4(4)
C(4)	99(7)	78(7)	154(10)	-17(7)	0(6)	5(5)
C(5)	41(3)	51(4)	63(4)	-1(3)	5(3)	-3(3)
C(6)	68(4)	47(4)	68(4)	-7(3)	2(3)	-5(3)
C(7)	84(5)	49(4)	81(5)	6(4)	-17(4)	-12(4)
C(8)	58(4)	56(4)	53(3)	2(3)	5(3)	-6(3)
C(9)	79(4)	68(5)	45(3)	4(4)	6(3)	-5(4)
C(10)	78(5)	81(5)	62(4)	10(4)	3(4)	-4(4)
C(11)	84(5)	127(9)	54(4)	9(5)	-3(4)	15(5)
C(12)	86(5)	90(7)	57(4)	-14(4)	-2(4)	-18(5)
C(13)	117(7)	81(6)	72(5)	-16(5)	-12(5)	-17(5)
C(14)	86(5)	77(6)	67(5)	-7(4)	-8(4)	-11(4)
C(15)	91(5)	66(5)	62(4)	-2(4)	13(4)	7(4)
C(16)	120(8)	109(10)	228(14)	-76(11)	22(9)	23(7)
C(17)	64(4)	67(5)	102(6)	-14(4)	-10(4)	-15(3)
C(18)	111(7)	181(12)	75(5)	-18(7)	-31(5)	9(7)

Table 5. Hydrogen coordinates (x 104) and isotropic displacement parameters (A2 x 103).

	x	y	z	U(eq)
H(4O)	10086	-3140	8227	348
H(1)	13820	312	9438	65
H(3A)	15313	-1273	8443	98
H(3B)	13136	-1282	7673	98
H(4)	14608	-3344	8733	135
H(5)	13288	960	8030	62
H(6)	10498	2674	8951	74
H(7A)	11052	4139	7869	89
H(7B)	12609	3149	7412	89
H(8)	10756	1380	6776	67
H(10)	5752	2715	6000	89
H(11)	2489	1933	5003	108
H(13)	4085	-1570	5843	111
H(14)	7426	-796	6789	94
H(15A)	8623	619	9477	109
H(15B)	10831	1225	10103	109
H(15C)	10260	-225	10159	109
H(16A)	15720	-4387	7597	229
H(16B)	17305	-3140	7750	229
H(16C)	15044	-3210	7004	229
H(17A)	15648	2731	8719	119
H(17B)	14633	2592	9604	119
H(17C)	14300	3874	9101	119
H(18A)	-1212	1012	4575	190
H(18B)	-1984	-149	3977	190
H(18C)	377	667	3839	190

^1H and ^{13}C NMR spectra for aldol adducts 10a-e obtained with (c-Hex) $_2\text{BCl}$