Unusual Highly Regioselective Direct Aldol Additions with a Moisture Resistant and Highly Efficient Titanium Catalyst

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Supporting Information:

Full characterisation of all isolated new compounds and NMR-data for all isolated compounds.

All reagents were used as obtained by the supplier without further purification. TLC was carried out using plates (Kieselgel 60 F₂₅₄, Merck KGaA, Darmstadt) with hexane-ethylacetate (80:20) as mobile phase. Flash-CC was carried out with silica gel as stationary and hexane-ethylacetate (gradient) as mobile phase. ¹H NMR and ¹³C NMR data were collected by using a Bruker DPX 300 spectrometer as solution in CDCl₃ with CHCl₃ (δ = 7.24 and 77.0) as internal standard. IR-spectra were recorded on a Perkin-Elmer IR-881 spectrograph. X-ray data sets were collected using a STOE IPDS1 image plate single crystal diffractometer using MoK_α-radiation. The structures were solved by direct methods and refined by full matrix least squares on *F*² by using SHELX97. All non-hydrogen atoms were refined anisotropically to give the final *R* values.

rac-Ti₄(μ-BINOLato)₆(μ₃-OH)₄: Dark red rectangular crystals, mp >270 °C

¹H NMR: δ = 3.81 (s, 4 H, OH), 5.59 (d, *J* = 8.7 Hz, 12 H), 6.98–7.20 (m, 24 H, ar), 7.41 (t, *J* = 7.9 Hz, 12 H, ar), 7.99 (d, *J* = 7.9 Hz, 12 H, ar).

¹³C NMR: δ = 117.3, 118.3, 124.8, 125.3, 126.6, 126.9, 127.9, 129.9, 130.6, 133.2, 160.4.

IR (KBr): 3501, 3053, 1617, 1583, 1499, 1426, 1353, 1332, 1235, 1074, 1033, 1004, 976, 820, 791, 765, 691, 670, 636, 611.

MS (ESI, relative intensity, %): 1970.9 (1), 1969.9 (3), 1968.9 (6), 1967.9 (15), 1966.9 (31), 1965.9 (56), 1964.9 (84), 1963.9 (100), 1962.9 (89), 1961.9 (51), 1960.9 (29), 1959.9 (10), 1958.9 (4).

Ti₄(μ-*R*-BINOLato)₆(μ₃-OH)₄:

¹H NMR: δ = 3.81 (s, 4 H, OH), 5.59 (d, *J* = 8.7 Hz, 12 H), 6.98–7.20 (m, 24 H, ar), 7.41 (t, *J* = 7.9 Hz, 12 H, ar), 7.99 (d, *J* = 7.9 Hz, 12 H, ar).

¹³C NMR: δ = 117.3, 118.3, 124.8, 125.3, 126.6, 126.9, 127.9, 129.9, 130.6, 133.2, 160.4.

5, 4β-hydroxy-1β,4α-dimethylbicyclo[3.2.1]octane-7,8-dione:

colorless crystals, mp 168 °C, above 120 °C sublimation.

¹H NMR: δ = 1.04 (s, 3 H, CH₃), 1.38 (s, 3 H, CH₃), 1.65–1.91 (m, 4 H, CH₂CH₂), 2.05–2.15 (m, 1 H), 2.51–2.60 (m, 1 H), 2.80–2.91 (m, 1 H).

¹³C NMR: δ = 11.8, 28.4 (2 signals), 32.1, 38.4, 42.6, 57.3, 80.5, 211.0, 213.9.

syn-3a: *syn*-3-Butyl-4-hydroxy-4-phenyl-butan-2-one¹. Colorless oil.

¹H NMR: δ = 0.69 (t, 7.2 Hz, 3 H, CH₃), 0.90–1.65 m, 6 H, CH₂CH₂CH₂), 1.83 (s, 3H, CH₃), 2.73 (dt, *J*₁ = 4.9 Hz, *J*₂ = 6.0 Hz, 1 H, CH), 4.69 (d, 6.0 Hz, 1 H, CHOH), 7.10–7.25 (m, 5 H, ar).

¹³C NMR: δ = 13.8, 22.8, 27.1, 29.9, 31.8, 59.6, 74.1, 126.1, 127.6, 128.4, 142.0, 213.2.

¹ Mahrwald, R.; Gündogan, B. *J. Am. Chem. Soc.* **1998**, *120*, 413–414.

anti-3a: *anti*-3-Butyl-4-hydroxy-4-phenyl-butan-2-one¹. Colorless oil.

¹H NMR: δ = 0.74 (t, J = 7.2 Hz, 3 H, CH₃), 0.90–1.65 m, 6 H, CH₂CH₂CH₂), 1.83 (s, 3 H, CH₃), 2.33 (dt, $J_1 = J_2$ = 7.5 Hz, 1 H, CH), 4.99 (dd, J_1 = 4.2 Hz, J_2 = 8.7 Hz, 1 H, CHOH), 7.10–7.25 (m, 5 H, ar).

¹³C NMR: δ = 13.9, 22.4, 23.4, 29.9, 31.3, 43.7, 69.9, 125.6, 127.6, 128.4, 142.8, 211.7.

syn-3b: *syn*-4-Hydroxy-3-methyl-4-phenyl-butan-2-one². Colorless oil.

¹H NMR: δ = 0.95–1.05 (d, J = 7.5 Hz, 3 H, CH₃), 2.12 (s, 3 H, CH₃), 2.75 (dd, J_1 = 4.2 Hz, J_2 = 7.2 Hz, 1 H, CH), 3.08 (s, br, 1 H, OH) 4.97 (d, J = 4.2 Hz, 1 H, CHOH), 7.15–7.33 (m, 5 H, ar).

¹³C NMR: δ = 10.1, 29.3, 53.2, 73.0, 125.7, 127.8, 128.2, 141.7, 213.4.

anti-3b: *anti*-4-Hydroxy-3-methyl-4-phenyl-butan-2-one³. Colorless oil.

¹H NMR: δ = 0.80 (d, J = 7.2 Hz, 3 H, CH₃), 2.03 (s, 3 H, CH₃), 2.84 (dd, J_1 = 7.2 Hz, J_2 = 8.8 Hz, 1 H, CH), 3.08 (s, br, 1 H, OH) 4.63 (d, J = 8.8 Hz, 1 H, CHOH), 7.15–7.33 (m, 5 H, ar).

¹³C NMR: δ = 13.9, 29.9, 53.6, 76.4, 126.5, 127.8, 128.4, 141.9, 213.4.

² Denmark, S.E.; Pham, S.M. *J. Org. Chem.* **2003**, 68, 5045–5055.

³ Vicario, J.L.; Badia, D.; Dominguez, E.; Rodriguez, M.; Corriillo, L. *J. Org. Chem.* **2000**, 65, 3745–3760.

syn-3c: *syn*-1-Hydroxy-2-methyl-1-phenyl-pentan-3-one⁴. Colorless oil.

¹H NMR: δ = 0.93 (t, J = 7.2 Hz, 3 H, CH₃), 1.01 (d, J = 7.4 Hz, 3 H, CH₃), 2.18–2.50 (m, 2 H, CH₂), 2.73 (dq, J_1 = 7.2 Hz, J_2 = 4.1 Hz, 1 H, CHCH₃), 4.98 (d, J = 4.1 Hz, 1 H, CHOH), 7.13–7.30 (m, 5 H, ar).

¹³C NMR: δ = 7.5, 10.6, 35.4, 52.3, 73.3, 125.8, 127.3, 128.6, 141.8, 216.3.

anti-3c: *anti*-1-Hydroxy-2-methyl-1-phenyl-pentan-3-one⁵. Colorless oil.

¹H NMR: δ = 0.89 (d, J = 7.3 Hz, 3 H, CH₃), 0.98 (t, J = 7.1 Hz, 3 H, CH₃), 2.18–2.50 (m, 2 H, CH₂), 2.82 (dq, J_1 = 7.1 Hz, J_2 = 8.3 Hz, 1 H, CHCH₃), 4.68 (d, J = 8.3 Hz, 1 H, CHOH), 7.13–7.30 (m, 5 H, ar).

¹³C NMR: δ = 7.4, 14.4, 36.4, 52.6, 76.6, 125.9, 128.4, 128.6, 142.3, 216.1.

syn-3d: *syn*-4-Hydroxy-3,4-diphenyl-butan-2-one⁶. Colorless oil.

¹H NMR: δ = 1.43 (s, 3 H, CH₃), 3.49 (d, J = 4.2 Hz, 1 H, CH), 4.92 (d, J = 4.1 Hz, 1 H, CHOH), 7.25–7.70 (m, 10 H, ar).

anti-3d: *anti*-4-Hydroxy-3,4-diphenyl-butan-2-one¹. Colorless crystals, mp 94–95 °C

⁴ Ward, D. E.; Ihennigut, V. *Tetrahedron Lett.* **2004**, 45, 8347–8350.

⁵ Wie, H.-X.; Richard, L.; Shao, H.; Jiali, P.; Paul, W. *Tetrahedron* **2004**, 60, 11829–11835.

⁶ Noyori, R.; Nishida, I.; Sakata, J. *J. Am. Chem. Soc.* **1983**, 105, 1598–1608.

^1H NMR: δ = 1.98 (s, 3 H, CH_3), 3.82 (d, J = 9.4 Hz, 1 H, CH), 5.06 (d, J = 9.4 Hz, 1 H, CHOH), 7.31–7.68 (m, 10 H, ar).

^{13}C NMR: δ = 30.2, 67.2, 75.8, 126.5, 127.4, 127.5, 127.8, 128.6, 128.9, 134.7, 140.8, 209.6.

syn-3e: *syn*-1-Hydroxy-1-(3-methoxy-phenyl)-2-methyl-pentan-3-one⁷. Colorless oil.

^1H NMR: δ = 0.94 (t, J = 7.2 Hz, 3 H, CH_3), 1.00 (d, J = 7.2 Hz, 3 H, CH_3), 2.17–2.56 (m, 2 H, CH_2), 2.75 (dd, J_1 = 7.2 Hz, J_2 = 4.2 Hz, 1 H, $\text{CHC}=\text{O}$), 3.72 (s, 3 H, CH_3), 4.92 (d, J = 4.2 Hz, 1 H, CHOH), 6.67–7.23 (m, 4 H, ar).

^{13}C NMR: δ = 7.3, 10.6, 35.3, 52.2, 55.1, 73.1, 111.4, 112.7, 118.1, 129.1, 143.6, 159.4, 216.0.

anti-3e: *anti*-1-Hydroxy-1-(3-methoxy-phenyl)-2-methyl-pentan-3-one⁷. Colorless oil.

^1H NMR: δ = 0.84 (d, J = 7.5 Hz, 3 H, CH_3), 0.90 (t, J = 7.2 Hz, 3 H, CH_3), 2.17–2.56 (m, 2 H, CH_2), 2.84 (dd, J_1 = 7.2 Hz, J_2 = 8.3 Hz, 1 H, $\text{CHC}=\text{O}$), 3.72 (s, 3 H, CH_3), 4.61 (d, J = 8.3 Hz, 1 H, CHOH), 6.65–7.23 (m, 4 H, ar).

^{13}C NMR: δ = 7.4, 14.3, 36.3, 52.4, 55.1, 76.5, 111.8, 113.3, 118.9, 129.3, 143.8, 159.6, 216.1.

⁷ Banno, K. *Bull. Chem. Soc. Jpn.* **1976**, 49, 2284–2289.

syn-3f: *syn*-1-(4-Chloro-phenyl)-1-hydroxy-2-methyl-pentan-3-one⁸. Colorless oil.

¹H NMR: δ = 0.92 (t, J = 7.2 Hz, 3 H, CH₃), 0.97 (d, J = 7.2 Hz, 3 H, CH₃), 2.17–2.55 (m, 2 H, CH₂), 2.70 (dd, J_1 = 7.2 Hz, J_2 = 4.2 Hz, 1 H, CHC=O), 4.64 (d, J = 4.1 Hz, 1 H, CHOH), 7.10–7.20 (m, 4 H, ar).

¹³C NMR: δ = 7.4, 10.4, 35.3, 52.0, 72.5, 127.3, 128.3, 132.9, 140.3, 216.1.

anti-3f: *anti*-1-(4-Chloro-phenyl)-1-hydroxy-2-methyl-pentan-3-one⁹. Pale yellow oil.

¹H NMR: δ = 0.83 (d, J = 7.2 Hz, 3 H, CH₃), 0.94 (t, J = 7.2 Hz, 3 H, CH₃), 2.17–2.55 (m, 2 H, CH₂), 2.78 (dd, J_1 = 7.2 Hz, J_2 = 8.3 Hz, 1 H, CHC=O), 4.64 (d, J = 8.3 Hz, 1 H, CHOH), 7.10–7.20 (m, 4 H, ar).

¹³C NMR: δ = 7.3, 14.3, 36.4, 52.4, 75.8, 127.8, 128.5, 133.4, 140.7, 215.9.

anti-3g: *anti*-4-(4-Ethoxy-phenyl)-4-hydroxy-3-methyl-butan-2-one. Pale yellow solid, mp 61–62 °C.

¹H NMR: δ = 0.65 (d, J = 7.2 Hz, 3 H, CH₃), 1.48 (t, J = 7.2 Hz, 3 H, CH₃), 2.27 (s, 3 H, CH₃), 2.89 (dq, J_1 = 6.8 Hz, J_2 = 10.2 Hz, 1 H, CHC=O), 3.99 (d, J = 6.8 Hz, 1 H, CHOH), 4.07 (q, J = 7.2 Hz, 2 H, CH₂O), 6.86 (d, J = 8.7 Hz, 2 H, ar), 9.68 (d, 8.7 Hz, 2 H, ar).

¹³C NMR: δ = 13.3, 14.8, 30.3, 53.1, 63.2, 80.3, 114.2, 129.1, 129.7, 158.9, 211.8.

IR (KBr): 3470, 3026, 3037, 2957, 2933, 1710, 1608, 1510, 1474, 1358, 1289, 1247, 1171, 1114, 1046.

Anal. Calcd. for C₁₃H₁₈O₃: C, 70.24, H, 8.16. Found: C, 70.01, H, 8.13.

MS (EI, relative intensity, %): 203.1 (48), 190.1 (29), 179.1 (43), 175.1 (100), 161.1 (27).

⁸ Kobayashi, S.; Wakabayashi, T. *Tetrahedron Lett.* **1998**, 39, 5389–5392.

⁹ Seki, A.; Takizawa, Y.; Ishiwata, F.; Asami, M. *Chem. Lett.* **2003**, 32, 342–343.

HRMS (ESI) $[M-H]^-$ Calcd. 221.1178, found, 221.1175.

syn-3h: *syn*-4-(4-Ethoxy-phenyl)-4-hydroxy-3-butyl-butan-2-one. Colorless crystals. mp 54–60 °C.

^1H NMR: δ = 0.65 (t, J = 7.2 Hz, 3 H, CH_3), 0.91–1.20 (m, 6 H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.81 (t, J = 7.2 Hz, 3 H, CH_3), 2.09 (s, 3 H, CH_3), 2.80 (dt, J_1 = 4.1 Hz, J_2 = 8.3 Hz, 1 H, $\text{CHC}=\text{O}$), 3.95 (q, J = 7.2 Hz, 2 H, CH_2), 4.62 (d, J = 6.8 Hz, 1 H, $\text{CH}-\text{OH}$), 6.77 (d, J = 8.6 Hz, 2 H, ar), 7.14 (d, J = 8.6 Hz, 2 H, ar).

^{13}C NMR: δ = 13.7, 14.8, 22.7, 29.1, 29.3, 31.8, 59.4, 63.4, 75.5, 114.4, 127.5, 134.4, 158.6, 213.9.

IR (KBr): 3463, 2976, 2930, 2883, 1722, 1612, 1542, 1249, 1213, 1040, 832.

Anal. Calcd. for $\text{C}_{16}\text{H}_{24}\text{O}_3$: C, 72.69, H, 9.15. Found: C, 73.02, H, 9.01.

MS (EI, relative intensity, %): 243.1 (5), 225.1 (100), 215.1 (12), 183.1 (45), 77.0 (72).

HRMS (ESI) $[M-H]^-$: Calcd. 263.1647, found, 263.1644.

anti-3h: *anti*-4-(4-Ethoxy-phenyl)-4-hydroxy-3-butyl-butan-2-one. Colorless oil.

^1H NMR: δ = 0.59 (t, J = 7.2 Hz, 3 H, CH_3), 0.74–1.20 (m, 6 H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.82 (t, J = 7.2 Hz, 3 H, CH_3), 2.15 (s, 3 H, CH_3), 2.68 (dt, J_1 = 7.5 Hz, J_2 = 10.2 Hz, 1 H, $\text{CHC}=\text{O}$), 3.71 (d, J = 10.2 Hz, $\text{CH}-\text{OH}$), 3.94 (dq, J_1 = 9.4 Hz, J_2 = 7.2 Hz, 2 H, CH_2), 7.74–7.88 (2x d, J_1 = J_2 = 8.7 Hz, 4 H, ar).

^{13}C NMR: δ = 13.7, 14.9, 22.5, 28.4, 29.3, 31.6, 59.2, 63.3, 79.7, 114.2, 129.2, 129.9, 159.0, 212.1.

IR (KBr): 3490, 2981, 2934, 2912, 2879, 1714, 1609, 1511, 1249, 1172, 1113, 1049, 835.

Anal. Calcd. for $\text{C}_{16}\text{H}_{24}\text{O}_3$: C, 72.69, H, 9.15. Found: C, 72.88, H, 8.93.

MS (EI, relative intensity, %): 243.1 (2), 225.1 (100), 215.0 (12), 85.0 (32), 77.0 (72).

HRMS (ESI) $[M-H]^-$: Calcd. 263.1647, found, 263.1644.

syn-3i: *syn*-4-Hydroxy-3-methyl-6-phenyl-hex-5-yn-2-one. Colorless oil.

^1H NMR: δ = 1.29 (d, J = 7.5 Hz, 3 H, CH_3), 2.16 (s, 3 H, CH_3), 2.81 (dt, J_1 = 4.14, J_2 = 7.2 Hz, 1 H, CH), 3.17 (d, br, J = 4.9 Hz, 1 H, OH), 4.82 (dd, J_1 = J_2 = 4.9 Hz, 1 H, CHOH), 7.18–7.45 (m, 5 H, ar).

^{13}C NMR: δ = 13.7, 29.9, 52.1, 63.5, 85.7, 87.7, 122.3, 128.3, 131.7, 211.7.

IR (KBr): 3400, 3096, 3035, 2978, 2881, 2865, 1706, 1652, 1488, 1358, 1086, 1026, 1001, 754, 691.

Anal. Calcd. for $\text{C}_{13}\text{H}_{14}\text{O}_2$: C, 77.20, H, 6.98. Found: C, 76.97, H, 7.08.

MS (EI, relative intensity, %): 201.1 (8), 187.1 (99), 131.0 (100), 103.1 (41), 77.0 (38), 43 (87).

HRMS (ESI) $[M-H]^-$: Calcd. 201.0921, found, 201.0923.

anti-3i: *anti*-4-Hydroxy-3-methyl-6-phenyl-hex-5-yn-2-one. Colorless oil.

^1H NMR: δ = 1.19 (d, J = 7.5 Hz, 3 H, CH_3), 2.16 (s, 3 H, CH_3), 2.75 (dt, J_1 = J_2 = 7.2 Hz, 1 H, CH), 3.17 (d, br, J = 7.9 Hz, 1 H, OH), 4.67 (dd, J_1 = 7.0 Hz, J_2 = 7.9 Hz, 1 H, CHOH), 7.18–7.45 (m, 5 H, ar).

^{13}C NMR: δ = 13.7, 29.9, 52.7, 64.6, 85.9, 88.0, 122.3, 128.3, 131.7, 211.9.

IR (KBr): 3442, 3094, 2977, 2829, 2869, 1704, 1489, 1355, 1116, 1086, 1026, 1000, 750, 690.

Anal. Calcd. for $\text{C}_{13}\text{H}_{14}\text{O}_2$: C, 77.20, H, 6.98. Found: C, 76.97, H, 7.08.

MS (EI, relative intensity, %): 201.1 (12), 187.1 (100), 131.0 (83), 103.1 (47), 91.1 (9), 77.0 (32), 43 (59).

HRMS (ESI) $[M-H]^-$: Calcd. 201.0921, found, 201.0923.

syn-3j-anti-3j-mixture: Pale yellow oil. Not separable by CC.

IR (KBr): 3437, 2933, 2878, 1706, 1455, 1416, 1356, 1243, 1213, 1168, 1024, 695.

Anal. Calcd. for $C_9H_{12}O_2S$: C, 58.67, H, 6.56, S, 17.40. Found: C, 58.89, H, 6.64, S, 17.42.

MS (EI, relative intensity, %): 184 (100), 167 (57), 151 (84).

HRMS Calcd. $[M+Na]^+$ 207.0451, found, 207.0450.

syn-3j: *syn*-4-Hydroxy-3-methyl-4-thiophen-2-yl-butan-2-one.

1H NMR: δ = 1.14 (d, J = 7.7 Hz, 3 H, CH_3), 2.09 (s, 3 H, CH_3), 2.81–2.98 (m, 1H, $CHC=O$), 5.24 (d, J = 4.4 Hz, 1 H, $CHOH$), 7.13–7.22 (m, 3 H, ar).

^{13}C NMR: δ = 10.9, 25.6, 53.7, 70.1, 123.6, 124.3, 126.7, 145.7, 212.9.

anti-3j: *anti*-4-Hydroxy-3-methyl-4-thiophen-2-yl-butan-2-one.

1H NMR: 0.92 (d, J = 7.1 Hz, 3 H, CH_3), 2.18 (s, 3 H, CH_3), 2.81–2.98 (m, 1H, $CHC=O$), 4.96 (d, J = 8.2 Hz, 1 H, $CHOH$), 6.80–6.95 (m, 3 H, ar).

^{13}C NMR: δ = 14.2, 28.8, 54.0, 72.4, 124.9, 125.2, 126.6, 145.9, 213.1.

3k: 1-Hydroxy-2,2-dimethyl-1-phenyl-pentan-3-one. Colorless oil.

^1H NMR: δ = 0.96 (t, J = 7.2 Hz, 3 H, CH_3), 0.94 (s, 3 H, CH_3), 1.06 (s, 3 H, CH_3), 2.33 (dq, J_1 = 7.2 Hz, J_2 = 6.0 Hz, 1 H, CH), 3.08 (s, br, 1 H, OH) 4.82 (s, 1 H, CHOH), 7.15–7.40 (m, 5 H, ar).

^{13}C NMR: δ = 7.8, 18.4, 22.9, 31.7, 51.8, 78.7, 127.6, 127.7, 140.3, 218.5.

IR (KBr): 3482, 3063, 3031, 2975, 2937, 2878, 1700, 1450, 1362, 1097, 1045, 1025, 1000, 972, 703.

Anal. Calcd. for $\text{C}_{13}\text{H}_{18}\text{O}_2$: C, 75.69, H, 8.80. Found: C, 75.27, H, 8.42.

MS (EI, relative intensity, %): 206.2 (60), 188.1 (100), 173.1 (14), 163.1 (32), 159.1 (64), 149.1 (51), 145.1 (24), 77.1 (30).

HRMS (ESI) $[\text{M}+\text{H}]^+$: Calcd. 207.1380, found, 207.1383.

3l: 5-Hydroxy-4,4-dimethyl-7-phenyl-hept-6-yn-3-one. Colourless oil.

^1H NMR: δ = 0.98 (t, J = 7.2 Hz, 3 H, CH_3), 1.17 (s, 3 H, CH_3), 1.30 (s, 3 H, CH_3), 2.43 (dq, J_1 = 7.2 Hz, J_2 = 6.0 Hz, 1 H, CH), 3.08 (s, br, 1 H, OH) 4.82 (s, 1 H, CHOH), 7.15–7.40 (m, 5 H, ar).

^{13}C NMR: δ = 7.7, 19.4, 22.3, 31.4, 52.0, 68.7, 86.0, 87.4, 128.2, 131.6, 216.5.

IR (KBr): 3454, 3080, 3059, 3022, 2947, 1701, 1488, 1442, 1362, 1098, 1068, 1050, 1025, 1001, 756, 690.

Anal. Calcd. for $\text{C}_{15}\text{H}_{18}\text{O}_2$: C, 78.23, H, 7.88. Found: C, 77.82, H, 7.94.

MS (EI, relative intensity, %): 230.1 (2), 215.1 (82), 187.1 (19), 131.0 (100), 100.1 (58), 85.1 (25), 77.0 (47).

HRMS (ESI) $[\text{M}-\text{H}]^-$: Calcd. 229.1229, found, 229.1227.

syn-8a1: *syn*-2-(Hydroxy-phenyl-methyl)-2-methyl-cyclopentanone¹⁰. Colorless oil.

¹H NMR: δ = 1.11 (s, 3 H, CH₃), 1.43–1.53 (m, 1 H, CH₂), 1.72–1.88 (m, 2 H, CH₂), 1.96–2.09 (m, 1 H, CH₂), 2.38–2.50 (m, 1 H, CH₂), 4.22 (s, br, 1 H, OH), 4.81 (s, 1 H, CH), 7.78–7.88 (m, 5 H, ar).

¹³C NMR: δ = 16.0, 18.3, 33.8, 38.0, 52.3, 76.6, 127.0, 127.5, 127.7, 139.5, 225.7.

anti-8a1: *anti*-2-(Hydroxy-phenyl-methyl)-2-methyl-cyclopentanone¹⁰. Colorless oil.

¹H NMR: δ = 1.11 (s, 3 H CH₃), 1.43–1.53 (m, 1 H, CH₂), 1.72–1.88 (m, 2 H, CH₂), 1.96–2.09 (m, 1 H, CH₂), 2.38–2.50 (m, 1 H, CH₂), 4.22 (s, br, 1 H, OH), 4.81 (s, 1 H, CH), 7.78–7.88 (m, 5 H, ar).

¹³C NMR: δ = 16.0, 18.3, 33.8, 38.0, 52.3, 76.6, 127.0, 127.5, 127.7, 139.5, 225.7.

syn-8a2: *syn*-2-(1-Hydroxy-3-phenyl-prop-2-ynyl)-2-methyl-cyclopentanone. Colourless crystals, mp.: 86–89 °C

¹H NMR: δ = 1.19 (s, 3 H CH₃), 1.69–2.48 (m, 6 H, CH₂–CH₂–CH₂), 3.22 (s, br, 1 H, OH), 4.59 (s, 1 H, CHOH), 7.12–7.40 (m, 5 H, ar).

¹³C NMR: δ = 17.6, 18.7, 33.4, 38.3, 52.8, 76.2, 85.6, 86.7, 122.2, 128.2, 128.5, 131.7, 223.4.

IR (KBr): 3437, 3060, 2964, 2928, 2881, 1713, 1487, 1443, 1402, 1377, 1167, 1051, 997, 765, 693.

Anal. Calcd. for C₁₅H₁₆O₂: C, 78.92, H, 7.06. Found: C, 78.46, H, 6.99.

MS (EI, relative intensity, %): 213.1 (2), 181.2 (100), 153.1 (28), 131.1 (83), 98.1 (41), 83.1 (23).

¹⁰ Duhamel, P.; Cahard, D.; Quemel, Y.; Poisier, J.-M. *J. Org. Chem.* **1996**, *61*, 2232–2235.

HRMS (ESI) $[M-H]^-$: Calcd. 227.1078, found, 227.1078.

anti-8a2: *anti*-2-(1-Hydroxy-3-phenyl-prop-2-ynyl)-2-methyl-cyclopentanone. Pale yellow crystals, mp 86–89 °C.

^1H NMR: δ = 1.09 (s, 3 H CH_3), 1.62–2.38 (m, 6 H, $\text{CH}_2\text{--CH}_2\text{--CH}_2$), 2.85 (s, br, 1 H OH), 4.56 (s, 1 H, CHOH), 7.12–7.40 (m, 5 H, ar).

^{13}C NMR: δ = 18.8, 20.3, 31.5, 39.0, 53.3, 76.3, 85.9, 87.7, 122.3, 128.3, 128.5, 131.7, 222.9.

IR (KBr): 3430, 3079, 3061, 2965, 2927, 2883, 1720, 1487, 1442, 1370, 1326, 1165, 1070, 1044, 998, 764, 694.

Anal. Calcd. for $\text{C}_{15}\text{H}_{16}\text{O}_2$: C, 78.92, H, 7.06. Found: C, 78.80, H, 7.35.

MS (EI, relative intensity, %): 213.1, 181, 153.1, 131.1, 98.1, 83.1.

HRMS (ESI) $[M+H]^+$: Calcd. 229.1223, found, 229.1223.

syn-8a3: *syn*-2-[(4-Ethoxy-phenyl)-hydroxy-methyl]-2-methyl-cyclopentanone. Colorless crystals, mp 84–86 °C.

^1H NMR: δ = 0.72 (s, 3 H, CH_3), 1.31 (t, 3 H, J = 7.1 Hz, CH_3), 1.52–2.43 (m, 6 H, $\text{CH}_2\text{--CH}_2\text{--CH}_2$), 3.92 (q, J = 7.1 Hz, 2 H, CH_2O), 4.66 (s, 1 H, CH), 6.74 (d, J = 6.1 Hz, 2 H, ar), 7.10–7.14 (d, J = 6.2 Hz, 2 H, ar).

^{13}C NMR: δ = 14.7, 18.5, 20.6, 29.7, 38.9, 53.9, 63.3, 76.7, 113.8, 128.1, 133.1, 158.4, 224.0.

IR (KBr): 3455, 2980, 2955, 2866, 1719, 1608, 1513, 1470, 1455, 1297, 1248, 1174, 1049, 922, 832.

Anal. Calcd. for $\text{C}_{15}\text{H}_{20}\text{O}_3$: C, 72.55, H, 8.12. Found: C, 72.41, H, 8.08.

MS (EI, relative intensity, %): 248.1 (11), 136.1 (20), 112.1 (100), 97.1 (23), 77.0 (24).

HRMS $[M]^+$: Calcd. 248.1412, found, 248.1413.

***anti*-8a3:** *anti*-2-[(4-Ethoxy-phenyl)-hydroxy-methyl]-2-methyl-cyclopentanone. Colorless oil

^1H NMR: δ = 0.96 (s, 3 H, CH_3), 1.17 (t, 3 H, J = 7.1 Hz, CH_3) 1.52–2.43 (m, 6 H, $\text{CH}_2\text{--CH}_2\text{--CH}_2$), 4.00 (q, J = 7.1 Hz, 2 H, CH_2O), 4.63 (s, 1 H, CH), 6.74 (d, 6.0 Hz, 2 H, ar), 7.12 (d, 6.1 Hz, 2 H, ar).

^{13}C NMR: δ = 14.6, 15.9, 18.4, 34.0, 38.0, 52.5, 63.3, 63.9, 76.4, 114.7, 132.0, 164.0, 226.0

IR (KBr): 3480, 3095, 1599, 1510, 1393, 1302, 1245, 1160, 1114, 1008, 920, 834.

Anal. Calcd. for $\text{C}_{15}\text{H}_{20}\text{O}_3$: C, 72.55, H, 8.12. Found: C, 72.51, H, 8.12.

MS (EI, relative intensity, %): 248.1 (100), 230.1 (20), 152.0 (19), 112.1 (98), 97.1 (22), 77.0 (24).

HRMS $[\text{M}]^+$: Calcd. 248.1412, found, 248.1413.

***syn*-8a4:** *syn*-2-[(4-Chloro-phenyl)-hydroxy-methyl]-2-methyl-cyclopentanone. Colorless crystals, mp 114–115 °C.

^1H NMR: δ = 0.72 (s, 3 H, CH_3), 1.10–2.41 (m, 6 H, $\text{CH}_2\text{--CH}_2\text{--CH}_2$), 4.65 (s, 1 H, CHOH), 7.10–7.25 (m, 4 H, ar).

^{13}C NMR: δ = 18.3, 20.3, 29.2, 38.7, 53.8, 75.9, 127.8, 128.3, 133.1, 139.7, 223.8.

IR (KBr): 3391, 3066, 2961, 2871, 1725, 1588, 1487, 1396, 1366, 1320, 1284, 1261, 1169, 1089, 1070, 1051, 1011, 825, 743.

Anal. Calcd. for $\text{C}_{13}\text{H}_{15}\text{O}_2\text{Cl}$: C, 65.41, H, 6.33, Cl, 14.85. Found: C, 65.32, H, 6.23, Cl, 14.53.

MS (EI, relative intensity, %): 238.1 (1), 167.0 (4), 141 (75), 97.1 (64), 77.0 (100).

HRMS $[\text{M}]^+$: Calcd. 238.0761, found, 238.0761.

anti-8a4: *anti*-2-[(4-Chloro-phenyl)-hydroxy-methyl]-2-methyl-cyclopentanone. Colorless oil.

^1H NMR: δ = 0.92 (s, 3 H, CH_3), 1.10–2.41 (m, 6 H, $\text{CH}_2\text{--CH}_2\text{--CH}_2$), 4.63 (s, 1 H, CHOH), 7.10–7.25 (m, 4 H, ar).

^{13}C NMR: δ = 15.9, 18.3, 33.7, 37.8, 52.2, 76.1, 127.8, 128.4, 133.1, 138.1, 225.4.

IR (KBr): 3370, 3067, 2960, 2926, 2871, 1724, 1589, 1487, 1396, 1366, 1285, 1169, 1089, 1053, 1011, 857, 743, 649, 609.

Anal. Calcd. for $\text{C}_{13}\text{H}_{15}\text{O}_2\text{Cl}$: C, 65.41, H, 6.33, Cl, 14.85. Found: C, 65.26, H, 6.38, Cl, 14.59.

MS (EI, relative intensity, %): 220.1 (1), 141.0 (28), 98.1 (100), 77.0 (31).

HRMS $[\text{M}]^+$: Calcd. 238.0761, found, 238.0761.

syn-8a5: *syn*-2-[(3-Methoxy-phenyl)-hydroxy-methyl]-2-methyl-cyclopentanone. Colorless oil.

^1H NMR: δ = 0.63 (s, 3 H CH_3), 1.21–2.43 (m, 6 H, $\text{CH}_2\text{--CH}_2\text{--CH}_2$), 3.89 (d, J = 4.2 Hz, 1 H, OH), 3.60 (s, 3H, OCH_3), 4.55 (d, J = 4.2 Hz, 1 H, CHOH), 6.80–7.30 (m, 4 H, ar).

^{13}C NMR: δ = 18.3, 20.4, 29.5, 38.7, 53.6, 54.9, 76.6, 112.70, 112.73, 119.5, 128.7, 142.8, 159.0, 223.7.

IR (KBr): 3473, 3167, 2961, 2876, 1730, 1598, 1547, 1485, 1434, 1401, 1317, 1279, 1256, 1161.

Anal. Calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_3$: C, 71.77, H, 7.74. Found: C, 71.97, H, 7.96.

MS (EI, relative intensity, %): 134.1 (8), 216.1 (2), 135.0 (22), 109.1 (31), 98.1 (100), 83.0 (19).

HRMS $[M]^+$: Calcd. 234.1256, found, 234.1256.

anti-8a5: *anti*-2-[(3-Methoxy-phenyl)-hydroxy-methyl]-2-methyl-cyclopentanone. Colorless oil.

^1H NMR: δ = 1.11 (s, 3 H CH_3), 1.51–2.43 (m, 6 H, $\text{CH}_2\text{--CH}_2\text{--CH}_2$), 3.84 (s, 3 H, OCH_3), 4.19 (s, 1 H, OH), 4.80 (s, 1 H, CHOH), 6.80–7.30 (m, 4 H, ar).

^{13}C NMR: δ = 16.0, 18.4, 33.9, 37.9, 52.3, 55.1, 76.6, 112.7, 112.9, 119.5, 128.7, 141.2, 159.1, 225.7.

IR (KBr): 3471, 3074, 2963, 2873, 2835, 1599, 1582, 1485, 1460, 1434, 1401, 1315, 1256, 1160, 1040, 789, 764, 735, 697.

Anal. Calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_3$: C, 71.77, H, 7.74. Found: C, 71.85, H, 7.87.

MS (EI, relative intensity, %): 134.1 (7), 216.1 (2), 173.1 (1), 135.0 (43), 109.1 (61), 98.1 (100), 83.0 (18), 77.0 (18).

HRMS $[M]^+$: Calcd. 234.1256, found, 234.1256.

syn-8b1: *syn*-2-(Hydroxy-phenyl-methyl)-2-methyl-cyclohexanone¹¹. Colorless oil.

^1H NMR: δ = 0.97 (s, 3 H, CH_3), 1.15–2.70 (m, 8 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 4.99 (s, 1 H, CHOH), 7.15–7.50 (m, 5 H, ar).

¹¹ Mukayama, T; Banno, K.; Narasaka, K. *J. Am. Chem. Soc.* **1974**, 96, 7503–7509.

anti-8b1: *anti*-2-(Hydroxy-phenyl-methyl)-2-methyl-cyclohexanone¹⁰. Colorless oil.

¹H NMR: δ = 1.09 (s, 3 H, CH₃), 1.15–2.70 (m, 8 H, CH₂CH₂CH₂CH₂), 4.88 (s, 1 H, CHOH), 7.15–7.50 (m, 5 H, ar).

syn-9b1: *syn*-2-(Hydroxy-phenyl-methyl)-6-methyl-cyclohexanone¹⁰. Colorless oil.

¹H NMR: δ = 0.96 (d, 7.1 Hz, 3 H, CH₃), 1.15–2.70 (m, 8 H, CHCH₂CH₂CH₂CH), 4.68–4.74 (d, J = 8.7 Hz, 1 H, CHOH), 7.15–7.50 (m, 5H, ar).

anti-9b2: *anti*-2-(Hydroxy-phenyl-methyl)-6-methyl-cyclohexanone¹⁰. Colorless oil.

¹H NMR: δ = 0.83 (d, 7.1 Hz, 3 H, CH₃), 1.15–2.70 (m, 8 H, CHCH₂CH₂CH₂CH), 4.77 (d, J = 9.42 Hz, 1 H, CHOH), 7.15–7.50 (m, 5H, ar).

syn-8b2: *syn*-2-(1-Hydroxy-3-phenyl-prop-2-ynyl)-2-methyl-cyclohexanone. Colorless oil.

¹H NMR: δ = 1.42 (s, 3 H, CH₃), 1.65–2.60 (m, 8 H, CH₂CH₂CH₂CH₂), 3.70 (s, 1 H, CHOH), 4.90 (s, 1 H, CHOH), 7.29–7.46 (m, 5 H, ar).

¹³C NMR: δ = 16.9, 20.5, 27.2, 32.5, 38.7, 52.6, 67.9, 85.7, 86.6, 122.3, 128.0, 128.2, 131.5, 215.9.

IR (KBr): 3450, 3058, 2936, 2867, 1699, 1488, 1440, 1373, 1126, 1042, 756, 691.

Anal. Calcd. for C₁₆H₁₈O₂: C, 79.31, H, 7.49. Found: C, 79.30, H, 7.49.

MS (EI, relative intensity, %): 242.1 (7), 227.1 (28), 131.1 (70), 112.1 (100), 97.1 (36), 77.0 (27).

HRMS (ESI) $[M+H]^+$: Calcd. 243.1380, found, 243.1378.

anti-8b2: *anti*-2-(1-Hydroxy-3-phenyl-prop-2-ynyl)-2-methyl-cyclohexanone. Colorless oil.

^1H NMR: δ = 1.31 (s, 3 H, CH_3), 1.65–2.50 (m, 8 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 3.50 (s, br, 1 H, CHOH), 4.83 (s, 1 H, CHOH), 7.29–7.46 (m, 5 H, ar).

^{13}C NMR: δ = 20.5, 20.6, 26.3, 36.1, 39.0, 53.2, 67.6, 85.9, 87.2, 122.4, 127.9, 128.1, 131.5, 216.5.

IR (KBr): 3450, 3059, 2936, 2865, 1703, 1488, 1442, 1312, 1238, 1121, 1069, 757, 688.

Anal. Calcd. for $\text{C}_{16}\text{H}_{18}\text{O}_2$: C, 79.31, H, 7.49. Found: C, 79.10, H, 7.36.

MS (EI, relative intensity, %): 242.1 (28), 227.1 (34), 131.0 (69), 112.1 (100), 97.1 (37), 77.0 (28).

HRMS (ESI) $[M-H]^-$: Calcd. 241.1243, found, 241.1243.

syn-8b4: *syn*-2-[Hydroxy-(4-chloro-phenyl)-methyl]-2-methyl-cyclohexanone. Colorless oil.

^1H NMR: δ = 1.10 (s, 3 H, CH_3), 1.25–2.70 (m, 8 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 3.72 (s, 3 H, OCH_3), 4.86 (s, CHOH), 6.82–7.20 (m, 4 H, ar).

^{13}C NMR: δ = 15.7, 20.4, 21.3, 27.1, 31.0, 39.2, 76.4, 127.7, 129.3, 133.1, 137.8, 217.7.

IR (KBr): 3535, 2975, 2864, 1691, 1543, 1488, 1460, 1448, 1396, 1376, 1309, 1270, 1190, 1170, 1088, 1050, 1013, 995, 832.

Anal. Calcd. for $\text{C}_{14}\text{H}_{17}\text{O}_2\text{Cl}$: C, 66.53, H, 6.78, Cl, 14.03. Found: C, 66.38, H, 6.77, Cl, 13.73.

HRMS (ESI) $[M+H]^+$: Calcd. 249.1491, found, 249.1488.

anti-8b4: *anti*-2-[Hydroxy-(4-chloro-phenyl)-methyl]-2-methyl-cyclohexanone. Colorless crystals, mp 68–70 °C.

^1H NMR: δ = 0.95 (s, 3 H, CH_3), 1.15–2.60 (m, 8 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 4.84 (s, CHOH), 7.05–7.25 (m, 4 H, ar).

^{13}C NMR: δ = 20.3, 20.5, 27.1, 36.8, 38.9, 52.4, 76.9, 127.7, 129.3, 133.2, 137.4, 219.0

IR (KBr): 3509, 2977, 2939, 2864, 1687, 1486, 1461, 1308, 1280, 1221, 1190, 1124, 1086, 1011, 831, 795.

Anal. Calcd. for $\text{C}_{14}\text{H}_{17}\text{O}_2\text{Cl}$: C, 66.53, H, 6.78, Cl, 14.03, Found: C, 66.08, H, 6.72, Cl, 13.73.

HRMS (ESI) $[\text{M}+\text{H}]^+$: Calcd. 253.0995, found, 249.0993.

syn-8b5: *syn*-2-[Hydroxy-(3-methoxy-phenyl)-methyl]-2-methyl-cyclohexanone. Colorless oil.

^1H NMR: δ = 1.00 (s, 3 H, CH_3), 1.25–2.70 (m, 8 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 3.72 (s, 3 H, OCH_3), 4.99 (s, CHOH), 6.82–7.20 (m, 4 H, ar).

^{13}C NMR: δ = 20.5, 21.5, 26.4, 31.2, 37.0, 39.3, 54.5, 74.5, 112.6, 113.8, 120.5, 128.4, 141.0, 159.0 219.0.

IR (KBr): 3446, 2936, 2835, 1701, 1599, 1583, 1485, 1450, 1434, 1395, 1313, 1256, 1156, 1040.

Anal. Calcd. for $\text{C}_{15}\text{H}_{20}\text{O}_3$: C, 72.55, H, 8.12. Found: C, 72.41, H, 8.08.

HRMS (ESI) $[\text{M}+\text{H}]^+$: Calcd. Calcd. 253.0995, found, 249.0993.

anti-8b5: *anti*-2-[Hydroxy-(3-methoxy-phenyl)-methyl]-2-methyl-cyclohexanone. Colorless oil.

^1H NMR: δ = 1.10 (s, 3 H, CH_3), 1.25–2.70 (m, 8 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 3.72 (s, 3 H, OCH_3), 4.86 (s, CHOH), 6.82–7.20 (m, 4 H, ar).

^{13}C NMR: δ = 15.9, 20.6, 27.2, 37.0, 39.2, 52.6, 55.1, 77.3, 112.8, 113.8, 120.5, 128.4, 140.6, 159.0, 217.8.

IR (KBr): 3460, 2940, 2835, 1700, 1600, 1583, 1485, 1450, 1320, 1256, 1156, 1123, 1040.

Anal. Calcd. for $\text{C}_{15}\text{H}_{20}\text{O}_3$: C, 72.55, H, 8.12. Found: C, 72.51, H, 8.12.

HRMS (ESI) $[\text{M}+\text{H}]^+$: Calcd. 249.1491, found, 249.1488.

syn-11a: *syn*-1-(2,5-Diphenyl-[1,3]dioxolan-4-yl)-ethanone. Colorless oil.

^1H NMR: δ = 2.31 (s, 3 H, CH_3), 4.40 (d, J = 6.78 Hz, 1 H, CH), 5.15 (d, J = 6.79 Hz, 1 H, CH), 6.00 (s, CH), 7.25–7.66 (m, 10 H, ar).

^{13}C NMR: δ = 27.2, 80.8, 105.0, 126.6, 126.8, 128.5, 128.6, 128.7, 129.8, 136.1, 137.7, 207.6.

IR (KBr): 3068, 3033, 2955, 1723, 1452, 1317, 1271, 1177, 1110, 1070, 1026, 758, 711.

Anal. Calcd. for $\text{C}_{17}\text{H}_{16}\text{O}_3$: C, 76.10, H, 6.01. Found: C, 75.91, H, 6.22.

MS (EI, relative intensity, %): 239.1 (1), 225.1 (30), 196.1 (14), 162.1 (31), 146.1 (24), 119.1 (100), 105.0 (79), 91.1 (99), 77.0 (44).

HRMS (ESI) $[\text{M}-\text{H}]^-$: Calcd. 267.1021, found, 267.1022.

anti-**11a**: *anti*-1-(2,5-Diphenyl-[1,3]dioxolan-4-yl)-ethanone. Colorless oil.

^1H NMR: δ = 1.77 (s, 3 H, CH₃), 4.23 (d, J = 8.67 Hz, 1 H, CH), 5.48 (d, J = 8.67 Hz, 1 H, CH), 6.01 (s, CH), 7.25–7.66 (m, 10 H, ar).

^{13}C NMR: δ = 27.8, 80.9, 84.9, 104.4, 126.6, 126.9, 128.4, 128.5, 128.7, 129.8, 135.4, 135.7, 206.5.

IR (KBr): 3032, 1722, 1722, 1704, 1689, 1601, 1684, 1494, 1492, 1452, 1419, 1325, 1272, 1177, 1110, 1070, 1026, 935, 709.

Anal. Calcd. for C₁₇H₁₆O₃: C, 76.10, H, 6.01. Found: C, 76.00, H, 6.32.

MS (EI, relative intensity, %): 267.1 (0.5), 239.1 (1), 225.1 (22), 196.1 (18), 162.1 (30), 146.1 (37), 119.1 (100), 105.0 (79), 91.1 (91), 77.0 (60).

HRMS (ESI) [M–H][–]: Calcd. 267.1021, found, 267.1022.

syn-**12a**: *syn*-1,5-Dimethyl-3-phenyl-2,6,8-trioxa-bicyclo[3.2.1]octan-4-ol. Colorless solid.

^1H NMR: δ = 1.56 (s, 3 H, CH₃), 1.62 (s, 3 H, CH₃), 1.85 (d, J = 9.0 Hz, 1 H, OH), 3.40 (dd, J_1 = 2.25 Hz, J_2 = 9.0 Hz, 1 H, CH), 3.76 (d, J = 8.3 Hz, 1 H, CH), 4.20 (d, J = 8.7 Hz, 1 H, CH), 5.16 (d, J = 2.6 Hz, 1 H, CH), 7.25–7.40 (m, 5 H, ar).

^{13}C NMR: δ = 20.4, 20.7, 70.6, 72.0, 75.3, 104.4, 108.7, 126.1, 127.8, 128.4, 137.4.

IR (KBr): 3478, 3058, 3034, 2905, 2357, 1244, 1226, 1187, 1088, 1075, 1037, 868.

Anal. Calcd. for C₁₃H₁₆O₄: C, 66.09, H, 6.83. Found: C, 65.82, H, 6.99.

MS (EI, relative intensity, %): 235.1 (0.5), 205.1 (1), 163.1 (6), 145.1 (9), 121.1 (26), 91.1 (100), 77.0 (20).

HRMS (ESI) [M]⁺: Calcd. 236.1049, found, 236.149.

anti-12a: *anti*-1,5-Dimethyl-3-phenyl-2,6,8-trioxa-bicyclo[3.2.1]octan-4-ol. Colorless solid.

^1H NMR: δ = 1.55 (s, 3 H, CH_3), 1.61 (s, 3 H, CH_3), 1.76 (d, J = 9.0 Hz, 1 H, OH), 3.25 (dd, $J_1 = J_2 = 9.9$ Hz, 1 H, CH), 3.81 (d, J = 8.3 Hz, 1 H, CH), 4.25 (d, J = 8.3 Hz, 1 H, CH), 4.54 (d, J = 8.3 Hz, 1 H, CH), 7.25–7.40 (m, 5 H, ar).

^{13}C NMR: δ = 19.8, 20.4, 72.8, 74.1, 79.0, 104.4, 108.7, 127.2, 128.5, 138.4 (one aryl signal is hidden under the 127.2 or 128.5 signal).

IR (KBr): 3486, 3446, 3064, 3034, 2944, 2905, 2894, 1452, 1383, 1248, 1228, 1206, 1186, 1144, 1098, 1076, 1045, 1012, 915, 903, 848, 797, 755, 702.

Anal. Calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_4$: C, 66.09, H, 6.83. Found: C, 66.04, H, 6.82.

MS (EI, relative intensity, %): 205.1 (0.5), 163.1 (3), 145.1 (10), 121.1 (42), 91.1 (100), 77.0 (18).

HRMS (ESI) $[\text{M}]^+$: Calcd. 236.1049, found, 236.149.

syn-12b: *syn*-1,5-Dimethyl-3-phenylethynyl-2,6,8-trioxa-bicyclo[3.2.1]octan-4-ol. Pale yellow solid.

^1H NMR: δ = 1.50 (s, 6 H, 2 x CH_3), 2.52 (s, br, 1 H, OH), 3.31 (s, br, 1 H, CH), 3.66 (d, J = 8.67 Hz, 1 H, CH), 4.08 (d, J = 8.66 Hz, 1 H, CH), 5.05 (d, J = 2.64 Hz, 1 H, CH), 7.25–7.50 (m, 5 H, ar).

^{13}C NMR: δ = 20.4, 20.6, 67.0, 69.5, 71.8, 83.5, 87.6, 104.6, 108.3, 121.8, 128.2, 128.8, 132.0.

IR (KBr): 3456, 3078, 2993, 2972, 2900, 1718, 1597, 1490, 1444, 1406, 1383, 1369, 1226, 1196, 1184, 1087, 1022, 881, 863, 838, 779, 759, 693.

Anal. Calcd. for $\text{C}_{15}\text{H}_{16}\text{O}_4$: C, 69.22, H, 6.20. Found: C, 68.95, H, 6.10.

MS (EI, relative intensity, %): 259.1 (3), 202.1 (12), 187.1 (32), 144.1 (100), 105.0 (85), 77.0 (45).

HRMS (ESI) $[M+H]^+$: Calcd. 261.1121, found, 261.1124.

anti-**12b**: *anti*-1,5-Dimethyl-3-phenylethynyl-2,6,8-trioxa-bicyclo[3.2.1]octan-4-ol. Colorless solid.

^1H NMR: δ = 1.49 (s, 3 H, CH_3), 1.50 (s, 3 H, CH_3), 2.44 (d, J = 8.29 Hz, 1 H, OH), 3.63 (dd, $J_1 = J_2$ = 8.29 Hz, 1 H, CH), 3.67 (d, J = 8.7 Hz, 1 H, CH), 4.04 (d, J = 8.3 Hz, 1 H, CH), 4.50 (d, J = 8.7 Hz, 1 H, CH), 7.25–7.40 (m, 5 H, ar).

^{13}C NMR: δ = 19.7, 20.2, 68.0, 72.5, 72.8, 85.2, 86.0, 104.1, 108.5, 121.9, 128.1, 128.7, 131.9.

IR (KBr): 3461, 3421, 3097, 3000, 2939, 2878, 1490, 1382, 1252, 1252, 1227, 1210, 1186, 1150, 1071, 1021, 887, 876, 876, 815, 757, 693.

Anal. Calcd. for $\text{C}_{15}\text{H}_{16}\text{O}_4$: C, 69.22, H, 6.20. Found: C, 69.04, H, 6.39.

MS (EI, relative intensity, %): 260.1 (1), 215.1 (1), 187.1 (4), 144.1 (100), 115.1 (52), 89.0 (4).

HRMS (ESI) $[M+H]^+$: Calcd. 261.1121, found, 261.1124.

Table 1. Crystal data and structure refinement for *rac*-Ti₄(μ-BINOLato)₆(μ₃-OH)₄.

Empirical formula	C ₁₂₀ H ₇₆ O ₁₆ Ti ₄	
Formula weight	1965.41	
Temperature	180(2) K	
Wavelength	71.073 pm	
Crystal system	cubic	
Space group	<i>F</i> -43 <i>c</i>	
Unit cell dimensions	a = 3234.8(5) pm	α = 90°.
	b = 3234.8(5) pm	β = 90°.
	c = 3234.8(5) pm	γ = 90°.
Volume	33.85(1) nm ³	
Z	8	
Density (calculated)	0.771 Mg/m ³	
Absorption coefficient	0.222 mm ⁻¹	
F(000)	8096	
Crystal size	0.48 x 0.40 x 0.40 mm ³	
Theta range for data collection	2.82 to 22.48°.	
Index ranges	0 ≤ h ≤ 20, 0 ≤ k ≤ 24, 4 ≤ l ≤ 34	
Reflections collected	978	
Independent reflections	978 [<i>R</i> (int) = 0.0000]	
Completeness to theta = 22.48°	97.8 %	
Max. and min. transmission	0.9165 and 0.9010	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	978 / 0 / 106	
Goodness-of-fit on F ²	0.865	
Final R indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0501, <i>wR</i> 2 = 0.1213	
R indices (all data)	<i>R</i> 1 = 0.0718, <i>wR</i> 2 = 0.1316	
Absolute structure parameter	0.15(10)	
Largest diff. peak and hole	0.205 and -0.206 e.Å ⁻³	

Table 2. Crystal data and structure refinement for **5**, 4 β -hydroxy-1 β ,4 α -dimethylbicyclo[3.2.1]octane-7,8-dione, C₁₀H₁₄O₃.

Empirical formula	C ₁₀ H ₁₄ O ₃	
Formula weight	182.21	
Temperature	180(2) K	
Wavelength	71.073 μ m	
Crystal system	Orthorhombic	
Space group	<i>Pna</i> 2 ₁	
Unit cell dimensions	<i>a</i> = 1202.4(2) μ m	α = 90°.
	<i>b</i> = 1069.31(15) μ m	β = 90°.
	<i>c</i> = 712.49(10) μ m	γ = 90°.
Volume	0.9161(3) nm ³	
Z	4	
Density (calculated)	1.321 Mg/m ³	
Absorption coefficient	0.097 mm ⁻¹	
F(000)	392	
Crystal size	0.64 x 0.48 x 0.40 mm ³	
Theta range for data collection	2.55 to 25.23°.	
Index ranges	$-14 \leq h \leq 14$, $-12 \leq k \leq 12$, $-8 \leq l \leq 8$	
Reflections collected	5683	
Independent reflections	1643 [<i>R</i> (int) = 0.0285]	
Completeness to theta = 25.23°	99.1 %	
Max. and min. transmission	0.9624 and 0.9408	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1643 / 1 / 175	
Goodness-of-fit on F ²	1.073	
Final R indices [<i>I</i> > 2sigma(<i>I</i>)]	<i>R</i> 1 = 0.0252, <i>wR</i> 2 = 0.0614	
R indices (all data)	<i>R</i> 1 = 0.0266, <i>wR</i> 2 = 0.0618	
Absolute structure parameter	-0.3(8)	
Extinction coefficient	0.012(7)	

Largest diff. peak and hole	0.200 and $-0.147 \text{ e.}\text{\AA}^{-3}$
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Table 3. Crystal data and structure refinement for ***syn-8a4***, $\text{C}_{13} \text{H}_{15} \text{O}_2 \text{Cl}$

Empirical formula	$\text{C}_{13} \text{H}_{15} \text{O}_2 \text{Cl}$	
Formula weight	238.70	
Temperature	180(2) K	
Wavelength	71.073 pm	
Crystal system	Monoclinic	
Space group	$P2_1/a$	
Unit cell dimensions	$a = 1248.9(3) \text{ pm}$	$\alpha = 90^\circ$.
	$b = 823.2(3) \text{ pm}$	$\beta = 90^\circ$.
	$c = 1274.6(3) \text{ pm}$	$\gamma = 90^\circ$.
Volume	$1233.7(6) \text{ nm}^3$	
Z	4	
Density (calculated)	1.347 Mg/m^3	
Absorption coefficient	0.23 mm^{-1}	
F(000)	144	
Crystal size	$0.50 \times 0.40 \times 0.20 \text{ mm}^3$	
Theta range for data collection	1.70 to 26.00° .	
Index ranges	$-15 \leq h \leq 14$, $0 \leq k \leq 12$, $0 \leq l \leq 8$	
Reflections collected	2604	
Independent reflections	2604 [$R(\text{int}) = 0.0117$]	
Completeness to $\theta = 25.23^\circ$	96.1 %	
Max. and min. transmission	0.9210 and 0.8320	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2604 / 0 / 206	
Goodness-of-fit on F^2	1.108	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.044$, $wR2 = 0.0110$	

R indices (all data)	$R1 = 0.060, wR2 = 0.0126$
Absolute structure parameter	$-0.3(8)$
Extinction coefficient	$0.0010(13)$
Largest diff. peak and hole	0.363 and $-0.260 \text{ e.}\text{\AA}^{-3}$