SUPPLEMENTARY MATERIAL

Synthesis and Characterization of $t\text{Bu}_2\text{PN}=\text{P}(i\text{BuNCH}_2\text{CH}_2)_3\text{N}$: A New Bulky Electron-Rich Phosphine for Efficient Pd-Assisted Suzuki-Miyaura Cross- Coupling Reactions

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Experimental Section

Reagents and General Procedures. All reactions were carried out under dry argon using standard Schlenk techniques. Solvents were purified employing standard procedures¹ and were freshly distilled prior to use. Pro-azaphosphatranes **1a** and **1b** were prepared using literature procedures,^{2a,b} although they are also commercially available. Chlorophosphines and all other reagents were purchased from commercial sources and were used without further purification. Ammonia gas was condensed and dried over sodium prior to use. Compounds **2c** and **2e** were prepared using literature procedure.^{2c} Melting points were uncorrected. ¹H and ¹³C NMR spectra were recorded on a 400 or a 300 MHz NMR spectrometer. Proton spectra were calibrated with the signal due to residual protio-solvent. ³¹P{¹H} NMR spectra were recorded on a 162 MHz NMR spectrometer using 85% H₃PO₄ as the external standard. Thin layer chromatography (TLC) was performed using commercial 60 mesh silica gel plates visualized with short-wavelength UV (254 nm) light. X-ray data collections and structure solutions were conducted at the Iowa State Molecular Structure Laboratory.

Table 2. Pd(OAc)₂/4c catalyzed Suzuki cross-coupling of aryl bromides with arylboronic acids^a

Entry	Arylhalide	Arylboronic acid	Time (h)	Product	Yield (%) ^b
1			8		97 (Lit: 15-99) ^d 89 ^c
2			16		98 (Lit: 87-100) ^e
3			16		93 (Lit: 85-94) ^f
4			10		98 (Lit: 87-94) ^g
5			8		99 (Lit: 87-99) ^h 91 ^c
6			12		96 (Lit: 42) ⁱ
7			8		94 (Lit: 72-100) ^j 87 ^c
8			10		100 (Lit: 82-99) ^k
9			16		97 (Lit: 93) ^l
10			14		91 (Lit: 83-97) ^m
11			16		99 (Lit 86-91) ⁿ
12			14		96 (Lit: 73-96) ^o
13			14		92 (Lit: 26-96) ^p
14			16		95 (Lit:46-98) ^q

^a Reaction conditions: 2.0 mmol of aryl halide, 3.0 mmol of arylboronic acid, 4.0 mmol of Cs₂CO₃,

1.0 mol% Pd(OAc)₂, 2.0 mol% ligand **4c**, 5 mL of toluene, 80⁰C, 8 - 16 h. ^b Isolated yields (average of two runs). ^c Reaction using ligand **4c** pre-exposed to the atmosphere. ^d Refs 3a-3e, 3p, 4, 5d ^e Refs 3p, 4 ^f Refs 3f, 3g, 5b ^g Refs 3h, 3i ^h Refs 3j-3l ⁱ Ref 5i ^j Refs 3a, 3b, 3f, 3g, 3j, 3m, 3y, 3ab, 3af. ^k Refs 3n, 3o ^l Ref 3p ^m Refs 3p, 3aa, 3ab, 3ae ⁿ Refs 3q, 3r ^o Refs 3i, 3s, 3t ^p Refs 3u, 3v. ^q Refs 3a, 3ab, 3ad.

Table 3. Pd(OAc)₂/**4c** catalyzed Suzuki cross-coupling of aryl chlorides with arylboronic acids^a

Entry	Arylhalide	Arylboronic acid	Time (h)	Product	Yield (%) ^b
1			10		98 (Lit: 24-96) ^c
2			12		96 (Lit: 42-99) ^d
3			10		98 (Lit: 66-100) ^e
4			12		97 (Lit: 92-100) ^f
5			16		95 (Lit: 62-99) ^g
6			12		92 (Lit: 22-100) ^h
7			16		96 (Lit: 48-100) ⁱ
8			18		97 (Lit: 64-98) ^j
9			18		93 (Lit: 65-99) ^k

^aReaction conditions: 2.0 mmol of aryl halide, 3.0 mmol of arylboronic acid, 4.0 mmol of Cs₂CO₃, 2.0 mol% Pd(OAc)₂, 4.0 mol% ligand **4c**, 5 mL of toluene, 80⁰C, 10 - 18 h. ^b Isolated yields (average of two runs). ^c Refs 3m, 3af, 3ag. ^d Refs 3a, 3g, 5a, 5g. ^e Refs 3j, 3m, 3x, 5e. ^f Refs 3i, 3m, 3p, 3x, 3z, 3ah. ^g Refs 3i, 3j, 3p, 3z, 3ab, 3ai. ^h Refs 3a, 3e, 3g, 3i, 3j, 3p, 3x, 3z, 3ao-3ar, 3av, 5c, 5h. ⁱ Refs 3b, 3i, 3j, 3p, 3z, 3aj-3an, 3av, 5a, 5c, 5f. ^j Refs 3b, 3ak. ^k Refs 3b, 3ag, 3al, 3an, 3ao, 5a.

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^3P NMR, in CD_3CN

^{31}P NMR, in C_6D_6

^{31}P NMR, in C_6D_6

^3P NMR, in C_6D_6

^{31}P NMR, in C_6D_6

¹H NMR, in CDCl₃

Current Data Parameters
NAME JVK-925-H-CDCl3.fid
EXPNO 1
PROCNO 1

7.762
7.755
7.751
7.743
7.675
7.671
7.666
7.657
7.654
7.651
7.562
7.559
7.542
7.537
7.526
7.523
7.498
7.495
7.491
7.476

Entry 1, Table 2 & 3

^{13}C NMR, in CDCl_3

Current Data Parameters
NAME JVK-925-C-CDCl3.fid
EXPNO 1
PROCNO 1

Entry 1, Table 2 & 3

¹H NMR, in CDCl₃

JVK-857 After column
in CDCl₃

Current Data Parameters
NAME JVK-857-H-CDCl₃.fid
EXPNO 1
PROCNO 1

Entry 2, Table 2 & 3

¹³C NMR, in CDCl₃

Current Data Parameters
NAME JVK-857-C-CDCl3.fid
EXPNO 1
PROCNO 1

Entry 2, Table 2 & 3

JVK-801 4-Br-Ph-CN+ o-tolyl-B(OH)2
After column, white solid

¹H NMR, in CDCl₃

Current Data Parameters
NAME JVK-801-H-CDCl3.fid
EXPNO 1
PROCNO 1

Entry 3, Table 2

¹H NMR, in CDCl₃

JVK-880 White solid after column
in CDCl₃

Current Data Parameters
NAME JVK-880-H-CDCl₃-1.fid
EXPNO 1
PROCNO 1

7.532
7.529
7.521
7.517
7.490
7.487
7.484
7.474
7.469
7.469
7.450
7.406
7.405
7.404
7.401
7.399
7.393
7.391
7.388
7.386
7.385
7.380
7.373
7.368
7.314
7.311
7.295
7.292
7.276
7.273
7.256
7.252
7.249
7.246
7.229
7.226

Entry 4, Table 2

JVK-880

^{13}C NMR, in CDCl_3

Current Data Parameters
NAME JVK-880-C-CDCl3-1.fid
EXPNO 1
PROCNO 1

161.149
158.689
135.982
130.963
130.929
129.299
129.229
129.200
129.169
129.087
128.610
127.830
124.536
124.499
116.370
116.143

77.556
77.236
76.922

Entry 4, Table 2

¹H NMR, in CDCl₃

JVK-838 After column,
Ph-B(OH)2 + 3-Br-C6H4-COOCH3
in CDCl₃

Current Data Parameters
NAME JVK-838-H-CDCl3-pure.fid
EXPNO 1
PROCNO 1

Entry 5, Table 2

¹³C NMR, in CDCl₃

Current Data Parameters
NAME JVK-838-C-CDCl3-pure.fid
EXPNO 1
PROCNO 1

Entry 5, Table 2

¹H NMR, in CDCl₃

JVK-865 colorless oil after column
in CDCl₃

Current Data Parameters
NAME JVK-865-H-CDCl₃.fid
EXPNO 1
PROCNO 1

8.243	7.540	7.564	7.576	7.582	7.596	7.615	7.616	7.709	7.713	7.714	7.717	7.728	7.732	7.733	7.849	7.868	7.870	7.907	7.927	7.939	7.940	7.959	7.960	7.962	8.144	8.147	8.148	8.152	8.164	8.167	8.168	8.171	8.233	8.234	8.237	8.238	8.242	8.243
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Entry 6, Table 2

¹³C NMR, in CDCl₃

JVK-865 colorless oil after column
in CDCl₃

Current Data Parameters
NAME JVK-865-C-CDCl₃.fid
EXPNO 1
PROCNO 1

Entry 6, Table 2

¹H NMR, in CDCl₃

JVK-856 White solid after column
in CDCl₃

Current Data Parameters
NAME JVK-856-H-CDCl₃.fid
EXPNO 1
PROCNO 1

8.060
8.039
7.713
7.692
7.657
7.654
7.635
7.507
7.489
7.470
7.435
7.417
7.270

Entry 7, Table 2
Entry 6, Table 3

^{13}C NMR, in CDCl_3

JVK-856 After column
in CDCl_3

Current Data Parameters
NAME JVK-856-C- CDCl_3 .fid
EXPNO 1
PROCNO 1

Entry 7, Table 2
Entry 6, Table 3

¹H NMR, in CDCl₃

JVK-862 white solid after column
in CDCl₃

Current Data Parameters
NAME JVK-862-H-CDCl₃.fid
EXPNO 1
PROCNO 1

7.914
7.903
7.901
7.882
7.633
7.629
7.617
7.612
7.583
7.565
7.562
7.559
7.545
7.542
7.525
7.521
7.498
7.495
7.478
7.474
7.460
7.457
7.442
7.439

Entry 8, Table 2

¹³C NMR, in CDCl₃

JVK-862 White solid after column
in CDCl₃

Current Data Parameters
NAME JVK-862-C-CDCl₃.fid
EXPNO 1
PROCNO 1

Entry 8, Table 2

¹H NMR, in CDCl₃

JVK-844 White solid after column
in CDCl₃

Current Data Parameters
NAME JVK-844-H-CDCl₃.fid
EXPNO 1
PROCNO 1

7.527
7.516
7.511
7.408
7.393
7.390
7.389
7.383
7.369
7.321
7.319
7.301
7.300
7.298
7.123
7.120
7.104
7.062
7.042

3.877

2.476

Entry 9, Table 2

¹³C NMR, in CDCl₃

JVK-844 After column
in CDCl₃

Current Data Parameters
NAME JVK-844-C-CDCl₃.fid
EXPNO 1
PROCNO 1

Entry 9, Table 2

¹H NMR, in CDCl₃

JVK-832 white solid in CDCl₃

Current Data Parameters
NAME JVK-832-H-CDCl₃.fid
EXPNO 1
PROCNO 1

Entry 10, Table 2

^{13}C NMR, in CDCl_3

JVK-832 White solid in CDCl_3 //After column

Current Data Parameters
NAME JVK-832-C- CDCl_3 .fid
EXPNO 1
PROCNO 1

Entry 10, Table 2

¹H NMR, in CDCl₃

JVK-843 colorless oil after column
in CDCl₃

Current Data Parameters
NAME JVK-843-H-CDCl₃.fid
EXPNO 1
PROCNO 1

8.030
8.029
8.008
7.982
7.963
7.930
7.922
7.915
7.907
7.608
7.590
7.587
7.578
7.574
7.570
7.563
7.557
7.555
7.548
7.540
7.517
7.513
7.508
7.505
7.500
7.496
7.491
7.487
7.476
7.471
7.389
7.388
7.368
7.270
2.533

Entry 11, Table 2

JVK-843 After column
in CDCl₃

¹³C NMR, in CDCl₃

Current Data Parameters
NAME JVK-843-C-CDCl₃.fid
EXPNO 1
PROCNO 1

Entry 11, Table 2

¹H NMR, in CDCl₃

JVK-836 Pale yellow solid
Ph-B(OH)₂ + p-Me₂N-C₆H₄-Br

Current Data Parameters
NAME JVK-836-H-CDCl₃.fid
EXPNO 1
PROCNO 1

7.591
7.588
7.570
7.567
7.541
7.519
7.416
7.396
7.270
6.842
6.820

Entry 12, Table 2

¹³C NMR, in CDCl₃

JVK-836 After column, white solid
Ph-B(OH)₂ + p-Me₂N-C₆H₄-Br

Entry 12, Table 2

Current Data Parameters
NAME JVK-836-C-CDCl₃.fid
EXPNO 1
PROCNO 1

¹H NMR, in CDCl₃

JVK-833 After column, white solid
in CDCl₃

Current Data Parameters
NAME JVK-833-H-CDCl₃-2.fid
EXPNO 1
PROCNO 1

7.507
7.490
7.485
7.481
7.464
7.459
7.270
7.269
6.973
6.957
6.951
6.828
6.811
6.806

3.859
3.853

3.002
2.997

Entry 13, Table 2

JVK-833 After column, white solid
in CDCl₃

¹³C NMR, in CDCl₃

Current Data Parameters
NAME JVK-833-C-CDCl₃-2.fid
EXPNO 1
PROCNO 1

Entry 13, Table 2

JVK-829 White solid after column
4-Br-anisole + p-MeO-C6H4B(OH)2

¹H NMR, in CDCl₃

Current Data Parameters
NAME JVK-829-H-CDCl3.fid
EXPNO 1
PROCNO 1

7.502
7.480
7.270
6.983
6.961

Entry 14, Table 2

JVK-829 White solid after column
4-Br-anisole + p-MeO-C₆H₄B(OH)₂

¹³C NMR, in CDCl₃

Current Data Parameters
NAME JVK-829-C-CDCl3.fid
EXPNO 1
PROCNO 1

Entry 14, Table 2

¹H NMR, in CDCl₃

JVK-838 white solid in CDCl₃
from 4-Cl-C₆D₄-COOMe + Ph-B(OH)₂

Current Data Parameters
NAME JVK-838-H-CDCl₃.fid
EXPNO 1
PROCNO 1

8.135
8.108
7.691
7.664
7.662
7.657
7.652
7.629
7.485
7.459
7.430
7.273
7.272
7.270

Entry 3, Table 3

^{13}C NMR, in CDCl_3

JVK-838 White solid in CDCl_3 //After column

Current Data Parameters
NAME JVK-838-C- CDCl_3 .fid
EXPNO 1
PROCNO 1

Entry 3, Table 3

JVK-858 After column
in CDCl₃

¹H NMR, in CDCl₃

Current Data Parameters
NAME JVK-858-H-CDCl₃.fid
EXPNO 1
PROCNO 1

Entry 4, Table 3

JVK-858 After column
in CDCl₃

¹³C NMR, in CDCl₃

Current Data Parameters
NAME JVK-858-C-CDCl₃.fid
EXPNO 1
PROCNO 1

Entry 4, Table 3

¹H NMR, in CDCl₃

JVK-873 After column
oil, slowly solidified
in CDCl₃

Current Data Parameters
NAME JVK-873-H-CDCl3.fid
EXPNO 1
PROCNO 1

10.057
7.963
7.959
7.947
7.943
7.758
7.753
7.741
7.737
7.655
7.651
7.646
7.638
7.634
7.632
7.515
7.512
7.494
7.490
7.479
7.475
7.454
7.450
7.447
7.433

Entry 5, Table 3

JVK-873 After column
oil Solidified
in CDCl₃

¹³C NMR, in CDCl₃

Current Data Parameters
NAME JVK-873-C-CDCl₃.fid
EXPNO 1
PROCNO 1

Entry 5, Table 3

¹H NMR, in CDCl₃

JVK-867 Oil crystallized after column
in CDCl₃

Current Data Parameters
NAME JVK-867-H-CDCl₃.fid
EXPNO 1
PROCNO 1

7.736
7.732
7.717
7.715
7.712
7.649
7.645
7.633
7.629
7.577
7.559
7.556
7.543
7.539
7.475
7.457
7.392
7.373

Entry 7, Table 3

JVK-867 Oil crystallized after column
in CDCl₃

¹³C NMR, in CDCl₃

Current Data Parameters
NAME JVK-867-C-CDCl₃.fid
EXPNO 1
PROCNO 1

Entry 7, Table 3

¹H NMR, in CDCl₃

JVK-868 Colorless oil after column
in CDCl₃

Current Data Parameters
NAME JVK-868-H-CDCl₃.fid
EXPNO 1
PROCNO 1

7.476
7.473
7.470
7.461
7.460
7.454
7.449
7.441
7.436
7.316
7.313
7.312
7.309
7.297
7.294
7.293
7.290
7.265
7.259
7.255
7.025
7.022
7.018
7.016
7.004
7.002
6.998
6.995
3.944

Entry 8, Table 3

^{13}C NMR, in CDCl_3

JVK-868 Colorless oil after column
in CDCl_3

Current Data Parameters
NAME JVK-868-C- CDCl_3 .fid
EXPNO 1
PROCNO 1

Entry 8, Table 3

JVK-866 Colorless oil after column
After 6% Ethyl acetate:Hexane
in CDCl₃

¹H NMR, in CDCl₃

Current Data Parameters
NAME JVK-866-H-CDCl₃.fid
EXPNO 1
PROCNO 1

7.848
7.844
7.842
7.840
7.838
7.834
7.824
7.820
7.819
7.814
7.565
7.561
7.556
7.547
7.544
7.541
7.536
7.472
7.470
7.465
7.452
7.448
7.436
7.433
7.400
7.397
7.394
7.384
7.378
7.360
7.336
7.334
7.324
7.322
7.316
7.314
7.304
7.302

Entry 9, Table 3

JVK-866 Colorless oil after column
After 6% Ethyl acetate:Hexane
in CDCl₃

¹³C NMR, in CDCl₃

Current Data Parameters
NAME JVK-866-C-CDCl₃.fid
EXPNO 1
PROCNO 1

148.429
148.274
137.762
136.590
134.335
129.076
128.101
127.125
123.557

77.551
77.232
76.914

Entry 9, Table 3

Crystallographic Experimental Section for **2d**

Data Collection

A pale yellow crystal with approximate dimensions $0.27 \times 0.20 \times 0.10 \text{ mm}^3$ was selected under ambient conditions. The crystal was mounted and centered in the X-ray beam by using a video camera. The crystal evaluation and data collection were performed at 197 K on a Bruker CCD-1000 diffractometer with Mo K_α ($\lambda = 0.71073 \text{ \AA}$) radiation and the detector to crystal distance of 5.03 cm. The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 30 frames collected at intervals of 0.3° in a 10° range about ω with the exposure time of 10 seconds per frame. A total of 101 reflections was obtained. The reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of 961 strong reflections from the actual data collection. The data were collected using the full sphere routine. A total of 22381 data were harvested by collecting four sets of frames with 0.3° scans in ω with an exposure time 10 sec per frame. This dataset was corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements [1] using SADABS software [2].

Structure Solution and Refinement

The systematic absences in the diffraction data were consistent for the space groups $P2_1/n$ [2] yielded chemically reasonable and computationally stable results of refinement. The position of heavy atom was found by the direct methods. The remaining atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined in full-matrix anisotropic. All hydrogen atoms were placed in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. Final least-squares refinement of 232 parameters against 5952 independent reflections converged to R (based on F^2 for $I \geq 2\sigma$) and wR (based on F^2 for $I \geq 2\sigma$) of 0.027 and 0.072, respectively.

The ORTEP diagram was drawn at 50% probability level. H-atoms were omitted for clarity.

The resulting CIF file has been tested with PLATON [3] software. The results and comments have been included to output package (Platon.txt file in ASCII format).

References

- [1] Blessing, R.H. *Acta Cryst.* **1995**, *A51*, 33-38.
- [2] All software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-Ray Systems, Madison, WI).
- [3] A.L.Spek, *J.Appl.Cryst.* 36, 7-13.

Table 1. Crystal data and structure refinement for **2d**.

Empirical formula	C ₁₈ H ₃₉ I ₂ N ₄ P	
Formula weight	596.30	
Temperature	197(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 16.650(3) Å	α = 90°.
	b = 10.1806(19) Å	β = 118.770(3)°.
	c = 16.742(3) Å	γ = 90°.
Volume	2487.6(8) Å ³	
Z	4	
Density (calculated)	1.592 Mg/m ³	
Absorption coefficient	2.602 mm ⁻¹	
F(000)	1184	
Crystal size	0.27 x 0.20 x 0.10 mm ³	
Theta range for data collection	1.42 to 28.32°.	
Index ranges	-22 ≤ h ≤ 21, -13 ≤ k ≤ 13, -22 ≤ l ≤ 22	
Reflections collected	22381	
Independent reflections	5952 [R(int) = 0.0366]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1 and 0.84	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5952 / 0 / 232	
Goodness-of-fit on F ²	0.769	
Final R indices [I > 2σ(I)]	R1 = 0.0267, wR2 = 0.0721	
R indices (all data)	R1 = 0.0363, wR2 = 0.0848	
Largest diff. peak and hole	1.475 and -0.335 e.Å ⁻³	

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o| \text{ and } wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2d**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
I(1)	4186(1)	7003(1)	98(1)	36(1)
I(2)	1130(1)	1848(1)	777(1)	36(1)
C(1)	2543(2)	8373(3)	1515(2)	32(1)
C(2)	1630(2)	7675(3)	1142(2)	35(1)
C(3)	2872(2)	9350(3)	322(2)	31(1)
C(4)	3722(2)	10225(3)	782(3)	44(1)
C(5)	3563(4)	11358(5)	119(4)	87(2)
C(6)	3914(2)	10757(4)	1707(3)	48(1)
C(7)	1172(2)	6403(3)	-722(2)	35(1)
C(8)	1027(2)	5849(3)	34(2)	33(1)
C(9)	2312(2)	4982(3)	-894(2)	36(1)
C(10)	2251(3)	5206(5)	-1836(3)	58(1)
C(11)	1380(4)	5782(7)	-2535(3)	93(2)
C(12)	2465(4)	3876(6)	-2128(4)	87(2)
C(13)	2854(2)	4607(3)	1462(2)	34(1)
C(14)	2179(2)	5406(3)	1629(2)	33(1)
C(15)	4351(2)	5809(3)	2132(2)	29(1)
C(16)	4985(2)	4608(3)	2446(2)	37(1)
C(17)	5838(3)	4953(4)	3334(3)	55(1)
C(18)	5231(2)	4135(4)	1731(3)	49(1)
N(1)	2888(2)	8183(2)	856(2)	28(1)
N(2)	2139(2)	6166(2)	-490(2)	30(1)
N(3)	3456(2)	5533(2)	1316(2)	29(1)
N(4)	1792(2)	6362(2)	880(2)	28(1)
P(1)	2911(1)	6665(1)	536(1)	25(1)

Table 3. Bond lengths [Å] and angles [°] for **2d**.

I(1)-P(1)	2.5814(8)	C(7)-C(8)	1.508(4)	C(13)-H(13B)	0.9900
C(1)-N(1)	1.482(3)	C(7)-H(7A)	0.9900	C(14)-N(4)	1.470(4)
C(1)-C(2)	1.513(4)	C(7)-H(7B)	0.9900	C(14)-H(14A)	0.9900
C(1)-H(1A)	0.9900	C(8)-N(4)	1.471(4)	C(14)-H(14B)	0.9900
C(1)-H(1B)	0.9900	C(8)-H(8A)	0.9900	C(15)-N(3)	1.485(4)
C(2)-N(4)	1.471(4)	C(8)-H(8B)	0.9900	C(15)-C(16)	1.534(4)
C(2)-H(2A)	0.9900	C(9)-N(2)	1.477(4)	C(15)-H(15A)	0.9900
C(2)-H(2B)	0.9900	C(9)-C(10)	1.547(5)	C(15)-H(15B)	0.9900
C(3)-N(1)	1.479(3)	C(9)-H(9A)	0.9900	C(16)-C(18)	1.519(5)
C(3)-C(4)	1.531(4)	C(9)-H(9B)	0.9900	C(16)-C(17)	1.522(5)
C(3)-H(3A)	0.9900	C(10)-C(11)	1.477(7)	C(16)-H(16)	1.0000
C(3)-H(3B)	0.9900	C(10)-C(12)	1.539(6)	C(17)-H(17A)	0.9800
C(4)-C(6)	1.523(5)	C(10)-H(10)	1.0000	C(17)-H(17B)	0.9800
C(4)-C(5)	1.533(6)	C(11)-H(11A)	0.9800	C(17)-H(17C)	0.9800
C(4)-H(4)	1.0000	C(11)-H(11B)	0.9800	C(18)-H(18A)	0.9800
C(5)-H(5A)	0.9800	C(11)-H(11C)	0.9800	C(18)-H(18B)	0.9800
C(5)-H(5B)	0.9800	C(12)-H(12A)	0.9800	C(18)-H(18C)	0.9800
C(5)-H(5C)	0.9800	C(12)-H(12B)	0.9800	N(1)-P(1)	1.642(2)
C(6)-H(6A)	0.9800	C(12)-H(12C)	0.9800	N(2)-P(1)	1.654(2)
C(6)-H(6B)	0.9800	C(13)-N(3)	1.480(3)	N(3)-P(1)	1.648(2)
C(6)-H(6C)	0.9800	C(13)-C(14)	1.517(4)	N(4)-P(1)	2.219(2)
C(7)-N(2)	1.483(4)	C(13)-H(13A)	0.9900		
N(1)-C(1)-C(2)	107.6(2)	H(2A)-C(2)-H(2B)	108.8	C(3)-C(4)-H(4)	108.7
N(1)-C(1)-H(1A)	110.2	N(1)-C(3)-C(4)	114.8(2)	C(5)-C(4)-H(4)	108.7
C(2)-C(1)-H(1A)	110.2	N(1)-C(3)-H(3A)	108.6	C(4)-C(5)-H(5A)	109.5
N(1)-C(1)-H(1B)	110.2	C(4)-C(3)-H(3A)	108.6	C(4)-C(5)-H(5B)	109.5
C(2)-C(1)-H(1B)	110.2	N(1)-C(3)-H(3B)	108.6	H(5A)-C(5)-H(5B)	109.5
H(1A)-C(1)-H(1B)	108.5	C(4)-C(3)-H(3B)	108.6	C(4)-C(5)-H(5C)	109.5
N(4)-C(2)-C(1)	105.0(2)	H(3A)-C(3)-H(3B)	107.5	H(5A)-C(5)-H(5C)	109.5
N(4)-C(2)-H(2A)	110.8	C(6)-C(4)-C(3)	114.1(3)	H(5B)-C(5)-H(5C)	109.5
C(1)-C(2)-H(2A)	110.8	C(6)-C(4)-C(5)	110.3(3)	C(4)-C(6)-H(6A)	109.5
N(4)-C(2)-H(2B)	110.8	C(3)-C(4)-C(5)	106.1(3)	C(4)-C(6)-H(6B)	109.5
C(1)-C(2)-H(2B)	110.8	C(6)-C(4)-H(4)	108.7	H(6A)-C(6)-H(6B)	109.5

C(4)-C(6)-H(6C)	109.5	C(10)-C(12)-H(12B)	109.5	H(17B)-C(17)-H(17C)	109.5
H(6A)-C(6)-H(6C)	109.5	H(12A)-C(12)-H(12B)	109.5	C(16)-C(18)-H(18A)	109.5
H(6B)-C(6)-H(6C)	109.5	C(10)-C(12)-H(12C)	109.5	C(16)-C(18)-H(18B)	109.5
N(2)-C(7)-C(8)	108.2(2)	H(12A)-C(12)-H(12C)	109.5	H(18A)-C(18)-H(18B)	109.5
N(2)-C(7)-H(7A)	110.1	H(12B)-C(12)-H(12C)	109.5	C(16)-C(18)-H(18C)	109.5
C(8)-C(7)-H(7A)	110.1	N(3)-C(13)-C(14)	108.0(2)	H(18A)-C(18)-H(18C)	109.5
N(2)-C(7)-H(7B)	110.1	N(3)-C(13)-H(13A)	110.1	H(18B)-C(18)-H(18C)	109.5
C(8)-C(7)-H(7B)	110.1	C(14)-C(13)-H(13A)	110.1	C(3)-N(1)-C(1)	116.4(2)
H(7A)-C(7)-H(7B)	108.4	N(3)-C(13)-H(13B)	110.1	C(3)-N(1)-P(1)	123.73(19)
N(4)-C(8)-C(7)	105.1(2)	C(14)-C(13)-H(13B)	110.1	C(1)-N(1)-P(1)	116.33(18)
N(4)-C(8)-H(8A)	110.7	H(13A)-C(13)-H(13B)	108.4	C(9)-N(2)-C(7)	116.1(2)
C(7)-C(8)-H(8A)	110.7	N(4)-C(14)-C(13)	104.9(2)	C(9)-N(2)-P(1)	120.1(2)
N(4)-C(8)-H(8B)	110.7	N(4)-C(14)-H(14A)	110.8	C(7)-N(2)-P(1)	115.12(19)
C(7)-C(8)-H(8B)	110.7	C(13)-C(14)-H(14A)	110.8	C(13)-N(3)-C(15)	115.4(2)
H(8A)-C(8)-H(8B)	108.8	N(4)-C(14)-H(14B)	110.8	C(13)-N(3)-P(1)	114.69(18)
N(2)-C(9)-C(10)	114.5(3)	C(13)-C(14)-H(14B)	110.8	C(15)-N(3)-P(1)	121.52(19)
N(2)-C(9)-H(9A)	108.6	H(14A)-C(14)-H(14B)	108.8	C(14)-N(4)-C(8)	114.0(2)
C(10)-C(9)-H(9A)	108.6	N(3)-C(15)-C(16)	112.7(2)	C(14)-N(4)-C(2)	114.6(2)
N(2)-C(9)-H(9B)	108.6	N(3)-C(15)-H(15A)	109.1	C(8)-N(4)-C(2)	114.3(2)
C(10)-C(9)-H(9B)	108.6	C(16)-C(15)-H(15A)	109.1	C(14)-N(4)-P(1)	103.61(16)
H(9A)-C(9)-H(9B)	107.6	N(3)-C(15)-H(15B)	109.1	C(8)-N(4)-P(1)	104.25(16)
C(11)-C(10)-C(12)	112.7(4)	C(16)-C(15)-H(15B)	109.1	C(2)-N(4)-P(1)	104.34(16)
C(11)-C(10)-C(9)	115.1(3)	H(15A)-C(15)-H(15B)	107.8	N(1)-P(1)-N(3)	119.35(13)
C(12)-C(10)-C(9)	106.4(4)	C(18)-C(16)-C(17)	111.4(3)	N(1)-P(1)-N(2)	119.99(13)
C(11)-C(10)-H(10)	107.4	C(18)-C(16)-C(15)	112.6(3)	N(3)-P(1)-N(2)	117.66(13)
C(12)-C(10)-H(10)	107.4	C(17)-C(16)-C(15)	108.4(3)	N(1)-P(1)-N(4)	83.84(10)
C(9)-C(10)-H(10)	107.4	C(18)-C(16)-H(16)	108.1	N(3)-P(1)-N(4)	84.75(10)
C(10)-C(11)-H(11A)	109.5	C(17)-C(16)-H(16)	108.1	N(2)-P(1)-N(4)	84.08(10)
C(10)-C(11)-H(11B)	109.5	C(15)-C(16)-H(16)	108.1	N(1)-P(1)-I(1)	96.80(9)
H(11A)-C(11)-H(11B)	109.5	C(16)-C(17)-H(17A)	109.5	N(3)-P(1)-I(1)	95.93(8)
C(10)-C(11)-H(11C)	109.5	C(16)-C(17)-H(17B)	109.5	N(2)-P(1)-I(1)	94.59(8)
H(11A)-C(11)-H(11C)	109.5	H(17A)-C(17)-H(17B)	109.5	N(4)-P(1)-I(1)	178.67(7)
H(11B)-C(11)-H(11C)	109.5	C(16)-C(17)-H(17C)	109.5		
C(10)-C(12)-H(12A)	109.5	H(17A)-C(17)-H(17C)	109.5		

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2d**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I(1)	34(1)	42(1)	42(1)	-4(1)	27(1)	-6(1)
I(2)	31(1)	33(1)	43(1)	1(1)	17(1)	2(1)
C(1)	38(2)	31(1)	36(2)	-3(1)	24(1)	0(1)
C(2)	36(2)	32(1)	45(2)	-1(1)	27(1)	3(1)
C(3)	33(1)	28(1)	32(1)	3(1)	16(1)	0(1)
C(4)	47(2)	38(2)	59(2)	-12(2)	35(2)	-15(1)
C(5)	151(5)	52(3)	89(3)	-12(2)	82(4)	-47(3)
C(6)	40(2)	45(2)	55(2)	-15(2)	20(2)	-14(2)
C(7)	25(1)	41(2)	35(2)	3(1)	11(1)	0(1)
C(8)	22(1)	34(1)	42(2)	1(1)	15(1)	-4(1)
C(9)	37(2)	35(2)	38(2)	-9(1)	19(1)	-7(1)
C(10)	61(2)	72(3)	45(2)	-18(2)	29(2)	-9(2)
C(11)	93(4)	145(6)	46(2)	8(3)	37(3)	-6(4)
C(12)	115(4)	88(4)	79(3)	-44(3)	64(3)	-20(3)
C(13)	28(1)	31(1)	42(2)	8(1)	18(1)	1(1)
C(14)	32(1)	35(1)	37(2)	8(1)	21(1)	0(1)
C(15)	29(1)	30(1)	30(1)	-2(1)	14(1)	2(1)
C(16)	27(1)	37(2)	40(2)	1(1)	11(1)	5(1)
C(17)	43(2)	60(2)	44(2)	-2(2)	6(2)	10(2)
C(18)	39(2)	48(2)	53(2)	-9(2)	18(2)	12(2)
N(1)	32(1)	24(1)	33(1)	1(1)	19(1)	-1(1)
N(2)	29(1)	33(1)	29(1)	-3(1)	14(1)	-3(1)
N(3)	24(1)	28(1)	35(1)	5(1)	14(1)	1(1)
N(4)	27(1)	28(1)	35(1)	2(1)	19(1)	2(1)
P(1)	25(1)	24(1)	28(1)	0(1)	15(1)	-1(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2d**.

	x	y	z	U(eq)
H(1A)	2466	9321	1593	39
H(1B)	2982	8003	2116	39
H(2A)	1433	7610	1611	42
H(2B)	1153	8148	607	42
H(3A)	2327	9885	196	37
H(3B)	2801	9051	-271	37
H(4)	4267	9709	860	53
H(5A)	3351	11006	-495	131
H(5B)	4137	11839	314	131
H(5C)	3098	11955	114	131
H(6A)	3369	11211	1647	72
H(6B)	4429	11374	1931	72
H(6C)	4068	10028	2139	72
H(7A)	755	5970	-1306	42
H(7B)	1041	7357	-787	42
H(8A)	432	6143	-29	40
H(8B)	1037	4877	27	40
H(9A)	1863	4297	-957	43
H(9B)	2931	4643	-469	43
H(10)	2753	5826	-1745	69
H(11A)	870	5213	-2622	140
H(11B)	1395	5860	-3112	140
H(11C)	1299	6654	-2336	140
H(12A)	1987	3240	-2216	131
H(12B)	3060	3556	-1654	131
H(12C)	2485	3984	-2700	131
H(13A)	3224	4038	1994	40
H(13B)	2521	4042	919	40
H(14A)	1693	4835	1619	39
H(14B)	2495	5858	2226	39

H(15A)	4243	6103	2635	35
H(15B)	4659	6534	1990	35
H(16)	4660	3879	2572	44
H(17A)	6233	4178	3565	83
H(17B)	5657	5241	3784	83
H(17C)	6171	5662	3225	83
H(18A)	5586	4815	1625	73
H(18B)	4669	3953	1161	73
H(18C)	5598	3330	1945	73

Crystallographic Experimental Section for **3a**

Data Collection

A colorless crystal was selected under ambient conditions and covered with Paratone-N oil. The crystal was mounted and centered in the X-ray beam under the stream of cold nitrogen by using a video camera. The crystal evaluation and data collection were performed at 193 K on a Bruker CCD-1000 diffractometer with Mo K α ($\lambda = 0.71073$ Å) radiation and the detector to crystal distance of 5.03 cm. The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 30 frames collected at intervals of 0.3° in a 10° range about ω with the exposure time of 10 seconds per frame. The obtained reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of strong reflections from the actual data collection.

The data were collected using the full sphere routine by collecting four sets of frames with 0.3° scans in ω with an exposure time 10 sec per frame. This dataset was corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements [1] using SADABS software [2].

Structure Solution and Refinement

The systematic absences in the diffraction data were consistent for the space groups Pna2₁ [2] yielded chemically reasonable and computationally stable results of refinement. The position of almost all non-hydrogen atoms were found by direct methods. The remaining atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined in full-matrix anisotropic approximation. All hydrogen atoms were placed in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

The ORTEP diagram was drawn at 50% probability level. H-atoms were omitted for clarity. The resulting CIF file has been tested with PLATON [3] software. The results and comments have been included in the output package (Platon_VER112.doc). Two chemically equivalent, but structurally independent molecules were found in an asymmetric unit of monoclinic cell.

References

- [1] Blessing, R.H. *Acta Cryst.* **1995**, *A51*, 33-38.
- [2] All software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-Ray Systems, Madison, WI).
- [3] A.L.Spek, *J.Appl.Cryst.* 36, 7-13.

Table 1. Crystal data and structure refinement for **3a**.

Empirical formula	C ₁₈ H ₃₉ N ₅ P	
Formula weight	356.51	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pna2(1)	
Unit cell dimensions	a = 20.503(4) Å	α = 90°.
	b = 11.297(2) Å	β = 90°.
	c = 18.369(4) Å	γ = 90°.
Volume	4254.6(14) Å ³	
Z	8	
Density (calculated)	1.113 Mg/m ³	
Absorption coefficient	0.139 mm ⁻¹	
F(000)	1576	
Crystal size	0.40 x 0.20 x 0.20 mm ³	
Theta range for data collection	1.99 to 28.31°.	
Index ranges	-27 ≤ h ≤ 27, -15 ≤ k ≤ 14, -22 ≤ l ≤ 24	
Reflections collected	37473	
Independent reflections	9964 [R(int) = 0.0312]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1 and 0.85	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9964 / 1 / 445	
Goodness-of-fit on F ²	1.029	
Final R indices [I > 2σ(I)]	R1 = 0.0343, wR2 = 0.0895	
R indices (all data)	R1 = 0.0405, wR2 = 0.0950	
Absolute structure parameter	0.00(5)	
Largest diff. peak and hole	0.404 and -0.173 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3a**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
P(1)	7448(1)	6994(1)	7826(1)	25(1)
P(2)	9273(1)	2640(1)	6229(1)	25(1)
C(1)	6118(1)	6954(1)	7927(1)	31(1)
C(2)	5930(1)	8155(2)	8249(1)	37(1)
C(3)	6742(1)	5757(2)	8818(1)	32(1)
C(4)	6456(1)	4520(2)	8706(1)	37(1)
C(5)	6878(1)	3763(2)	8220(1)	56(1)
C(6)	6351(1)	3947(2)	9448(1)	64(1)
C(7)	7266(1)	8653(2)	8908(1)	34(1)
C(8)	6808(1)	9584(2)	8580(1)	38(1)
C(9)	8333(1)	8607(2)	8274(1)	34(1)
C(10)	8808(1)	8487(2)	8914(1)	36(1)
C(11)	9449(1)	9089(3)	8711(1)	75(1)
C(12)	8907(1)	7213(2)	9131(1)	61(1)
C(13)	7136(1)	8944(1)	6996(1)	35(1)
C(14)	6476(1)	9354(2)	7287(1)	38(1)
C(15)	7092(1)	6968(2)	6405(1)	33(1)
C(16)	7540(1)	7170(2)	5751(1)	38(1)
C(17)	8232(1)	6799(3)	5913(1)	62(1)
C(18)	7263(1)	6501(2)	5095(1)	65(1)
C(19)	9395(1)	4795(1)	6915(1)	31(1)
C(20)	9674(1)	4511(1)	7663(1)	34(1)
C(21)	10177(1)	4312(1)	5918(1)	28(1)
C(22)	10096(1)	5385(1)	5416(1)	35(1)
C(23)	9631(1)	5134(2)	4797(1)	49(1)
C(24)	10759(1)	5773(2)	5130(1)	51(1)
C(25)	8541(1)	2225(2)	7460(1)	32(1)
C(26)	8808(1)	3094(2)	8027(1)	36(1)
C(27)	8001(1)	3217(1)	6414(1)	30(1)
C(28)	7413(1)	2396(2)	6289(1)	35(1)
C(29)	7563(1)	1438(2)	5736(1)	47(1)

C(30)	6831(1)	3142(2)	6052(1)	50(1)
C(31)	10249(1)	2105(2)	7210(1)	33(1)
C(32)	9968(1)	2433(2)	7956(1)	37(1)
C(33)	9639(1)	447(1)	6641(1)	32(1)
C(34)	10198(1)	-320(1)	6346(1)	38(1)
C(35)	10392(1)	38(2)	5581(1)	52(1)
C(36)	9988(1)	-1615(2)	6375(1)	53(1)
N(1)	6751(1)	6486(1)	8157(1)	27(1)
N(2)	7693(1)	8061(1)	8386(1)	29(1)
N(3)	7266(1)	7673(1)	7049(1)	29(1)
N(4)	6356(1)	9123(1)	8047(1)	37(1)
N(5)	7941(1)	5971(1)	7717(1)	35(1)
N(6)	9590(1)	3985(1)	6327(1)	27(1)
N(7)	8580(1)	2614(1)	6702(1)	28(1)
N(8)	9774(1)	1718(1)	6667(1)	30(1)
N(9)	9492(1)	3367(1)	7945(1)	35(1)
N(10)	9167(1)	2320(1)	5412(1)	36(1)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for **3a**.

P(1)-N(5)	1.5467(12)	C(3)-N(1)	1.467(2)	C(7)-H(7A)	0.9900
P(1)-N(1)	1.6553(12)	C(3)-C(4)	1.529(2)	C(7)-H(7B)	0.9900
P(1)-N(2)	1.6628(13)	C(3)-H(3A)	0.9900	C(8)-N(4)	1.446(2)
P(1)-N(3)	1.6642(14)	C(3)-H(3B)	0.9900	C(8)-H(8A)	0.9900
P(2)-N(10)	1.5586(15)	C(4)-C(5)	1.508(3)	C(8)-H(8B)	0.9900
P(2)-N(6)	1.6630(12)	C(4)-C(6)	1.525(3)	C(9)-N(2)	1.4643(19)
P(2)-N(7)	1.6655(13)	C(4)-H(4)	1.0000	C(9)-C(10)	1.533(2)
P(2)-N(8)	1.6692(13)	C(5)-H(5A)	0.9800	C(9)-H(9A)	0.9900
C(1)-N(1)	1.4637(18)	C(5)-H(5B)	0.9800	C(9)-H(9B)	0.9900
C(1)-C(2)	1.530(2)	C(5)-H(5C)	0.9800	C(10)-C(12)	1.507(3)
C(1)-H(1A)	0.9900	C(6)-H(6A)	0.9800	C(10)-C(11)	1.527(2)
C(1)-H(1B)	0.9900	C(6)-H(6B)	0.9800	C(10)-H(10)	1.0000
C(2)-N(4)	1.448(2)	C(6)-H(6C)	0.9800	C(11)-H(11A)	0.9800
C(2)-H(2A)	0.9900	C(7)-N(2)	1.4610(19)	C(11)-H(11B)	0.9800
C(2)-H(2B)	0.9900	C(7)-C(8)	1.533(2)	C(11)-H(11C)	0.9800

C(12)-H(12A)	0.9800	C(20)-H(20A)	0.9900	C(28)-H(28)	1.0000
C(12)-H(12B)	0.9800	C(20)-H(20B)	0.9900	C(29)-H(29A)	0.9800
C(12)-H(12C)	0.9800	C(21)-N(6)	1.4649(18)	C(29)-H(29B)	0.9800
C(13)-N(3)	1.463(2)	C(21)-C(22)	1.531(2)	C(29)-H(29C)	0.9800
C(13)-C(14)	1.528(2)	C(21)-H(21A)	0.9900	C(30)-H(30A)	0.9800
C(13)-H(13A)	0.9900	C(21)-H(21B)	0.9900	C(30)-H(30B)	0.9800
C(13)-H(13B)	0.9900	C(22)-C(23)	1.511(3)	C(30)-H(30C)	0.9800
C(14)-N(4)	1.441(2)	C(22)-C(24)	1.522(2)	C(31)-N(8)	1.4618(19)
C(14)-H(14A)	0.9900	C(22)-H(22)	1.0000	C(31)-C(32)	1.533(2)
C(14)-H(14B)	0.9900	C(23)-H(23A)	0.9800	C(31)-H(31A)	0.9900
C(15)-N(3)	1.469(2)	C(23)-H(23B)	0.9800	C(31)-H(31B)	0.9900
C(15)-C(16)	1.530(2)	C(23)-H(23C)	0.9800	C(32)-N(9)	1.438(2)
C(15)-H(15A)	0.9900	C(24)-H(24A)	0.9800	C(32)-H(32A)	0.9900
C(15)-H(15B)	0.9900	C(24)-H(24B)	0.9800	C(32)-H(32B)	0.9900
C(16)-C(17)	1.510(3)	C(24)-H(24C)	0.9800	C(33)-N(8)	1.4633(19)
C(16)-C(18)	1.531(3)	C(25)-N(7)	1.4631(19)	C(33)-C(34)	1.535(2)
C(16)-H(16)	1.0000	C(25)-C(26)	1.532(2)	C(33)-H(33A)	0.9900
C(17)-H(17A)	0.9800	C(25)-H(25A)	0.9900	C(33)-H(33B)	0.9900
C(17)-H(17B)	0.9800	C(25)-H(25B)	0.9900	C(34)-C(35)	1.516(3)
C(17)-H(17C)	0.9800	C(26)-N(9)	1.443(2)	C(34)-C(36)	1.526(2)
C(18)-H(18A)	0.9800	C(26)-H(26A)	0.9900	C(34)-H(34)	1.0000
C(18)-H(18B)	0.9800	C(26)-H(26B)	0.9900	C(35)-H(35A)	0.9800
C(18)-H(18C)	0.9800	C(27)-N(7)	1.4660(19)	C(35)-H(35B)	0.9800
C(19)-N(6)	1.4706(18)	C(27)-C(28)	1.538(2)	C(35)-H(35C)	0.9800
C(19)-C(20)	1.523(2)	C(27)-H(27A)	0.9900	C(36)-H(36A)	0.9800
C(19)-H(19A)	0.9900	C(27)-H(27B)	0.9900	C(36)-H(36B)	0.9800
C(19)-H(19B)	0.9900	C(28)-C(29)	1.517(3)	C(36)-H(36C)	0.9800
C(20)-N(9)	1.442(2)	C(28)-C(30)	1.526(2)		
N(5)-P(1)-N(1)	110.64(7)	N(10)-P(2)-N(7)	112.26(7)	C(2)-C(1)-H(1A)	108.4
N(5)-P(1)-N(2)	115.10(7)	N(6)-P(2)-N(7)	107.09(6)	N(1)-C(1)-H(1B)	108.4
N(1)-P(1)-N(2)	106.57(7)	N(10)-P(2)-N(8)	113.89(7)	C(2)-C(1)-H(1B)	108.4
N(5)-P(1)-N(3)	112.36(7)	N(6)-P(2)-N(8)	106.10(6)	H(1A)-C(1)-H(1B)	107.4
N(1)-P(1)-N(3)	106.29(7)	N(7)-P(2)-N(8)	105.21(7)	N(4)-C(2)-C(1)	114.74(13)
N(2)-P(1)-N(3)	105.30(7)	N(1)-C(1)-C(2)	115.61(13)	N(4)-C(2)-H(2A)	108.6
N(10)-P(2)-N(6)	111.76(7)	N(1)-C(1)-H(1A)	108.4	C(1)-C(2)-H(2A)	108.6

N(4)-C(2)-H(2B)	108.6	N(4)-C(8)-H(8B)	108.7	N(4)-C(14)-H(14B)	108.3
C(1)-C(2)-H(2B)	108.6	C(7)-C(8)-H(8B)	108.7	C(13)-C(14)-H(14B)	108.3
H(2A)-C(2)-H(2B)	107.6	H(8A)-C(8)-H(8B)	107.6	H(14A)-C(14)-H(14B)	107.4
N(1)-C(3)-C(4)	114.02(13)	N(2)-C(9)-C(10)	115.11(13)	N(3)-C(15)-C(16)	113.96(13)
N(1)-C(3)-H(3A)	108.7	N(2)-C(9)-H(9A)	108.5	N(3)-C(15)-H(15A)	108.8
C(4)-C(3)-H(3A)	108.7	C(10)-C(9)-H(9A)	108.5	C(16)-C(15)-H(15A)	108.8
N(1)-C(3)-H(3B)	108.7	N(2)-C(9)-H(9B)	108.5	N(3)-C(15)-H(15B)	108.8
C(4)-C(3)-H(3B)	108.7	C(10)-C(9)-H(9B)	108.5	C(16)-C(15)-H(15B)	108.8
H(3A)-C(3)-H(3B)	107.6	H(9A)-C(9)-H(9B)	107.5	H(15A)-C(15)-H(15B)	107.7
C(5)-C(4)-C(6)	111.66(17)	C(12)-C(10)-C(11)	112.0(2)	C(17)-C(16)-C(18)	111.52(19)
C(5)-C(4)-C(3)	112.22(14)	C(12)-C(10)-C(9)	111.94(16)	C(17)-C(16)-C(15)	111.55(15)
C(6)-C(4)-C(3)	108.82(16)	C(11)-C(10)-C(9)	108.63(15)	C(18)-C(16)-C(15)	108.77(16)
C(5)-C(4)-H(4)	108.0	C(12)-C(10)-H(10)	108.1	C(17)-C(16)-H(16)	108.3
C(6)-C(4)-H(4)	108.0	C(11)-C(10)-H(10)	108.1	C(18)-C(16)-H(16)	108.3
C(3)-C(4)-H(4)	108.0	C(9)-C(10)-H(10)	108.1	C(15)-C(16)-H(16)	108.3
C(4)-C(5)-H(5A)	109.5	C(10)-C(11)-H(11A)	109.5	C(16)-C(17)-H(17A)	109.5
C(4)-C(5)-H(5B)	109.5	C(10)-C(11)-H(11B)	109.5	C(16)-C(17)-H(17B)	109.5
H(5A)-C(5)-H(5B)	109.5	H(11A)-C(11)-H(11B)	109.5	H(17A)-C(17)-H(17B)	109.5
C(4)-C(5)-H(5C)	109.5	C(10)-C(11)-H(11C)	109.5	C(16)-C(17)-H(17C)	109.5
H(5A)-C(5)-H(5C)	109.5	H(11A)-C(11)-H(11C)	109.5	H(17A)-C(17)-H(17C)	109.5
H(5B)-C(5)-H(5C)	109.5	H(11B)-C(11)-H(11C)	109.5	H(17B)-C(17)-H(17C)	109.5
C(4)-C(6)-H(6A)	109.5	C(10)-C(12)-H(12A)	109.5	C(16)-C(18)-H(18A)	109.5
C(4)-C(6)-H(6B)	109.5	C(10)-C(12)-H(12B)	109.5	C(16)-C(18)-H(18B)	109.5
H(6A)-C(6)-H(6B)	109.5	H(12A)-C(12)-H(12B)	109.5	H(18A)-C(18)-H(18B)	109.5
C(4)-C(6)-H(6C)	109.5	C(10)-C(12)-H(12C)	109.5	C(16)-C(18)-H(18C)	109.5
H(6A)-C(6)-H(6C)	109.5	H(12A)-C(12)-H(12C)	109.5	H(18A)-C(18)-H(18C)	109.5
H(6B)-C(6)-H(6C)	109.5	H(12B)-C(12)-H(12C)	109.5	H(18B)-C(18)-H(18C)	109.5
N(2)-C(7)-C(8)	115.06(14)	N(3)-C(13)-C(14)	115.78(13)	N(6)-C(19)-C(20)	115.46(12)
N(2)-C(7)-H(7A)	108.5	N(3)-C(13)-H(13A)	108.3	N(6)-C(19)-H(19A)	108.4
C(8)-C(7)-H(7A)	108.5	C(14)-C(13)-H(13A)	108.3	C(20)-C(19)-H(19A)	108.4
N(2)-C(7)-H(7B)	108.5	N(3)-C(13)-H(13B)	108.3	N(6)-C(19)-H(19B)	108.4
C(8)-C(7)-H(7B)	108.5	C(14)-C(13)-H(13B)	108.3	C(20)-C(19)-H(19B)	108.4
H(7A)-C(7)-H(7B)	107.5	H(13A)-C(13)-H(13B)	107.4	H(19A)-C(19)-H(19B)	107.5
N(4)-C(8)-C(7)	114.30(14)	N(4)-C(14)-C(13)	115.79(13)	N(9)-C(20)-C(19)	114.56(13)
N(4)-C(8)-H(8A)	108.7	N(4)-C(14)-H(14A)	108.3	N(9)-C(20)-H(20A)	108.6
C(7)-C(8)-H(8A)	108.7	C(13)-C(14)-H(14A)	108.3	C(19)-C(20)-H(20A)	108.6

N(9)-C(20)-H(20B)	108.6	N(9)-C(26)-H(26B)	108.7	N(9)-C(32)-H(32B)	108.6
C(19)-C(20)-H(20B)	108.6	C(25)-C(26)-H(26B)	108.7	C(31)-C(32)-H(32B)	108.6
H(20A)-C(20)-H(20B)	107.6	H(26A)-C(26)-H(26B)	107.6	H(32A)-C(32)-H(32B)	107.5
N(6)-C(21)-C(22)	114.77(13)	N(7)-C(27)-C(28)	114.05(13)	N(8)-C(33)-C(34)	115.12(13)
N(6)-C(21)-H(21A)	108.6	N(7)-C(27)-H(27A)	108.7	N(8)-C(33)-H(33A)	108.5
C(22)-C(21)-H(21A)	108.6	C(28)-C(27)-H(27A)	108.7	C(34)-C(33)-H(33A)	108.5
N(6)-C(21)-H(21B)	108.6	N(7)-C(27)-H(27B)	108.7	N(8)-C(33)-H(33B)	108.5
C(22)-C(21)-H(21B)	108.6	C(28)-C(27)-H(27B)	108.7	C(34)-C(33)-H(33B)	108.5
H(21A)-C(21)-H(21B)	107.6	H(27A)-C(27)-H(27B)	107.6	H(33A)-C(33)-H(33B)	107.5
C(23)-C(22)-C(24)	110.93(15)	C(29)-C(28)-C(30)	111.15(16)	C(35)-C(34)-C(36)	111.20(16)
C(23)-C(22)-C(21)	111.92(14)	C(29)-C(28)-C(27)	111.81(14)	C(35)-C(34)-C(33)	111.84(15)
C(24)-C(22)-C(21)	109.82(15)	C(30)-C(28)-C(27)	108.84(15)	C(36)-C(34)-C(33)	108.52(15)
C(23)-C(22)-H(22)	108.0	C(29)-C(28)-H(28)	108.3	C(35)-C(34)-H(34)	108.4
C(24)-C(22)-H(22)	108.0	C(30)-C(28)-H(28)	108.3	C(36)-C(34)-H(34)	108.4
C(21)-C(22)-H(22)	108.0	C(27)-C(28)-H(28)	108.3	C(33)-C(34)-H(34)	108.4
C(22)-C(23)-H(23A)	109.5	C(28)-C(29)-H(29A)	109.5	C(34)-C(35)-H(35A)	109.5
C(22)-C(23)-H(23B)	109.5	C(28)-C(29)-H(29B)	109.5	C(34)-C(35)-H(35B)	109.5
H(23A)-C(23)-H(23B)	109.5	H(29A)-C(29)-H(29B)	109.5	H(35A)-C(35)-H(35B)	109.5
C(22)-C(23)-H(23C)	109.5	C(28)-C(29)-H(29C)	109.5	C(34)-C(35)-H(35C)	109.5
H(23A)-C(23)-H(23C)	109.5	H(29A)-C(29)-H(29C)	109.5	H(35A)-C(35)-H(35C)	109.5
H(23B)-C(23)-H(23C)	109.5	H(29B)-C(29)-H(29C)	109.5	H(35B)-C(35)-H(35C)	109.5
C(22)-C(24)-H(24A)	109.5	C(28)-C(30)-H(30A)	109.5	C(34)-C(36)-H(36A)	109.5
C(22)-C(24)-H(24B)	109.5	C(28)-C(30)-H(30B)	109.5	C(34)-C(36)-H(36B)	109.5
H(24A)-C(24)-H(24B)	109.5	H(30A)-C(30)-H(30B)	109.5	H(36A)-C(36)-H(36B)	109.5
C(22)-C(24)-H(24C)	109.5	C(28)-C(30)-H(30C)	109.5	C(34)-C(36)-H(36C)	109.5
H(24A)-C(24)-H(24C)	109.5	H(30A)-C(30)-H(30C)	109.5	H(36A)-C(36)-H(36C)	109.5
H(24B)-C(24)-H(24C)	109.5	H(30B)-C(30)-H(30C)	109.5	H(36B)-C(36)-H(36C)	109.5
N(7)-C(25)-C(26)	115.82(13)	N(8)-C(31)-C(32)	115.57(13)	C(1)-N(1)-C(3)	115.49(12)
N(7)-C(25)-H(25A)	108.3	N(8)-C(31)-H(31A)	108.4	C(1)-N(1)-P(1)	122.33(10)
C(26)-C(25)-H(25A)	108.3	C(32)-C(31)-H(31A)	108.4	C(3)-N(1)-P(1)	120.59(10)
N(7)-C(25)-H(25B)	108.3	N(8)-C(31)-H(31B)	108.4	C(7)-N(2)-C(9)	115.88(13)
C(26)-C(25)-H(25B)	108.3	C(32)-C(31)-H(31B)	108.4	C(7)-N(2)-P(1)	123.81(11)
H(25A)-C(25)-H(25B)	107.4	H(31A)-C(31)-H(31B)	107.4	C(9)-N(2)-P(1)	119.34(11)
N(9)-C(26)-C(25)	114.37(13)	N(9)-C(32)-C(31)	114.79(13)	C(13)-N(3)-C(15)	115.84(13)
N(9)-C(26)-H(26A)	108.7	N(9)-C(32)-H(32A)	108.6	C(13)-N(3)-P(1)	123.36(11)
C(25)-C(26)-H(26A)	108.7	C(31)-C(32)-H(32A)	108.6	C(15)-N(3)-P(1)	119.63(10)

C(14)-N(4)-C(2)	119.22(15)	C(19)-N(6)-P(2)	122.72(10)	C(31)-N(8)-P(2)	123.54(10)
C(14)-N(4)-C(8)	118.75(14)	C(25)-N(7)-C(27)	116.05(12)	C(33)-N(8)-P(2)	118.74(10)
C(2)-N(4)-C(8)	119.05(15)	C(25)-N(7)-P(2)	123.24(11)	C(32)-N(9)-C(26)	120.09(14)
C(21)-N(6)-C(19)	116.35(11)	C(27)-N(7)-P(2)	119.59(10)	C(32)-N(9)-C(20)	119.20(13)
C(21)-N(6)-P(2)	119.74(9)	C(31)-N(8)-C(33)	116.21(13)	C(26)-N(9)-C(20)	118.68(13)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
P(1)	24(1)	26(1)	27(1)	2(1)	2(1)	4(1)
P(2)	25(1)	23(1)	26(1)	-3(1)	-2(1)	-1(1)
C(1)	24(1)	34(1)	35(1)	2(1)	0(1)	3(1)
C(2)	26(1)	37(1)	49(1)	-2(1)	4(1)	8(1)
C(3)	32(1)	38(1)	26(1)	4(1)	3(1)	2(1)
C(4)	34(1)	38(1)	39(1)	10(1)	0(1)	-2(1)
C(5)	64(1)	35(1)	69(1)	-6(1)	13(1)	-7(1)
C(6)	76(2)	59(1)	56(1)	26(1)	7(1)	-7(1)
C(7)	32(1)	36(1)	33(1)	-6(1)	1(1)	3(1)
C(8)	38(1)	32(1)	45(1)	-8(1)	3(1)	7(1)
C(9)	30(1)	39(1)	32(1)	6(1)	-1(1)	-4(1)
C(10)	29(1)	49(1)	29(1)	2(1)	0(1)	-3(1)
C(11)	39(1)	135(3)	50(1)	15(1)	-4(1)	-32(1)
C(12)	68(1)	60(1)	56(1)	4(1)	-23(1)	20(1)
C(13)	40(1)	30(1)	35(1)	8(1)	-1(1)	2(1)
C(14)	40(1)	29(1)	46(1)	6(1)	-7(1)	8(1)
C(15)	36(1)	34(1)	29(1)	2(1)	1(1)	-2(1)
C(16)	47(1)	38(1)	29(1)	5(1)	7(1)	2(1)
C(17)	47(1)	89(2)	52(1)	25(1)	18(1)	17(1)
C(18)	90(2)	70(2)	36(1)	-10(1)	13(1)	-16(1)
C(19)	34(1)	23(1)	35(1)	-6(1)	4(1)	1(1)
C(20)	35(1)	32(1)	35(1)	-12(1)	-1(1)	-1(1)
C(21)	26(1)	29(1)	31(1)	-5(1)	1(1)	-3(1)
C(22)	43(1)	27(1)	36(1)	-3(1)	5(1)	-5(1)

C(23)	50(1)	50(1)	46(1)	13(1)	-9(1)	-5(1)
C(24)	57(1)	48(1)	49(1)	-3(1)	8(1)	-22(1)
C(25)	31(1)	37(1)	28(1)	4(1)	1(1)	-2(1)
C(26)	37(1)	43(1)	27(1)	-2(1)	3(1)	0(1)
C(27)	25(1)	32(1)	32(1)	4(1)	-2(1)	-1(1)
C(28)	28(1)	47(1)	32(1)	8(1)	-2(1)	-7(1)
C(29)	47(1)	45(1)	51(1)	-2(1)	-5(1)	-13(1)
C(30)	29(1)	70(1)	50(1)	8(1)	-6(1)	0(1)
C(31)	30(1)	31(1)	39(1)	-6(1)	-9(1)	3(1)
C(32)	39(1)	39(1)	32(1)	-4(1)	-11(1)	3(1)
C(33)	36(1)	24(1)	38(1)	-2(1)	-1(1)	1(1)
C(34)	35(1)	28(1)	50(1)	-9(1)	-9(1)	5(1)
C(35)	46(1)	53(1)	57(1)	-12(1)	10(1)	5(1)
C(36)	56(1)	28(1)	74(2)	-11(1)	-13(1)	3(1)
N(1)	25(1)	29(1)	29(1)	4(1)	1(1)	2(1)
N(2)	26(1)	31(1)	30(1)	-3(1)	1(1)	1(1)
N(3)	33(1)	29(1)	25(1)	3(1)	0(1)	4(1)
N(4)	32(1)	33(1)	45(1)	0(1)	0(1)	6(1)
N(5)	32(1)	33(1)	40(1)	-2(1)	4(1)	10(1)
N(6)	28(1)	22(1)	30(1)	-5(1)	2(1)	-2(1)
N(7)	25(1)	31(1)	29(1)	3(1)	0(1)	-1(1)
N(8)	31(1)	23(1)	34(1)	-4(1)	-7(1)	3(1)
N(9)	34(1)	34(1)	35(1)	-3(1)	-1(1)	0(1)
N(10)	44(1)	37(1)	28(1)	-6(1)	-3(1)	-1(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3a**.

	x	y	z	U(eq)
<hr/>				
H(1A)	5777	6372	8060	38
H(1B)	6119	7024	7390	38
H(2A)	5480	8349	8092	45
H(2B)	5926	8087	8786	45

H(3A)	6484	6171	9195	38
H(3B)	7194	5677	9001	38
H(4)	6021	4609	8466	44
H(5A)	7301	3632	8455	84
H(5B)	6944	4164	7753	84
H(5C)	6663	2999	8138	84
H(6A)	6176	3147	9382	96
H(6B)	6041	4422	9731	96
H(6C)	6767	3904	9708	96
H(7A)	7540	9040	9282	40
H(7B)	6998	8045	9156	40
H(8A)	6556	9957	8979	46
H(8B)	7075	10210	8348	46
H(9A)	8269	9460	8172	40
H(9B)	8536	8248	7838	40
H(10)	8619	8918	9340	43
H(11A)	9764	8988	9107	112
H(11B)	9372	9934	8629	112
H(11C)	9623	8730	8265	112
H(12A)	9119	6785	8732	91
H(12B)	8484	6850	9237	91
H(12C)	9184	7178	9566	91
H(13A)	7169	9180	6479	42
H(13B)	7483	9371	7265	42
H(14A)	6438	10217	7204	46
H(14B)	6129	8964	6999	46
H(15A)	6639	7161	6262	40
H(15B)	7105	6119	6538	40
H(16)	7540	8035	5634	45
H(17A)	8389	7220	6345	93
H(17B)	8512	6991	5497	93
H(17C)	8246	5944	6003	93
H(18A)	7545	6627	4672	98
H(18B)	6824	6794	4987	98
H(18C)	7243	5653	5207	98
H(19A)	8913	4790	6949	37

H(19B)	9530	5607	6779	37
H(20A)	10156	4554	7636	41
H(20B)	9527	5127	8010	41
H(21A)	10313	3625	5620	34
H(21B)	10532	4480	6268	34
H(22)	9911	6049	5711	43
H(23A)	9575	5852	4503	73
H(23B)	9208	4889	4993	73
H(23C)	9809	4500	4491	73
H(24A)	10960	5120	4859	77
H(24B)	11040	5992	5540	77
H(24C)	10704	6456	4807	77
H(25A)	8782	1470	7507	38
H(25B)	8078	2062	7577	38
H(26A)	8556	3840	7997	43
H(26B)	8737	2757	8518	43
H(27A)	8117	3598	5946	36
H(27B)	7873	3850	6758	36
H(28)	7303	2006	6762	43
H(29A)	7671	1804	5267	71
H(29B)	7181	926	5677	71
H(29C)	7934	965	5905	71
H(30A)	6938	3562	5601	74
H(30B)	6726	3717	6434	74
H(30C)	6454	2626	5969	74
H(31A)	10484	2802	7015	40
H(31B)	10573	1465	7278	40
H(32A)	9765	1718	8171	44
H(32B)	10332	2673	8279	44
H(33A)	9249	316	6333	39
H(33B)	9531	174	7139	39
H(34)	10585	-216	6672	45
H(35A)	10761	-447	5420	78
H(35B)	10518	875	5577	78
H(35C)	10022	-82	5252	78
H(36A)	9625	-1742	6036	79

H(36B)	9848	-1812	6870	79
H(36C)	10356	-2121	6237	79

Crystallographic Experimental Section for 4c

Data Collection

A colorless crystal was selected under ambient conditions. The crystal was mounted and centered in the X-ray beam by using a video camera. The crystal evaluation and data collection were performed room temperature on a Bruker CCD-1000 diffractometer with Mo K_α ($\lambda = 0.71073$ Å) radiation and the detector to crystal distance of 5.03 cm. The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 30 frames collected at intervals of 0.3° in a 10° range about ω with the exposure time of 10 seconds per frame. The obtained reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of strong reflections from the actual data collection. The data were collected using the full sphere routine by collecting four sets of frames with 0.3° scans in ω with an exposure time 10 sec per frame. This dataset was corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements [1] using SADABS software [2].

Structure Solution and Refinement

The systematic absences in the diffraction data were consistent for the space groups $P1$ and $P\bar{1}$ [2]. The E -statistics strongly suggested the centrosymmetric space group $P\bar{1}$ yielded chemically reasonable and computationally stable results of refinement. The position of almost all non-hydrogen atoms were found by direct methods. The remaining atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined in full-matrix anisotropic approximation. All hydrogen atoms were placed in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

The ORTEP diagram was drawn at 50% probability level. H-atoms were omitted for clarity. The resulting CIF file has been tested with PLATON [3] software. The results and comments have been included in the output package (Platon_Ver115.doc).

References

- [1] Blessing, R.H. *Acta Cryst.* **1995**, *A51*, 33-38.
- [2] All software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-Ray Systems, Madison, WI).
- [3] A.L.Spek, *J.Appl.Cryst.* 36, 7-13.

Table 1. Crystal data and structure refinement for **4c**.

Empirical formula	C ₂₆ H ₅₇ N ₅ P ₂	
Formula weight	501.71	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.0374(18) Å	α = 89.909(3)°.
	b = 10.3404(19) Å	β = 86.599(3)°.
	c = 16.234(3) Å	γ = 66.722(3)°.
Volume	1544.6(5) Å ³	
Z	2	
Density (calculated)	1.079 Mg/m ³	
Absorption coefficient	0.162 mm ⁻¹	
F(000)	556	
Crystal size	0.40 x 0.30 x 0.20 mm ³	
Theta range for data collection	1.26 to 28.39°.	
Index ranges	-13 ≤ h ≤ 13, -13 ≤ k ≤ 13, -19 ≤ l ≤ 20	
Reflections collected	13743	
Independent reflections	6876 [R(int) = 0.0216]	
Completeness to theta = 25.00°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1 and 0.81	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6876 / 0 / 310	
Goodness-of-fit on F ²	1.008	
Final R indices [I > 2σ(I)]	R1 = 0.0490, wR2 = 0.1299	
R indices (all data)	R1 = 0.0666, wR2 = 0.1468	
Largest diff. peak and hole	0.904 and -0.480 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4c**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
P(1)	1271(1)	3138(1)	2174(1)	32(1)
P(2)	3567(1)	4147(1)	2615(1)	40(1)
C(1)	2189(2)	904(2)	1063(1)	46(1)
C(2)	869(3)	1036(3)	600(2)	59(1)
C(3)	2895(2)	2911(2)	744(1)	39(1)
C(4)	4442(2)	2015(2)	397(1)	44(1)
C(5)	5454(2)	1225(3)	1051(1)	57(1)
C(6)	5014(3)	2984(3)	-73(2)	69(1)
C(7)	-593(2)	1861(2)	2622(1)	50(1)
C(8)	-662(3)	1046(3)	1853(2)	61(1)
C(9)	1810(2)	995(2)	3240(1)	51(1)
C(10)	1244(5)	883(4)	4121(2)	104(1)
C(11)	2550(5)	-63(4)	4594(2)	119(2)
C(12)	265(5)	2140(5)	4551(2)	114(1)
C(13)	-803(2)	4200(2)	1038(1)	51(1)
C(14)	-1446(3)	3093(3)	939(2)	63(1)
C(15)	-1377(2)	5241(2)	2473(1)	51(1)
C(16)	-1572(3)	6764(2)	2512(2)	61(1)
C(17)	-2611(4)	7502(3)	3250(2)	102(1)
C(18)	-2034(4)	7560(3)	1735(2)	101(1)
C(19)	4349(3)	3578(3)	3648(1)	64(1)
C(20)	5158(4)	1976(4)	3535(2)	91(1)
C(21)	3223(4)	3927(5)	4383(2)	102(1)
C(22)	5490(4)	4165(4)	3829(2)	95(1)
C(23)	2836(3)	6137(2)	2579(2)	56(1)
C(24)	1791(3)	6902(3)	3308(2)	80(1)
C(25)	4097(3)	6628(3)	2488(2)	86(1)
C(26)	2079(3)	6483(2)	1764(2)	65(1)
N(1)	2236(2)	2235(2)	1340(1)	35(1)
N(2)	775(2)	2026(2)	2723(1)	39(1)
N(3)	-281(2)	4318(2)	1850(1)	40(1)

N(4)	-500(2)	1658(2)	1078(1)	59(1)
N(5)	2052(2)	3834(2)	2703(1)	39(1)

Table 3. Bond lengths [Å] and angles [°] for **4c**.

P(1)-N(5)	1.5484(15)	C(7)-H(7B)	0.9700	C(16)-H(16)	0.9800
P(1)-N(2)	1.6621(15)	C(8)-N(4)	1.438(3)	C(17)-H(17A)	0.9600
P(1)-N(1)	1.6654(15)	C(8)-H(8A)	0.9700	C(17)-H(17B)	0.9600
P(1)-N(3)	1.6690(15)	C(8)-H(8B)	0.9700	C(17)-H(17C)	0.9600
P(2)-N(5)	1.6727(16)	C(9)-N(2)	1.464(2)	C(18)-H(18A)	0.9600
P(2)-C(19)	1.887(2)	C(9)-C(10)	1.529(4)	C(18)-H(18B)	0.9600
P(2)-C(23)	1.895(2)	C(9)-H(9A)	0.9700	C(18)-H(18C)	0.9600
C(1)-N(1)	1.468(2)	C(9)-H(9B)	0.9700	C(19)-C(20)	1.535(4)
C(1)-C(2)	1.521(3)	C(10)-C(12)	1.433(5)	C(19)-C(22)	1.535(3)
C(1)-H(1A)	0.9700	C(10)-C(11)	1.538(5)	C(19)-C(21)	1.533(4)
C(1)-H(1B)	0.9700	C(10)-H(10)	0.9800	C(20)-H(20A)	0.9600
C(2)-N(4)	1.442(3)	C(11)-H(11A)	0.9600	C(20)-H(20B)	0.9600
C(2)-H(2A)	0.9700	C(11)-H(11B)	0.9600	C(20)-H(20C)	0.9600
C(2)-H(2B)	0.9700	C(11)-H(11C)	0.9600	C(21)-H(21A)	0.9600
C(3)-N(1)	1.467(2)	C(12)-H(12A)	0.9600	C(21)-H(21B)	0.9600
C(3)-C(4)	1.532(3)	C(12)-H(12B)	0.9600	C(21)-H(21C)	0.9600
C(3)-H(3A)	0.9700	C(12)-H(12C)	0.9600	C(22)-H(22A)	0.9600
C(3)-H(3B)	0.9700	C(13)-N(3)	1.469(3)	C(22)-H(22B)	0.9600
C(4)-C(5)	1.515(3)	C(13)-C(14)	1.532(3)	C(22)-H(22C)	0.9600
C(4)-C(6)	1.522(3)	C(13)-H(13A)	0.9700	C(23)-C(24)	1.525(3)
C(4)-H(4)	0.9800	C(13)-H(13B)	0.9700	C(23)-C(26)	1.536(4)
C(5)-H(5A)	0.9600	C(14)-N(4)	1.437(3)	C(23)-C(25)	1.539(3)
C(5)-H(5B)	0.9600	C(14)-H(14A)	0.9700	C(24)-H(24A)	0.9600
C(5)-H(5C)	0.9600	C(14)-H(14B)	0.9700	C(24)-H(24B)	0.9600
C(6)-H(6A)	0.9600	C(15)-N(3)	1.479(3)	C(24)-H(24C)	0.9600
C(6)-H(6B)	0.9600	C(15)-C(16)	1.510(3)	C(25)-H(25A)	0.9600
C(6)-H(6C)	0.9600	C(15)-H(15A)	0.9700	C(25)-H(25B)	0.9600
C(7)-N(2)	1.467(2)	C(15)-H(15B)	0.9700	C(25)-H(25C)	0.9600
C(7)-C(8)	1.528(3)	C(16)-C(18)	1.500(4)	C(26)-H(26A)	0.9600
C(7)-H(7A)	0.9700	C(16)-C(17)	1.527(4)	C(26)-H(26B)	0.9600

C(26)-H(26C)	0.9600				
N(5)-P(1)-N(2)	111.27(8)	H(5A)-C(5)-H(5B)	109.5	C(10)-C(11)-H(11B)	109.5
N(5)-P(1)-N(1)	115.40(8)	C(4)-C(5)-H(5C)	109.5	H(11A)-C(11)-H(11B)	109.5
N(2)-P(1)-N(1)	106.31(8)	H(5A)-C(5)-H(5C)	109.5	C(10)-C(11)-H(11C)	109.5
N(5)-P(1)-N(3)	111.92(8)	H(5B)-C(5)-H(5C)	109.5	H(11A)-C(11)-H(11C)	109.5
N(2)-P(1)-N(3)	104.45(8)	C(4)-C(6)-H(6A)	109.5	H(11B)-C(11)-H(11C)	109.5
N(1)-P(1)-N(3)	106.74(8)	C(4)-C(6)-H(6B)	109.5	C(10)-C(12)-H(12A)	109.5
N(5)-P(2)-C(19)	102.02(10)	H(6A)-C(6)-H(6B)	109.5	C(10)-C(12)-H(12B)	109.5
N(5)-P(2)-C(23)	102.81(9)	C(4)-C(6)-H(6C)	109.5	H(12A)-C(12)-H(12B)	109.5
C(19)-P(2)-C(23)	108.69(12)	H(6A)-C(6)-H(6C)	109.5	C(10)-C(12)-H(12C)	109.5
N(1)-C(1)-C(2)	115.72(17)	H(6B)-C(6)-H(6C)	109.5	H(12A)-C(12)-H(12C)	109.5
N(1)-C(1)-H(1A)	108.3	N(2)-C(7)-C(8)	116.70(18)	H(12B)-C(12)-H(12C)	109.5
C(2)-C(1)-H(1A)	108.3	N(2)-C(7)-H(7A)	108.1	N(3)-C(13)-C(14)	116.82(18)
N(1)-C(1)-H(1B)	108.3	C(8)-C(7)-H(7A)	108.1	N(3)-C(13)-H(13A)	108.1
C(2)-C(1)-H(1B)	108.3	N(2)-C(7)-H(7B)	108.1	C(14)-C(13)-H(13A)	108.1
H(1A)-C(1)-H(1B)	107.4	C(8)-C(7)-H(7B)	108.1	N(3)-C(13)-H(13B)	108.1
N(4)-C(2)-C(1)	114.67(19)	H(7A)-C(7)-H(7B)	107.3	C(14)-C(13)-H(13B)	108.1
N(4)-C(2)-H(2A)	108.6	N(4)-C(8)-C(7)	115.60(18)	H(13A)-C(13)-H(13B)	107.3
C(1)-C(2)-H(2A)	108.6	N(4)-C(8)-H(8A)	108.4	N(4)-C(14)-C(13)	116.45(18)
N(4)-C(2)-H(2B)	108.6	C(7)-C(8)-H(8A)	108.4	N(4)-C(14)-H(14A)	108.2
C(1)-C(2)-H(2B)	108.6	N(4)-C(8)-H(8B)	108.4	C(13)-C(14)-H(14A)	108.2
H(2A)-C(2)-H(2B)	107.6	C(7)-C(8)-H(8B)	108.4	N(4)-C(14)-H(14B)	108.2
N(1)-C(3)-C(4)	116.47(15)	H(8A)-C(8)-H(8B)	107.4	C(13)-C(14)-H(14B)	108.2
N(1)-C(3)-H(3A)	108.2	N(2)-C(9)-C(10)	116.1(2)	H(14A)-C(14)-H(14B)	107.3
C(4)-C(3)-H(3A)	108.2	N(2)-C(9)-H(9A)	108.3	N(3)-C(15)-C(16)	116.90(19)
N(1)-C(3)-H(3B)	108.2	C(10)-C(9)-H(9A)	108.3	N(3)-C(15)-H(15A)	108.1
C(4)-C(3)-H(3B)	108.2	N(2)-C(9)-H(9B)	108.3	C(16)-C(15)-H(15A)	108.1
H(3A)-C(3)-H(3B)	107.3	C(10)-C(9)-H(9B)	108.3	N(3)-C(15)-H(15B)	108.1
C(5)-C(4)-C(6)	111.22(19)	H(9A)-C(9)-H(9B)	107.4	C(16)-C(15)-H(15B)	108.1
C(5)-C(4)-C(3)	113.49(17)	C(12)-C(10)-C(9)	118.7(3)	H(15A)-C(15)-H(15B)	107.3
C(6)-C(4)-C(3)	107.69(17)	C(12)-C(10)-C(11)	115.8(3)	C(18)-C(16)-C(15)	115.2(2)
C(5)-C(4)-H(4)	108.1	C(9)-C(10)-C(11)	107.5(3)	C(18)-C(16)-C(17)	111.3(3)
C(6)-C(4)-H(4)	108.1	C(12)-C(10)-H(10)	104.3	C(15)-C(16)-C(17)	109.2(2)
C(3)-C(4)-H(4)	108.1	C(9)-C(10)-H(10)	104.3	C(18)-C(16)-H(16)	106.9
C(4)-C(5)-H(5A)	109.5	C(11)-C(10)-H(10)	104.3	C(15)-C(16)-H(16)	106.9
C(4)-C(5)-H(5B)	109.5	C(10)-C(11)-H(11A)	109.5	C(17)-C(16)-H(16)	106.9

C(16)-C(17)-H(17A)	109.5	C(19)-C(21)-H(21B)	109.5	H(25A)-C(25)-H(25B)	109.5
C(16)-C(17)-H(17B)	109.5	H(21A)-C(21)-H(21B)	109.5	C(23)-C(25)-H(25C)	109.5
H(17A)-C(17)-H(17B)	109.5	C(19)-C(21)-H(21C)	109.5	H(25A)-C(25)-H(25C)	109.5
C(16)-C(17)-H(17C)	109.5	H(21A)-C(21)-H(21C)	109.5	H(25B)-C(25)-H(25C)	109.5
H(17A)-C(17)-H(17C)	109.5	H(21B)-C(21)-H(21C)	109.5	C(23)-C(26)-H(26A)	109.5
H(17B)-C(17)-H(17C)	109.5	C(19)-C(22)-H(22A)	109.5	C(23)-C(26)-H(26B)	109.5
C(16)-C(18)-H(18A)	109.5	C(19)-C(22)-H(22B)	109.5	H(26A)-C(26)-H(26B)	109.5
C(16)-C(18)-H(18B)	109.5	H(22A)-C(22)-H(22B)	109.5	C(23)-C(26)-H(26C)	109.5
H(18A)-C(18)-H(18B)	109.5	C(19)-C(22)-H(22C)	109.5	H(26A)-C(26)-H(26C)	109.5
C(16)-C(18)-H(18C)	109.5	H(22A)-C(22)-H(22C)	109.5	H(26B)-C(26)-H(26C)	109.5
H(18A)-C(18)-H(18C)	109.5	H(22B)-C(22)-H(22C)	109.5	C(1)-N(1)-C(3)	115.98(15)
H(18B)-C(18)-H(18C)	109.5	C(24)-C(23)-C(26)	111.1(2)	C(1)-N(1)-P(1)	122.74(13)
C(20)-C(19)-C(22)	106.9(2)	C(24)-C(23)-C(25)	110.4(2)	C(3)-N(1)-P(1)	119.74(12)
C(20)-C(19)-C(21)	110.2(3)	C(26)-C(23)-C(25)	106.0(2)	C(9)-N(2)-C(7)	116.28(16)
C(22)-C(19)-C(21)	109.0(2)	C(24)-C(23)-P(2)	114.60(18)	C(9)-N(2)-P(1)	120.13(13)
C(20)-C(19)-P(2)	103.37(17)	C(26)-C(23)-P(2)	104.00(14)	C(7)-N(2)-P(1)	122.89(13)
C(22)-C(19)-P(2)	112.0(2)	C(25)-C(23)-P(2)	110.24(18)	C(13)-N(3)-C(15)	116.40(16)
C(21)-C(19)-P(2)	114.93(19)	C(23)-C(24)-H(24A)	109.5	C(13)-N(3)-P(1)	122.54(13)
C(19)-C(20)-H(20A)	109.5	C(23)-C(24)-H(24B)	109.5	C(15)-N(3)-P(1)	118.29(13)
C(19)-C(20)-H(20B)	109.5	H(24A)-C(24)-H(24B)	109.5	C(14)-N(4)-C(8)	118.7(2)
H(20A)-C(20)-H(20B)	109.5	C(23)-C(24)-H(24C)	109.5	C(14)-N(4)-C(2)	119.3(2)
C(19)-C(20)-H(20C)	109.5	H(24A)-C(24)-H(24C)	109.5	C(8)-N(4)-C(2)	118.4(2)
H(20A)-C(20)-H(20C)	109.5	H(24B)-C(24)-H(24C)	109.5	P(1)-N(5)-P(2)	137.36(11)
H(20B)-C(20)-H(20C)	109.5	C(23)-C(25)-H(25A)	109.5		
C(19)-C(21)-H(21A)	109.5	C(23)-C(25)-H(25B)	109.5		

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4c**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
P(1)	33(1)	31(1)	32(1)	2(1)	-5(1)	-13(1)
P(2)	39(1)	45(1)	37(1)	-7(1)	-1(1)	-19(1)
C(1)	53(1)	41(1)	48(1)	-10(1)	-1(1)	-22(1)
C(2)	69(2)	62(1)	56(1)	-12(1)	-10(1)	-37(1)
C(3)	42(1)	41(1)	33(1)	2(1)	-4(1)	-15(1)
C(4)	44(1)	49(1)	39(1)	-7(1)	0(1)	-18(1)
C(5)	45(1)	58(1)	55(1)	-7(1)	-7(1)	-7(1)
C(6)	61(2)	79(2)	68(2)	4(1)	14(1)	-32(1)
C(7)	45(1)	52(1)	61(1)	8(1)	-2(1)	-28(1)
C(8)	54(1)	60(1)	82(2)	1(1)	-11(1)	-36(1)
C(9)	59(1)	43(1)	52(1)	15(1)	-13(1)	-21(1)
C(10)	142(3)	97(2)	56(2)	22(2)	-22(2)	-26(2)
C(11)	172(4)	115(3)	83(2)	53(2)	-66(3)	-63(3)
C(12)	127(3)	167(4)	61(2)	-15(2)	21(2)	-75(3)
C(13)	45(1)	54(1)	50(1)	11(1)	-19(1)	-15(1)
C(14)	54(1)	77(2)	65(2)	4(1)	-24(1)	-32(1)
C(15)	39(1)	48(1)	57(1)	3(1)	3(1)	-9(1)
C(16)	50(1)	51(1)	76(2)	-6(1)	-3(1)	-15(1)
C(17)	88(2)	77(2)	131(3)	-43(2)	30(2)	-26(2)
C(18)	135(3)	46(2)	117(3)	21(2)	-47(2)	-25(2)
C(19)	62(1)	103(2)	44(1)	2(1)	-16(1)	-48(1)
C(20)	87(2)	103(2)	90(2)	40(2)	-49(2)	-39(2)
C(21)	104(2)	192(4)	40(1)	3(2)	-6(1)	-90(3)
C(22)	83(2)	158(3)	75(2)	1(2)	-28(2)	-78(2)
C(23)	56(1)	47(1)	73(2)	-13(1)	9(1)	-30(1)
C(24)	73(2)	68(2)	98(2)	-39(2)	17(2)	-31(1)
C(25)	81(2)	74(2)	124(3)	-8(2)	9(2)	-54(2)
C(26)	68(2)	42(1)	84(2)	10(1)	3(1)	-21(1)
N(1)	39(1)	34(1)	35(1)	-2(1)	-4(1)	-16(1)
N(2)	40(1)	38(1)	42(1)	7(1)	-5(1)	-19(1)
N(3)	35(1)	39(1)	41(1)	4(1)	-7(1)	-10(1)

N(4)	57(1)	64(1)	65(1)	0(1)	-15(1)	-31(1)
N(5)	42(1)	40(1)	37(1)	-4(1)	-4(1)	-19(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4c**.

	x	y	z	U(eq)
H(1A)	2226	332	1542	55
H(1B)	3055	404	708	55
H(2A)	834	1601	118	71
H(2B)	992	106	408	71
H(3A)	2904	3750	1006	47
H(3B)	2275	3215	285	47
H(4)	4389	1323	2	53
H(5A)	6409	711	798	85
H(5B)	5099	582	1314	85
H(5C)	5496	1883	1455	85
H(6A)	5113	3647	306	103
H(6B)	4346	3481	-477	103
H(6C)	5944	2435	-345	103
H(7A)	-1368	2793	2618	60
H(7B)	-790	1392	3103	60
H(8A)	94	105	1863	73
H(8B)	-1589	954	1882	73
H(9A)	2651	1231	3268	61
H(9B)	2137	77	2969	61
H(10)	668	317	4063	125
H(11A)	3253	352	4597	179
H(11B)	2985	-976	4328	179
H(11C)	2228	-154	5151	179
H(12A)	-54	1901	5077	172
H(12B)	-560	2603	4231	172
H(12C)	754	2758	4632	172
H(13A)	2	3993	628	61
H(13B)	-1537	5111	912	61
H(14A)	-2298	3342	1318	75
H(14B)	-1770	3147	384	75

H(15A)	-1120	4845	3012	61
H(15B)	-2308	5213	2369	61
H(16)	-624	6770	2621	73
H(17A)	-3565	7547	3157	153
H(17B)	-2650	8439	3315	153
H(17C)	-2274	6985	3740	153
H(18A)	-1302	7137	1297	152
H(18B)	-2160	8521	1821	152
H(18C)	-2935	7533	1588	152
H(20A)	5523	1576	4050	137
H(20B)	5954	1771	3129	137
H(20C)	4503	1580	3354	137
H(21A)	3647	3339	4836	153
H(21B)	2395	3762	4227	153
H(21C)	2924	4898	4547	153
H(22A)	5011	5143	3988	142
H(22B)	6118	4068	3343	142
H(22C)	6054	3653	4269	142
H(24A)	1246	7863	3169	120
H(24B)	2332	6878	3780	120
H(24C)	1136	6448	3433	120
H(25A)	3742	7578	2299	129
H(25B)	4832	6024	2096	129
H(25C)	4504	6588	3013	129
H(26A)	1361	6087	1759	98
H(26B)	2786	6091	1310	98
H(26C)	1618	7486	1714	98