Supporting Information

Umpolung of a Hydrogen Atom of Water by Using a Hexacoordinated Phosphate and Its Application to Deuteride Reduction Reactions of Carbonyl Compounds

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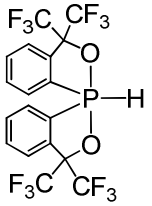
Contents



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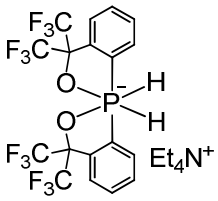
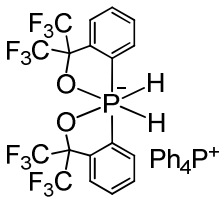


2a



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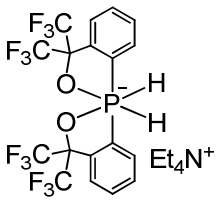

2a-*d*$_2$

1. General experimental procedures

Solvents were dried and purified before use by an MBRAUN MB-SPS solvent purification system. All reactions were carried out under argon atmosphere. All NMR spectra were measured with a JEOL AL400 spectrometer. Tetramethylsilane (TMS) was used as an external standard for the ^{1}H NMR (400 MHz), and ^{13}C NMR (100 MHz) spectra. CF_3CO_2H (δ –77.7) was used as an external standard for the ^{19}F NMR (376 MHz) spectra. FAB-Mass spectral data were obtained on JEOL JMS-700P. Infrared (IR) spectra were recorded on a JASCO V-530. Melting points were recorded with a Yanaco micro melting point apparatus and uncorrected. Elemental analyses were performed by the Microanalytical Laboratory of Department of Chemistry, Faculty of Science, The University of Tokyo. Phosphorane **1** was prepared according to the reported procedure[1].

2. Experimental procedures

Synthesis of dihydrophosphate 2a via the reaction of hydrophosphorane 1 with lithium naphthalenide

A THF solution of lithium naphthalenide (0.34 M, 8.8 ml, 3.0 mmol) was added to a THF solution (20 ml) of phosphorane **1** (516 mg, 1.0 mmol) at –78 ˚C under an argon atmosphere. After being stirred for 30 minutes, the reaction mixture was warmed to room temperature. The reaction mixture was quenched with water (1 ml) and stirred for 1 hour. Aqueous solution (5 ml) of tetraethylammonium bromide (315 mg, 1.5 mmol) was added to the reaction mixture, and then the solvents were removed under reduced pressure to give crude solid. Washing the solid with water and diethyl ether and recrystallization of the solid from acetone/$CHCl_3$ gave dihydrophosphate **2a** (296 mg, 46%) as colorless crystals.

Synthesis of dihydrophosphate 2a via the reaction of hydrophosphorane 1 with lithium aluminum hydride

A THF solution (30 ml) of phosphorane **1** (1.03 g, 2.0 mmol) was added to lithium aluminum hydride (0.15 g, 4.1 mmol) at room temperature. After stirring for 1 hour, the reaction mixture was cooled to 0 ˚C and slowly quenched with water (1 ml). After stirring for 30 minutes, the reaction mixture was filtered and the residue was washed with THF (3 × 10 ml). The combined filtrate and washings were added to aqueous solution (10 ml) of tetraethylammonium bromide (0.63 g, 3.0 mmol). After stirring for 10 minutes, solvents were removed under reduced pressure and the resulting solid was washed with water and ether. Recrystallization of the solid from acetone/ether gave dihydrophosphate **2a** (0.94 g, 73%).

2a: Colorless crystals, mp 136-137 ˚C (decomp). ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.15 (tt, $^3J_{HH}$ = 7.3 Hz, $^3J_{NH}$ = 1.7 Hz, 12H), 3.19 (q, $^3J_{HH}$ = 7.3 Hz, 8H), 6.78 (d, $^1J_{PH}$ = 342.4 Hz, 2H), 7.30-7.45 (m, 8H); ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 7.2 (s), 51.5 (t, $^1J_{NC}$ = 3 Hz), 77.4 (sept, $^2J_{CF}$ = 29 Hz), 123.7 (q, $^1J_{CF}$ = 289 Hz), 124.2 (d, J_{PC} = 16 Hz), 124.6 (q, $^1J_{CF}$ = 286 Hz), 125.1 (d, J_{PC} = 20 Hz), 127.8 (d, J_{PC} = 3 Hz), 129.1 (d, J_{PC} = 18 Hz), 129.8 (d, J_{PC} = 21 Hz), 150.3 (d, J_{PC} = 174 Hz); ^{19}F NMR (376 MHz, DMSO-d_6) δ –75.79 (q, $^4J_{FF}$ = 7.5 Hz, 6F), –75.50 (q, $^4J_{FF}$ = 7.5 Hz, 6F); ^{31}P NMR (162 MHz, DMSO-d_6) δ –169.1 (t, $^1J_{PH}$ = 342.5 Hz); MS (FAB, negative) *m/z* 517 $[M–Et_4N]^–$; MS (FAB, positive) *m/z* 130 $[Et_4N]^+$. Anal. Calcd for $C_{26}H_{30}F_{12}NO_2P$: C, 48.23; H, 4.67; N, 2.16. Found: C, 48.46; H, 4.84; N, 2.26.

Synthesis of dihydrophosphate 2b

Acetone (1 ml) was poured to a mixture of dihydrophosphate **2a** (194 mg, 0.30 mmol) and tetraphenylphosphonium iodide (140 mg, 0.30 mmol), and the suspension was stirred for 10 minutes at room temperature. After addition of water (10 ml), the resulting solid was filtered and washed with water. Recrystallization of the solid from CH_2Cl_2/hexane gave dihydrophosphate **2b** (233 mg, 91%).

Synthesis of dihydrophosphate 2b via the reaction of hydrophosphorane 1 with lithium aluminum hydride

A THF solution (5 ml) of phosphorane **1** (103 mg, 0.20 mmol) was added to lithium aluminum hydride (15 mg, 0.40 mmol) at room temperature. After stirring for 1 hour, the reaction mixture was cooled to 0 ˚C and slowly quenched with water (0.1 ml). After stirring for 30 minutes, the reaction mixture was filtered and the residue was

washed with THF (3 × 5 ml). The combined filtrate and washings were poured onto tetraphenylphosphonium iodide (93 mg, 0.20 mmol) and water (1 ml) was added to the mixture. After stirring for 10 minutes, solvents were removed under reduced pressure to give a colorless solid. The solid was washed with water and diethyl ether and redissolved in THF. The solution was filtered and the filtrate was evaporated. Recrystallization of the solid from acetone/diethyl ether gave dihydrophosphate **2b** (90 mg, 52%).

2b: Colorless crystals, mp 142-143 ˚C (decomp). ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.79 (d, $^{1}J_{PH}$ = 342.4 Hz, 2H), 7.30-7.45 (m, 8H), 7.68-7.84 (m, 16H), 7.92-7.98 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 77.3 (sept, $^{2}J_{CF}$ = 28 Hz), 117.8 (d, $^{1}J_{PC}$ = 89 Hz), 123.7 (q, $^{1}J_{CF}$ = 286 Hz), 124.2 (d, J_{PC} = 17 Hz), 124.6 (q, $^{1}J_{CF}$ = 288 Hz), 125.1 (d, J_{PC} = 19 Hz), 127.8 (d, J_{PC} = 3 Hz), 129.1 (d, J_{PC} = 17 Hz), 129.8 (d, J_{PC} = 21 Hz), 130.5 (d, J_{PC} = 12 Hz), 134.6 (d, J_{PC} = 11 Hz), 135.4 (d, J_{PC} = 2 Hz), 150.3 (d, J_{PC} = 174 Hz); ^{19}F NMR (376 MHz, DMSO-d_6) δ –75.78 (q, $^{4}J_{FF}$ = 7.9 Hz, 6F), –75.50 (q, $^{4}J_{FF}$ = 7.9 Hz, 6F); ^{31}P NMR (162 MHz, DMSO-d_6) δ –169.1 (t, $^{1}J_{PH}$ = 342.4 Hz), 23.3 (s); MS (FAB, negative) *m*/*z* 517 [M–Ph_4P]$^-$; MS (FAB, positive) *m*/*z* 339 [Ph_4P]$^+$. Anal. Calcd for $C_{42}H_{30}F_{12}O_2P_2$: C, 58.89; H, 3.53. Found: C, 58.91; H, 3.74.

H-D exchange experiments of dihydrophosphate 2a with D_2O

Deuterium oxide (0.05 ml, 2.8 mmol) was added to a DMSO-d_6 solution (0.5 ml) of **2a** (13 mg, 0.020 mmol). After standing the reaction mixture for 10 hours at room temperature, ^{1}H NMR spectrum showed no change.

Deuterium oxide (0.05 ml, 2.8 mmol) and triethylamine (0.03 ml, 0.2 mmol) were added to a DMSO-d_6 solution (0.5 ml) of **2a** (13 mg, 0.020 mmol). After standing the reaction mixture for 10 hours at room temperature, ^{1}H NMR spectrum showed no change.

Deuterium oxide (0.05 ml, 2.8 mmol) and acetic acid (1 μl, 0.02 mmol) were added to a DMSO-d_6 solution (0.5 ml) of **2a** (13 mg, 0.020 mmol). After standing the reaction mixture for 30 minutes at room temperature, ^{1}H, ^{19}F, and ^{31}P NMR spectra showed formation of dihydro-d_2-phosphate **2a-*d*$_2$** (90%, 95%D, estimated by ^{1}H and ^{19}F NMR spectroscopy). ^{31}P NMR (162 MHz, DMSO-d_6) δ –170.2 (quint, $^{1}J_{PD}$ = 52 Hz).

Synthesis of dihydro-*d*$_2$-phosphate 2a-*d*$_2$

Deuterium oxide (1.0 ml, 55 mmol) and acetic acid (0.01 M in THF, 1.5 ml, 0.015 mmol) were added to a THF solution (20 ml) of **2a** (324 mg, 0.50 mmol) at room temperature. After stirring for 30 minutes, evaporation and recrystallization from acetone/ether gave dihydro-d_2-phosphate **2a-*d*$_2$** (262 mg, 81%, 98%D).

Reduction of carbonyl compounds with dihydrophosphate 2a

A mixture of **2a** (129 mg, 0.20 mmol) and 4-phenylbenzaldehyde (37 mg, 0.20 mmol) was dissolved in THF (5 ml) and refluxed for 10 hours. After addition of aqueous solution of ammonium chloride, extraction with diethyl ether and evaporation gave a crude solid. The solid was separated by silica-gel chromatography to give **1** (82 mg, 80%) and 4-phenylbenzyl alcohol (31 mg, 85%). The products were identified by comparison of the data of ^{1}H

NMR, GC-MS, and TLC with those of the authentic samples.

The reaction of **2a** (129 mg, 0.20 mmol) with 4-phenylbenzaldehyde (37 mg, 0.20 mmol) in the presence of lithium chloride (9 mg, 0.2 mmol) at room temperature for 1 hour gave **1** (92 mg, 89%) and 4-phenylbenzyl alcohol (33 mg, 90%).

The reaction of **2a** (129 mg, 0.20 mmol) with 4-phenylbenzaldehyde (37 mg, 0.20 mmol) in the presence of acetic acid (0.06 ml, 1 mmol) at room temperature for 1 hour gave **1** (82 mg, 79%) and 4-phenylbenzyl alcohol (32 mg, 88%).

The reaction of **2a** (129 mg, 0.20 mmol) with hydrocinnamaldehyde (27 mg, 0.20 mmol) in the presence of lithium chloride (9 mg, 0.2 mmol) at room temperature for 1 hour gave **1** (88 mg, 85%) and 3-phenyl-1-propanol (20 mg, 72%).

The reaction of **2a** (129 mg, 0.20 mmol) with cinnamaldehyde (27 mg, 0.20 mmol) in the presence of acetic acid (0.35 ml, 6.0 mmol) at room temperature for 1 hour gave **1** (91 mg, 88%) and a mixture of cinnamyl alcohol and 3-phenyl-1-propanol (18 mg). Their yields were estimated to be 55% and 12%, respectively, by ^{1}H NMR spectroscopy.

The reaction of **2a** (129 mg, 0.20 mmol) with 4-acetylbiphenyl (39 mg, 0.20 mmol) in the presence of lithium chloride (85 mg, 2.0 mmol) at room temperature for 20 hours gave **1** (88 mg, 75%) and α-methyl-4-biphenylmethanol (24 mg, 61%).

Reduction of 4-phenylbenzaldehyde with dihydro-d_2-phosphate 2a-d_2

According to the general procedure for the reduction of carbonyl compounds with **2a**, a reaction of **2a-d_2** (130 mg, 0.20 mmol) with 4-phenylbenzaldehyde (37 mg, 0.20 mmol) in the presence of lithium chloride (9 mg, 0.2 mmol) at room temperature for 1 hour gave **1** (89 mg, 87%) and α-*d*-4-biphenylmethanol (31 mg, 83%, 95%D).

A similar reaction in the presence of water (0.4 ml, 22 mmol) gave **1** (92 mg, 89%) and α-*d*-4-biphenylmethanol (32 mg, 87%, 88%D).

One pot reaction of the H-D exchange of dihydrophosphate 2a and reduction of 4-phenylbenzaldehyde

Deuterium oxide (1.0 ml, 55 mmol) and acetic acid (0.017 ml, 0.30 mmol) were added to a THF solution (5 ml) of **2a** (129 mg, 0.20 mmol) at room temperature. After stirring for 30 minutes, a THF solution (3 ml) of 4-phenylbenzaldehyde (37 mg, 0.20 mmol) was added to it, and the reaction mixture was stirred for 1 hour at room temperature. Extraction with diethyl ether and evaporation gave a crude solid. Work up according to the general procedure for the reduction of carbonyl compounds gave **1** (88 mg, 85%) and α-*d*-4-biphenylmethanol (30 mg, 82%, 97%D).

3. NMR spectra of **2a** and **2b**

The ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectral charts of dihydrophosphates **2a** and **2b** are shown in Figures S1-S8.

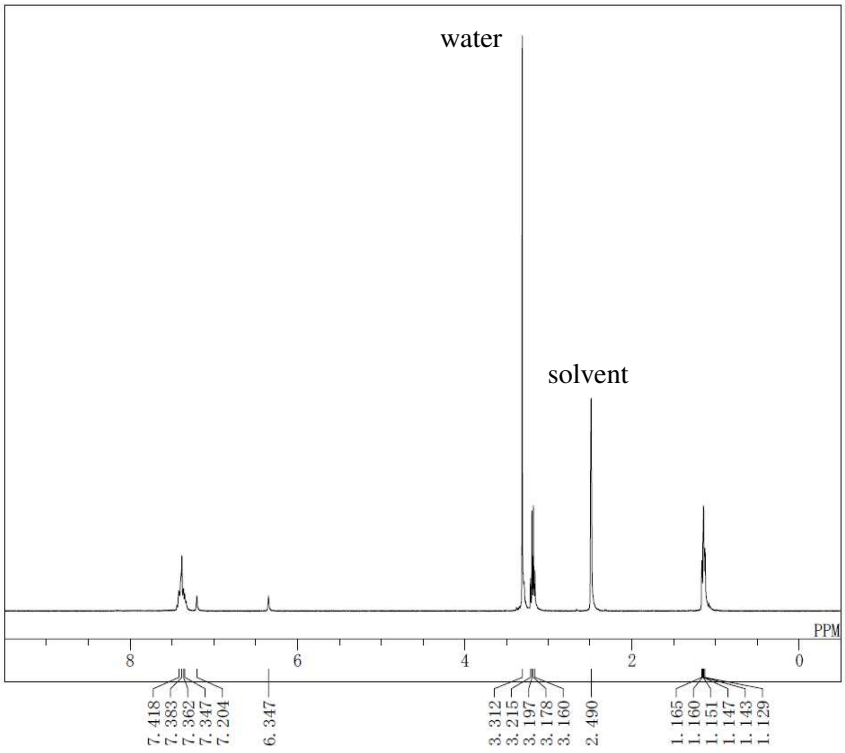

Figure S1. ^{1}H NMR spectrum of dihydrophosphate **2a** in DMSO-d_6.

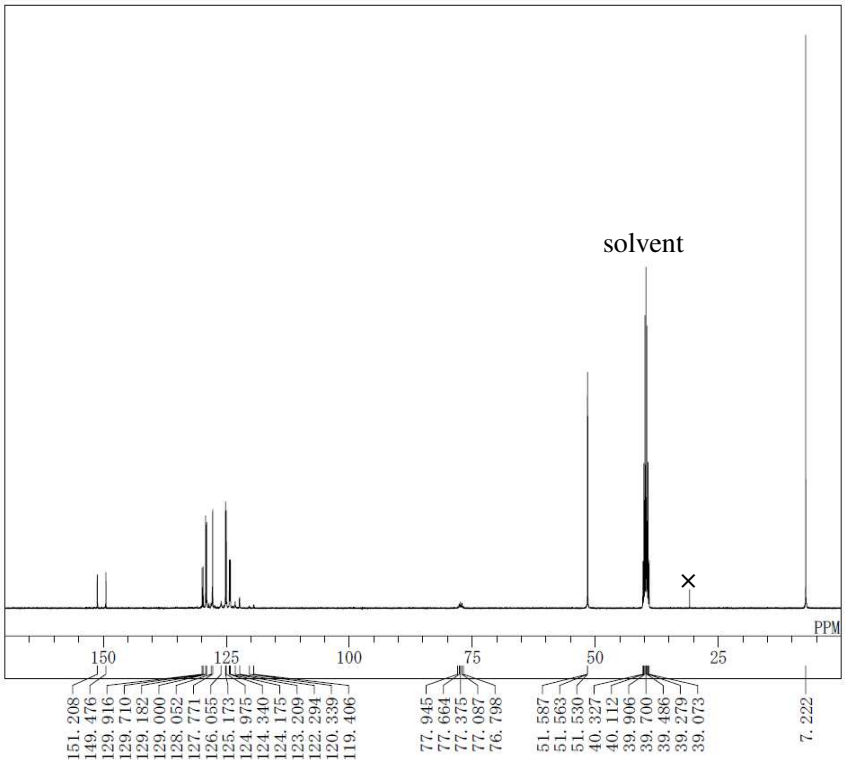

Figure S2. ^{13}C NMR spectrum of dihydrophosphate **2a** in DMSO-d_6.

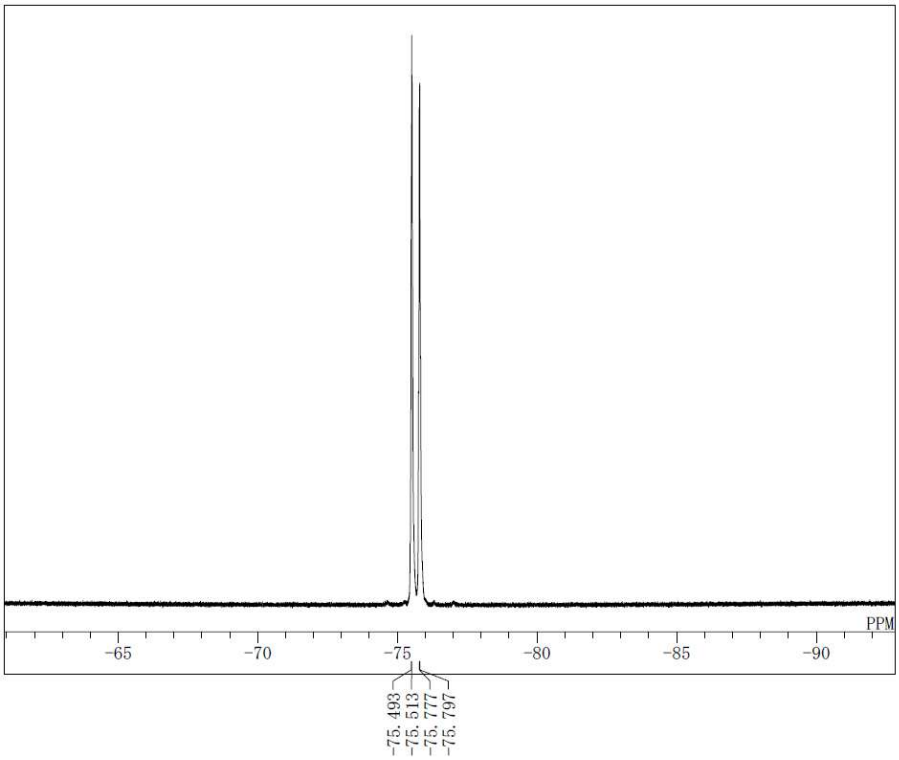

Figure S3. ^{19}F NMR spectrum of dihydrophosphate **2a** in DMSO-d_6.

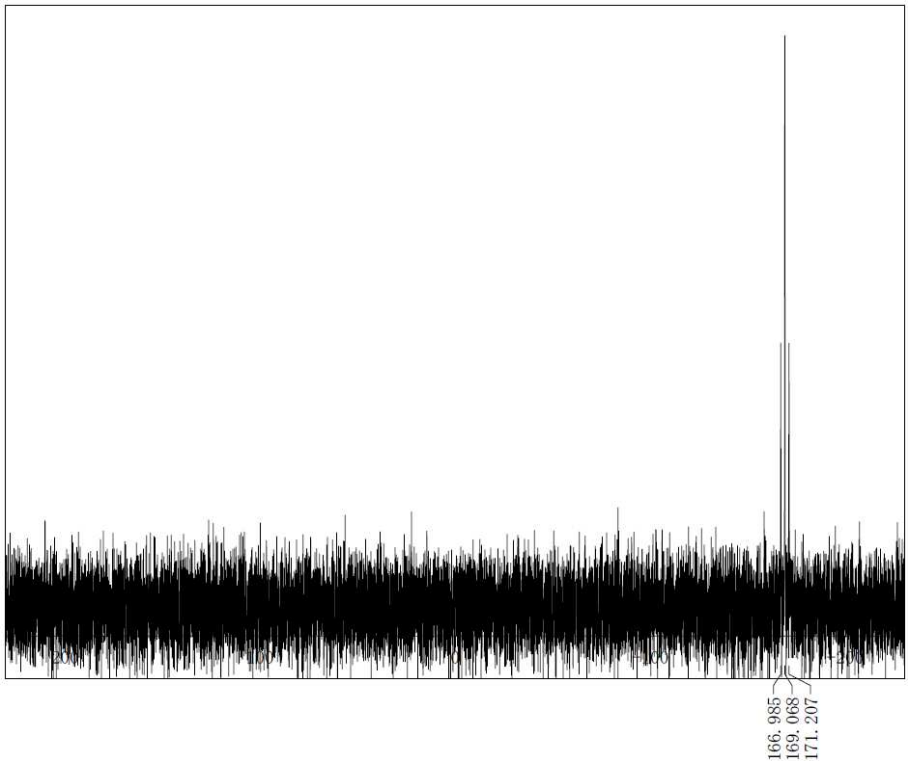

Figure S4. ^{31}P NMR spectrum of dihydrophosphate **2a** in DMSO-d_6.

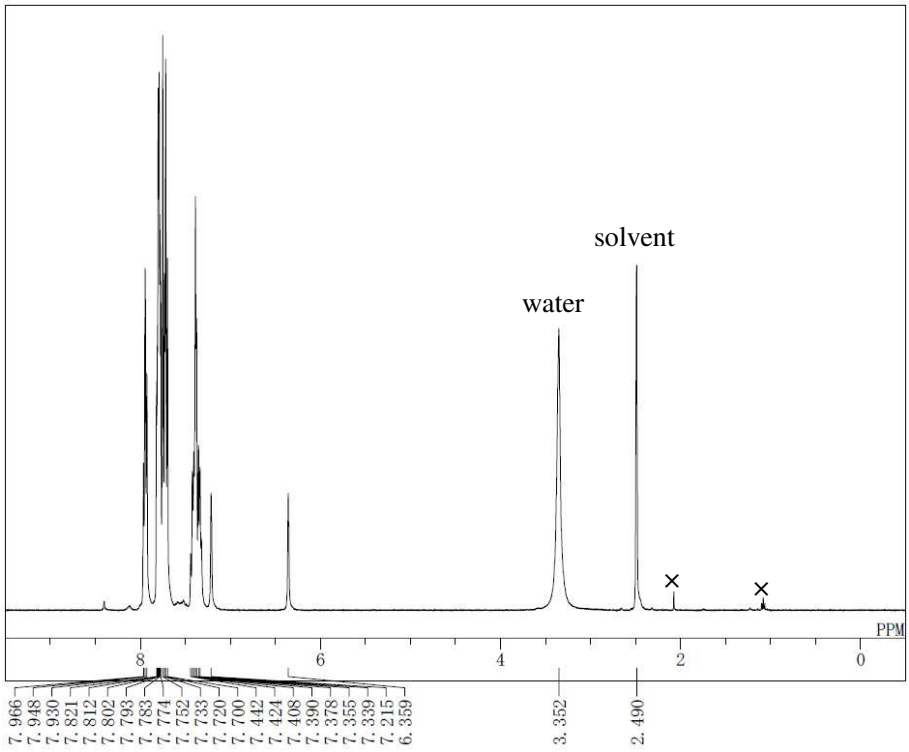

Figure S5. ^{1}H NMR spectrum of dihydrophosphate **2b** in DMSO-d_6.

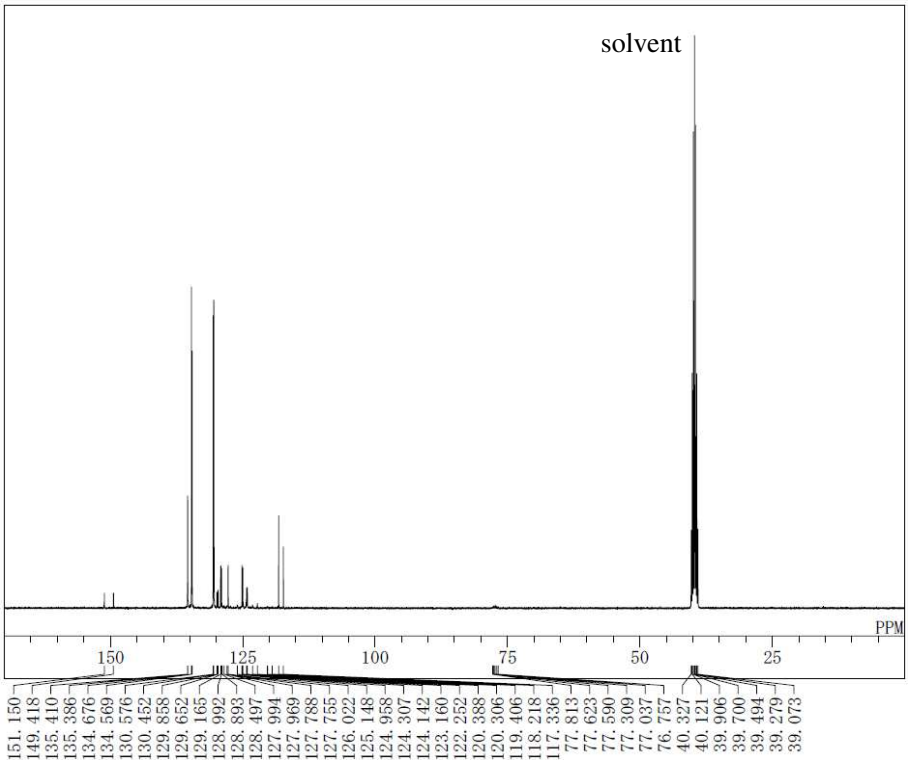

Figure S6. ^{13}C NMR spectrum of dihydrophosphate **2b** in DMSO-d_6.

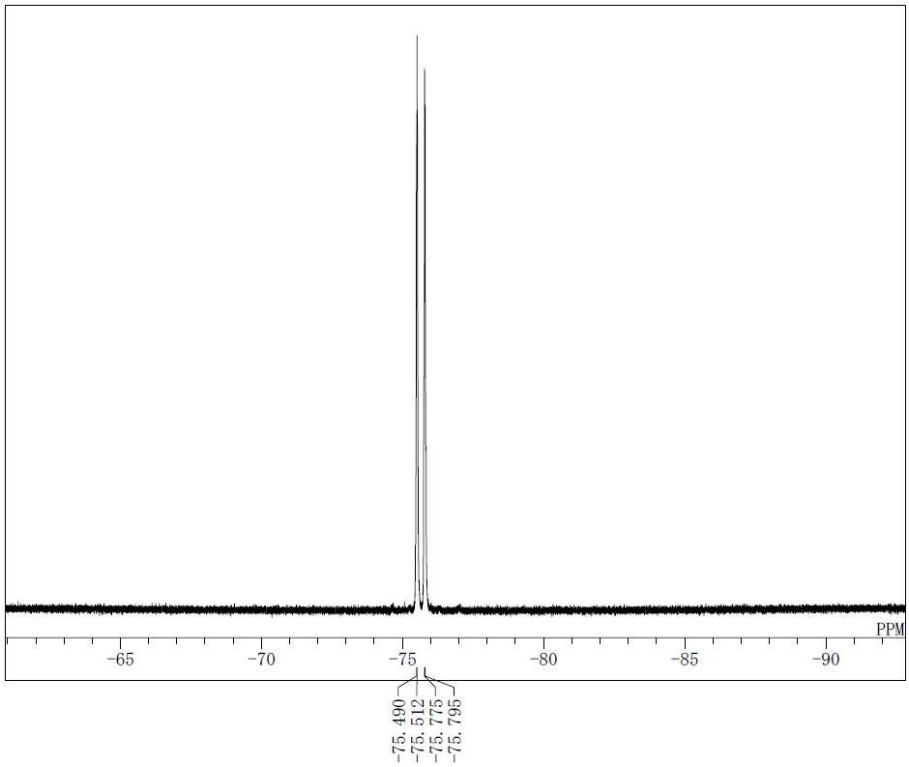

Figure S7. ^{19}F NMR spectrum of dihydrophosphate **2b** in DMSO-d_6.

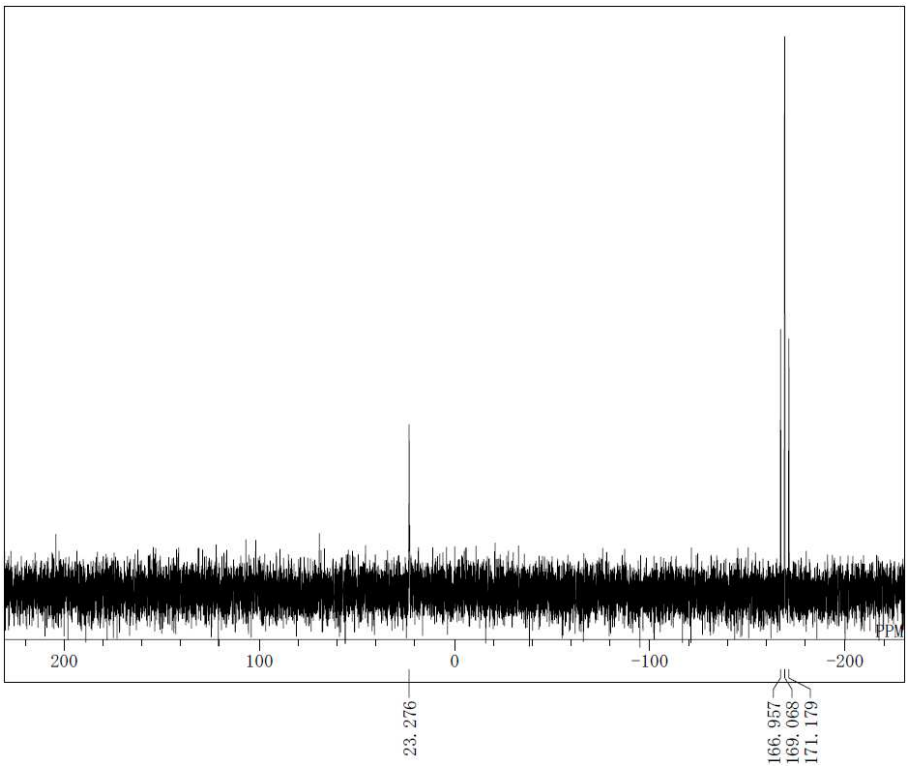

Figure S8. ^{31}P NMR spectrum of dihydrophosphate **2b** in DMSO-d_6.

.4. IR spectra of **2a**, **2b**, and, **2a-d_2**

All IR spectra were obtained in KBr pellets. The IR spectral charts of **2a**, **2b** and **2a-d_2** are shown in Figures S9-S11.

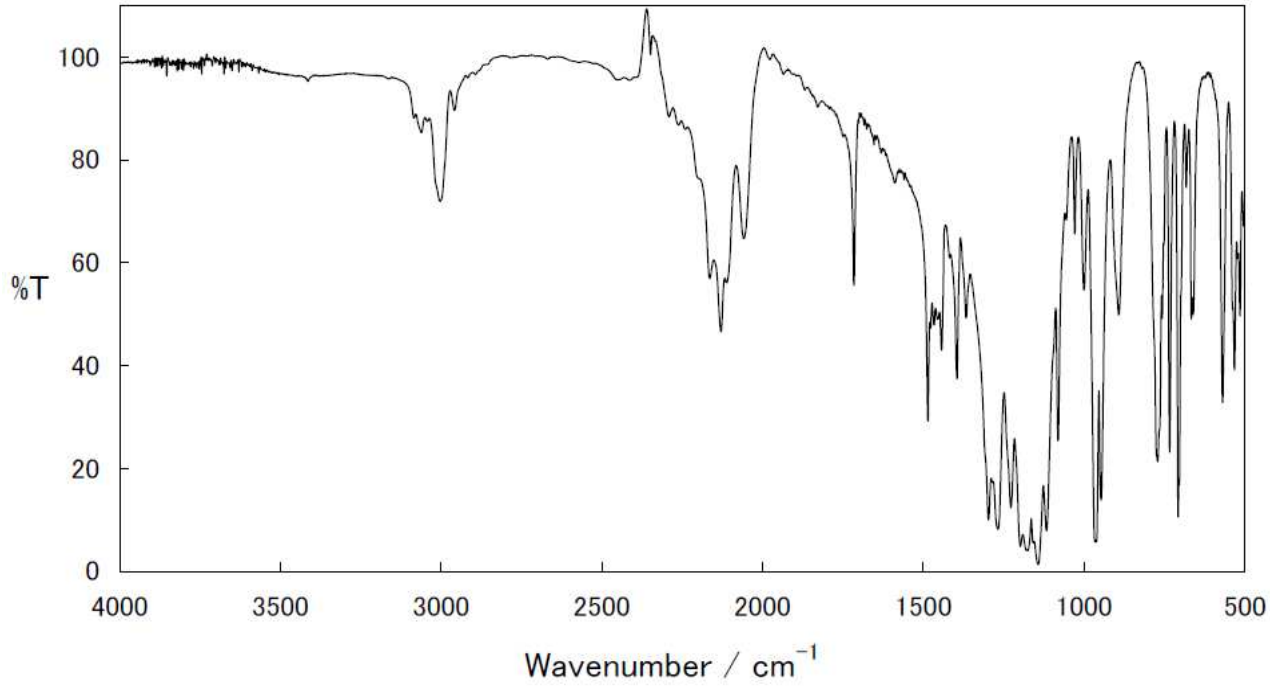

Figure S9. IR spectrum of dihydrophosphate **2a**.

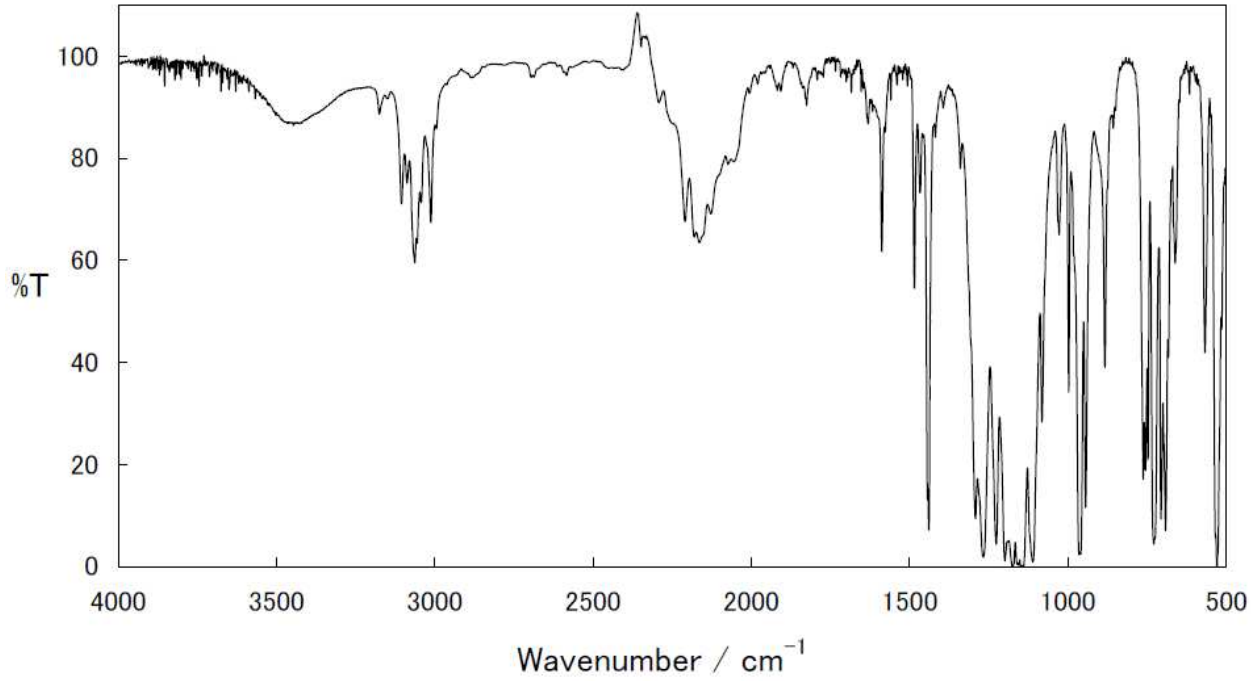

Figure S10. IR spectrum of dihydrophosphate **2b**.

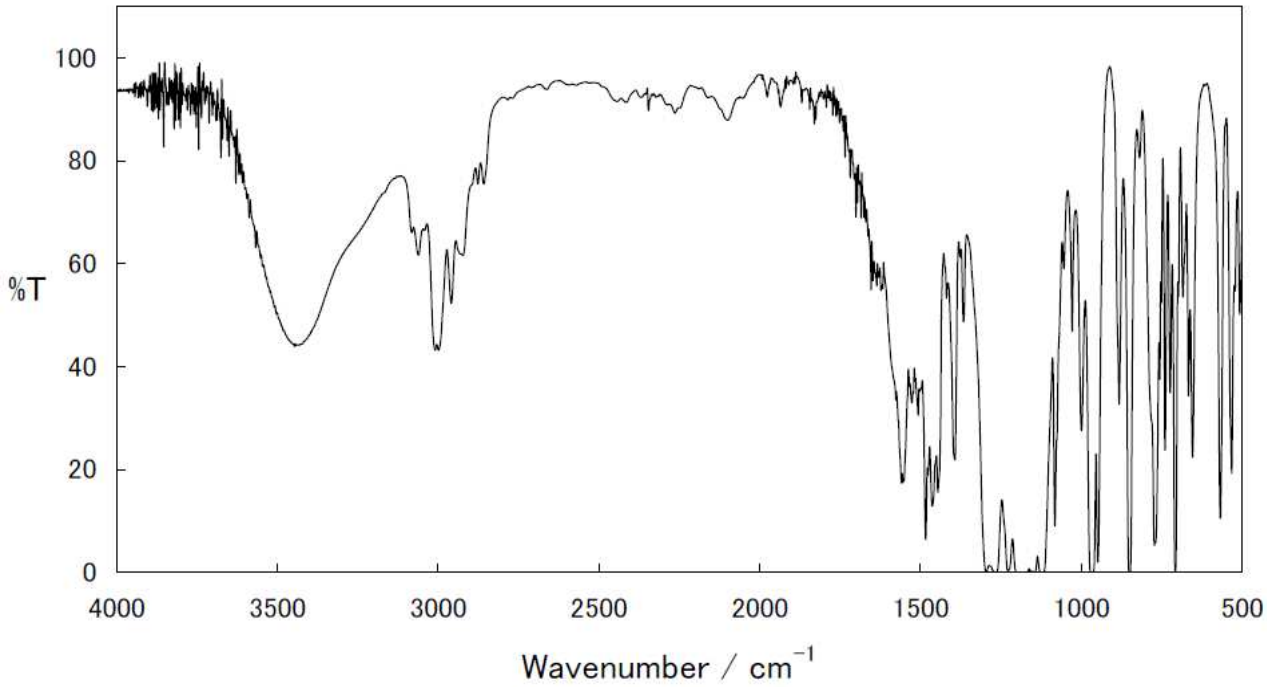

Figure S11. IR spectrum of dideuterophosphate **2a-*d*$_2$**.

5. X-ray crystallographic analysis of **2b**

Colorless crystals of **2b** were obtained by recrystallization from CH_2Cl_2 and used for the X-ray diffraction data collection on a Rigaku Mercury charge-coupled device diffractometer with a graphite-monochromated Mo–Kα radiation. Data were collected and processed using CrystalClear (Rigaku)[2]. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SHELXS-97) and expanded using Fourier techniques[3]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. The crystal data are summarized in Table S1. Atomic coordinates and equivalent isotropic displacement parameters are summarized in Table S2. Bond lengths and angles are shown in Table S3. Hydrogen coordinates and isotropic displacement parameters are shown in Table S4. Torsion angles are shown in Table S5. More crystal data are available at the Cambridge Crystallographic Data Centre, deposition no. CCDC 729102.

Table S1. Crystal data and structure refinement for dihydrophosphate **2b**

Empirical formula	C42 H30 F12 O2 P2	
Formula weight	856.60	
Temperature	120(2) K	
Wavelength	0.71070 Å	
Crystal system	Monoclinic	
Space group	*P*2/*n*	
Unit cell dimensions	a = 13.8932(17) Å	α = 90°.
	b = 7.3216(9) Å	β = 98.415(3)°.
	c = 18.572(3) Å	γ = 90°.
Volume	1868.8(4) Å^3	
Z	2	
Density (calculated)	1.522 Mg/m^3	
Absorption coefficient	0.215 mm^{-1}	
F(000)	872	
Crystal size	0.18 × 0.16 × 0.08 mm^3	
Theta range for data collection	3.15 to 25.00°.	
Index ranges	-13<=h<=16, -8<=k<=8, -22<=l<=17	
Reflections collected	11729	
Independent reflections	3248 [R(int) = 0.0265]	
Completeness to theta = 25.00°	98.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9830 and 0.9583	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3248 / 0 / 267	
Goodness-of-fit on F^2	1.064	
Final R indices [I>2sigma(I)]	R1 = 0.0377, wR2 = 0.0981	
R indices (all data)	R1 = 0.0470, wR2 = 0.1047	
Largest diff. peak and hole	0.411 and -0.325 e.Å^{-3}	

Table S2. Atomic coordinates (Å x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for dihydrophosphate **2b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	7500	2082(1)	7500	22(1)
C(1)	8450(2)	2326(3)	8297(1)	23(1)
C(2)	9316(2)	1366(3)	8391(1)	27(1)
C(3)	9963(2)	1545(3)	9032(1)	31(1)
C(4)	9733(2)	2672(3)	9578(1)	31(1)
C(5)	8865(2)	3643(3)	9494(1)	28(1)
C(6)	8230(1)	3456(3)	8849(1)	22(1)
C(7)	7235(1)	4386(3)	8646(1)	23(1)
O(1)	6845(1)	3913(2)	7946(1)	22(1)
C(8)	7342(2)	6477(3)	8686(1)	27(1)
F(1)	7983(1)	7061(2)	8273(1)	32(1)
F(2)	7652(1)	7089(2)	9366(1)	41(1)
F(3)	6508(1)	7342(2)	8460(1)	39(1)
C(9)	6527(2)	3744(3)	9159(1)	31(1)
F(4)	6407(1)	1933(2)	9111(1)	46(1)
F(5)	6829(1)	4116(2)	9864(1)	44(1)
F(6)	5642(1)	4475(2)	9005(1)	45(1)
P(2)	7500	6905(1)	2500	17(1)
C(10)	6861(1)	8371(3)	1817(1)	19(1)
C(11)	6272(1)	9734(3)	2047(1)	23(1)
C(12)	5763(1)	10901(3)	1541(1)	26(1)
C(13)	5855(2)	10731(3)	813(1)	28(1)
C(14)	6442(2)	9395(3)	585(1)	30(1)
C(15)	6947(1)	8203(3)	1083(1)	24(1)
C(16)	8330(1)	5437(3)	2126(1)	18(1)
C(17)	7937(1)	4113(3)	1617(1)	23(1)
C(18)	8551(2)	2943(3)	1325(1)	25(1)
C(19)	9548(2)	3061(3)	1536(1)	24(1)
C(20)	9933(1)	4329(3)	2045(1)	23(1)
C(21)	9326(1)	5532(3)	2340(1)	21(1)

Table S3. Bond lengths [Å] and angles [°] for dihydrophosphate **2b**.

P(1)-C(1)	1.842(2)	C(14)-C(15)	1.386(3)
P(1)-C(1)#1	1.842(2)	C(14)-H(9)	0.9500
P(1)-O(1)	1.8788(14)	C(15)-H(10)	0.9500
P(1)-O(1)#1	1.8788(14)	C(16)-C(21)	1.384(3)
P(1)-H(1)	1.354(18)	C(16)-C(17)	1.407(3)
C(1)-C(2)	1.382(3)	C(17)-C(18)	1.376(3)
C(1)-C(6)	1.386(3)	C(17)-H(11)	0.9500
C(2)-C(3)	1.390(3)	C(18)-C(19)	1.386(3)
C(2)-H(2)	0.9500	C(18)-H(12)	0.9500
C(3)-C(4)	1.380(3)	C(19)-C(20)	1.377(3)
C(3)-H(3)	0.9500	C(19)-H(13)	0.9500
C(4)-C(5)	1.388(3)	C(20)-C(21)	1.387(3)
C(4)-H(4)	0.9500	C(20)-H(14)	0.9500
C(5)-C(6)	1.388(3)	C(21)-H(15)	0.9500
C(5)-H(5)	0.9500		
C(6)-C(7)	1.537(3)	C(1)-P(1)-C(1)#1	168.88(13)
C(7)-O(1)	1.378(2)	C(1)-P(1)-O(1)	85.02(7)
C(7)-C(8)	1.538(3)	C(1)#1-P(1)-O(1)	87.05(7)
C(7)-C(9)	1.541(3)	C(1)-P(1)-O(1)#1	87.05(7)
C(8)-F(1)	1.328(2)	C(1)#1-P(1)-O(1)#1	85.02(8)
C(8)-F(3)	1.333(2)	O(1)-P(1)-O(1)#1	88.97(9)
C(8)-F(2)	1.351(2)	C(1)-P(1)-H(1)	92.4(8)
C(9)-F(6)	1.333(2)	C(1)#1-P(1)-H(1)	95.1(8)
C(9)-F(4)	1.338(3)	O(1)-P(1)-H(1)	176.0(8)
C(9)-F(5)	1.344(2)	O(1)#1-P(1)-H(1)	87.9(8)
P(2)-C(16)#2	1.7891(19)	C(2)-C(1)-C(6)	119.54(19)
P(2)-C(16)	1.7891(19)	C(2)-C(1)-P(1)	124.07(16)
P(2)-C(10)#2	1.7939(19)	C(6)-C(1)-P(1)	116.23(15)
P(2)-C(10)	1.7940(19)	C(1)-C(2)-C(3)	120.1(2)
C(10)-C(15)	1.391(3)	C(1)-C(2)-H(2)	119.9
C(10)-C(11)	1.397(3)	C(3)-C(2)-H(2)	119.9
C(11)-C(12)	1.385(3)	C(4)-C(3)-C(2)	119.7(2)
C(11)-H(6)	0.9500	C(4)-C(3)-H(3)	120.1
C(12)-C(13)	1.382(3)	C(2)-C(3)-H(3)	120.1
C(12)-H(7)	0.9500	C(3)-C(4)-C(5)	120.9(2)
C(13)-C(14)	1.380(3)	C(3)-C(4)-H(4)	119.5
C(13)-H(8)	0.9500	C(5)-C(4)-H(4)	119.5

C(6)-C(5)-C(4)	118.6(2)	C(12)-C(11)-C(10)	119.80(18)
C(6)-C(5)-H(5)	120.7	C(12)-C(11)-H(6)	120.1
C(4)-C(5)-H(5)	120.7	C(10)-C(11)-H(6)	120.1
C(1)-C(6)-C(5)	121.08(19)	C(13)-C(12)-C(11)	119.84(19)
C(1)-C(6)-C(7)	111.79(17)	C(13)-C(12)-H(7)	120.1
C(5)-C(6)-C(7)	127.13(18)	C(11)-C(12)-H(7)	120.1
O(1)-C(7)-C(6)	109.60(16)	C(14)-C(13)-C(12)	120.48(19)
O(1)-C(7)-C(8)	108.54(16)	C(14)-C(13)-H(8)	119.8
C(6)-C(7)-C(8)	110.65(16)	C(12)-C(13)-H(8)	119.8
O(1)-C(7)-C(9)	107.95(16)	C(13)-C(14)-C(15)	120.4(2)
C(6)-C(7)-C(9)	110.21(16)	C(13)-C(14)-H(9)	119.8
C(8)-C(7)-C(9)	109.84(17)	C(15)-C(14)-H(9)	119.8
C(7)-O(1)-P(1)	116.51(11)	C(14)-C(15)-C(10)	119.43(19)
F(1)-C(8)-F(3)	106.90(17)	C(14)-C(15)-H(10)	120.3
F(1)-C(8)-F(2)	106.53(17)	C(10)-C(15)-H(10)	120.3
F(3)-C(8)-F(2)	106.25(16)	C(21)-C(16)-C(17)	120.05(18)
F(1)-C(8)-C(7)	111.12(16)	C(21)-C(16)-P(2)	122.15(15)
F(3)-C(8)-C(7)	112.62(17)	C(17)-C(16)-P(2)	117.77(14)
F(2)-C(8)-C(7)	112.99(17)	C(18)-C(17)-C(16)	119.47(18)
F(6)-C(9)-F(4)	106.40(17)	C(18)-C(17)-H(11)	120.3
F(6)-C(9)-F(5)	105.95(18)	C(16)-C(17)-H(11)	120.3
F(4)-C(9)-F(5)	106.47(17)	C(17)-C(18)-C(19)	120.13(19)
F(6)-C(9)-C(7)	113.37(18)	C(17)-C(18)-H(12)	119.9
F(4)-C(9)-C(7)	110.24(18)	C(19)-C(18)-H(12)	119.9
F(5)-C(9)-C(7)	113.90(18)	C(20)-C(19)-C(18)	120.52(19)
C(16)#2-P(2)-C(16)	106.21(12)	C(20)-C(19)-H(13)	119.7
C(16)#2-P(2)-C(10)#2	111.39(8)	C(18)-C(19)-H(13)	119.7
C(16)-P(2)-C(10)#2	110.72(8)	C(19)-C(20)-C(21)	120.11(19)
C(16)#2-P(2)-C(10)	110.72(8)	C(19)-C(20)-H(14)	119.9
C(16)-P(2)-C(10)	111.38(8)	C(21)-C(20)-H(14)	119.9
C(10)#2-P(2)-C(10)	106.49(13)	C(16)-C(21)-C(20)	119.71(19)
C(15)-C(10)-C(11)	120.05(18)	C(16)-C(21)-H(15)	120.1
C(15)-C(10)-P(2)	122.39(15)	C(20)-C(21)-H(15)	120.1
C(11)-C(10)-P(2)	117.56(15)		

Symmetry transformations used to generate equivalent atoms: #1 -x+3/2,y,-z+3/2 #2 -x+3/2,y,-z+1/2

Table S4. Hydrogen coordinates (Å x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for dihydrophosphate **2b**.

	x	y	z	U(eq)
H(1)	8028(13)	840(30)	7186(10)	18(5)
H(2)	9469	583	8016	32
H(3)	10560	894	9095	37
H(4)	10174	2784	10017	37
H(5)	8710	4420	9871	34
H(6)	6220	9859	2549	28
H(7)	5353	11816	1694	31
H(8)	5511	11540	467	34
H(9)	6500	9291	83	36
H(10)	7348	7280	925	28
H(11)	7253	4028	1476	27
H(12)	8291	2052	978	30
H(13)	9969	2260	1327	29
H(14)	10617	4380	2195	28
H(15)	9592	6416	2687	25

Table S5. Torsion angles [°] for dihydrophosphate **2b**.

C(1)#1-P(1)-C(1)-C(2)	-133.05(18)	O(1)-C(7)-C(9)-F(6)	-59.2(2)
O(1)-P(1)-C(1)-C(2)	-177.73(18)	C(6)-C(7)-C(9)-F(6)	-178.86(17)
O(1)#1-P(1)-C(1)-C(2)	-88.51(18)	C(8)-C(7)-C(9)-F(6)	59.0(2)
C(1)#1-P(1)-C(1)-C(6)	51.65(15)	O(1)-C(7)-C(9)-F(4)	60.0(2)
O(1)-P(1)-C(1)-C(6)	6.97(15)	C(6)-C(7)-C(9)-F(4)	-59.7(2)
O(1)#1-P(1)-C(1)-C(6)	96.19(16)	C(8)-C(7)-C(9)-F(4)	178.14(16)
C(6)-C(1)-C(2)-C(3)	-0.4(3)	O(1)-C(7)-C(9)-F(5)	179.55(17)
P(1)-C(1)-C(2)-C(3)	-175.60(16)	C(6)-C(7)-C(9)-F(5)	59.9(2)
C(1)-C(2)-C(3)-C(4)	0.6(3)	C(8)-C(7)-C(9)-F(5)	-62.3(2)
C(2)-C(3)-C(4)-C(5)	-0.4(3)	C(16)#2-P(2)-C(10)-C(15)	-111.59(16)
C(3)-C(4)-C(5)-C(6)	0.2(3)	C(16)-P(2)-C(10)-C(15)	6.35(19)
C(2)-C(1)-C(6)-C(5)	0.2(3)	C(10)#2-P(2)-C(10)-C(15)	127.17(18)
P(1)-C(1)-C(6)-C(5)	175.69(15)	C(16)#2-P(2)-C(10)-C(11)	69.25(17)
C(2)-C(1)-C(6)-C(7)	-179.45(18)	C(16)-P(2)-C(10)-C(11)	-172.80(14)
P(1)-C(1)-C(6)-C(7)	-3.9(2)	C(10)#2-P(2)-C(10)-C(11)	-51.99(13)
C(4)-C(5)-C(6)-C(1)	0.0(3)	C(15)-C(10)-C(11)-C(12)	0.8(3)
C(4)-C(5)-C(6)-C(7)	179.53(19)	P(2)-C(10)-C(11)-C(12)	-179.98(15)
C(1)-C(6)-C(7)-O(1)	-3.0(2)	C(10)-C(11)-C(12)-C(13)	-1.1(3)
C(5)-C(6)-C(7)-O(1)	177.45(18)	C(11)-C(12)-C(13)-C(14)	0.6(3)
C(1)-C(6)-C(7)-C(8)	-122.63(18)	C(12)-C(13)-C(14)-C(15)	0.1(3)
C(5)-C(6)-C(7)-C(8)	57.8(3)	C(13)-C(14)-C(15)-C(10)	-0.3(3)
C(1)-C(6)-C(7)-C(9)	115.69(19)	C(11)-C(10)-C(15)-C(14)	-0.1(3)
C(5)-C(6)-C(7)-C(9)	-63.9(3)	P(2)-C(10)-C(15)-C(14)	-179.26(15)
C(6)-C(7)-O(1)-P(1)	8.57(19)	C(16)#2-P(2)-C(16)-C(21)	-123.05(18)
C(8)-C(7)-O(1)-P(1)	129.51(14)	C(10)#2-P(2)-C(16)-C(21)	-1.98(19)
C(9)-C(7)-O(1)-P(1)	-111.48(15)	C(10)-P(2)-C(16)-C(21)	116.32(16)
C(1)-P(1)-O(1)-C(7)	-8.98(14)	C(16)#2-P(2)-C(16)-C(17)	54.65(13)
C(1)#1-P(1)-O(1)-C(7)	178.83(14)	C(10)#2-P(2)-C(16)-C(17)	175.71(14)
O(1)#1-P(1)-O(1)-C(7)	-96.10(13)	C(10)-P(2)-C(16)-C(17)	-65.98(17)
O(1)-C(7)-C(8)-F(1)	-65.0(2)	C(21)-C(16)-C(17)-C(18)	-1.3(3)
C(6)-C(7)-C(8)-F(1)	55.3(2)	P(2)-C(16)-C(17)-C(18)	-179.08(15)
C(9)-C(7)-C(8)-F(1)	177.20(16)	C(16)-C(17)-C(18)-C(19)	0.5(3)
O(1)-C(7)-C(8)-F(3)	54.9(2)	C(17)-C(18)-C(19)-C(20)	0.9(3)
C(6)-C(7)-C(8)-F(3)	175.20(16)	C(18)-C(19)-C(20)-C(21)	-1.6(3)
C(9)-C(7)-C(8)-F(3)	-62.9(2)	C(17)-C(16)-C(21)-C(20)	0.7(3)
O(1)-C(7)-C(8)-F(2)	175.32(15)	P(2)-C(16)-C(21)-C(20)	178.34(14)
C(6)-C(7)-C(8)-F(2)	-64.4(2)	C(19)-C(20)-C(21)-C(16)	0.7(3)
C(9)-C(7)-C(8)-F(2)	57.5(2)		

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