# Photochemistry and Photophysics of Cholesta-5,7,9(11)-trien-3β-ol in Ethanol

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**Supporting Information:** Figure S1, ^{1}H NMR spectrum of the final product mixture from the irradiation of HOCTL in Ar outgassed ethanol. Figure S2, the UV spectrum of $HOE_2$. Figures S3-S6, ^{1}H NMR spectra of $HOD_1$, $HOD_2$, $HOE_1$ and $HOE_2$, respectively. Figure S7, COSY ^{1}H NMR spectrum of $HOE_1$. Figure S8, NOESY ^{1}H NMR spectrum of $HOE_1$. Figure S9, Expanded region of Figure S7 showing the correlation between the vinyl H at $C_{11}$ and the H-6 proton. Figure S10, NOESY ^{1}H NMR spectrum of $HOE_1$ in $CD_3OD$. Figure S11, ^{1}H NMR spectrum of HORP2 in $CD_3Cl$. Figure S12, Time evolution of UV spectra from the 313 nm irradiation of CTL in ethanol. Figure S13, Combination coefficient plot for the spectra in Figure S12. X-ray structures: Tables S1-S7 of X-ray data consisting of crystallographic parameters, positional parameters, bond distances, bond angles, and torsional angles for HOCTL. Tables S8-S14 and Tables S15-S21 for HOCTLP and HORP2, respectively. Table S22, Hydrogen Atom Coordinates ($Å × 10^4$) and Isotropic Displacement Parameters ($Å2 × 10^3$) for HORP2. Reference [1] in Supporting Information is cited as reference [20] in the manuscript.
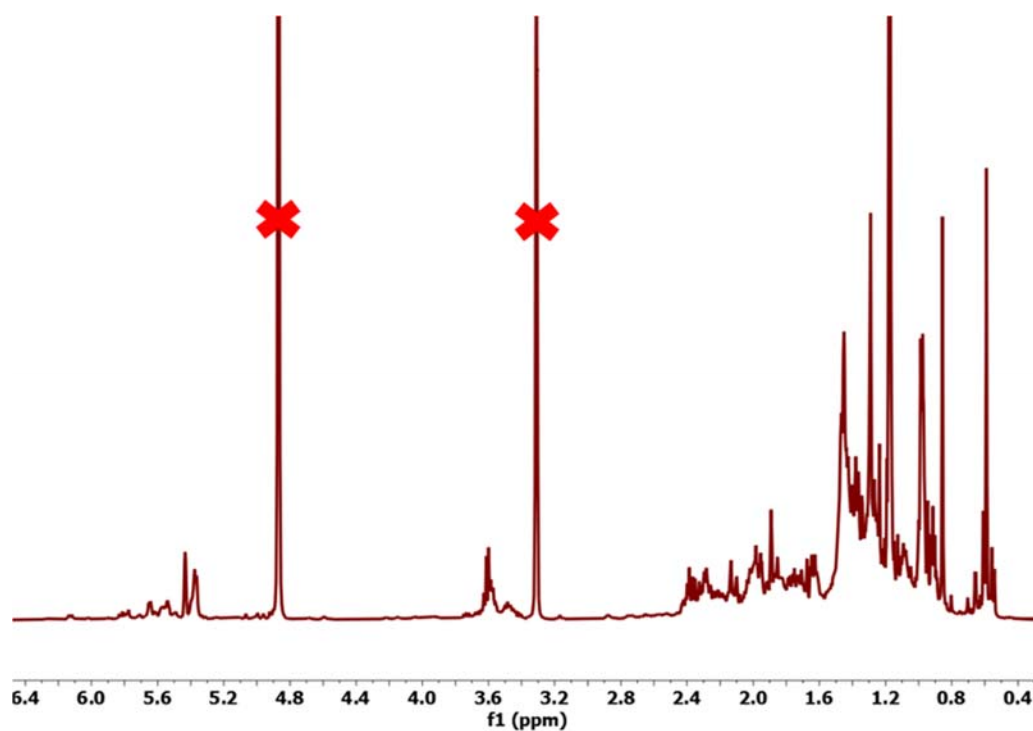
**Figure S1**. $^1$H NMR spectrum in $CD_3OD$ of photoproduct mixture from the irradiation of HOCTL in Ar outgassed ethanol. The crossed out peaks belong to partially protonated solvent.
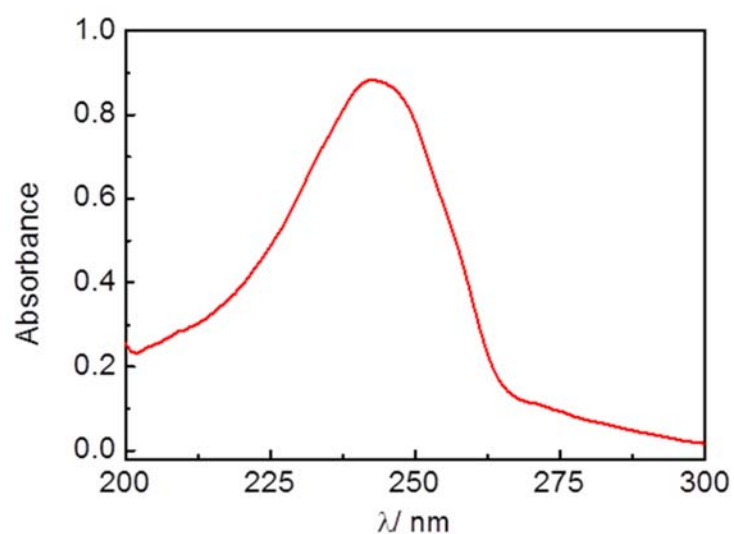


**Figure S2.** The UV spectrum of $HOE_2$.
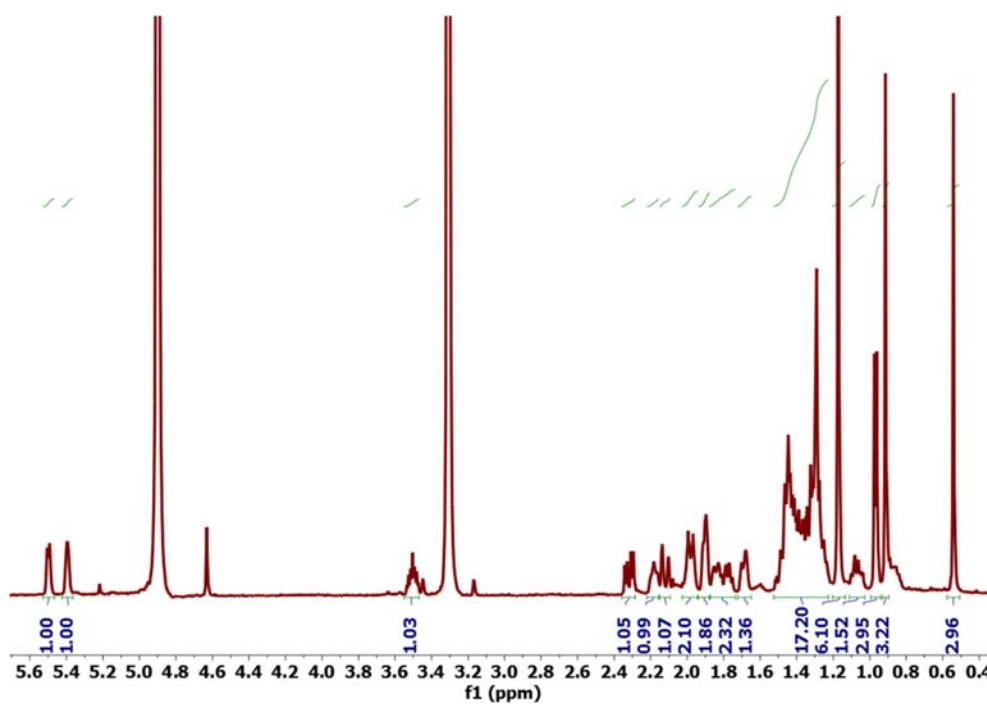
**Figure S3.** $^1$H NMR spectrum of HOD$_1$, in CD$_3$OD.
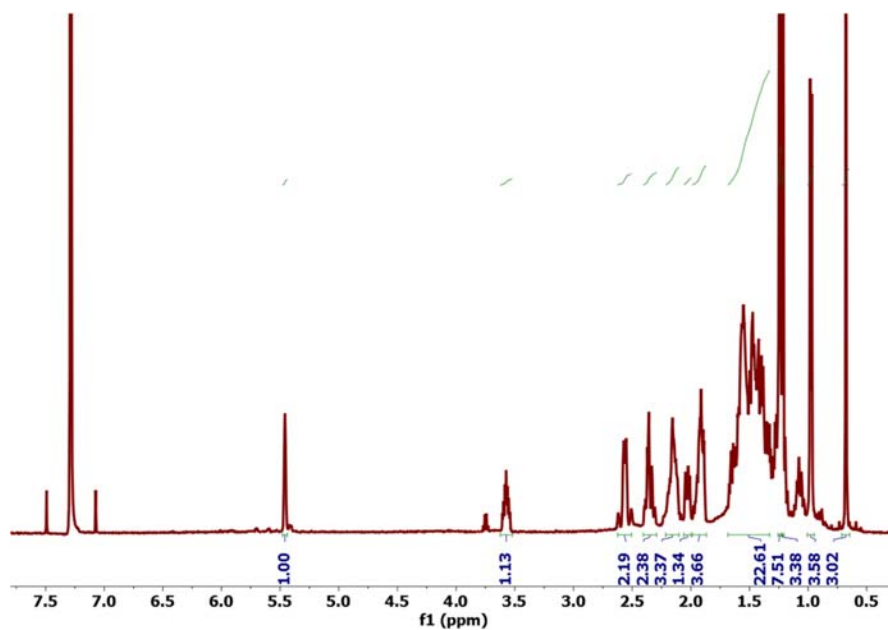


**Figure S4.** $^1$H NMR spectrum of HOD$_2$, in CDCl$_3$.

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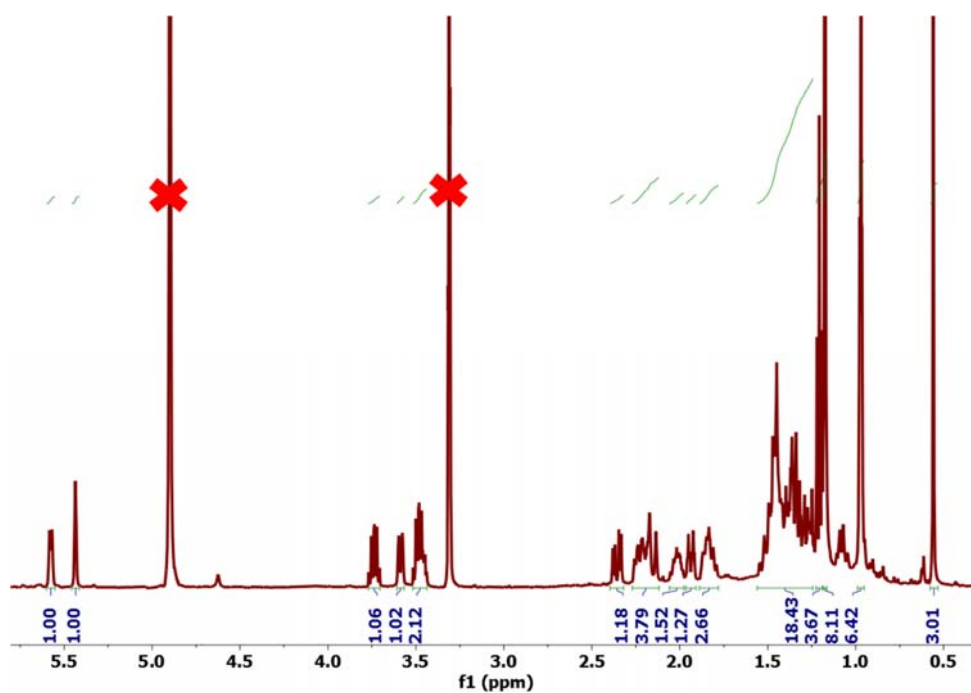
**Figure S5.** $^1$H NMR spectrum of HOE$_1$ in CD$_3$OD.

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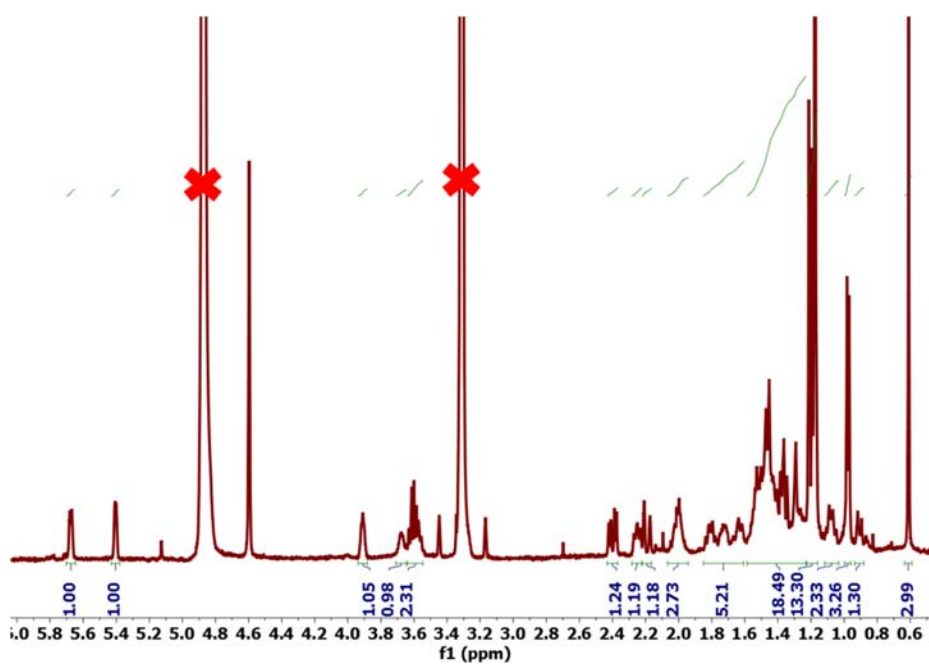


**Figure S6.** $^1$H NMR spectrum of HOE$_2$ in CD$_3$OD.
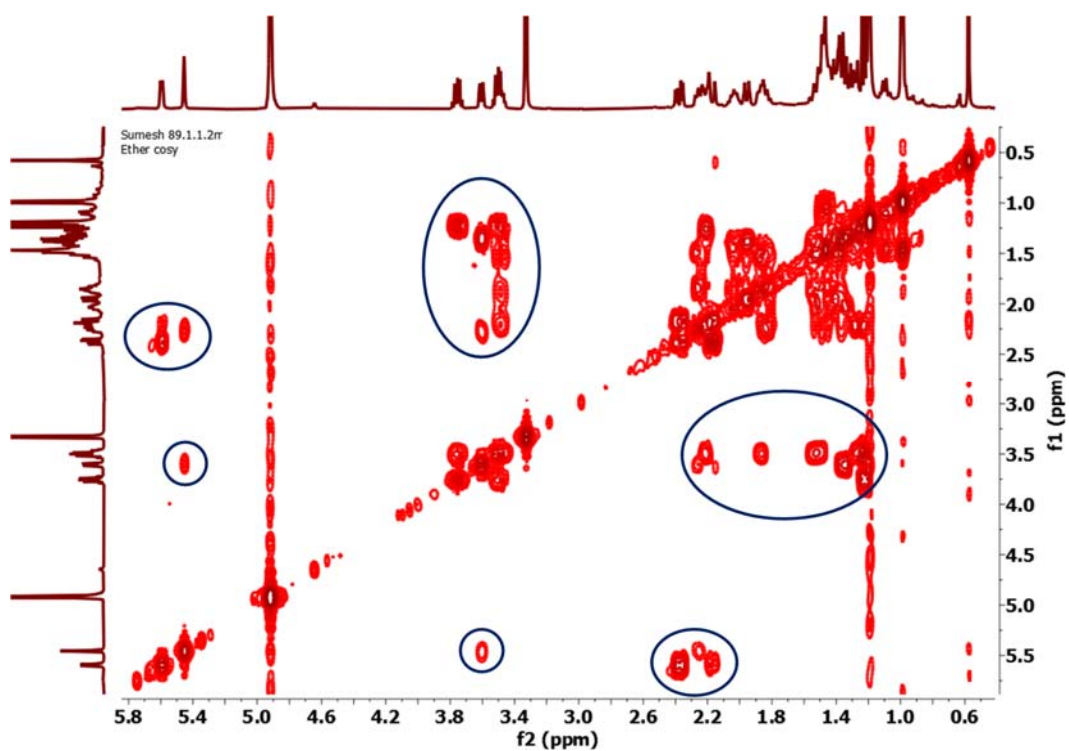
**Figure S7.** COSY $^1$H NMR spectrum of HOE$_1$ in CD$_3$OD.
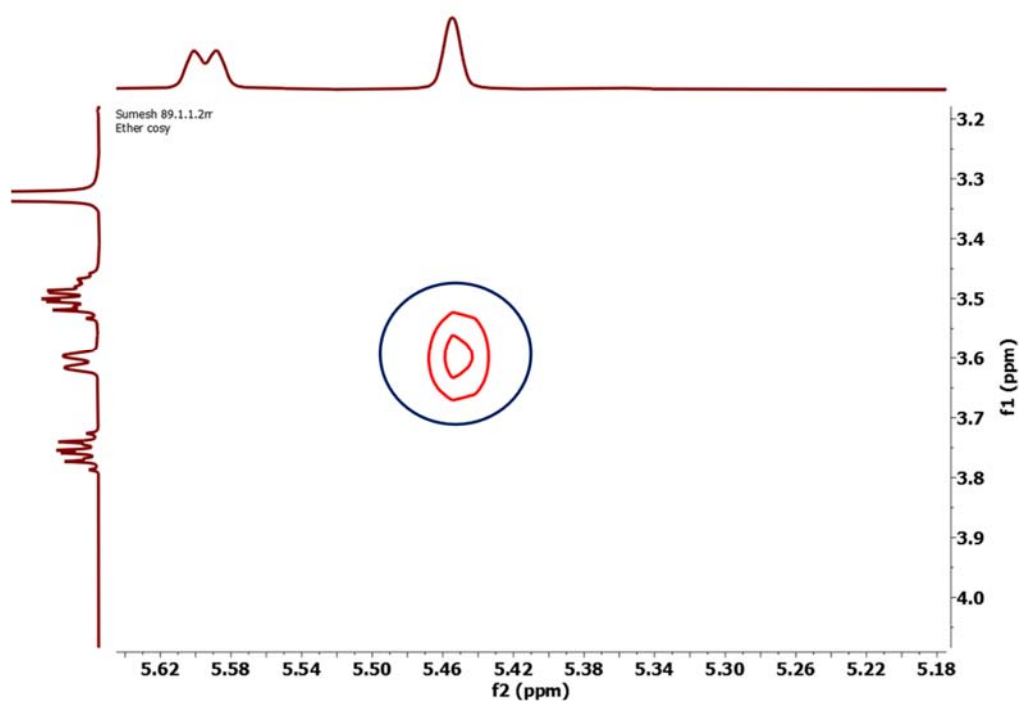


**Figure S8.** Expanded region of Figure S7 showing the correlation between vinyl H at C$_7$ and the H at C$_6$.
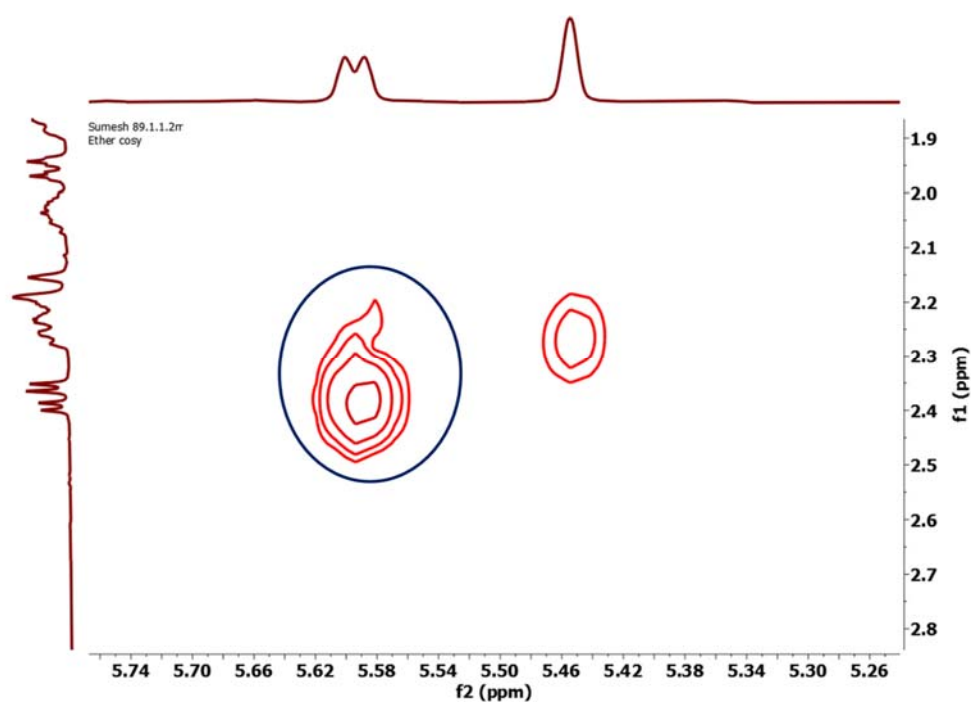
**Figure S9.** Expanded region of Figure S7 showing the correlation between the vinyl H at $C_{11}$ and the H-6 proton.
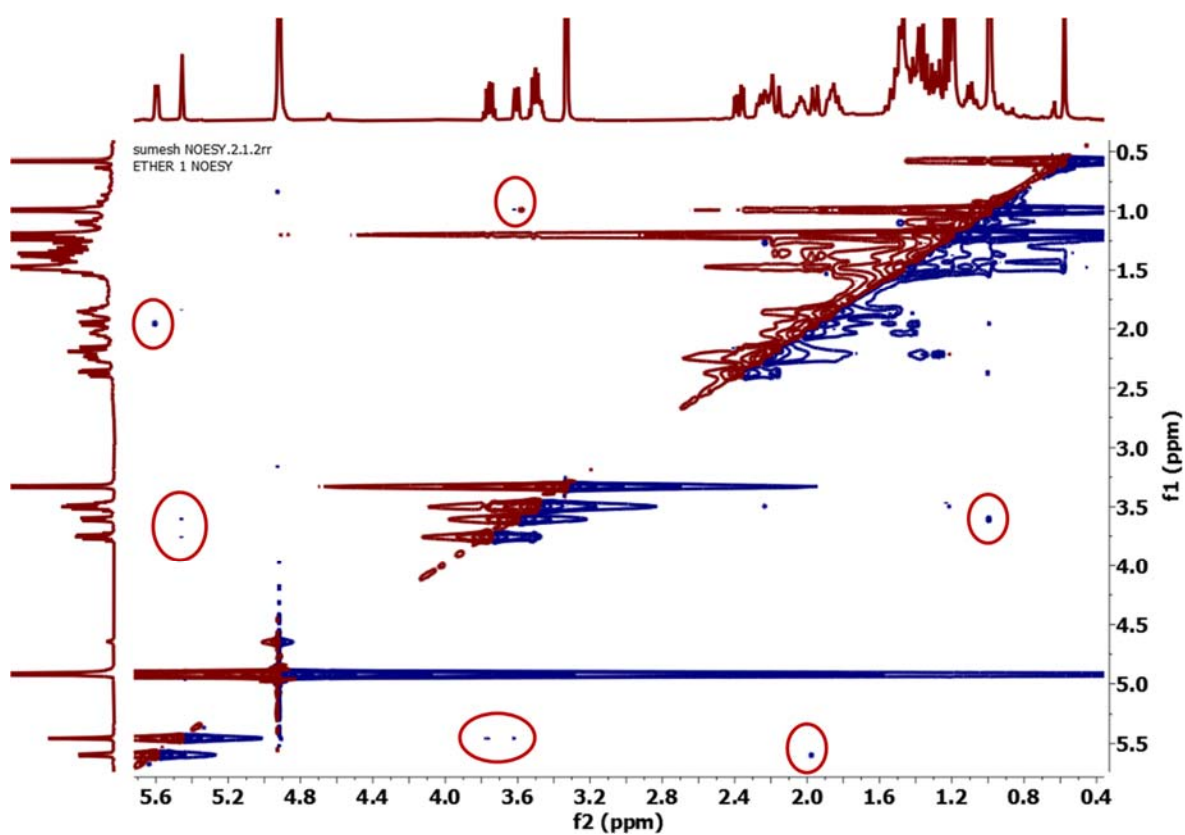
**Figure S10.** NOESY $^1$H NMR spectrum of HOE$_1$ in CD$_3$OD.
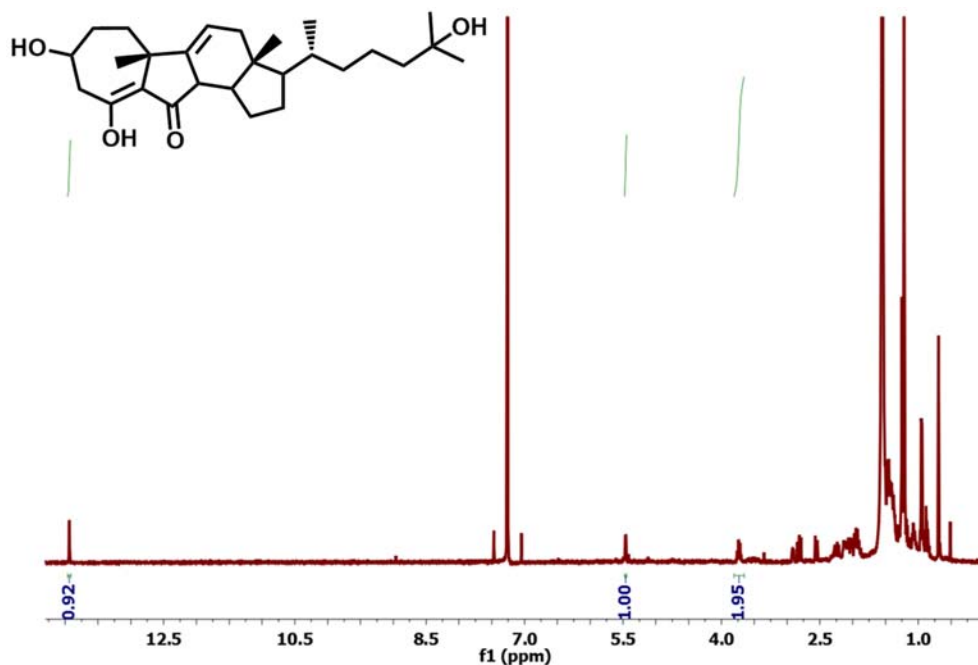


**Figure S11.** $^1$H NMR spectrum of HORP$_2$ in CD$_3$Cl.
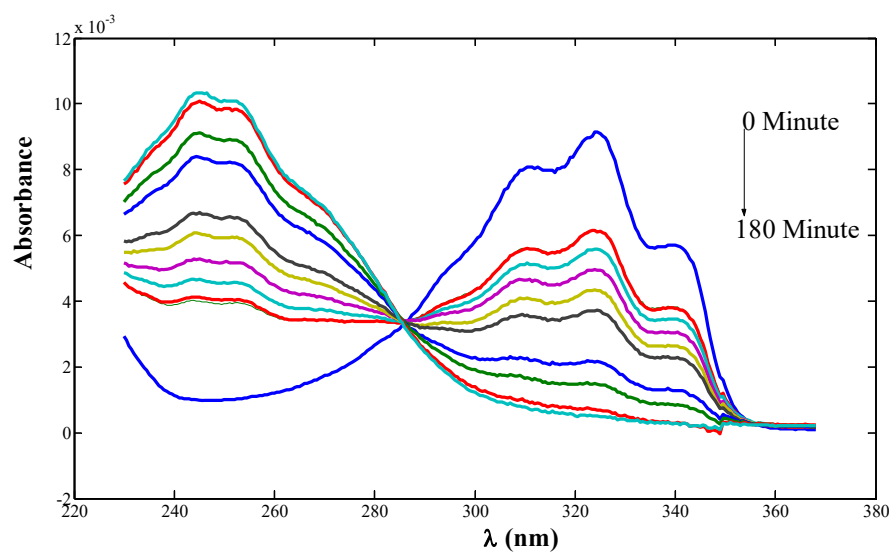


**Figure S12.** Time evolution of UV spectra from the 313 nm irradiation of CTL in ethanol. PCA of the spectral matrix in Figure S12 revealed a two component system. The combination coefficient plot, Figure S13, shows that the spectral points strictly adhere to the normalization line.
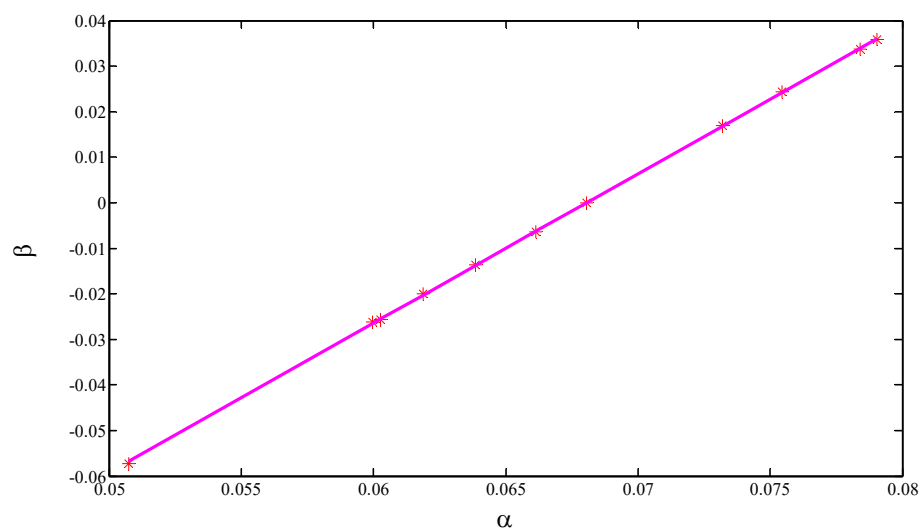
**Figure S13.** Combination coefficient plot for the spectra in Figure S12.

**Crystal Structures**

**Structural Information**



ConDiene123.mol

**HOD$_1$** Structure
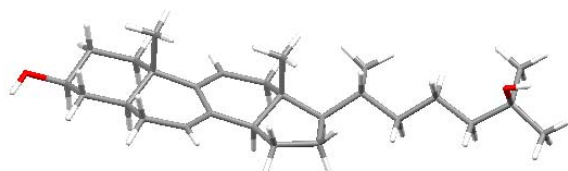


**Table S1** Crystal data and structure refinement

| Crystal name | HOD$_1$ |
|---|---|
| Empirical formula | $C_{27}H_{44}O_2$ |
| Formula weight | 400.62 |
| Temperature/K | 150.00(11) |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| $a$/Å | 7.1933(2) |
| $b$/Å | 9.6267(2) |
| $c$/Å | 34.9761(9) |

| | |
|---|---|
| $\alpha/°$ | 90 |
| $\beta/°$ | 90 |
| $\gamma/°$ | 90 |
| Volume/Å$^3$ | 2422.02(10) |
| $Z$ | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.099 |
| $\mu$/mm$^{-1}$ | 0.506 |
| $F$(000) | 888.0 |
| Crystal size/mm$^3$ | 0.332 × 0.242 × 0.068 |
| Radiation | Cu Kα ($\lambda$ = 1.54184) |
| $2\Theta$ range for data collection/° | 5.054 to 155.784 |
| Index ranges | -9 ≤ h ≤ 9, -9 ≤ k ≤ 12, -44 ≤ l ≤ 43 |
| Reflections collected | 18127 |
| Independent reflections | 4953 [$R_{int}$ = 0.1169, $R_{sigma}$ = 0.0732] |
| Data/restraints/parameters | 4953/0/270 |
| Goodness-of-fit on $F^2$ | 1.061 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0972, $wR_2$ = 0.2568 |
| Final R indexes [all data] | $R_1$ = 0.1073, $wR_2$ = 0.2643 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.34/-0.32 |
| Flack parameter | 0.2(4) |

**Table S2** Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for HOD$_1$. U$_{eq}$ is defined as 1/3 of the trace of the orthogonalised U$_{IJ}$ tensor.

| Atom | $x$ | $y$ | $Z$ | U(eq) |
|---|---|---|---|---|
| C1 | 2043(8) | 8205(6) | 824.3(17) | 36.9(12) |
| C2 | 3594(9) | 7205(6) | 951.5(17) | 37.2(12) |
| C3 | 3917(8) | 7284(6) | 1379.7(16) | 35.5(12) |
| C4 | 2156(7) | 7046(5) | 1619.9(15) | 29.3(11) |
| C5 | 617(8) | 8039(6) | 1477.9(16) | 35.7(12) |
| C6 | 290(9) | 7940(7) | 1044.5(17) | 39.5(13) |
| C7 | 1495(10) | 5527(6) | 1595.6(17) | 39.7(13) |
| C8 | 5518(8) | 6400(7) | 1506.4(18) | 41.8(14) |
| C9 | 5825(8) | 6454(6) | 1923.0(18) | 38.8(13) |
| C10 | 4497(7) | 6912(5) | 2172.5(15) | 28.6(11) |
| C11 | 2647(8) | 7305(5) | 2045.6(16) | 30.2(11) |

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| Atom | x | y | Z | U(eq) |
|------|------|------|------|------|
| C12 | 1371(9) | 7709(6) | 2303.6(16) | 37.7(13) |
| C13 | 1702(8) | 7790(6) | 2729.0(16) | 33.8(12) |
| C14 | 3265(7) | 6812(5) | 2852.2(14) | 25.0(10) |
| C15 | 4913(8) | 7127(6) | 2589.3(16) | 33.9(12) |
| C16 | 2615(9) | 5295(5) | 2815.2(17) | 34.0(12) |
| C17 | 6557(8) | 6407(7) | 2770.4(17) | 41.6(14) |
| C18 | 6196(9) | 6550(7) | 3202.9(19) | 43.8(15) |
| C19 | 4192(8) | 7062(5) | 3247.9(16) | 30.7(11) |
| C20 | 3205(8) | 6463(6) | 3607.8(15) | 33.1(12) |
| C21 | 1252(9) | 6999(8) | 3659.3(19) | 48.0(15) |
| C22 | 4364(10) | 6739(6) | 3969.9(16) | 40.0(14) |
| C23 | 3813(12) | 5826(6) | 4310.2(16) | 45.4(16) |
| C24 | 4949(16) | 6123(6) | 4658.5(17) | 63(3) |
| C25 | 4500(20) | 5246(7) | 5017.6(19) | 84(4) |
| C26 | 5660(40) | 5714(12) | 5342(2) | 198(13) |
| C27 | 2430(20) | 5263(13) | 5105(4) | 146(9) |
| O1 | 1677(7) | 8099(5) | 425.0(12) | 44.6(11) |
| O2 | 5018(8) | 3842(4) | 4924.3(12) | 44.4(11) |

**Table S3** Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for $HOD_1$. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a*^2U_{11}+2hka*b*U_{12}+\ldots]$.

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|------|------|------|------|------|------|------|
| C1 | 26(3) | 37(3) | 48(3) | -3(2) | -2(2) | -5(2) |
| C2 | 28(3) | 36(3) | 47(3) | -1(2) | 5(2) | -1(2) |
| C3 | 27(3) | 34(3) | 46(3) | -3(2) | 5(2) | 5(2) |
| C4 | 22(2) | 22(2) | 43(3) | -1(2) | -1(2) | 0(2) |
| C5 | 22(2) | 39(3) | 46(3) | -3(2) | -4(2) | 5(2) |
| C6 | 31(3) | 40(3) | 48(3) | -3(2) | -4(2) | 5(2) |
| C7 | 34(3) | 32(3) | 53(3) | -5(2) | -2(3) | -11(3) |
| C8 | 16(3) | 52(4) | 58(3) | 3(3) | 6(2) | 8(2) |
| C9 | 18(2) | 41(3) | 58(3) | 2(3) | 4(2) | 9(2) |
| C10 | 16(2) | 22(2) | 48(3) | 2.8(19) | 4(2) | 1.0(18) |
| C11 | 22(2) | 27(2) | 42(3) | -4(2) | 0(2) | 1(2) |

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| C12 | 31(3) | 36(3) | 46(3) | -1(2) | -4(2) | 13(2) |
| C13 | 22(3) | 29(3) | 51(3) | -6(2) | -2(2) | 8(2) |
| C14 | 19(2) | 16(2) | 40(3) | 1.0(17) | 4(2) | -6.6(18) |
| C15 | 16(2) | 33(3) | 52(3) | 8(2) | 3(2) | -1(2) |
| C16 | 34(3) | 21(2) | 47(3) | 0(2) | 3(2) | -8(2) |
| C17 | 16(2) | 56(4) | 53(3) | 10(3) | -3(2) | 2(3) |
| C18 | 26(3) | 48(4) | 57(4) | 15(3) | -6(3) | -5(3) |
| C19 | 23(2) | 20(2) | 49(3) | 3(2) | -2(2) | -3.9(19) |
| C20 | 30(3) | 26(2) | 42(3) | 0(2) | 2(2) | -4(2) |
| C21 | 32(3) | 60(4) | 52(3) | -3(3) | 4(3) | 9(3) |
| C22 | 44(3) | 32(3) | 44(3) | 5(2) | 0(3) | -5(3) |
| C23 | 62(5) | 30(3) | 44(3) | 8(2) | 4(3) | -1(3) |
| C24 | 123(8) | 27(3) | 41(3) | 8(2) | -2(4) | -12(4) |
| C25 | 183(13) | 30(3) | 38(3) | 7(3) | 14(5) | 18(5) |
| C26 | 480(40) | 73(7) | 38(4) | 14(4) | -58(11) | -72(14) |
| C27 | 240(20) | 91(8) | 111(8) | 63(7) | 114(12) | 106(11) |
| O1 | 49(3) | 42(2) | 43(2) | 1.2(18) | -3(2) | -2(2) |
| O2 | 57(3) | 29(2) | 47(2) | 7.8(16) | 4(2) | -0.1(19) |

**Table S4** Bond Lengths for $HOD_1$.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| C1 | C2 | 1.539(8) | C13 | C14 | 1.528(7) |
| C1 | C6 | 1.499(8) | C14 | C15 | 1.531(7) |
| C1 | O1 | 1.425(7) | C14 | C16 | 1.539(6) |
| C2 | C3 | 1.517(8) | C14 | C19 | 1.555(7) |
| C3 | C4 | 1.537(7) | C15 | C17 | 1.510(8) |
| C3 | C8 | 1.499(8) | C17 | C18 | 1.541(9) |
| C4 | C5 | 1.545(7) | C18 | C19 | 1.532(8) |
| C4 | C7 | 1.540(7) | C19 | C20 | 1.556(8) |
| C4 | C11 | 1.550(8) | C20 | C21 | 1.507(9) |
| C5 | C6 | 1.537(8) | C20 | C22 | 1.539(8) |
| C8 | C9 | 1.475(9) | C22 | C23 | 1.532(8) |

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|------|------|----------|------|------|----------|
| C9 | C10 | 1.366(8) | C23 | C24 | 1.494(10) |
| C10 | C11 | 1.454(7) | C24 | C25 | 1.547(9) |
| C10 | C15 | 1.503(8) | C25 | C26 | 1.481(18) |
| C11 | C12 | 1.345(8) | C25 | C27 | 1.52(2) |
| C12 | C13 | 1.509(8) | C25 | O2 | 1.439(9) |

**Table S5** Bond Angles for HOD$_1$.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|------|------|------|---------|------|------|------|---------|
| C6 | C1 | C2 | 110.8(5) | C13 | C14 | C16 | 109.7(5) |
| O1 | C1 | C2 | 111.9(5) | C13 | C14 | C19 | 118.1(4) |
| O1 | C1 | C6 | 109.6(5) | C15 | C14 | C16 | 111.9(4) |
| C3 | C2 | C1 | 111.4(5) | C15 | C14 | C19 | 99.9(4) |
| C2 | C3 | C4 | 113.9(5) | C16 | C14 | C19 | 110.6(4) |
| C8 | C3 | C2 | 112.4(5) | C10 | C15 | C14 | 113.7(4) |
| C8 | C3 | C4 | 112.8(5) | C10 | C15 | C17 | 120.0(5) |
| C3 | C4 | C5 | 108.8(4) | C17 | C15 | C14 | 105.3(4) |
| C3 | C4 | C7 | 111.5(5) | C15 | C17 | C18 | 103.8(5) |
| C3 | C4 | C11 | 108.3(5) | C19 | C18 | C17 | 106.7(5) |
| C5 | C4 | C11 | 111.8(4) | C14 | C19 | C20 | 117.8(4) |
| C7 | C4 | C5 | 110.4(5) | C18 | C19 | C14 | 105.2(5) |
| C7 | C4 | C11 | 106.0(4) | C18 | C19 | C20 | 113.1(5) |
| C6 | C5 | C4 | 112.9(5) | C21 | C20 | C19 | 113.3(5) |
| C1 | C6 | C5 | 111.6(5) | C21 | C20 | C22 | 110.3(5) |
| C9 | C8 | C3 | 112.8(5) | C22 | C20 | C19 | 110.8(5) |
| C10 | C9 | C8 | 122.5(5) | C23 | C22 | C20 | 113.6(5) |
| C9 | C10 | C11 | 121.9(5) | C24 | C23 | C22 | 112.5(6) |
| C9 | C10 | C15 | 121.7(5) | C23 | C24 | C25 | 116.3(8) |
| C11 | C10 | C15 | 116.3(4) | C26 | C25 | C24 | 109.7(10) |
| C10 | C11 | C4 | 117.4(5) | C26 | C25 | C27 | 113.4(12) |
| C12 | C11 | C4 | 122.4(5) | C27 | C25 | C24 | 111.2(9) |
| C12 | C11 | C10 | 119.7(5) | O2 | C25 | C24 | 105.9(6) |
| C11 | C12 | C13 | 124.7(5) | O2 | C25 | C26 | 108.2(10) |

| Atom | Atom | Atom | Angle/° | | Atom | Atom | Atom | Angle/° |
|------|------|------|---------|-|------|------|------|---------|
| C12 | C13 | C14 | 111.2(4) | | O2 | C25 | C27 | 108.1(9) |
| C13 | C14 | C15 | 106.2(4) | | | | | |

**Table S6** Torsion Angles for HOD$_1$.

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---------|---|---|---|---|---------|
| C1 | C2 | C3 | C4 | 54.5(6) | C12 | C13 | C14 | C15 | 51.2(6) |
| C1 | C2 | C3 | C8 | -175.7(5) | C12 | C13 | C14 | C16 | -69.8(6) |
| C2 | C1 | C6 | C5 | 55.9(7) | C12 | C13 | C14 | C19 | 162.2(5) |
| C2 | C3 | C4 | C5 | -52.5(6) | C13 | C14 | C15 | C10 | -59.5(5) |
| C2 | C3 | C4 | C7 | 69.5(6) | C13 | C14 | C15 | C17 | 167.2(5) |
| C2 | C3 | C4 | C11 | -174.2(4) | C13 | C14 | C19 | C18 | -150.1(5) |
| C2 | C3 | C8 | C9 | -179.2(5) | C13 | C14 | C19 | C20 | 82.7(6) |
| C3 | C4 | C5 | C6 | 52.7(6) | C14 | C15 | C17 | C18 | -35.1(6) |
| C3 | C4 | C11 | C10 | -34.7(6) | C14 | C19 | C20 | C21 | -58.5(6) |
| C3 | C4 | C11 | C12 | 153.6(5) | C14 | C19 | C20 | C22 | 177.0(5) |
| C3 | C8 | C9 | C10 | 18.0(9) | C15 | C10 | C11 | C4 | -177.9(5) |
| C4 | C3 | C8 | C9 | -48.7(7) | C15 | C10 | C11 | C12 | -6.0(7) |
| C4 | C5 | C6 | C1 | -56.3(7) | C15 | C14 | C19 | C18 | -35.7(5) |
| C4 | C11 | C12 | C13 | 171.3(5) | C15 | C14 | C19 | C20 | -162.9(4) |
| C5 | C4 | C11 | C10 | -154.6(5) | C15 | C17 | C18 | C19 | 11.6(6) |
| C5 | C4 | C11 | C12 | 33.7(7) | C16 | C14 | C15 | C10 | 60.2(6) |
| C6 | C1 | C2 | C3 | -55.0(6) | C16 | C14 | C15 | C17 | -73.1(6) |
| C7 | C4 | C5 | C6 | -70.0(6) | C16 | C14 | C19 | C18 | 82.3(5) |
| C7 | C4 | C11 | C10 | 85.0(6) | C16 | C14 | C19 | C20 | -44.9(6) |
| C7 | C4 | C11 | C12 | -86.7(6) | C17 | C18 | C19 | C14 | 15.5(6) |
| C8 | C3 | C4 | C5 | 177.9(5) | C17 | C18 | C19 | C20 | 145.4(5) |
| C8 | C3 | C4 | C7 | -60.2(7) | C18 | C19 | C20 | C21 | 178.3(5) |
| C8 | C3 | C4 | C11 | 56.1(6) | C18 | C19 | C20 | C22 | 53.7(6) |
| C8 | C9 | C10 | C11 | 3.5(9) | C19 | C14 | C15 | C10 | 177.3(4) |
| C8 | C9 | C10 | C15 | -172.3(5) | C19 | C14 | C15 | C17 | 44.0(5) |
| C9 | C10 | C11 | C4 | 6.1(7) | C19 | C20 | C22 | C23 | -162.5(5) |
| C9 | C10 | C11 | C12 | 178.0(6) | C20 | C22 | C23 | C24 | -179.5(6) |

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| C9 | C10 | C15 | C14 | -146.5(5) | C21 | C20 | C22 | C23 | 71.2(7) |
| C9 | C10 | C15 | C17 | -20.7(8) | C22 | C23 | C24 | C25 | -179.8(7) |
| C10 | C11 | C12 | C13 | -0.1(9) | C23 | C24 | C25 | C26 | -176.9(12) |
| C10 | C15 | C17 | C18 | -164.8(5) | C23 | C24 | C25 | C27 | -50.7(11) |
| C11 | C4 | C5 | C6 | 172.2(5) | C23 | C24 | C25 | O2 | 66.5(12) |
| C11 | C10 | C15 | C14 | 37.4(6) | O1 | C1 | C2 | C3 | -177.6(5) |
| C11 | C10 | C15 | C17 | 163.3(5) | O1 | C1 | C6 | C5 | 179.8(5) |
| C11 | C12 | C13 | C14 | -24.5(8) | | | | | |

**Table S7** Hydrogen Atom Coordinates ($\text{Å}\times10^4$) and Isotropic Displacement Parameters ($\text{Å}^2\times10^3$) for $HOD_1$.

| Atom | $x$ | $Y$ | $z$ | U(eq) |
|---|---|---|---|---|
| H1 | 2459.65 | 9175.25 | 879.42 | 44 |
| H2A | 3249.05 | 6243.32 | 880.94 | 45 |
| H2B | 4759.58 | 7442.65 | 816 | 45 |
| H3 | 4302.19 | 8263.98 | 1431.79 | 43 |
| H5A | -556.7 | 7818.53 | 1612.66 | 43 |
| H5B | 964.3 | 9004.74 | 1543.68 | 43 |
| H6A | -186.29 | 7003.25 | 980.92 | 47 |
| H6B | -663.43 | 8627.5 | 968.11 | 47 |
| H7A | 2365.26 | 4928.98 | 1734.74 | 60 |
| H7B | 1444.57 | 5238.98 | 1327.04 | 60 |
| H7C | 254.99 | 5447.27 | 1709.41 | 60 |
| H8A | 5280.98 | 5425.62 | 1429.9 | 50 |
| H8B | 6659.78 | 6713.86 | 1374.24 | 50 |
| H9 | 6990.16 | 6159.17 | 2021.68 | 47 |
| H12 | 175.35 | 7962 | 2211.5 | 45 |
| H13A | 545.08 | 7539.73 | 2865.94 | 41 |
| H13B | 2031.33 | 8755.18 | 2799.52 | 41 |
| H15 | 5157.62 | 8143.79 | 2618.47 | 41 |
| H16A | 3585.27 | 4674.25 | 2912.76 | 51 |
| H16B | 2374.18 | 5081.83 | 2545.7 | 51 |
| H16C | 1472.99 | 5162.58 | 2963.45 | 51 |

| Atom | x | Y | z | U(eq) |
|------|------|------|------|-------|
| H17A | 7736.27 | 6866.14 | 2697.38 | 50 |
| H17B | 6611.02 | 5418.27 | 2693.68 | 50 |
| H18A | 6356.73 | 5641.58 | 3331.65 | 53 |
| H18B | 7074.03 | 7222.67 | 3317.61 | 53 |
| H19 | 4258.99 | 8091.55 | 3284.09 | 37 |
| H20 | 3124.39 | 5433.35 | 3574.24 | 40 |
| H21A | 1265.54 | 8016.68 | 3660.09 | 72 |
| H21B | 750.91 | 6660.66 | 3902.69 | 72 |
| H21C | 470.76 | 6667.08 | 3448.78 | 72 |
| H22A | 5691.99 | 6578.71 | 3910.52 | 48 |
| H22B | 4221.16 | 7726.59 | 4043.3 | 48 |
| H23A | 2483.85 | 5980.35 | 4369.83 | 54 |
| H23B | 3968.4 | 4837.26 | 4238.96 | 54 |
| H24A | 4790.1 | 7115.36 | 4724.81 | 76 |
| H24B | 6274.37 | 5980.27 | 4593.47 | 76 |
| H26A | 5554.56 | 5049.74 | 5553.19 | 297 |
| H26B | 5243.65 | 6631.2 | 5427.5 | 297 |
| H26C | 6964.55 | 5770.78 | 5260.15 | 297 |
| H27A | 1735.11 | 4928.73 | 4881.67 | 220 |
| H27B | 2037.1 | 6214.12 | 5165.09 | 220 |
| H27C | 2171.61 | 4658.61 | 5324.12 | 220 |
| H1A | 2649.73 | 8279.78 | 301.86 | 67 |
| H2 | 5227.29 | 3398.03 | 5126.54 | 67 |

**HOD$_2$** Structure



UnconjDiene.mol
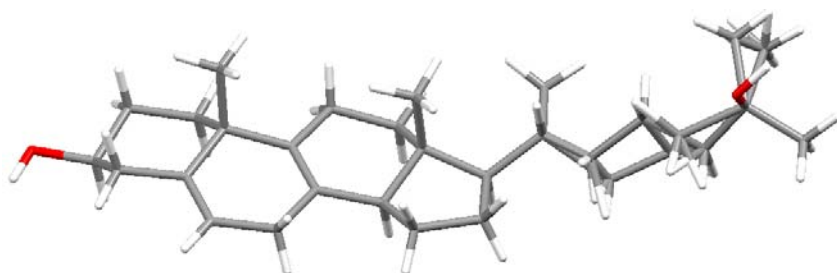
**Table S8** Crystal data and structure refinement

| Crystal name | HOD$_2$ |
|---|---|
| Molecular Formula | C$_{27}$H$_{44}$O$_2$ |
| Formula Weight | 400.62 |
| Temperature/$K$ | 149.98(10) |
| Crystal System | Orthorhombic |
| Space Group | $P$212121 |
| $a$ [Å] | 7.33440(10) |
| $b$ [Å] | 9.6312(2) |
| $c$ [Å] | 34.4304(9) |
| [°] | 90 |
| [°] | 90 |
| [°] | 90 |
| V[Å$^3$] | 2432.13(9) |
| $Z$ | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.094 |
| $\mu$/mm$^{-1}$ | 0.504 |
| $F$(000) | 888.0 |
| Crystal size/mm$^3$ | 0.13 × 0.1 × 0.04 |
| Radiation | Cu K$\alpha$ ($\lambda$ = 1.54184) |
| 2$\Theta$ range for data collection/° | 5.134 to 155.072 |
| Index ranges | -9 ≤ $h$ ≤ 9, -8 ≤ $k$ ≤ 12, -43 ≤ $l$ ≤ 43 |
| Reflections collected | 24631 |
| Independent reflections | 5079 [$R_{int}$ = 0.0329, $R_{sigma}$ = 0.0205] |
| Data/restraints/parameters | 5079/0/321 |
| Goodness-of-fit on $F^2$ | 1.198 |
| Final R indexes [$I$>=2$\sigma$ ($I$)] | $R_1$ = 0.0796, $wR_2$ = 0.1851 |
| Final R indexes [all data] | $R_1$ = 0.0847, $wR_2$ = 0.1877 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.23/-0.22 |
| Flack parameter | 0.11(2) |

**Table S9** Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for $HOD_2$. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.

| Atom | X | y | z | U(eq) |
|------|------|------|------|-------|
| C1 | 2710(7) | 8334(6) | 847.7(17) | 53.9(14) |
| C2 | 905(7) | 8232(6) | 1061.1(17) | 52.3(14) |
| C3 | 1175(6) | 8328(5) | 1497.3(17) | 47.4(13) |
| C4 | 2500(6) | 7222(5) | 1668.9(17) | 44.0(12) |
| C005 | 4866(6) | 7564(5) | 2680.0(17) | 43.9(12) |
| C5 | 4230(6) | 7202(5) | 1425.8(17) | 47.6(13) |
| C6 | 3990(7) | 7191(6) | 992.9(17) | 55.8(15) |
| C7 | 1602(7) | 5763(5) | 1641.1(19) | 54.2(15) |
| C8 | 5879(6) | 7132(5) | 1583.4(16) | 45.1(12) |
| C9 | 6211(6) | 7070(5) | 2005.1(17) | 47.4(14) |
| C10 | 4558(6) | 7379(5) | 2252.9(17) | 40.2(12) |
| C11 | 2891(6) | 7510(5) | 2098.2(16) | 39.2(11) |
| C12 | 1254(6) | 7843(5) | 2349.7(16) | 44.8(12) |
| C13 | 1655(6) | 8137(5) | 2778.8(16) | 41.4(12) |
| C14 | 3196(6) | 7217(5) | 2933.2(17) | 43.0(12) |
| C15 | 2681(7) | 5675(5) | 2890(2) | 62.3(18) |
| C16 | 6425(6) | 6802(6) | 2883.2(18) | 55.1(15) |
| C17 | 5956(7) | 6953(6) | 3317.4(17) | 55.5(15) |
| C18 | 3947(6) | 7517(5) | 3340.2(17) | 49.0(13) |
| C19 | 2951(7) | 6935(7) | 3697(2) | 73(2) |
| C20 | 922(7) | 7362(7) | 3708(2) | 70.0(19) |
| C21 | 3936(13) | 7691(12) | 4122(3) | 51(2) |
| C22 | 3412(15) | 7114(10) | 4513(2) | 41(2) |
| C23 | 4110(20) | 6194(14) | 4725(4) | 54(3) |
| C24 | 3526(8) | 5055(8) | 4989(2) | 75(2) |
| C25 | 4291(14) | 5622(9) | 5359(2) | 103(3) |
| C26 | 1457(19) | 5129(16) | 5111(4) | 58(3) |
| C27 | 3777(17) | 6928(12) | 4001(3) | 29(2) |
| C28 | 3184(15) | 5986(11) | 4341(3) | 42(2) |
| C29 | 4110(16) | 5636(13) | 4565(3) | 39(2) |
| C30 | 1423(17) | 4674(15) | 4919(4) | 52(3) |

| Atom | X | y | z | U(eq) |
|---|---|---|---|---|
| O1 | 2401(5) | 8234(5) | 440.2(12) | 62.0(11) |
| O2 | 4291(5) | 3702(5) | 4930.2(12) | 60.0(11) |

**Table S10** Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for $HOD_2$. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a*^2U_{11}+2hka*b*U_{12}+...]$.

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| C1 | 31(2) | 59(3) | 72(4) | -19(3) | 1(2) | -4(2) |
| C2 | 29(2) | 52(3) | 77(4) | -7(3) | -2(3) | 3(2) |
| C3 | 24(2) | 39(3) | 78(4) | -8(2) | 3(2) | 2(2) |
| C4 | 21.4(19) | 33(2) | 77(4) | -7(2) | 1(2) | 0.6(18) |
| C005 | 17.7(18) | 33(2) | 81(4) | 13(2) | -1(2) | -0.5(18) |
| C5 | 26(2) | 37(3) | 80(4) | -19(3) | 3(2) | 1(2) |
| C6 | 29(2) | 58(3) | 80(4) | -24(3) | 0(3) | 2(2) |
| C7 | 41(3) | 39(3) | 83(4) | -14(3) | -3(3) | -9(2) |
| C8 | 24(2) | 42(3) | 69(4) | -10(2) | 4(2) | 1(2) |
| C9 | 19(2) | 29(2) | 94(4) | 1(2) | 5(2) | 3.1(18) |
| C10 | 20(2) | 27(2) | 73(3) | 2(2) | 4(2) | 0.8(17) |
| C11 | 22.5(19) | 29(2) | 66(3) | -6(2) | 2(2) | -1.4(17) |
| C12 | 21(2) | 43(3) | 71(4) | -11(2) | 1(2) | 4(2) |
| C13 | 22(2) | 32(2) | 70(3) | -1(2) | 3(2) | 3.3(17) |
| C14 | 22(2) | 27(2) | 80(4) | 10(2) | 7(2) | 0.9(17) |
| C15 | 33(3) | 31(2) | 124(6) | 8(3) | 17(3) | -1(2) |
| C16 | 22(2) | 57(3) | 87(4) | 24(3) | 0(2) | 5(2) |
| C17 | 28(2) | 61(3) | 78(4) | 38(3) | 5(3) | 6(2) |
| C18 | 27(2) | 43(3) | 78(4) | 25(3) | 5(2) | 6(2) |
| C19 | 34(3) | 81(5) | 105(6) | 52(4) | 24(3) | 20(3) |
| C20 | 38(3) | 86(5) | 86(4) | 34(4) | 17(3) | 20(3) |
| C21 | 44(5) | 69(7) | 38(5) | -6(5) | -5(4) | 5(5) |
| C22 | 64(6) | 42(5) | 16(4) | -5(4) | 3(4) | 8(5) |
| C23 | 62(8) | 56(8) | 43(7) | -3(6) | -14(7) | -13(7) |
| C24 | 44(3) | 78(5) | 102(6) | 44(4) | 5(4) | 9(3) |
| C25 | 136(8) | 78(5) | 96(6) | 7(5) | 17(6) | -16(6) |
| C26 | 53(7) | 63(9) | 58(9) | 10(7) | 18(7) | 19(7) |

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|------|----------|----------|----------|----------|----------|----------|
| C27 | 44(6) | 23(5) | 22(5) | 0(4) | -10(5) | -3(5) |
| C28 | 50(6) | 51(6) | 23(4) | -2(4) | -5(5) | -6(5) |
| C29 | 37(5) | 54(7) | 26(6) | 3(5) | -8(5) | 4(5) |
| C30 | 36(6) | 64(9) | 56(9) | -2(6) | 11(6) | 14(6) |
| O1 | 36.3(19) | 79(3) | 71(3) | -24(2) | 1.5(19) | -1(2) |
| O2 | 43(2) | 77(3) | 60(3) | 23(2) | 8.2(19) | 0(2) |

**Table S11** Bond Lengths for $HOD_2$.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|------|------|----------|------|------|----------|
| C1 | C2 | 1.517(7) | C14 | C15 | 1.540(7) |
| C1 | C6 | 1.531(8) | C14 | C18 | 1.533(8) |
| C1 | O1 | 1.425(7) | C16 | C17 | 1.541(8) |
| C2 | C3 | 1.518(8) | C17 | C18 | 1.572(6) |
| C3 | C4 | 1.558(7) | C18 | C19 | 1.537(8) |
| C4 | C5 | 1.520(7) | C19 | C20 | 1.544(7) |
| C4 | C7 | 1.555(7) | C19 | C21 | 1.785(12) |
| C4 | C11 | 1.531(8) | C19 | C27 | 1.207(12) |
| C005 | C10 | 1.498(8) | C21 | C22 | 1.507(12) |
| C005 | C14 | 1.540(6) | C22 | C23 | 1.256(16) |
| C005 | C16 | 1.528(6) | C23 | C24 | 1.487(14) |
| C5 | C6 | 1.501(8) | C24 | C25 | 1.495(11) |
| C5 | C8 | 1.327(7) | C24 | C26 | 1.577(14) |
| C8 | C9 | 1.473(8) | C24 | C29 | 1.621(12) |
| C9 | C10 | 1.512(6) | C24 | C30 | 1.604(14) |
| C10 | C11 | 1.340(6) | C24 | O2 | 1.433(8) |
| C11 | C12 | 1.515(6) | C27 | C28 | 1.543(14) |
| C12 | C13 | 1.533(7) | C28 | C29 | 1.083(14) |
| C13 | C14 | 1.531(6) | | | |

**Table S12** Bond Angles for HOD$_2$.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|------|------|------|---------|------|------|------|---------|
| C2 | C1 | C6 | 109.3(5) | C13 | C14 | C005 | 105.4(4) |
| O1 | C1 | C2 | 109.5(4) | C13 | C14 | C15 | 110.1(4) |
| O1 | C1 | C6 | 111.7(5) | C13 | C14 | C18 | 118.3(4) |
| C1 | C2 | C3 | 111.2(4) | C15 | C14 | C005 | 110.5(4) |
| C2 | C3 | C4 | 114.5(4) | C18 | C14 | C005 | 101.0(4) |
| C5 | C4 | C3 | 108.7(4) | C18 | C14 | C15 | 111.0(5) |
| C5 | C4 | C7 | 107.9(4) | C005 | C16 | C17 | 103.4(4) |
| C5 | C4 | C11 | 112.2(4) | C16 | C17 | C18 | 106.9(4) |
| C7 | C4 | C3 | 109.3(4) | C14 | C18 | C17 | 103.1(4) |
| C11 | C4 | C3 | 111.0(4) | C14 | C18 | C19 | 119.5(5) |
| C11 | C4 | C7 | 107.6(5) | C19 | C18 | C17 | 111.1(4) |
| C10 | C005 | C14 | 114.2(4) | C18 | C19 | C20 | 112.3(5) |
| C10 | C005 | C16 | 120.3(4) | C27 | C19 | C18 | 117.1(8) |
| C16 | C005 | C14 | 103.4(4) | C27 | C19 | C20 | 117.7(9) |
| C6 | C5 | C4 | 116.7(4) | C22 | C21 | C19 | 118.6(8) |
| C8 | C5 | C4 | 122.4(5) | C23 | C22 | C21 | 132.5(11) |
| C8 | C5 | C6 | 120.8(5) | C22 | C23 | C24 | 139.4(13) |
| C5 | C6 | C1 | 113.0(4) | C23 | C24 | C26 | 113.9(9) |
| C5 | C8 | C9 | 123.7(5) | C25 | C24 | C29 | 122.8(7) |
| C8 | C9 | C10 | 114.6(4) | C25 | C24 | C30 | 124.9(8) |
| C005 | C10 | C9 | 117.2(4) | C30 | C24 | C29 | 101.4(8) |
| C11 | C10 | C005 | 121.1(4) | O2 | C24 | C25 | 107.8(6) |
| C11 | C10 | C9 | 121.7(5) | O2 | C24 | C29 | 94.8(7) |
| C10 | C11 | C4 | 122.5(4) | O2 | C24 | C30 | 98.5(7) |
| C10 | C11 | C12 | 121.1(5) | C19 | C27 | C28 | 121.2(10) |
| C12 | C11 | C4 | 116.2(4) | C29 | C28 | C27 | 123.2(11) |
| C11 | C12 | C13 | 116.0(4) | C28 | C29 | C24 | 125.8(11) |
| C14 | C13 | C12 | 111.7(4) | | | | |

**Table S13** Torsion Angles for HOD₂.

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| C1 | C2 | C3 | C4 | -56.6(6) | C11 | C4 | C5 | C6 | -169.1(4) |
| C2 | C1 | C6 | C5 | -54.2(6) | C11 | C4 | C5 | C8 | 14.0(7) |
| C2 | C3 | C4 | C5 | 48.6(5) | C11 | C12 | C13 | C14 | -36.6(6) |
| C2 | C3 | C4 | C7 | -69.0(6) | C12 | C13 | C14 | C005 | 59.8(5) |
| C2 | C3 | C4 | C11 | 172.5(4) | C12 | C13 | C14 | C15 | -59.4(6) |
| C3 | C4 | C5 | C6 | -45.9(6) | C12 | C13 | C14 | C18 | 171.6(4) |
| C3 | C4 | C5 | C8 | 137.2(5) | C13 | C14 | C18 | C17 | -153.4(4) |
| C3 | C4 | C11 | C10 | -138.7(5) | C13 | C14 | C18 | C19 | 82.9(6) |
| C3 | C4 | C11 | C12 | 46.0(5) | C14 | C005 | C10 | C9 | -153.7(4) |
| C4 | C5 | C6 | C1 | 51.0(6) | C14 | C005 | C10 | C11 | 27.6(6) |
| C4 | C5 | C8 | C9 | -0.2(8) | C14 | C005 | C16 | C17 | -36.6(6) |
| C4 | C11 | C12 | C13 | -179.7(4) | C14 | C18 | C19 | C20 | -55.0(8) |
| C005 | C10 | C11 | C4 | -175.3(4) | C14 | C18 | C19 | C27 | 164.2(8) |
| C005 | C10 | C11 | C12 | -0.3(7) | C15 | C14 | C18 | C17 | 78.0(5) |
| C005 | C14 | C18 | C17 | -39.2(4) | C15 | C14 | C18 | C19 | -45.7(6) |
| C005 | C14 | C18 | C19 | -162.8(4) | C16 | C005 | C10 | C9 | -29.8(6) |
| C005 | C16 | C17 | C18 | 11.7(6) | C16 | C005 | C10 | C11 | 151.5(5) |
| C5 | C4 | C11 | C10 | -16.9(6) | C16 | C005 | C14 | C13 | 171.5(4) |
| C5 | C4 | C11 | C12 | 167.9(4) | C16 | C005 | C14 | C15 | -69.7(6) |
| C5 | C8 | C9 | C10 | -11.6(7) | C16 | C005 | C14 | C18 | 47.8(5) |
| C6 | C1 | C2 | C3 | 57.0(6) | C16 | C17 | C18 | C14 | 17.3(5) |
| C6 | C5 | C8 | C9 | -177.0(5) | C16 | C17 | C18 | C19 | 146.4(6) |
| C7 | C4 | C5 | C6 | 72.5(6) | C17 | C18 | C19 | C20 | -174.7(6) |
| C7 | C4 | C5 | C8 | -104.4(6) | C17 | C18 | C19 | C27 | 44.5(10) |
| C7 | C4 | C11 | C10 | 101.7(5) | C18 | C19 | C27 | C28 | -160.9(8) |
| C7 | C4 | C11 | C12 | -73.5(5) | C19 | C21 | C22 | C23 | 92.5(15) |
| C8 | C5 | C6 | C1 | -132.0(5) | C19 | C27 | C28 | C29 | 155.3(13) |
| C8 | C9 | C10 | C005 | -170.2(4) | C20 | C19 | C27 | C28 | 60.4(13) |
| C8 | C9 | C10 | C11 | 8.5(7) | C21 | C22 | C23 | C24 | -142.1(16) |
| C9 | C10 | C11 | C4 | 6.0(7) | C22 | C23 | C24 | C26 | -15(2) |
| C9 | C10 | C11 | C12 | -179.0(4) | C25 | C24 | C29 | C28 | -127.2(13) |

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| C10 | C005 | C14 | C13 | -56.0(5) | C27 | C28 | C29 | C24 | 160.6(10) |
| C10 | C005 | C14 | C15 | 62.9(6) | C30 | C24 | C29 | C28 | 18.3(16) |
| C10 | C005 | C14 | C18 | -179.6(4) | O1 | C1 | C2 | C3 | 179.7(4) |
| C10 | C005 | C16 | C17 | -165.4(4) | O1 | C1 | C6 | C5 | -175.6(4) |
| C10 | C11 | C12 | C13 | 5.0(7) | O2 | C24 | C29 | C28 | 118.0(14) |

**Table S14** Hydrogen Atom Coordinates ($Å×10^4$) and Isotropic Displacement Parameters ($Å^2×10^3$) for $HOD_2$.

| Atom | $x$ | $Y$ | $z$ | U(eq) |
|---|---|---|---|---|
| H1 | 3260.87 | 9238.57 | 904.25 | 65 |
| H2A | 322.7 | 7356.66 | 997.97 | 63 |
| H2B | 108.21 | 8976.25 | 976.12 | 63 |
| H3A | -2.08 | 8230.02 | 1622.92 | 57 |
| H3B | 1638.33 | 9244.7 | 1559.5 | 57 |
| H005 | 5100.98 | 8556.45 | 2718.36 | 53 |
| H6A | 3508.95 | 6295.74 | 914.46 | 67 |
| H6B | 5172.19 | 7305.3 | 870.67 | 67 |
| H7A | 2421.5 | 5077.67 | 1743.83 | 81 |
| H7B | 1340.78 | 5553.41 | 1374.23 | 81 |
| H7C | 489.83 | 5756.32 | 1788.04 | 81 |
| H8 | 6882.17 | 7120.63 | 1418.16 | 54 |
| H9A | 7164.06 | 7728.55 | 2069.89 | 57 |
| H9B | 6655.48 | 6150.17 | 2069.97 | 57 |
| H12A | 410.26 | 7068.79 | 2335.26 | 54 |
| H12B | 643.41 | 8646.66 | 2240.79 | 54 |
| H13A | 1991.37 | 9104.47 | 2809.2 | 50 |
| H13B | 560.78 | 7973.5 | 2930.44 | 50 |
| H15A | 2537.17 | 5455.37 | 2619.88 | 93 |
| H15B | 1556.86 | 5500.84 | 3024.29 | 93 |
| H15C | 3627.98 | 5108.66 | 2999.24 | 93 |
| H16A | 7590.25 | 7229.13 | 2824.24 | 66 |
| H16B | 6462.69 | 5832.86 | 2806.96 | 66 |
| H17A | 6789.93 | 7596.11 | 3441.77 | 67 |

| Atom | x | Y | z | U(eq) |
|---|---|---|---|---|
| H17B | 6047.52 | 6061.46 | 3447.13 | 67 |
| H18 | 4014.4 | 8527.98 | 3370.31 | 59 |
| H19 | 2925 | 5792.4 | 3660(20) | 100(30) |
| H20A | 828.79 | 8355.29 | 3698.72 | 105 |
| H20B | 374.01 | 7025.73 | 3942.86 | 105 |
| H20C | 302.59 | 6969 | 3488.08 | 105 |
| H21A | 5250.4 | 7619.18 | 4097.64 | 61 |
| H21B | 3637.02 | 8671.75 | 4120.89 | 61 |
| H22A | 2372.05 | 7519.19 | 4618.29 | 49 |
| H22 | 3880(90) | 7480(70) | 4787(18) | 80(20) |
| H23 | 5372.69 | 6237.74 | 4712.83 | 64 |
| H25A | 3969.61 | 5019.99 | 5570.46 | 155 |
| H25B | 3800.62 | 6531.06 | 5405.08 | 155 |
| H25C | 5594.65 | 5678.34 | 5339.01 | 155 |
| H26A | 709.01 | 4811.65 | 4900.53 | 87 |
| H26B | 1143.38 | 6070.77 | 5173.84 | 87 |
| H26C | 1258.39 | 4550.19 | 5334.43 | 87 |
| H27A | 4789.75 | 7499.4 | 4029.89 | 35 |
| H27 | 4616.3 | 6165.9 | 3950 | 160(100) |
| H28A | 1971.87 | 5706.06 | 4353.33 | 50 |
| H28 | 3540(90) | 4910(80) | 4290(19) | 80(20) |
| H29 | 5349.72 | 5671.06 | 4509.74 | 47 |
| H30A | 1309.69 | 4130.58 | 4686.47 | 78 |
| H30B | 727.07 | 5512.77 | 4892.43 | 78 |
| H30C | 973.4 | 4150.59 | 5136.08 | 78 |
| H1A | 3375.65 | 8295.82 | 324.89 | 93 |
| H2 | 3860(100) | 3080(80) | 5120(20) | 90(20) |

**Table S15** Atomic Occupancy for $HOD_2$.

| Atom | Occupancy | Atom | Occupancy | Atom | Occupancy |
|------|-----------|------|-----------|------|-----------|
| C21 | 0.6 | H21A | 0.6 | H21B | 0.6 |
| C22 | 0.5 | H22A | 0.5 | C23 | 0.5 |
| H23 | 0.5 | C26 | 0.5 | H26A | 0.5 |
| H26B | 0.5 | H26C | 0.5 | C27 | 0.4 |
| H27A | 0.4 | H27 | 0.4 | C28 | 0.5 |
| H28A | 0.5 | C29 | 0.5 | H29 | 0.5 |
| C30 | 0.5 | H30A | 0.5 | H30B | 0.5 |
| H30C | 0.5 | | | | |

Rearranged peroxide product $HORP_2$



s-7r-1123.cif
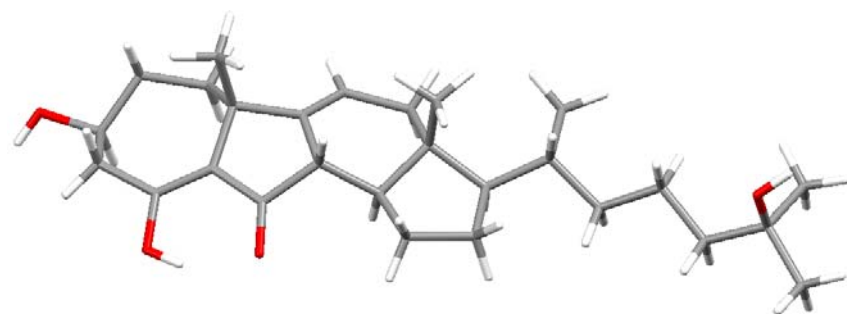


**Crystallography.** Single clear plate-shaped crystal of approximate dimension $0.60 \times 0.07 \times 0.03$ mm$^3$ was adhered to a Mitegen loop with Paratone oil. Crystallographic data were collected at temperature 149.99 K on a Rigaku-Oxford Diffraction XtaLAB-Synergy-S diffractometer with a Hypix-6000HE (Hybrid Photon Counting) detector, using Cu-Kα radiation of wavelength 1.54187 Å. The intensity data were measured by a ω-scan with 0.5° oscillations for each frame with the intensity that is more than 10:1 for data-to-parameter ratio. The program suite CrysAlis$^{Pro}$ was used for data collection, absorption correction, and data reduction. The structures were solved with the dual-space algorithm using SHELXT and were refined by full-matrix least-squares methods on $F^2$ with SHELXL-2014 using the GUI Olex2 [1]. The compound $C_{27}H_{42}O_4$ crystallized in the orthorhombic crystal system, with the space group $P2_12_12_1$. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted at calculated positions or if possible based on difference Fourier analysis and refined with a riding model or without restrictions.

**Table S16** Crystal data and structure refinement

| Crystal name | HORP$_2$ |
|---|---|
| Molecular Formula | C$_{27}$H$_{42}$O$_4$ |
| Formula Weight | 430.60 |
| Temperature [$K$] | 149.99(10) |
| Crystal System | orthorhombic |
| Space Group | $P2_12_12_1$ |
| $a$ [Å] | 7.52147(13) |
| $b$ [Å] | 9.40295(17) |
| $c$ [Å] | 35.0317(6) |
| [$\degree$] | 90 |
| [$\degree$] | 90 |
| [$\degree$] | 90 |
| V[Å$^3$] | 2477.59(8) |
| $Z$ | 4 |
| $\rho_{calc}$ [g/cm$^3$] | 1.154 |
| $\mu$/mm$^{-1}$ | 0.593 |
| $F$(000) | 944.0 |
| Crystal size [mm$^3$] | 0.596 × 0.069 × 0.029 |
| Radiation | Cu K$\alpha$ ($\lambda$ = 1.54184) |
| $2\Theta$ range for data collection [°] | 5.046 to 160.658 |
| Index ranges | -9 $\leq$ h $\leq$ 9, -9 $\leq$ k $\leq$ 11, -44 $\leq$ l $\leq$ 38 |
| Reflections collected | 25536 |
| Independent reflections | 5225 [$R_{int}$ = 0.0647, $R_{sigma}$ = 0.0443] |
| Data/restraints/parameters | 5225/0/289 |
| Goodness-of-fit on $F^2$ | 1.060 |
| Final R indexes [$I$>=2$\sigma$ ($I$)] | $R1$ = 0.0511, $wR_2$ = 0.1308 |
| Final R indexes [all data] | $R1$ = 0.0563, $wR_2$ = 0.1375 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.36/-0.22 |
| Flack parameter | 0.2(3) |

**Table S17** Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for HORP$_2$. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.

| Atom | $X$ | $y$ | $z$ | U(eq) |
|------|------|------|------|-------|
| O1 | 8570(3) | 2325(2) | 473.7(5) | 36.3(5) |
| O2 | 3574(2) | 3765(3) | 1142.2(6) | 42.7(5) |
| O4 | 4127(3) | 6205(2) | 4966.5(5) | 34.9(4) |
| C1 | 7874(4) | 2477(3) | 851.6(8) | 31.5(6) |
| C2 | 9458(3) | 2857(3) | 1101.9(8) | 29.1(5) |
| C3 | 9110(3) | 2889(3) | 1533.3(7) | 26.8(5) |
| C4 | 7934(3) | 4091(3) | 1685.4(7) | 25.6(5) |
| C5 | 5995(3) | 4022(3) | 1555.7(7) | 26.7(5) |
| C6 | 5338(3) | 3783(3) | 1201.0(8) | 31.0(6) |
| C7 | 6376(4) | 3573(4) | 840.5(8) | 35.9(6) |
| C8 | 8749(4) | 5557(3) | 1588.8(8) | 32.1(6) |
| C9 | 7676(3) | 4000(3) | 2118.5(7) | 25.6(5) |
| C10 | 5886(3) | 4630(3) | 2221.6(7) | 25.5(5) |
| C11 | 4808(3) | 4326(3) | 1867.1(8) | 26.7(5) |
| C12 | 8694(3) | 3350(3) | 2376.0(8) | 30.1(5) |
| C13 | 8222(3) | 3213(3) | 2794.6(8) | 31.6(6) |
| C14 | 6658(3) | 4167(3) | 2911.7(7) | 25.5(5) |
| C15 | 5212(3) | 4044(3) | 2598.4(7) | 25.5(5) |
| C16 | 3545(4) | 4708(3) | 2770.9(8) | 34.0(6) |
| C17 | 3713(4) | 4392(3) | 3201.7(8) | 32.0(6) |
| C18 | 5567(3) | 3701(3) | 3268.6(8) | 27.4(5) |
| C19 | 7303(4) | 5703(3) | 2955.2(9) | 36.4(6) |
| C20 | 8130(5) | 3402(5) | 3744.4(9) | 53.6(10) |
| C21 | 6298(4) | 4059(3) | 3667.7(7) | 33.3(6) |
| C22 | 4972(4) | 3594(3) | 3977.6(8) | 36.3(6) |
| C23 | 5292(4) | 4280(3) | 4368.0(8) | 34.7(6) |
| C24 | 3736(4) | 4019(3) | 4635.6(8) | 33.8(6) |
| C25 | 3875(4) | 4710(3) | 5031.6(8) | 33.1(6) |
| C26 | 5415(5) | 4099(3) | 5258.6(9) | 41.9(7) |
| C27 | 2124(4) | 4498(4) | 5247.8(9) | 43.2(7) |
| O3 | 3156(2) | 4374(2) | 1849.0(6) | 35.5(5) |

**Table S18** Anisotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for HORP$_2$. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| O1 | 28.7(9) | 53.9(12) | 26.3(9) | -4.5(9) | 0.3(8) | -7.7(9) |
| O2 | 15.7(8) | 82.4(16) | 30.1(10) | 2.4(11) | -5.3(8) | -1.0(9) |
| O4 | 38.7(10) | 37.5(10) | 28.7(9) | -4.0(8) | -7.7(8) | 2.5(8) |
| C1 | 25.9(12) | 42.3(14) | 26.2(13) | -0.8(11) | -1.3(10) | -5.7(11) |
| C2 | 19.8(11) | 36.9(13) | 30.5(13) | -0.9(11) | 0.0(10) | -1.2(10) |
| C3 | 19.6(11) | 31.1(12) | 29.7(13) | 0.7(10) | -1.0(9) | 0.1(9) |
| C4 | 16.4(10) | 33.1(12) | 27.5(12) | 1.8(10) | -2.9(9) | 0.5(9) |
| C5 | 17.6(10) | 32.2(12) | 30.3(13) | 4.3(10) | -0.7(9) | -1.2(9) |
| C6 | 16.4(11) | 44.8(15) | 31.8(14) | 5.6(12) | -2.5(10) | -1.5(10) |
| C7 | 24.2(12) | 58.6(18) | 24.9(12) | 2.7(12) | -2.5(11) | -0.7(12) |
| C8 | 25.7(12) | 35.8(13) | 34.9(14) | 2.1(11) | 1.0(11) | -3.5(11) |
| C9 | 18.3(11) | 29.2(11) | 29.4(13) | -2.0(10) | 0.5(9) | -0.9(9) |
| C10 | 19.3(11) | 27.5(11) | 29.7(12) | 2.0(10) | 0.1(10) | 0.8(9) |
| C11 | 19.5(11) | 29.7(12) | 30.9(13) | 4.2(10) | -1.2(10) | 0.7(9) |
| C12 | 19.5(11) | 42.0(14) | 28.7(12) | -2.1(11) | -1.7(10) | 4.0(10) |
| C13 | 22.0(11) | 45.9(15) | 27.0(13) | 0.4(11) | -1.8(10) | 8.8(11) |
| C14 | 20.1(11) | 29.9(12) | 26.5(12) | -2.3(10) | -1.6(9) | 2.0(9) |
| C15 | 17.7(10) | 29.9(12) | 29.0(13) | -0.1(10) | -1.3(9) | -0.8(9) |
| C16 | 19.9(11) | 47.3(15) | 34.8(14) | -0.5(12) | 2.2(11) | 5.4(11) |
| C17 | 23.2(12) | 38.0(13) | 34.8(14) | -2.5(11) | 3.1(10) | 2.0(11) |
| C18 | 25.5(12) | 28.0(11) | 28.6(12) | -3.2(10) | 1.6(10) | 1.4(10) |
| C19 | 34.8(14) | 38.8(14) | 35.6(15) | -3.2(12) | -1.0(12) | -8.2(12) |
| C20 | 36.8(16) | 95(3) | 28.7(14) | -4.3(16) | -2.5(13) | 20.3(18) |
| C21 | 30.4(13) | 44.5(15) | 24.9(12) | -3.8(11) | 1.1(11) | 0.6(12) |
| C22 | 38.2(15) | 41.2(15) | 29.6(14) | -3.4(12) | 0.2(12) | -1.1(12) |
| C23 | 34.5(14) | 41.1(15) | 28.5(13) | -2.4(11) | 1.0(11) | -0.1(12) |
| C24 | 33.0(13) | 40.9(14) | 27.6(13) | -2.9(11) | -0.9(11) | -1.0(12) |
| C25 | 34.4(14) | 39.1(14) | 25.9(13) | -1.8(11) | 0.8(11) | 1.8(11) |
| C26 | 50.8(17) | 42.3(15) | 32.5(15) | -2.6(13) | -8.4(13) | 9.7(14) |
| C27 | 44.0(17) | 51.7(17) | 33.8(15) | -5.8(14) | 9.1(13) | -2.2(14) |
| O3 | 16.3(8) | 55.0(12) | 35.3(10) | 4.0(9) | -1.2(7) | 4.0(8) |

**Table S19** Bond Lengths for HORP$_2$.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|------|------|----------|------|------|----------|
| O1 | C1 | 1.431(3) | C11 | O3 | 1.245(3) |
| O2 | C6 | 1.342(3) | C12 | C13 | 1.515(4) |
| O4 | C25 | 1.437(4) | C13 | C14 | 1.535(3) |
| C1 | C2 | 1.522(4) | C14 | C15 | 1.550(3) |
| C1 | C7 | 1.528(4) | C14 | C18 | 1.559(4) |
| C2 | C3 | 1.534(4) | C14 | C19 | 1.531(4) |
| C3 | C4 | 1.531(4) | C15 | C16 | 1.526(4) |
| C4 | C5 | 1.529(3) | C16 | C17 | 1.543(4) |
| C4 | C8 | 1.546(4) | C17 | C18 | 1.556(4) |
| C4 | C9 | 1.532(4) | C18 | C21 | 1.540(4) |
| C5 | C6 | 1.356(4) | C20 | C21 | 1.534(4) |
| C5 | C11 | 1.439(4) | C21 | C22 | 1.538(4) |
| C6 | C7 | 1.498(4) | C22 | C23 | 1.531(4) |
| C9 | C10 | 1.514(3) | C23 | C24 | 1.519(4) |
| C9 | C12 | 1.331(4) | C24 | C25 | 1.535(4) |
| C10 | C11 | 1.510(4) | C25 | C26 | 1.517(4) |
| C10 | C15 | 1.517(4) | C25 | C27 | 1.532(4) |

**Table S20** Bond Angles for HORP₂.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|------|------|------|---------|------|------|------|---------|
| O1 | C1 | C2 | 105.7(2) | C12 | C13 | C14 | 112.8(2) |
| O1 | C1 | C7 | 108.3(2) | C13 | C14 | C15 | 107.8(2) |
| C2 | C1 | C7 | 115.7(2) | C13 | C14 | C18 | 117.0(2) |
| C1 | C2 | C3 | 116.0(2) | C15 | C14 | C18 | 100.22(19) |
| C4 | C3 | C2 | 117.1(2) | C19 | C14 | C13 | 109.6(2) |
| C3 | C4 | C8 | 110.7(2) | C19 | C14 | C15 | 111.3(2) |
| C3 | C4 | C9 | 112.1(2) | C19 | C14 | C18 | 110.6(2) |
| C5 | C4 | C3 | 114.6(2) | C10 | C15 | C14 | 110.8(2) |
| C5 | C4 | C8 | 110.6(2) | C10 | C15 | C16 | 118.1(2) |
| C5 | C4 | C9 | 99.85(19) | C16 | C15 | C14 | 105.4(2) |
| C9 | C4 | C8 | 108.5(2) | C15 | C16 | C17 | 104.0(2) |
| C6 | C5 | C4 | 128.9(2) | C16 | C17 | C18 | 107.5(2) |
| C6 | C5 | C11 | 120.1(2) | C17 | C18 | C14 | 103.5(2) |
| C11 | C5 | C4 | 111.0(2) | C21 | C18 | C14 | 118.6(2) |
| O2 | C6 | C5 | 120.2(2) | C21 | C18 | C17 | 111.5(2) |
| O2 | C6 | C7 | 112.6(2) | C20 | C21 | C18 | 113.1(2) |
| C5 | C6 | C7 | 127.2(2) | C20 | C21 | C22 | 110.2(3) |
| C6 | C7 | C1 | 116.9(2) | C22 | C21 | C18 | 110.3(2) |
| C10 | C9 | C4 | 109.1(2) | C23 | C22 | C21 | 114.2(2) |
| C12 | C9 | C4 | 128.6(2) | C24 | C23 | C22 | 111.3(2) |
| C12 | C9 | C10 | 122.0(2) | C23 | C24 | C25 | 115.9(2) |
| C9 | C10 | C15 | 111.2(2) | O4 | C25 | C24 | 106.2(2) |
| C11 | C10 | C9 | 102.0(2) | O4 | C25 | C26 | 110.7(2) |
| C11 | C10 | C15 | 117.9(2) | O4 | C25 | C27 | 108.6(2) |
| C5 | C11 | C10 | 109.1(2) | C26 | C25 | C24 | 111.4(2) |
| O3 | C11 | C5 | 126.0(3) | C26 | C25 | C27 | 110.3(3) |
| O3 | C11 | C10 | 124.8(2) | C27 | C25 | C24 | 109.4(2) |
| C9 | C12 | C13 | 124.1(2) | | | | |

**Table S21** Torsion Angles for HORP$_2$.

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| O1 | C1 | C2 | C3 | -172.2(2) | C11 | C5 | C6 | O2 | -3.1(4) |
| O1 | C1 | C7 | C6 | 173.9(2) | C11 | C5 | C6 | C7 | 174.5(3) |
| O2 | C6 | C7 | C1 | -132.0(3) | C11 | C10 | C15 | C14 | 167.7(2) |
| C1 | C2 | C3 | C4 | -69.7(3) | C11 | C10 | C15 | C16 | -70.7(3) |
| C2 | C1 | C7 | C6 | -67.7(3) | C12 | C9 | C10 | C11 | -143.7(3) |
| C2 | C3 | C4 | C5 | 66.7(3) | C12 | C9 | C10 | C15 | -17.2(3) |
| C2 | C3 | C4 | C8 | -59.2(3) | C12 | C13 | C14 | C15 | 43.8(3) |
| C2 | C3 | C4 | C9 | 179.6(2) | C12 | C13 | C14 | C18 | 155.6(2) |
| C3 | C4 | C5 | C6 | -46.1(4) | C12 | C13 | C14 | C19 | -77.5(3) |
| C3 | C4 | C5 | C11 | 137.0(2) | C13 | C14 | C15 | C10 | -64.5(3) |
| C3 | C4 | C9 | C10 | -150.5(2) | C13 | C14 | C15 | C16 | 166.7(2) |
| C3 | C4 | C9 | C12 | 22.3(4) | C13 | C14 | C18 | C17 | -154.8(2) |
| C4 | C5 | C6 | O2 | -179.8(3) | C13 | C14 | C18 | C21 | 81.1(3) |
| C4 | C5 | C6 | C7 | -2.2(5) | C14 | C15 | C16 | C17 | -31.2(3) |
| C4 | C5 | C11 | C10 | 0.5(3) | C14 | C18 | C21 | C20 | -59.7(3) |
| C4 | C5 | C11 | O3 | 178.7(3) | C14 | C18 | C21 | C22 | 176.4(2) |
| C4 | C9 | C10 | C11 | 29.7(2) | C15 | C10 | C11 | C5 | -140.2(2) |
| C4 | C9 | C10 | C15 | 156.2(2) | C15 | C10 | C11 | O3 | 41.6(4) |
| C4 | C9 | C12 | C13 | -174.1(2) | C15 | C14 | C18 | C17 | -38.8(2) |
| C5 | C4 | C9 | C10 | -28.8(2) | C15 | C14 | C18 | C21 | -162.8(2) |
| C5 | C4 | C9 | C12 | 144.1(3) | C15 | C16 | C17 | C18 | 6.0(3) |
| C5 | C6 | C7 | C1 | 50.3(4) | C16 | C17 | C18 | C14 | 21.0(3) |
| C6 | C5 | C11 | C10 | -176.7(2) | C16 | C17 | C18 | C21 | 149.5(2) |
| C6 | C5 | C11 | O3 | 1.4(4) | C17 | C18 | C21 | C20 | -179.7(3) |
| C7 | C1 | C2 | C3 | 67.9(3) | C17 | C18 | C21 | C22 | 56.4(3) |
| C8 | C4 | C5 | C6 | 79.8(3) | C18 | C14 | C15 | C10 | 172.8(2) |
| C8 | C4 | C5 | C11 | -97.2(3) | C18 | C14 | C15 | C16 | 43.9(2) |
| C8 | C4 | C9 | C10 | 87.0(2) | C18 | C21 | C22 | C23 | -162.7(3) |
| C8 | C4 | C9 | C12 | -100.2(3) | C19 | C14 | C15 | C10 | 55.7(3) |
| C9 | C4 | C5 | C6 | -166.1(3) | C19 | C14 | C15 | C16 | -73.1(3) |
| C9 | C4 | C5 | C11 | 17.0(3) | C19 | C14 | C18 | C17 | 78.8(3) |

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| C9 | C10 | C11 | C5 | -18.1(3) | C19 | C14 | C18 | C21 | -45.3(3) |
| C9 | C10 | C11 | O3 | 163.7(3) | C20 | C21 | C22 | C23 | 71.7(3) |
| C9 | C10 | C15 | C14 | 50.5(3) | C21 | C22 | C23 | C24 | 168.3(3) |
| C9 | C10 | C15 | C16 | 172.1(2) | C22 | C23 | C24 | C25 | -177.7(2) |
| C9 | C12 | C13 | C14 | -12.4(4) | C23 | C24 | C25 | O4 | 56.3(3) |
| C10 | C9 | C12 | C13 | -2.1(4) | C23 | C24 | C25 | C26 | -64.3(3) |
| C10 | C15 | C16 | C17 | -155.6(2) | C23 | C24 | C25 | C27 | 173.4(3) |

**Table S22** Hydrogen Atom Coordinates ($Å×10^4$) and Isotropic Displacement Parameters ($Å^2×10^3$) for HORP$_2$.

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H1 | 7828 | 1894 | 337 | 54 |
| H2 | 3047 | 3980 | 1346 | 64 |
| H4 | 4589 | 6577 | 5161 | 52 |
| H1A | 7379 | 1543 | 937 | 38 |
| H2A | 9899 | 3805 | 1023 | 35 |
| H2B | 10419 | 2163 | 1051 | 35 |
| H3A | 8556 | 1973 | 1606 | 32 |
| H3B | 10273 | 2944 | 1665 | 32 |
| H7A | 6894 | 4501 | 766 | 43 |
| H7B | 5534 | 3293 | 637 | 43 |
| H8A | 8661 | 5726 | 1313 | 48 |
| H8B | 10002 | 5570 | 1666 | 48 |
| H8C | 8102 | 6302 | 1726 | 48 |
| H10 | 6024 | 5683 | 2247 | 31 |
| H12 | 9784 | 2948 | 2292 | 36 |
| H13A | 9274 | 3464 | 2950 | 38 |
| H13B | 7915 | 2210 | 2850 | 38 |
| H15 | 4965 | 3009 | 2560 | 31 |
| H16A | 2458 | 4268 | 2664 | 41 |
| H16B | 3509 | 5745 | 2723 | 41 |
| H17A | 2759 | 3734 | 3284 | 38 |
| H17B | 3608 | 5283 | 3350 | 38 |

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H18 | 5411 | 2646 | 3255 | 33 |
| H19A | 8137 | 5763 | 3170 | 55 |
| H19B | 6283 | 6326 | 3004 | 55 |
| H19C | 7901 | 6003 | 2720 | 55 |
| H20A | 8065 | 2369 | 3712 | 80 |
| H20B | 8499 | 3622 | 4006 | 80 |
| H20C | 8998 | 3797 | 3564 | 80 |
| H21 | 6426 | 5116 | 3684 | 40 |
| H22A | 3755 | 3833 | 3892 | 44 |
| H22B | 5039 | 2548 | 4006 | 44 |
| H23A | 6388 | 3882 | 4482 | 42 |
| H23B | 5465 | 5316 | 4335 | 42 |
| H24A | 3601 | 2980 | 4670 | 41 |
| H24B | 2641 | 4372 | 4511 | 41 |
| H26A | 6537 | 4333 | 5131 | 63 |
| H26B | 5288 | 3064 | 5275 | 63 |
| H26C | 5412 | 4506 | 5516 | 63 |
| H27A | 2186 | 4988 | 5494 | 65 |
| H27B | 1925 | 3480 | 5290 | 65 |
| H27C | 1141 | 4889 | 5097 | 65 |

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