

Optical Resolution of Dimethyl α -Hydroxy-Arylmethylphosphonates via Diastereomer Complex Formation Using Calcium Hydrogen *O,O'*-Dibenzoyl-(2*R*,3*R*)-Tartrate; X-Ray Analysis of the Complexes and Products

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Single crystal X-ray diffraction studies of diastereomeric complex Ca[(S)-1a • H-DBTA]₂

Single crystals of compound Ca[(S)-1a • H-DBTA]₂, suitable for X-ray diffraction, were obtained by slow evaporation of acetone. The crystals were introduced into perfluorinated oil and a suitable single crystal was carefully mounted on the top of a thin glass wire. Data collection was performed with an Bruker D8 Venture diffractometer equipped with a Bruker D8 Venture TXS rotating anode X-ray tube and a multilayer mirror optics monochromator and operating with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$).

Data collection was performed with the Bruker Instrument Service software;¹ SAINT software² was used for data reduction. Absorption correction using multiscan method within the SABABS software³ was applied. The structures were solved with SHELXS-97,⁴ refined with SHELXL-97⁵ and finally checked using PLATON.⁶ Details for data collection and structure refinement are summarized in Table S1.

Table S1. Details for X-ray data collection and structure refinement for compound Ca[(S)-1a • H-DBTA]₂.

Ca[(S)-1a • H-DBTA]₂	
Empirical formula	C ₅₄ H ₅₂ CaO ₂₄ P ₂
Formula mass	1186.97
T[K]	293(2)
Crystal size [mm]	0.10 × 0.03 × 0.02
Crystal description	colorless block
Crystal system	monoclinic
Space group	C2
a [Å]	28.790(2)
b [Å]	7.6772(6)
c [Å]	15.8661(15)
α [°]	90.0
β [°]	117.074(3)
γ [°]	90.0
V [Å ³]	3122.5(5)
Z	2
$\rho_{\text{calcd.}}$ [g cm ⁻³]	1.262
μ [mm ⁻¹]	0.227
F(000)	1236
Θ range [°]	3.73–25.24

Index ranges	-34 ≤ <i>h</i> ≤ 34 -9 ≤ <i>k</i> ≤ 9 -16 ≤ <i>l</i> ≤ 19
Reflns. collected	14544
Reflns. obsd.	4766
Reflns. unique	5614 (<i>R</i> _{int} = 0.0292)
<i>R</i> ₁ , <i>wR</i> ₂ (2σ data)	0.0526, 0.1326
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0643, 0.1407
GOOF on <i>F</i> ²	1.043
Peak/hole [e Å ⁻³]	0.422/-0.236

Table S2. Selected bond lengths (Å) of compound Ca[(S)-1a • H-DBTA]₂; symmetry codes: (i) 2 - *x*, *y*, 2 - *z*; (ii) 2 - *x*, -1 + *y*, 2 - *z*; (iii) *x*, -1 + *y*, *z*.

Ca1–O1	2.284(3)	C2–C7	1.392(8)
Ca1–O1 ⁱ	2.284(3)	C2–C1	1.513(8)
Ca1–O5 ⁱ	2.324(4)	C13–C14	1.379(9)
Ca1–O5	2.324(4)	C13–C18	1.385(8)
Ca1–O9 ⁱⁱ	2.332(3)	C23–C24	1.362(8)
Ca1–O9 ⁱⁱⁱ	2.332(3)	O4–C1	1.408(8)
O2–C8	1.365(9)	C27–C26	1.377(8)
O2–P1	1.528(6)	C7–C6	1.397(10)
P1–O1	1.463(3)	C25–C24	1.375(10)
P1–O3	1.564(4)	C25–C26	1.381(10)
P1–C1	1.802(6)	C14–C15	1.389(9)
O5–C10	1.205(5)	C5–C4	1.358(11)
O9–C20	1.247(5)	C5–C6	1.361(12)
O10–C20	1.242(6)	C3–C4	1.351(9)
O11–C21	1.334(6)	C15–C16	1.337(12)
O11–C19	1.427(5)	C16–C17	1.425(13)
O6–C10	1.264(6)	C18–C17	1.314(11)
O7–C12	1.340(6)	O8–C12	1.214(7)
O7–C11	1.425(5)	C11–C19	1.523(6)
C20–C19	1.535(6)	C22–C27	1.388(7)
C10–C11	1.532(6)	C22–C23	1.394(7)
O12–C21	1.215(6)	C22–C21	1.459(6)
C2–C3	1.350(8)	O3–C9	1.368(8)
C12–C13	1.463(8)		

Table S3. Selected bond angles (°) of compound Ca[(S)-1a • H-DBTA]₂; symmetry codes: (i) 2 - *x*, *y*, 2 - *z*; (ii) 2 - *x*, -1 + *y*, 2 - *z*; (iii) *x*, -1 + *y*, *z*.

O1–Ca1–O1 ⁱ	172.4(2)	C3–C2–C7	117.9(6)
O1–Ca1–O5 ⁱ	86.2(2)	C3–C2–C1	121.7(6)
O1 ⁱ –Ca1–O5 ⁱ	88.4(2)	C7–C2–C1	120.4(5)
O1–Ca1–O5	88.4(2)	O11–C19–C11	106.0(3)
O1 ⁱ –Ca1–O5	86.2(1)	O11–C19–C20	113.0(3)
O5 ⁱ –Ca1–O5	90.3(2)	C11–C19–C20	111.5(4)
O1–Ca1–O9 ⁱⁱ	97.0(1)	C14–C13–C18	117.4(6)
O1 ⁱ –Ca1–O9 ⁱⁱ	88.2(1)	C14–C13–C12	122.1(5)
O5 ⁱ –Ca1–O9 ⁱⁱ	87.9(1)	C18–C13–C12	120.6(6)
O5–Ca1–O9 ⁱⁱ	174.1(2)	C24–C23–C22	120.1(6)
O1–Ca1–O9 ⁱⁱⁱ	88.2(1)	O4–C1–C2	109.4(5)
O1 ⁱ –Ca1–O9 ⁱⁱⁱ	97.0(1)	O4–C1–P1	108.8(5)
O5 ⁱ –Ca1–O9 ⁱⁱⁱ	174.1(2)	C2–C1–P1	113.8(4)
O5–Ca1–O9 ⁱⁱⁱ	87.9(1)	C26–C27–C22	119.8(6)

O9 ⁱⁱ -Ca1-O9 ⁱⁱⁱ	94.4(2)	C2-C7-C6	121.1(6)
C8-O2-P1	131.0(5)	C24-C25-C26	119.1(6)
O1-P1-O2	114.4(3)	C13-C14-C15	119.2(7)
O1-P1-O3	113.5(2)	C27-C26-C25	120.7(6)
O2-P1-O3	104.0(4)	C4-C5-C6	119.5(7)
O1-P1-C1	111.6(3)	C5-C6-C7	118.5(7)
O2-P1-C1	107.5(3)	C23-C24-C25	121.1(6)
O3-P1-C1	105.0(3)	C2-C3-C4	120.9(7)
C10-O5-Ca1	149.0(3)	C3-C4-C5	122.1(7)
C21-O11-C19	117.5(3)	C16-C15-C14	121.8(8)
C12-O7-C11	116.6(4)	C15-C16-C17	118.9(7)
O10-C20-O9	127.2(4)	C17-C18-C13	124.3(8)
O10-C20-C19	117.7(4)	C18-C17-C16	118.1(8)
O9-C20-C19	115.1(4)	C27-C22-C21	118.7(5)
O5-C10-O6	127.0(4)	C23-C22-C21	122.2(4)
O5-C10-C11	116.5(4)	C9-O3-P1	123.3(4)
O6-C10-C11	116.4(4)	O12-C21-O11	121.8(5)
P1-O1-Ca1	162.0(2)	O12-C21-C22	125.4(5)
O7-C11-C19	107.3(3)	O11-C21-C22	112.8(4)
O7-C11-C10	112.4(3)	O8-C12-O7	121.2(5)
C19-C11-C10	108.3(4)	O8-C12-C13	126.0(5)
C27-C22-C23	119.2(5)	O7-C12-C13	112.7(4)

Table S4. Selected torsion angles (°) of compound Ca[(S)-**1a** • H-DBTA]₂.

C8-O2-P1-O1	11.4(11)	O8-C12-C13-C14	177.0(7)
C8-O2-P1-O3	135.8(10)	O7-C12-C13-C14	-3.4(8)
C8-O2-P1-C1	-113.2(10)	O8-C12-C13-C18	-5.1(9)
Ca1-O9-C20-O10	-57.1(7)	O7-C12-C13-C18	174.5(6)
Ca1-O9-C20-C19	121.2(4)	C27-C22-C23-C24	1.8(9)
Ca1-O5-C10-O6	0.2(11)	C21-C22-C23-C24	-178.0(5)
Ca1-O5-C10-C11	-177.4(5)	C3-C2-C1-O4	-30.9(8)
O2-P1-O1-Ca1	-85.8(10)	C7-C2-C1-O4	148.8(6)
O3-P1-O1-Ca1	155.0(9)	C3-C2-C1-P1	91.0(7)
C1-P1-O1-Ca1	36.6(10)	C7-C2-C1-P1	-89.2(7)
C12-O7-C11-C19	-174.2(4)	O1-P1-C1-O4	-48.3(5)
C12-O7-C11-C10	66.9(5)	O2-P1-C1-O4	78.0(5)
O5-C10-C11-O7	-169.7(4)	O3-P1-C1-O4	-171.7(4)
O6-C10-C11-O7	12.4(6)	O1-P1-C1-C2	-170.5(4)
O5-C10-C11-C19	71.9(5)	O2-P1-C1-C2	-44.2(5)
O6-C10-C11-C19	-106.0(5)	O3-P1-C1-C2	66.1(5)
O1-P1-O3-C9	31.1(8)	C23-C22-C27-C26	0.0(9)
O2-P1-O3-C9	-93.9(7)	C21-C22-C27-C26	179.9(5)
C1-P1-O3-C9	153.3(6)	C3-C2-C7-C6	-1.9(10)
C19-O11-C21-O12	2.0(7)	C1-C2-C7-C6	178.3(6)
C19-O11-C21-C22	-176.8(4)	C18-C13-C14-C15	0.8(11)
C27-C22-C21-O12	-13.0(8)	C12-C13-C14-C15	178.8(8)
C23-C22-C21-O12	166.8(6)	C22-C27-C26-C25	-1.1(10)
C27-C22-C21-O11	165.8(4)	C24-C25-C26-C27	0.3(11)
C23-C22-C21-O11	-14.4(7)	C4-C5-C6-C7	-0.5(12)
C11-O7-C12-O8	6.8(7)	C2-C7-C6-C5	1.6(12)
C11-O7-C12-C13	-172.8(4)	C22-C23-C24-C25	-2.7(10)
C21-O11-C19-C11	-159.3(3)	C26-C25-C24-C23	1.6(11)
C21-O11-C19-C20	78.2(5)	C7-C2-C3-C4	1.3(11)
O7-C11-C19-O11	-50.7(4)	C1-C2-C3-C4	-179.0(7)
C10-C11-C19-O11	70.9(4)	C2-C3-C4-C5	-0.3(13)
O7-C11-C19-C20	72.7(4)	C6-C5-C4-C3	-0.1(13)
C10-C11-C19-C20	-165.7(3)	C13-C14-C15-C16	3.3(15)
O10-C20-C19-O11	11.4(6)	C14-C15-C16-C17	-6.2(16)

O9–C20–C19–O11	-167.0(4)	C14–C13–C18–C17	-1.8(13)
O10–C20–C19–C11	-107.9(5)	C12–C13–C18–C17	-179.8(9)
O9–C20–C19–C11	73.7(5)	C13–C18–C17–C16	-1.1(15)
C15–C16–C17–C18	5.1(15)		

Single crystal X-ray diffraction studies of optically active α -hydroxyphosphonate (S)-1a

Single crystals of compound (S)-**1a**, suitable for X-ray diffraction, were obtained by slow evaporation of acetone. The crystals were introduced into perfluorinated oil and a suitable single crystal was carefully mounted on the top of a thin glass wire. Data collection was performed with an Oxford Xcalibur 3 diffractometer equipped with a Spellman generator (50 kV, 40 mA) and a Kappa CCD detector, operating with Mo-K α radiation ($\lambda = 0.71071 \text{ \AA}$).

Data collection and data reduction were performed with the CrysAlisPro software.⁷ Absorption correction using the multiscan method⁷ was applied. The structures were solved with SHELXS-97,⁴ refined with SHELXL-97⁵ and finally checked using PLATON.⁶ Details for data collection and structure refinement are summarized in Table S5.

Table S5. Details for X-ray data collection and structure refinement for compound (S)-**1a**.

(S)-1a	
Empirical formula	C ₉ H ₁₃ O ₄ P
Formula mass	216.16
T[K]	123(2)
Crystal size [mm]	0.35 × 0.08 × 0.04
Crystal description	colorless block
Crystal system	monoclinic
Space group	<i>P</i> 21
a [Å]	8.3225(6)
b [Å]	7.6670(5)
c [Å]	8.6598(6)
α [°]	90.0
β [°]	106.140(7)
γ [°]	90.0
V [Å ³]	530.79(7)
Z	2
$\rho_{\text{calcd.}}$ [g cm ⁻³]	1.353
μ [mm ⁻¹]	0.246
<i>F</i> (000)	228
Θ range [°]	3.61–25.24
Index ranges	-10 ≤ <i>h</i> ≤ 11 -10 ≤ <i>k</i> ≤ 10 -10 ≤ <i>l</i> ≤ 11
Reflns. collected	5336
Reflns. obsd.	1995
Reflns. unique	2604
	(<i>R</i> _{int} = 0.0513)
<i>R</i> ₁ , <i>wR</i> ₂ (2 σ data)	0.0533, 0.0744
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0800, 0.0856
GOOF on <i>F</i> ²	1.025
Peak/hole [e Å ⁻³]	0.349/-0.284

Table S6. Selected bond lengths (Å) of compound (S)-**1a**.

P1–O2	1.468(3)	C1–C2	1.509(5)
P1–O4	1.563(3)	C4–C5	1.369(6)
P1–O3	1.583(3)	C6–C5	1.370(6)
P1–C1	1.810(4)	C3–C2	1.382(5)
O1–C1	1.431(5)	C3–C4	1.389(5)

O3–C8	1.448(5)	C7–C6	1.381(6)
O4–C9	1.447(5)	C7–C2	1.383(5)

Table S7. Selected bond angles (°) of compound (S)-**1a**.

O2–P1–O4	115.9(2)	C7–C2–C1	119.8(4)
O2–P1–O3	113.2(2)	C5–C4–C3	120.8(4)
O4–P1–O3	102.8(2)	C5–C6–C7	120.2(5)
O2–P1–C1	115.3(2)	C4–C5–C6	119.6(4)
O4–P1–C1	102.3(2)	O1–C1–C2	113.3(3)
O3–P1–C1	106.0(2)	O1–C1–P1	103.4(3)
C8–O3–P1	119.9(3)	C2–C1–P1	114.1(3)
C9–O4–P1	120.0(3)	C3–C2–C7	118.8(4)
C2–C3–C4	119.8(4)	C3–C2–C1	121.3(4)
C6–C7–C2	120.8(5)		

Table S8. Selected torsion angles (°) of compound (S)-**1a**.

O2–P1–O3–C8	-41.0(3)	C4–C3–C2–C7	-1.4(6)
O4–P1–O3–C8	-166.7(3)	C4–C3–C2–C1	176.2(4)
C1–P1–O3–C8	86.3(3)	C6–C7–C2–C3	1.4(6)
O2–P1–O4–C9	-42.2(4)	C6–C7–C2–C1	-176.3(4)
O3–P1–O4–C9	81.8(3)	O1–C1–C2–C3	-22.5(5)
C1–P1–O4–C9	-168.4(3)	P1–C1–C2–C3	95.4(4)
O2–P1–C1–O1	63.1(3)	O1–C1–C2–C7	155.1(4)
O4–P1–C1–O1	-170.3(3)	P1–C1–C2–C7	-87.0(4)
O3–P1–C1–O1	-62.9(3)	C2–C3–C4–C5	0.4(6)
O2–P1–C1–C2	-60.3(4)	C2–C7–C6–C5	-0.2(7)
O4–P1–C1–C2	66.3(3)	C3–C4–C5–C6	0.8(7)
O3–P1–C1–C2	173.7(3)	C7–C6–C5–C4	-0.9(7)

*Single crystal X-ray diffraction studies of diastereomeric complex Ca[(R)-**1b** • H-DBTA]₂*

Single crystals of compound Ca[(R)-**1b** • H-DBTA]₂, suitable for X-ray diffraction, were obtained by slow evaporation of acetone. The crystals were introduced into perfluorinated oil and a suitable single crystal was carefully mounted on the top of a thin glass wire. Data collection was performed with an Oxford Xcalibur 3 diffractometer equipped with a Spellman generator (50 kV, 40 mA) and a Kappa CCD detector, operating with Mo-K α radiation ($\lambda = 0.71071 \text{ \AA}$).

Data collection and data reduction were performed with the CrysAlisPro software.⁷ Absorption correction using the multiscan method⁷ was applied. The structures were solved with SHELXS-97,⁴ refined with SHELXL-97⁵ and finally checked using PLATON.⁶ Details for data collection and structure refinement are summarized in Table S9.

Table S9. Details for X-ray data collection and structure refinement for compound Ca[(R)-**1b** • H-DBTA]₂.

<i>Ca[(R)-1b • H-DBTA]₂</i>	
Empirical formula	C ₅₆ H ₅₆ CaO ₂₆ P ₂
Formula mass	1247.02
T[K]	123(2)
Crystal size [mm]	0.40 × 0.15 × 0.10
Crystal description	colorless block
Crystal system	monoclinic
Space group	C2
a [Å]	30.7229(7)
b [Å]	7.6095(1)

c [Å]	14.5500(3)
α [°]	90.0
β [°]	115.956(3)
γ [°]	90.0
V [Å ³]	3058.47(12)
Z	2
ρ _{calcd.} [g cm ⁻³]	1.354
μ [mm ⁻¹]	0.238
F(000)	1300
Θ range [°]	2.57–25.24
Index ranges	-43 ≤ h ≤ 43 -10 ≤ k ≤ 10 -20 ≤ l ≤ 20
Reflns. collected	30960
Reflns. obsd.	8767
Reflns. unique	9307
	(R _{int} = 0.0263)
R ₁ , wR ₂ (2σ data)	0.0313, 0.0746
R ₁ , wR ₂ (all data)	0.0347, 0.0768
GOOF on F ²	1.032
Peak/hole [e Å ⁻³]	0.585/-0.267

Table S10. Selected bond lengths (Å) of compound *Ca[(R)-1b • H-DBTA]₂*. Symmetry codes: *i* 2-x, y, 1-z; *ii* x, 1+y, z; *iii* x, -1+y, z.

Ca1–O1 ^{<i>i</i>}	2.293(1)	C6–C5	1.390(3)
Ca1–O1	2.293(1)	C15–C16	1.390(3)
Ca1–O10	2.296(1)	C15–C14	1.392(3)
Ca1–O10 ^{<i>i</i>}	2.296(1)	C14–C19	1.391(3)
Ca1–O6	2.318(1)	C21–C12 ^{<i>iii</i>}	1.518(2)
Ca1–O6 ^{<i>i</i>}	2.318(1)	C24–C25	1.395(3)
P1–O1	1.476(1)	C8–C7	1.388(3)
P1–O3	1.558(2)	C8–C9	1.389(3)
P1–O2	1.568(2)	C19–C18	1.387(3)
P1–C3	1.812(2)	C18–C17	1.379(4)
O10–C20	1.238(2)	C17–C16	1.381(4)
O8–C13	1.348(2)	C25–C26	1.382(4)
O8–C12	1.429(2)	C26–C27	1.373(4)
O6–C11	1.233(2)	C28–C27	1.392(3)
O7–C11	1.268(2)	O4–C3	1.429(2)
C12–C21 ^{<i>ii</i>}	1.518(2)	O3–C2	1.433(3)
C12–C11	1.529(2)	O9–C13	1.208(2)
O12–C22	1.347(2)	C22–C23	1.483(2)
O12–C21	1.429(2)	C13–C14	1.482(2)
O2–C1	1.425(3)	C23–C24	1.388(3)
O13–C22	1.207(2)	C23–C28	1.394(3)
C20–O11	1.260(2)	C4–C5	1.395(3)
C20–C21	1.532(2)	C4–C9	1.409(2)
O5–C9	1.365(2)	C4–C3	1.505(3)
O5–C10	1.429(3)	C6–C7	1.385(3)

Table S11. Selected bond angles (°) of compound $Ca[(R)\text{-}1b \bullet H\text{-DBTA}]_2$. Symmetry codes: i 2 - x, y, 1 - z; ii x, 1 + y, z; iii x, -1 + y, z.

O1 ⁱ -Ca1-O1	177.0(1)	C19-C14-C15	120.3(2)
O1 ⁱ -Ca1-O10	95.2(1)	C19-C14-C13	117.8(2)
O1-Ca1-O10	86.8(1)	C15-C14-C13	121.9(2)
O1 ⁱ -Ca1-O10 ⁱ	86.8(1)	O12-C21-C12 ⁱⁱⁱ	107.8(1)
O1-Ca1-O10 ⁱ	95.2(1)	O12-C21-C20	112.3(1)
O10-Ca1-O10 ⁱ	95.9(1)	C12 ⁱⁱⁱ -C21-C20	109.4(1)
O1 ⁱ -Ca1-O6	84.7(1)	C23-C24-C25	119.0(2)
O1-Ca1-O6	93.3(1)	C7-C8-C9	120.0(2)
O10-Ca1-O6	86.2(1)	C6-C5-C4	121.3(2)
O10 ⁱ -Ca1-O6	171.4(1)	C18-C19-C14	120.0(2)
O1 ⁱ -Ca1-O6 ⁱ	93.3(1)	C17-C18-C19	119.7(2)
O1-Ca1-O6 ⁱ	84.7(1)	C6-C7-C8	120.8(2)
O10-Ca1-O6 ⁱ	171.4(1)	C18-C17-C16	120.5(2)
O10 ⁱ -Ca1-O6 ⁱ	86.2(1)	O5-C9-C8	124.3(2)
O6-Ca1-O6 ⁱ	93.0(1)	O5-C9-C4	115.5(2)
O1-P1-O3	114.5(1)	C8-C9-C4	120.2(2)
O1-P1-O2	114.4(1)	C26-C25-C24	120.1(2)
O3-P1-O2	104.2(1)	C27-C26-C25	120.9(2)
O1-P1-C3	115.9(1)	C27-C28-C23	119.6(2)
O3-P1-C3	105.7(1)	C17-C16-C15	120.5(2)
O2-P1-C3	100.9(1)	C26-C27-C28	119.8(2)
C20-O10-Ca1	144.5(1)	O13-C22-O12	122.7(2)
C13-O8-C12	114.8(1)	O13-C22-C23	124.8(2)
C11-O6-Ca1	145.0(1)	O12-C22-C23	112.5(2)
O8-C12-C21 ⁱⁱ	106.5(1)	O9-C13-O8	122.9(2)
O8-C12-C11	114.8(1)	O9-C13-C14	125.2(2)
C21 ⁱⁱ -C12-C11	110.3(1)	O8-C13-C14	111.9(2)
P1-O1-Ca1	170.7(1)	C24-C23-C28	120.6(2)
C22-O12-C21	114.4(1)	C24-C23-C22	122.1(2)
C1-O2-P1	124.0(1)	C28-C23-C22	117.3(2)
O10-C20-O11	127.2(2)	C5-C4-C9	118.5(2)
O10-C20-C21	115.3(1)	C5-C4-C3	122.7(2)
O11-C20-C21	117.4(1)	C9-C4-C3	118.6(2)
C9-O5-C10	117.3(2)	C7-C6-C5	119.3(2)
O6-C11-O7	127.0(2)	C16-C15-C14	119.0(2)
O6-C11-C12	115.5(1)	O4-C3-C4	113.0(2)
O7-C11-C12	117.5(1)	O4-C3-P1	106.5(1)
C2-O3-P1	123.8(1)	C4-C3-P1	116.0(1)

Table S12. Selected torsion angles (°) of compound $Ca[(R)\text{-}1b \bullet H\text{-DBTA}]_2$. Symmetry codes: i 2 - x, y, 1 - z; ii x, 1 + y, z; iii x, -1 + y, z.

C13-O8-C12-C21 ⁱⁱ	-170.6(1)	O8-C13-C14-C19	164.3(2)
C13-O8-C12-C11	67.0(2)	O9-C13-C14-C15	161.1(2)
O1-P1-O2-C1	-16.1(2)	O8-C13-C14-C15	-17.5(3)
O3-P1-O2-C1	109.6(2)	C22-O12-C21-C12 ⁱⁱⁱ	-165.3(1)
C3-P1-O2-C1	-141.3(2)	C22-O12-C21-C20	74.1(2)
Ca1-O10-C20-O11	-48.2(3)	O10-C20-C21-O12	-173.1(1)
Ca1-O10-C20-C21	133.1(2)	O11-C20-C21-O12	8.1(2)
Ca1-O6-C11-O7	-49.6(3)	O10-C20-C21-C12 ⁱⁱⁱ	67.3(2)
Ca1-O6-C11-C12	132.7(2)	O11-C20-C21-C12 ⁱⁱⁱ	-111.5(2)
O8-C12-C11-O6	-164.5(1)	C28-C23-C24-C25	0.1(4)
C21-C12-C11-O6	75.2(2)	C22-C23-C24-C25	179.3(2)
O8-C12-C11-O7	17.6(2)	C7-C6-C5-C4	-0.2(3)
C21-C12-C11-O7	-102.7(2)	C9-C4-C5-C6	-0.6(3)
O1-P1-O3-C2	-16.2(2)	C3-C4-C5-C6	-175.8(2)

O2–P1–O3–C2	-141.9(2)	C15–C14–C19–C18	-1.0(3)
C3–P1–O3–C2	112.3(2)	C13–C14–C19–C18	177.2(2)
C21–O12–C22–O13	10.1(2)	C14–C19–C18–C17	-0.6(4)
C21–O12–C22–C23	-169.7(1)	C5–C6–C7–C8	0.8(3)
C12–O8–C13–O9	-3.6(3)	C9–C8–C7–C6	-0.5(4)
C12–O8–C13–C14	175.1(1)	C19–C18–C17–C16	1.0(4)
O13–C22–C23–C24	174.7(2)	C10–O5–C9–C8	2.7(3)
O12–C22–C23–C24	-5.5(3)	C10–O5–C9–C4	-177.5(2)
O13–C22–C23–C28	-6.0(3)	C7–C8–C9–O5	179.3(2)
O12–C22–C23–C28	173.8(2)	C7–C8–C9–C4	-0.4(3)
C5–C4–C3–O4	86.2(2)	C5–C4–C9–O5	-178.8(2)
C9–C4–C3–O4	-89.0(2)	C3–C4–C9–O5	-3.4(3)
C5–C4–C3–P1	-37.1(2)	C5–C4–C9–C8	0.9(3)
C9–C4–C3–P1	147.7(2)	C3–C4–C9–C8	176.3(2)
O1–P1–C3–O4	-58.5(1)	C23–C24–C25–C26	-0.5(4)
O3–P1–C3–O4	173.8(1)	C24–C25–C26–C27	0.3(5)
O2–P1–C3–O4	65.7(1)	C24–C23–C28–C27	0.6(4)
O1–P1–C3–C4	68.1(2)	C22–C23–C28–C27	-178.7(2)
O3–P1–C3–C4	-59.5(2)	C18–C17–C16–C15	0.3(4)
O2–P1–C3–C4	-167.7(1)	C14–C15–C16–C17	-2.0(4)
C16–C15–C14–C19	2.3(3)	C25–C26–C27–C28	0.3(5)
C16–C15–C14–C13	-175.8(2)	C23–C28–C27–C26	-0.8(4)
O9–C13–C14–C19	-17.0(3)		

Single crystal X-ray diffraction studies of optically active α -hydroxyphosphonate (R)-1b

Single crystals of compound (R)-1b, suitable for X-ray diffraction, were obtained by slow evaporation of acetone. The crystals were introduced into perfluorinated oil and a suitable single crystal was carefully mounted on the top of a thin glass wire. Data collection was performed with an Oxford Xcalibur 3 diffractometer equipped with a Spellman generator (50 kV, 40 mA) and a Kappa CCD detector, operating with Mo-K α radiation ($\lambda = 0.71071 \text{ \AA}$).

Data collection and data reduction were performed with the CrysAlisPro software.⁷ Absorption correction using the multiscan method⁷ was applied. The structures were solved with SHELXS-97,⁴ refined with SHELXL-97⁵ and finally checked using PLATON.⁶ Details for data collection and structure refinement are summarized in Table S13.

Table S13. Details for X-ray data collection and structure refinement for compound (R)-1b.

(R)-1b	
Empirical formula	C ₁₀ H ₁₅ O ₅ P
Formula mass	246.19
T[K]	123(2)
Crystal size [mm]	0.40 × 0.07 × 0.07
Crystal description	colorless needle
Crystal system	orthorhombic
Space group	<i>P</i> 212121
a [Å]	7.5686(4)
b [Å]	9.8996(6)
c [Å]	15.4712(8)
α [°]	90.0
β [°]	90.0
γ [°]	90.0
V [Å ³]	1159.20(11)
Z	4
$\rho_{\text{calcd.}}$ [g cm ⁻³]	1.411
μ [mm ⁻¹]	0.240
<i>F</i> (000)	520
Θ range [°]	2.63–25.24
Index ranges	-10 ≤ <i>h</i> ≤ 10

	-14 ≤ <i>k</i> ≤ 14
	-22 ≤ <i>l</i> ≤ 22
Reflns. collected	23514
Reflns. obsd.	3020
Reflns. unique	3529
	(<i>R</i> _{int} = 0.0584)
<i>R</i> ₁ , <i>wR</i> ₂ (2σ data)	0.0379, 0.0842
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0503, 0.0910
GOOF on <i>F</i> ²	1.026
Peak/hole [e Å ⁻³]	0.340/-0.222

Table S14. Selected bond lengths (Å) of compound (*R*)-**1b**.

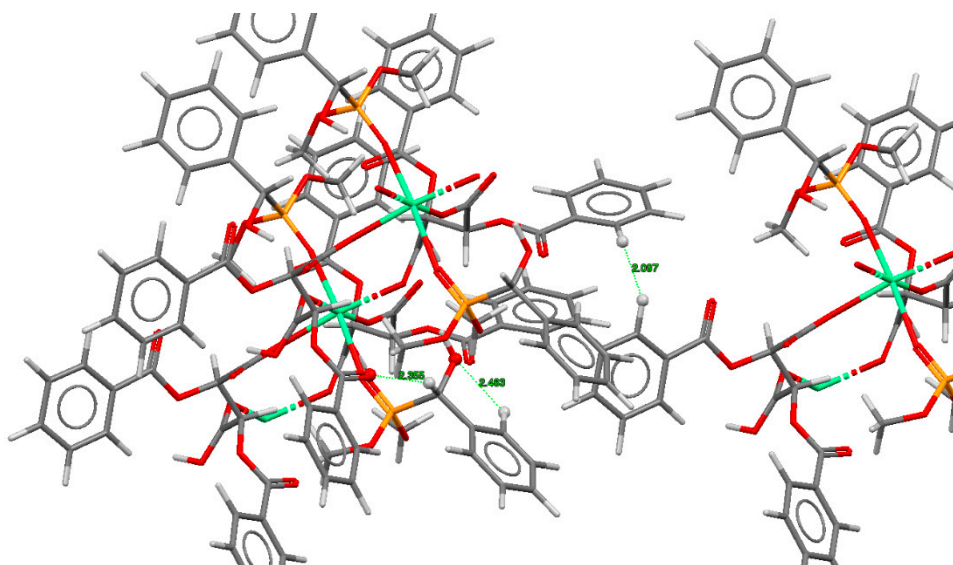
P1–O1	1.473(2)	O5–C10	1.429(3)
P1–O3	1.569(2)	C5–C6	1.392(4)
P1–O2	1.579(2)	C6–C7	1.383(4)
P1–C3	1.823(2)	C4–C9	1.406(3)
O3–C2	1.454(3)	C4–C3	1.518(3)
O4–C3	1.427(3)	C8–C7	1.386(4)
O2–C1	1.440(3)	C8–C9	1.395(3)
C4–C5	1.389(3)	C9–O5	1.365(3)

Table S15. Selected bond angles (°) of compound (*R*)-**1b**.

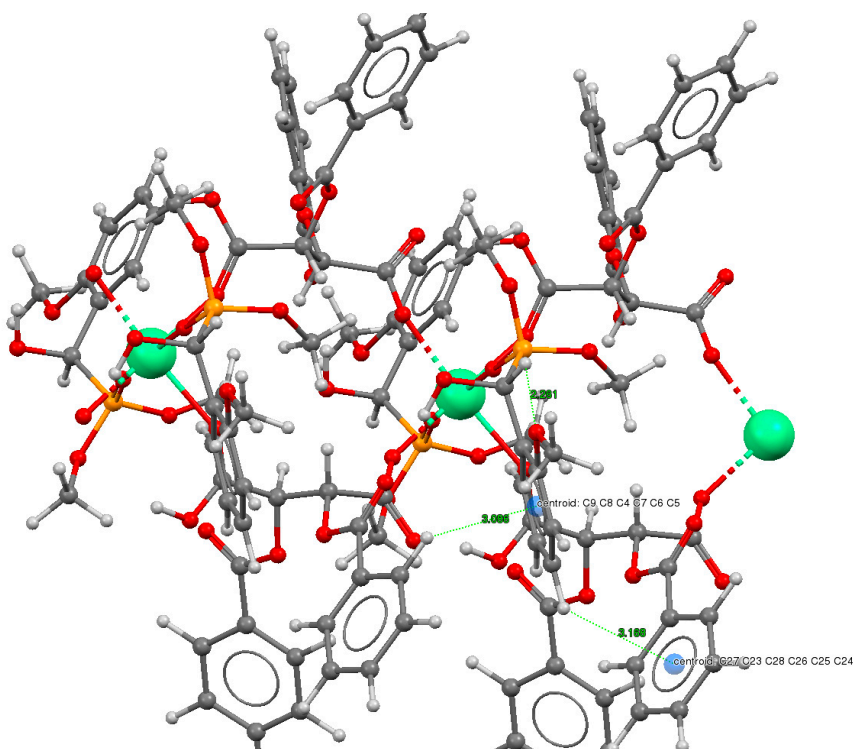
O1–P1–O3	111.0(1)	C7–C6–C5	119.4(3)
O1–P1–O2	114.8(1)	C6–C7–C8	120.9(2)
O3–P1–O2	103.1(1)	O4–C3–C4	112.3(2)
O1–P1–C3	113.9(1)	O4–C3–P1	104.9(1)
O3–P1–C3	107.4(1)	C4–C3–P1	111.0(2)
O2–P1–C3	105.9(1)	C7–C8–C9	119.5(3)
C2–O3–P1	121.7(2)	O5–C9–C8	124.2(2)
C1–O2–P1	121.8(2)	O5–C9–C4	115.5(2)
C5–C4–C9	118.7(2)	C8–C9–C4	120.3(2)
C5–C4–C3	121.2(2)	C9–O5–C10	117.9(2)
C9–C4–C3	120.1(2)	C4–C5–C6	121.1(3)

Table S16. Selected torsion angles (°) of compound (*R*)-**1b**.

O1–P1–O3–C2	165.3(2)	O2–P1–C3–C4	-175.6(2)
O2–P1–O3–C2	42.0(2)	C7–C8–C9–O5	178.2(2)
C3–P1–O3–C2	-69.6(2)	C7–C8–C9–C4	-0.6(4)
O1–P1–O2–C1	33.6(2)	C5–C4–C9–O5	-178.7(2)
O3–P1–O2–C1	154.4(2)	C3–C4–C9–O5	1.7(3)
C3–P1–O2–C1	-92.9(2)	C5–C4–C9–C8	0.1(3)
C5–C4–C3–O4	25.5(3)	C3–C4–C9–C8	-179.4(2)
C9–C4–C3–O4	-154.9(2)	C8–C9–O5–C10	-1.5(4)
C5–C4–C3–P1	-91.6(2)	C4–C9–O5–C10	177.3(2)
C9–C4–C3–P1	88.0(2)	C9–C4–C5–C6	0.5(3)
O1–P1–C3–O4	-64.1(2)	C3–C4–C5–C6	-180.0(2)
O3–P1–C3–O4	172.5(1)	C4–C5–C6–C7	-0.6(4)
O2–P1–C3–O4	62.9(2)	C5–C6–C7–C8	0.2(4)
O1–P1–C3–C4	57.4(2)	C9–C8–C7–C6	0.4(4)
O3–P1–C3–C4	-66.0(2)		



Supplementary Figure S1. A packing excerpt of $\text{Ca}[(S)\text{-1a}] \cdot (\text{H-DBTA})_2$ showing a central Ca-ion bound assembly with 2.35 Å between a benzyl C = O group and the H atom at the C_α atom as well as 2.43 Å of the O of the α -OH group to an o -H of **1a**. Relevant H atoms are drawn as small spheres.



Supplementary Figure S2. A packing excerpt of $\text{Ca}[(R)\text{-1b}] \cdot (\text{H-DBTA})_2$ showing a central Ca-ion bound assembly with the o -C-H distance to the center of the **1b** phenyl moiety at 3.09 Å. The p -C-H of the **1b** phenyl group approaches the next benzyl ring center at 3.17 Å.

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