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Supporting information for article:

Origin of the chemical stability of phosphine-phosphoramidites: structural study of an UPPhos-type crystal and application of UPPhos in the asymmetric hydrogenation of imines

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S1. Refinement

The isotropic displacement parameters of the hydrogen atoms were approximated from the *U*(eq) value of the atom they were bonded to (crystal data collection, structure refinement details are summarized in Table 1). Eight reflections were found to be shaded by the beamstop and removed from the data set.

Table S1 Experimental details

Crystal data	
Chemical formula	$C_{38}H_{35}NO_2P_2$
M_r	599.64
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	294
a, *b*, *c* (Å)	11.7931 (5), 10.4209 (5), 14.0792 (6)
β (°)	111.081 (2)
V (Å^3)	1614.5 (1)
Z, Z'	2, 1
Radiation type	Mo *Kα*
μ (mm^{-1})	0.17
Crystal size (mm)	0.60 x 0.38 x 0.31 (single crystal size)
Data collection	
Diffractometer	Rigaku R-AXIS-RAPID diffractometer
Absorption correction	Numerical Rigaku, (Higashi, 1999)
T_{min}, T_{max}	0.891, 0.964
No. of measured, independent and observed [$I > 2\sigma(I)$]reflections	46478, 5701, 4190
θ-range for data collection (°)	$3.101 \le \theta \le 25.027$
Index ranges	$-14 \le h \le 14$; $-12 \le k \le 12$; $-16 \le l \le 16$;
Completeness to 2θ max.	0.997
R_{int}	0.051
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.595

Refinement	
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0439, wR^2 = 0.0831
R indices (all data)	R_1 = 0.0658, wR^2 = 0.0899
Refinement method	Matrix least-squares of F^2
H-atom treatment	Atom parameters constrained
Data/restraints/parameters	5701, 1, 3914
Max. and mean shift/esd	0.000; 0.000
Largest diff. peak and hole $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.12, -0.15
Absolute structure	Flack x determined using 1519 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al*., 2013)
Absolute structure parameters:	
Flack parameter (x)	-0.02(3)
Hooft parameter (y)	-0.02(3)
Parsons parameter (z)	-0.02(3)

Computer programs: Crystal Clear V.1.4.1 (Rigaku/MSC, 2008), *SHELXL2015* (Sheldrick, 2015), Mercury (Macrae *et al*., 2008) and *PLATON* (Spek, 2009).

Atomic distances (Å)

P1-N1	1.641(3)	P1-O1'	1.667(3)
P1-O1	1.673(3)	P2-C1P	1.829(4)
P2-C7P	1.831(4)	P2-C15	1.870(4)
O1-C2	1.398(5)	O1'-C2'	1.401(5)
N1-C12	1.461(5)	N1-C11	1.483(5)
C1-C2	1.360(6)	C1-C9	1.446(6)
C1-C1'	1.486(6)	C2-C3	1.420(7)
C3-C4	1.357(8)	C4-C10	1.391(8)
C5-C6	1.348(8)	C5-C10	1.440(8)
C6-C7	1.376(8)	C7-C8	1.354(6)
C8-C9	1.409(6)	C9-C10	1.420(6)
C1'-C2'	1.366(5)	C1'-C9'	1.436(5)
C2'-C3'	1.404(6)	C3'-C4'	1.358(6)
C4'-C10'	1.408(6)	C5'-C6'	1.348(7)
C5'-C10'	1.419(6)	C6'-C7'	1.394(7)
C7'-C8'	1.366(6)	C8'-C9 '	1.414(5)

C9'-C10'	1.425(6)	C11-C14	1.525(6)
C11-C13	1.526(6)	C14-C15	1.532(6)
C15-C16	1.539(5)	C1P-C6P	1.384(6)
C1P-C2P	1.391(5)	C2P-C3P	1.384(6)
C3P-C4P	1.372(6)	C4P-C5P	1.366(6)
C5P-C6P	1.387(6)	C7P-C8P	1.397(5)
C7P-C12P	1.401(6)	C8P-C9P	1.378(6)
C9P-C10P	1.361(7)	C10P-C11P	1.365(8)
C11P-C12P	1.383(7)		

Bond angles (º)

N1-P1-O1'	96.8(2)	N1-P1-O1	107.8(2)
O1'-P1-O1	98.2(2)	C1P-P2-C7P	104.3(2)
C1P-P2-C15	103.3(2)	C7P-P2-C15	101.5(2)
C2-O1-P1	124.7(2)	C2'-O1'-P1	113.7(2)
C12-N1-C11	118.0(3)	C12-N1-P1	125.3(3)
C11-N1-P1	116.7(2)	C2-C1-C9	117.3(4)
C2-C1-C1'	120.5(4)	C9-C1-C1'	122.2(3)
C1-C2-O1	119.2(5)	C1-C2-C3	122.7(5)
O1-C2-C3	117.9(5)	C4-C3-C2	118.5(5)
C3-C4-C10	122.6(5)	C6-C5-C10	120.8(5)
C5-C6-C7	120.1(5)	C8-C7-C6	121.4(5)
C7-C8-C9	121.7(5)	C8-C9-C10	117.3(4)
C8-C9-C1	122.4(4)	C10-C9-C1	120.2(4)
C4-C10-C9	118.2(5)	C4-C10-C5	123.1(6)
C9-C10-C5	118.6(5)	C2'-C1'-C9'	117.4(4)
C2'-C1'-C1	119.8(4)	C9'-C1'-C1	122.7(3)
C1'-C2'-O1'	119.2(4)	C1'-C2'-C3'	123.2(4)
O1'-C2'-C3'	117.6(4)	C4'-C3'-C2'	119.4(4)
C3'-C4'-C10'	121.1(4)	C6'-C5'-C10'	120.5(5)
C5'-C6'-C7'	120.6(4)	C8'-C7'-C6'	120.9(5)
C7'-C8'-C9'	120.7(4)	C8'-C9'-C10'	117.9(4)
C8'-C9'-C1'	122.3(4)	C10'-C9'-C1'	119.8(4)

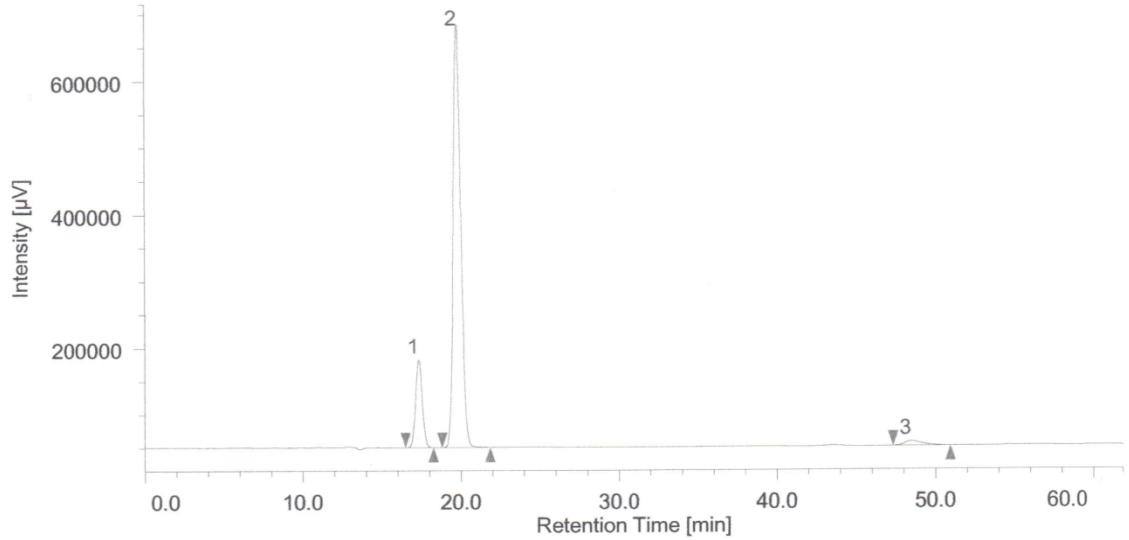
C4'-C10'-C5'	121.5(4)	C4'-C10'-C9'	118.9(4)
C5'-C10'-C9'	119.4(4)	N1-C11-C14	111.1(4)
N1-C11-C13	112.4(4)	C14-C11-C13	111.4(4)
C11-C14-C15	114.3(3)	C14-C15-C16	110.8(3)
C14-C15-P2	110.1(3)	C16-C15-P2	115.8(3)
C6P-C1P-C2P	117.1(4)	C6P-C1P-P2	122.6(3)
C2P-C1P-P2	119.9(4)	C3P-C2P-C1P	121.1(4)
C4P-C3P-C2P	121.0(4)	C5P-C4P-C3P	118.4(5)
C4P-C5P-C6P	121.2(5)	C1P-C6P-C5P	121.1(4)
C8P-C7P-C12P	116.3(4)	C8P-C7P-P2	126.5(3)
C12P-C7P-P2	117.1(4)	C9P-C8P-C7P	121.5(4)
C10P-C9P-C8P	120.5(5)	C9P-C10P-C11P	120.1(5)
C10P-C11P-C12P	120.0(5)	C11P-C12P-C7P	121.5(5)

Torsion angles (º)

N1-P1-O1-C2	-67.5(4)	O1'-P1-O1-C2	32.4(4)
N1-P1-O1'-C2'	168.2(3)	O1-P1-O1'-C2'	59.0(3)
O1'-P1-N1-C12	-36.8(5)	O1-P1-N1-C12	64.1(5)
O1'-P1-N1-C11	147.6(3)	O1-P1-N1-C11	-111.5(3)
C9-C1-C2-O1	176.4(3)	C1'-C1-C2-O1	-0.1(6)
C9-C1-C2-C3	-7.9(6)	C1'-C1-C2-C3	175.6(4)
P1-O1-C2-C1	-68.4(5)	P1-O1-C2-C3	115.6(4)
C1-C2-C3-C4	4.3(7)	O1-C2-C3-C4	-179.9(4)
C2-C3-C4-C10	1.0(8)	C10-C5-C6-C7	0.1(8)
C5-C6-C7-C8	-1.7(8)	C6-C7-C8-C9	1.4(7)
C7-C8-C9-C10	0.6(6)	C7-C8-C9-C1	178.5(4)
C2-C1-C9-C8	-171.3(4)	C1'-C1-C9-C8	5.1(5)
C2-C1-C9-C10	6.6(5)	C1'-C1-C9-C10	-177.0(4)
C3-C4-C10-C9	-2.1(7)	C3-C4-C10-C5	176.1(5)
C8-C9-C10-C4	176.2(4)	C1-C9-C10-C4	-1.7(6)

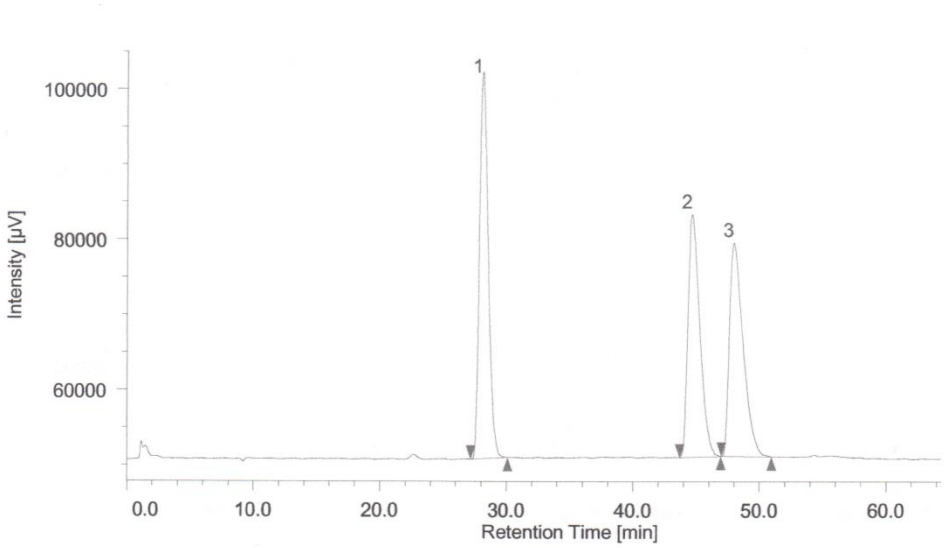
C8-C9-C10-C5	-2.0(6)	C1-C9-C10-C5	180.0(4)
C6-C5-C10-C4	-176.5(5)	C6-C5-C10-C9	1.7(7)
C2-C1-C1'-C2'	53.2(5)	C9-C1-C1'-C2'	-123.2(4)
C2-C1-C1'-C9'	-123.3(4)	C9-C1-C1'-C9'	60.4(5)
C9'-C1'-C2'-O1'	174.2(3)	C1-C1'-C2'-O1'	-2.5(5)
C9'-C1'-C2'-C3'	-5.7(5)	C1-C1'-C2'-C3'	177.6(4)
P1-O1'-C2'-C1'	-80.1(4)	P1-O1'-C2'-C3'	99.8(4)
C1'-C2'-C3'-C4'	2.4(6)	O1'-C2'-C3'-C4'	-177.5(3)
C2'-C3'-C4'-C10'	1.6(6)	C10'-C5'-C6'-C7'	-1.2(7)
C5'-C6'-C7'-C8'	0.5(7)	C6'-C7'-C8'-C9'	-0.1(7)
C7'-C8'-C9'-C10'	0.3(6)	C7'-C8'-C9'-C1'	176.5(4)
C2'-C1'-C9'-C8'	-171.0(4)	C1-C1'-C9'-C8'	5.6(6)
C2'-C1'-C9'-C10'	5.2(5)	C1-C1'-C9'-C10'	-178.3(3)
C3'-C4'-C10'-C5'	173.7(4)	C3'-C4'-C10'-C9'	-2.0(6)
C6'-C5'-C10'-C4'	-174.3(4)	C6'-C5'-C10'-C9'	1.4(6)
C8'-C9'-C10'-C4'	174.8(4)	C1'-C9'-C10'-C4'	-1.5(5)
C8'-C9'-C10'-C5'	-0.9(5)	C1'-C9'-C10'-C5'	-177.2(3)
C12-N1-C11-C14	65.0(5)	P1-N1-C11-C14	-119.0(3)
C12-N1-C11-C13	-60.6(6)	P1-N1-C11-C13	115.4(4)
N1-C11-C14-C15	58.1(5)	C13-C11-C14-C15	-175.8(4)
C11-C14-C15-C16	-169.3(4)	C11-C14-C15-P2	61.4(4)
C1P-P2-C15-C14	-175.4(3)	C7P-P2-C15-C14	76.7(3)
C1P-P2-C15-C16	58.0(4)	C7P-P2-C15-C16	-49.9(4)
C7P-P2-C1P-C6P	138.1(3)	C15-P2-C1P-C6P	32.2(4)
C7P-P2-C1P-C2P	-49.7(3)	C15-P2-C1P-C2P	-155.5(3)
C6P-C1P-C2P-C3P	0.1(6)	P2-C1P-C2P-C3P	-172.6(4)
C1P-C2P-C3P-C4P	0.0(7)	C2P-C3P-C4P-C5P	-0.4(7)
C3P-C4P-C5P-C6P	0.8(7)	C2P-C1P-C6P-C5P	0.2(7)
P2-C1P-C6P-C5P	172.7(4)	C4P-C5P-C6P-C1P	-0.7(8)
C1P-P2-C7P-C8P	-27.0(4)	C15-P2-C7P-C8P	80.2(4)
C1P-P2-C7P-C12P	156.1(3)	C15-P2-C7P-C12P	-96.7(3)
C12P-C7P-C8P-C9P	0.0(6)	P2-C7P-C8P-C9P	-177.0(3)
C7P-C8P-C9P-C10P	1.2(6)	C8P-C9P-C10P-C11P	-0.9(7)

C9P-C10P-C11P-C12I	-0.6(8)	C10P-C11P-C12P-C7P	1.8(7)
C8P-C7P-C12P-C11P	-1.5(6)	P2-C7P-C12P-C11P	175.8(4)



#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%
1	Unknown	2	17.321	3809645	131053	14.996	16.985
2	Unknown	2	19.743	21080854	633713	82.980	82.134
3	Unknown	2	48.445	514386	6797	2.025	0.881

Figure S1 HPLC chromatogram of quinaldine (**XI**) hydrogenation reaction mixture



#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%
1	Unknown	2	28.084	2463428	51428	33.643	43.650
2	Unknown	2	44.629	2094108	32301	28.599	27.416
3	Unknown	2	47.918	2132871	28427	29.129	24.128

Figure S2 HPLC chromatogram of *N*-(1-phenylethylidene)aniline (**VIII**) hydrogenation reaction mixture