Total Synthesis of (±)-Aspercyclide A and its C19 Methyl Ether

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Supporting Information — X-Ray Crystallography

Crystal data for **7a**: $C_{18}H_{25}BrO_3$, M = 369.29, monoclinic, $P2_1/c$ (no. 14), a = 7.80269(5), b = 14.86805(8), c = 15.69840(8) Å, β = 92.5603(5)°, V = 1819.37(2) Å^3, Z = 4, D_c = 1.348 g cm^{-3}, μ(Cu-Kα) = 3.154 mm^{-1}, T = 173 K, colourless plates, Oxford Diffraction Xcalibur PX Ultra diffractometer; 3516 independent measured reflections (R_{int} = 0.0294), F^2 refinement, R_1(obs) = 0.0255, wR_2(all) = 0.0761, 2910 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 143°], 201 parameters. CCDC 747554.

Crystal data for the benzoate ester of **8**: $C_{17}H_{15}BrO_4$, M = 363.20, monoclinic, Pn (no. 7), a = 8.02056(13), b = 6.60200(9), c = 14.6738(2) Å, β = 95.5928(15)°, V = 773.31(2) Å^3, Z = 2, D_c = 1.560 g cm^{-3}, μ(Cu-Kα) = 3.764 mm^{-1}, T = 173 K, colourless blocks, Oxford Diffraction Xcalibur PX Ultra diffractometer; 2700 independent measured reflections (R_{int} = 0.0173), F^2 refinement, R_1(obs) = 0.0254, wR_2(all) = 0.0724, 2634 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 143°], 200 parameters. The absolute structure of the benzoate of **8** was determined by a combination of *R*-factor tests [R_1^+ = 0.0254, R_1^- = 0.0352] and by use of the Flack parameter [x^+ = +0.00(2), x^- = +1.01(2)]. CCDC 747376.

Crystal data for **15a**: $C_{25}H_{28}O_6$, M = 424.47, monoclinic, $P2_1/c$ (no. 14), a = 18.7407(3), b = 8.56319(13), c = 13.73354(18) Å, β = 93.1039(14)°, V = 2200.73(6) Å^3, Z = 4, D_c = 1.281 g cm^{-3}, μ(Cu-Kα) = 0.743 mm^{-1}, T = 173 K, colourless canoe-shaped plates, Oxford Diffraction Xcalibur PX Ultra diffractometer; 4188 independent measured reflections (R_{int} =

0.0202), F^2 refinement, R_1(obs) = 0.0429, wR_2(all) = 0.1214, 3114 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 143°], 285 parameters. CCDC 747377.

The O(21)-bound hydrogen atom in the structure of **15a** was located from a ΔF map and refined freely subject to an O–H distance constraint of 0.90 Å. The O(21)–H···O(22) hydrogen bond has O···O and H···O separations of 2.613(2) and 1.80 Å respectively, with an O–H···O angle of 150°.

Fig. S1 The molecular structure of **7a**.

Fig. S2 The molecular structure of **7a** (50% probability ellipsoids).

Fig. S3 The molecular structure of the benzoate ester of **8**.

Fig. S4 The molecular structure of the benzoate ester of **8** (50% probability ellipsoids).

Fig. S5 The molecular structure of **15a** (50% probability ellipsoids).

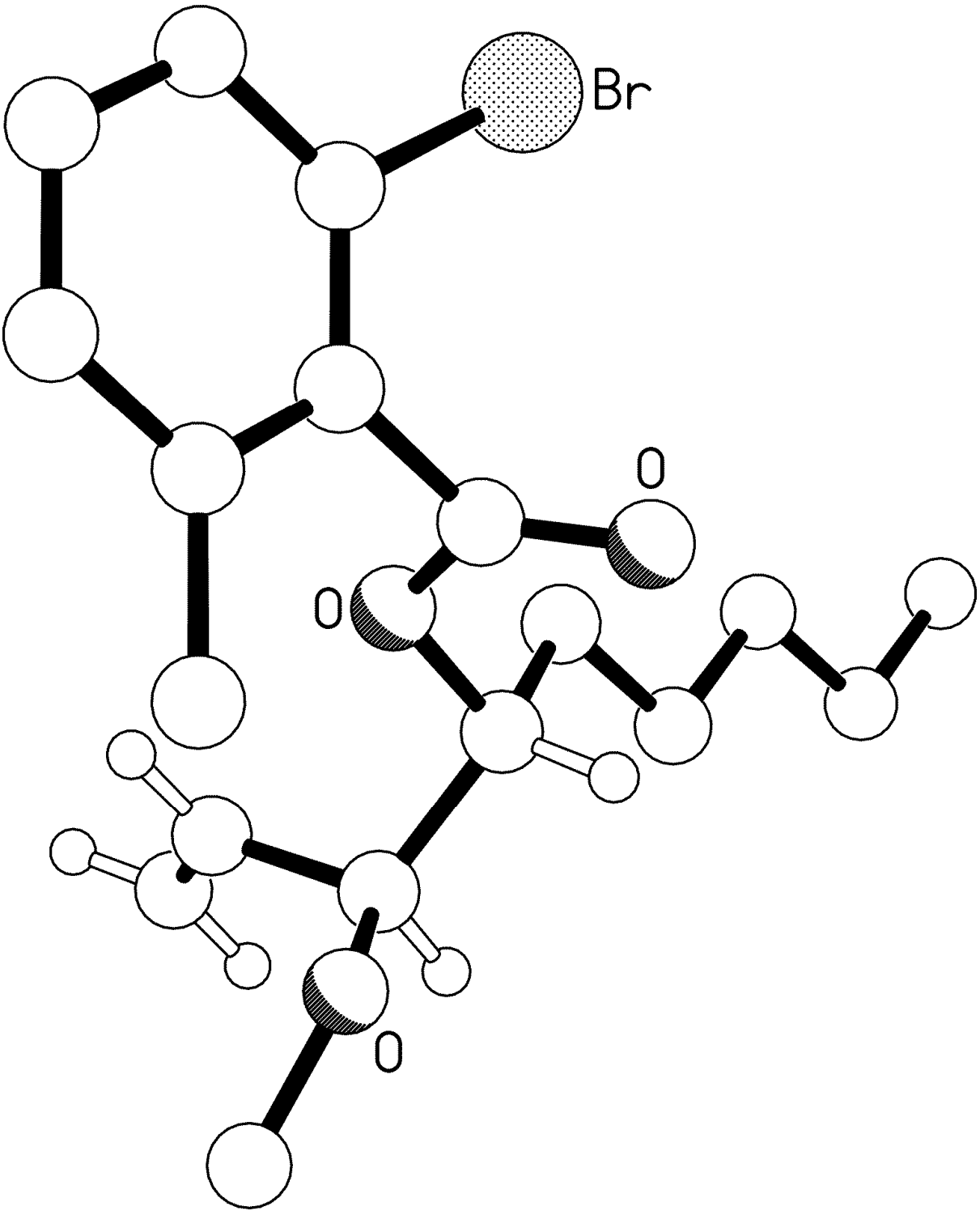
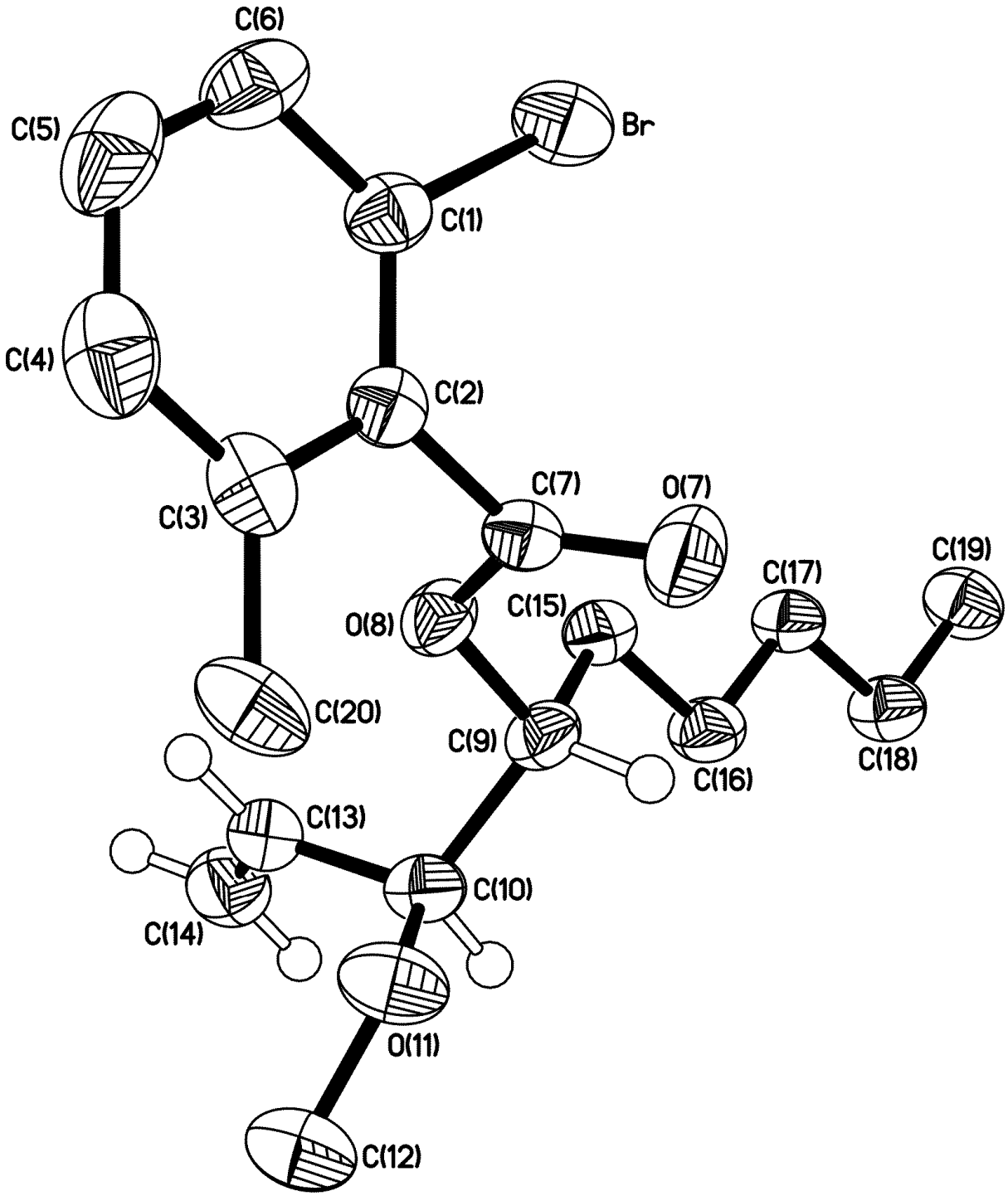


Fig. S1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C(5)
Br
C(1)
C(4)
C(2)
C(7)
O(7)
C(3)
C(19)
C(17)
C(15)
O(8)
C(20)
C(9)
C(16)
C(18)
C(13)
C(10)
C(14)
O(11)
C(12)

Fig. S2

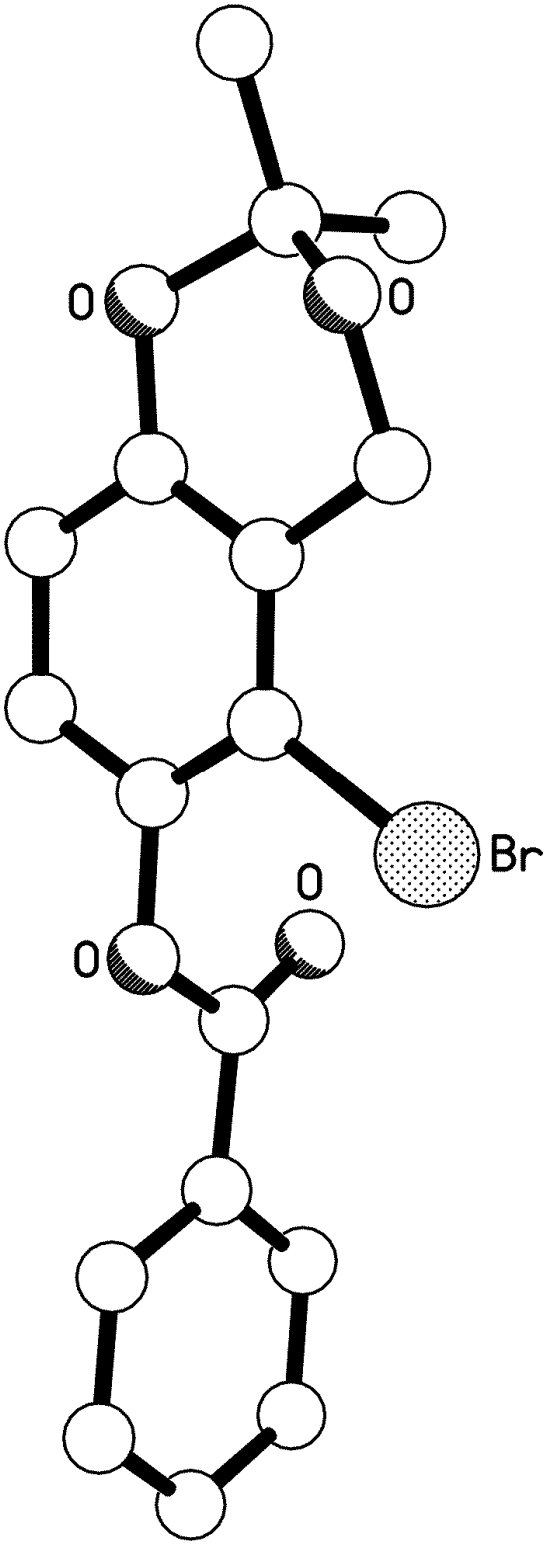
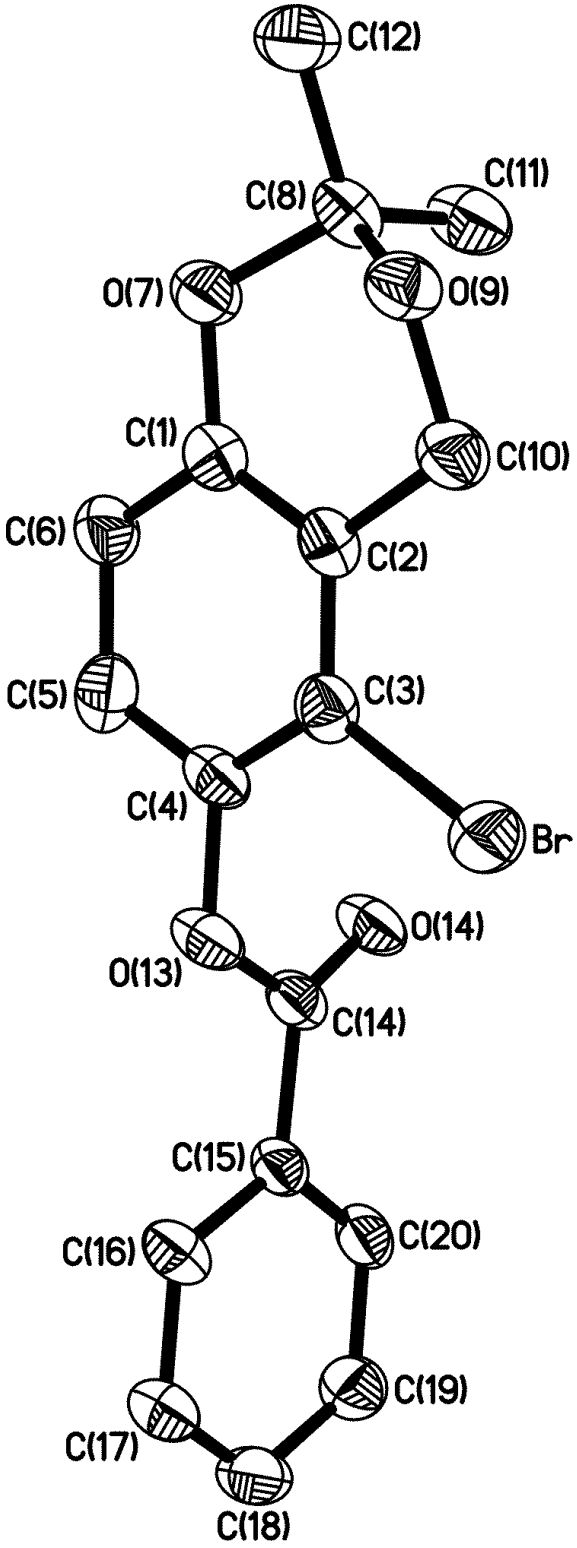


Fig. S3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C(11)
C(8)
O(7)
O(9)
C(1)
C(10)
C(6)
C(2)
C(5)
C(3)
C(4)
Br
O(14)
O(13)
C(14)
C(15)
C(16)
C(20)
C(19)
C(17)
C(18)

Fig. S4

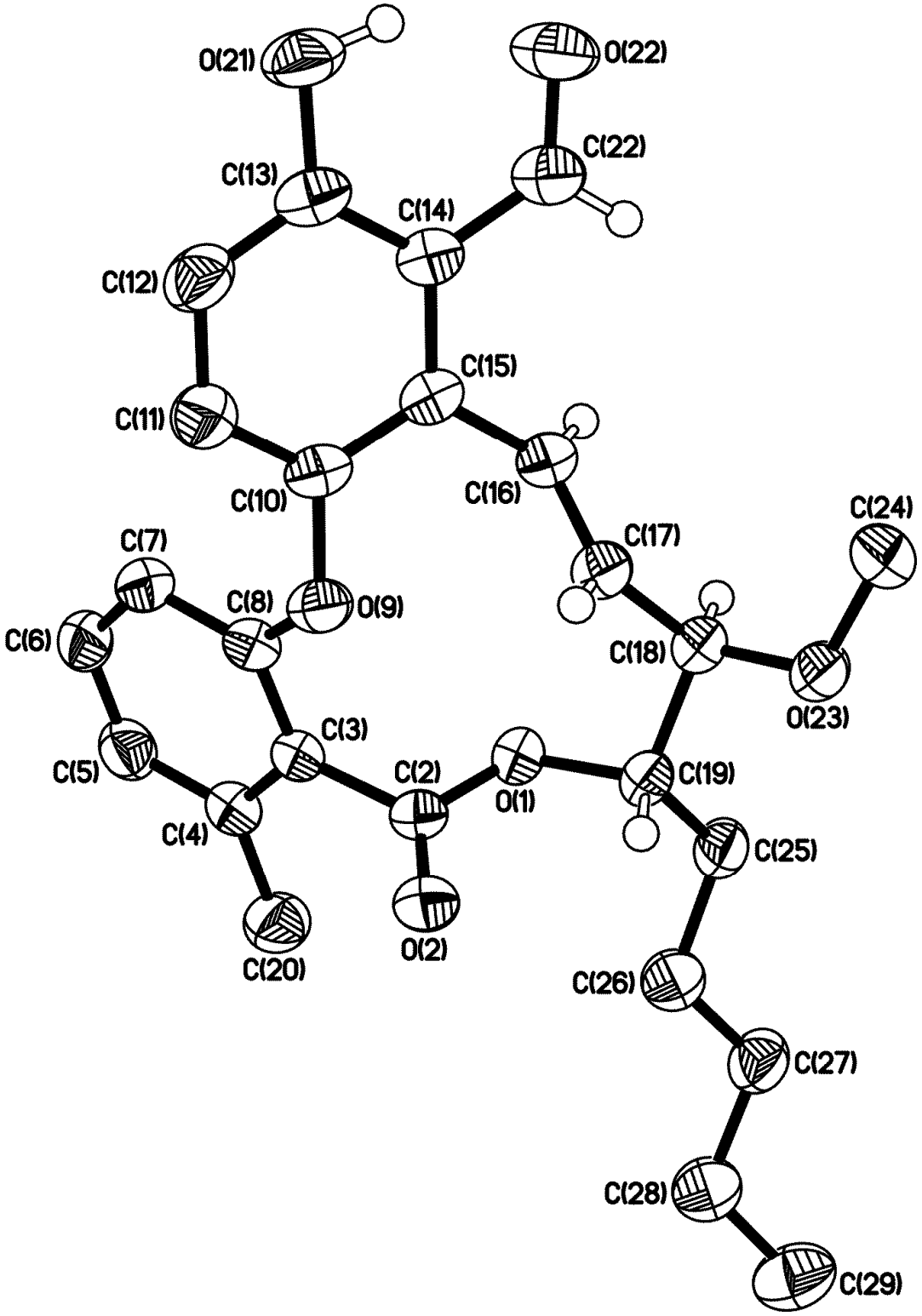
O(21)
O(22)
C(22)
C(13)
C(14)
C(12)
C(15)
C(11)
C(10)
C(16)
C(24)
C(7)
C(17)
C(8)
O(9)
C(6)
C(18)
O(23)
C(3)
C(5)
C(2)
O(1)
C(19)
C(4)
C(25)
O(2)
C(20)
C(26)
C(27)
C(28)
C(29)

Fig. S5