Improved Synthesis of Asymmetrical Substituted 1*H-1*,2,4-Diazaphospholes

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**Supplemental Materials**

**General Procedures**

*Preparation of imidoyl chloride (****1****)*: Oxalyl chloride (32 mL, 375 mmol) was added gradually to a solution of *N*,*N*-dimethylalkylamide(125 mmol) in 350 mL diethyl ether over a period of 1 h. During this time a white precipitate formed with evolution of gas. After stirring for 12 h at room temperature, the solution was filtrated and the resulting residue was washed with diethyl ether (3×100 mL) to afford **1** as white solid in high yield.

*Preparation of asymmetrical 1,3-bis(amino)-2-phosphaallyl chloride (****2****):* To a mixture of **1**(R1) (30 mmol) and **1**(R2) (30 mmol) in a ratio of 1:1 in 120 mL acetonitrile, P(SiMe3)3 (11 mL, 35 mmol) was slowly added within 1 h with a syringe. The resulting solution was stirred for 10 h at room temperature, then the solvent was removed under reduced pressure. The resulting residue was washed with ether (3 × 20 mL) to give **2** as dark-orange solid in good yield.

*Synthesis of asymmetrical 1H-1,2,4-diazaphosphole (****3****)*: To a solution of **2** (30 mmol) in chloroform (90 mL) was added anhydrous hydrazine (5.5 mL, 165 mmol). After stirring for 24 h at room temperature, the suspension was refluxed for 12 h and the solvent was then removed under reduced pressure. The resulting residue was extracted with diethyl ether (10 × 30 mL). The combined extract in diethyl ether was washed with water (2 × 100 mL). After drying with anhydrous sodium sulfate, the solvent was evaporated and the white solid residue was purified by column chromatography on silica-gel using ethylacetate-petroleum ether (6:9) as eluent.

 Crystallographic data for **3.**

Crystallographic data for **3a**

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

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 Identification code L2

 Empirical formula C6 H11 N2 P

 Formula weight 142.14

 Temperature 296(2) K

 Wavelength 0.71073 A

 Crystal system, space group Monoclinic, *C*2/*c*

 Unit cell dimensions *a* = 20.785(6) Å *α* = 90 deg.

 *b* = 9.875(3) Å *β* = 117.922(4) deg.

 *c* = 18.310(5) Å *γ* = 90 deg.

 Volume 3320.5(16) Å3

 Z, calculated density 16, 1.137 Mg/m3

 Absorption coefficient 0.253 mm-1

 F(000) 1216

 Crystal size 0.30 x 0.20 x 0.20 mm

 Theta range for data collection 2.22 to 25.04 deg.

 Limiting indices -24<=*h*<=24, -11<=*k*<=11, -21<=*l*<=21

 Reflections collected / unique 16631 / 2946 [*R*(int) = 0.0509]

 Completeness to theta = 25.04 100.0 %

 Absorption correction Semi-empirical from equivalents

 Max. and min. transmission 0.9511 and 0.9280

 Refinement method Full-matrix least-squares on *F*2

 Data / restraints / parameters 2946 / 36 / 169

 Goodness-of-fit on *F*2 1.057

 Final *R* indices [*I*>2*σ*(*I*)] *R*1 = 0.0801, *wR*2 = 0.2310

 *R* indices (all data) *R*1 = 0.1077, *wR*2 = 0.2633

 Largest diff. peak and hole 0.563 and -0.525 e.Å-3

Table S 2. Atomic coordinates ( x 104) and equivalent isotropic displacement parameters (Å2 x 103) for L2. U(eq) is defined as one third of the trace of the orthogonalized *Uij* tensor.

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 x y z U(eq)

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 P(1) 1195(1) 3924(1) 3022(1) 70(1)

 N(1) 830(3) 6257(4) 3315(3) 70(1)

 N(2) 997(2) 6470(4) 2699(3) 59(1)

 C(1) -588(3) 10269(6) 3157(4) 80(2)

 C(2) 657(3) 9921(5) 4103(3) 56(1)

 C(3) 1455(3) 9865(7) 4712(4) 80(2)

 C(4) 1898(4) 9751(9) 4258(5) 117(2)

 C(5) 1612(5) 8638(9) 5263(5) 123(3)

 C(6) 1669(5) 11150(9) 5216(6) 139(3)

 P(2) 85(1) 11315(2) 3844(1) 87(1)

 N(3) -378(3) 9026(4) 3143(3) 70(1)

 N(4) 322(2) 8817(4) 3673(3) 62(1)

 C(7) 904(3) 4983(5) 3552(3) 70(1)

 C(8) 1206(2) 5348(4) 2468(3) 52(1)

 C(9) 1412(3) 5430(6) 1786(4) 80(2)

 C(10) 1992(4) 6493(9) 1986(5) 111(2)

 C(11) 748(5) 5874(10) 981(4) 121(2)

 C(12) 1689(5) 4070(9) 1675(6) 128(3)

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 Table 3. Bond lengths [Å] and angles [deg] for **3a**.

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 P(1)-C(7) 1.719(6)

 P(1)-C(8) 1.740(5)

 N(1)-C(7) 1.317(6)

 N(1)-N(2) 1.342(6)

 N(1)-H(2) 0.8600

 N(2)-C(8) 1.328(6)

 C(1)-N(3) 1.308(7)

 C(1)-P(2) 1.720(6)

 C(1)-H(1) 0.9300

 C(2)-N(4) 1.334(6)

 C(2)-C(3) 1.504(8)

 C(2)-P(2) 1.734(5)

 C(3)-C(4) 1.506(9)

 C(3)-C(6) 1.508(9)

 C(3)-C(5) 1.511(9)

 C(4)-H(4A) 0.9600

 C(4)-H(4B) 0.9600

 C(4)-H(4C) 0.9600

 C(5)-H(5A) 0.9600

 C(5)-H(5B) 0.9600

 C(5)-H(5C) 0.9600

 C(6)-H(6A) 0.9600

 C(6)-H(6B) 0.9600

 C(6)-H(6C) 0.9600

 N(3)-N(4) 1.333(6)

 N(3)-H(3) 0.8600

 C(7)-H(7) 0.9300

 C(8)-C(9) 1.502(7)

 C(9)-C(10) 1.507(9)

 C(9)-C(12) 1.512(9)

 C(9)-C(11) 1.536(10)

 C(10)-H(10A) 0.9600

 C(10)-H(10B) 0.9600

 C(10)-H(10C) 0.9600

 C(11)-H(11A) 0.9600

 C(11)-H(11B) 0.9600

 C(11)-H(11C) 0.9600

 C(12)-H(12A) 0.9600

 C(12)-H(12B) 0.9600

 C(12)-H(12C) 0.9600

 C(7)-P(1)-C(8) 86.6(2)

 C(7)-N(1)-N(2) 113.0(4)

 C(7)-N(1)-H(2) 123.5

 N(2)-N(1)-H(2) 123.5

 C(8)-N(2)-N(1) 112.8(4)

 N(3)-C(1)-P(2) 114.4(4)

 N(3)-C(1)-H(1) 122.8

 P(2)-C(1)-H(1) 122.8

 N(4)-C(2)-C(3) 119.8(4)

 N(4)-C(2)-P(2) 112.7(4)

 C(3)-C(2)-P(2) 127.5(4)

 C(2)-C(3)-C(4) 109.9(5)

 C(2)-C(3)-C(6) 109.2(5)

 C(4)-C(3)-C(6) 108.6(7)

 C(2)-C(3)-C(5) 110.1(6)

 C(4)-C(3)-C(5) 108.2(6)

 C(6)-C(3)-C(5) 110.9(7)

 C(3)-C(4)-H(4A) 109.5

 C(3)-C(4)-H(4B) 109.5

 H(4A)-C(4)-H(4B) 109.5

 C(3)-C(4)-H(4C) 109.5

 H(4A)-C(4)-H(4C) 109.5

 H(4B)-C(4)-H(4C) 109.5

 C(3)-C(5)-H(5A) 109.5

 C(3)-C(5)-H(5B) 109.5

 H(5A)-C(5)-H(5B) 109.5

 C(3)-C(5)-H(5C) 109.5

 H(5A)-C(5)-H(5C) 109.5

 H(5B)-C(5)-H(5C) 109.5

 C(3)-C(6)-H(6A) 109.5

 C(3)-C(6)-H(6B) 109.5

 H(6A)-C(6)-H(6B) 109.5

 C(3)-C(6)-H(6C) 109.5

 H(6A)-C(6)-H(6C) 109.5

 H(6B)-C(6)-H(6C) 109.5

 C(1)-P(2)-C(2) 86.7(3)

 C(1)-N(3)-N(4) 113.1(4)

 C(1)-N(3)-H(3) 123.5

 N(4)-N(3)-H(3) 123.5

 N(3)-N(4)-C(2) 113.2(4)

 N(1)-C(7)-P(1) 114.3(4)

 N(1)-C(7)-H(7) 122.8

 P(1)-C(7)-H(7) 122.8

 N(2)-C(8)-C(9) 118.9(4)

 N(2)-C(8)-P(1) 113.2(4)

 C(9)-C(8)-P(1) 127.9(4)

 C(8)-C(9)-C(10) 110.0(5)

 C(8)-C(9)-C(12) 109.8(5)

 C(10)-C(9)-C(12) 109.9(6)

 C(8)-C(9)-C(11) 109.6(5)

 C(10)-C(9)-C(11) 107.0(6)

 C(12)-C(9)-C(11) 110.6(7)

 C(9)-C(10)-H(10A) 109.5

 C(9)-C(10)-H(10B) 109.5

 H(10A)-C(10)-H(10B) 109.5

 C(9)-C(10)-H(10C) 109.5

 H(10A)-C(10)-H(10C) 109.5

 H(10B)-C(10)-H(10C) 109.5

 C(9)-C(11)-H(11A) 109.5

 C(9)-C(11)-H(11B) 109.5

 H(11A)-C(11)-H(11B) 109.5

 C(9)-C(11)-H(11C) 109.5

 H(11A)-C(11)-H(11C) 109.5

 H(11B)-C(11)-H(11C) 109.5

 C(9)-C(12)-H(12A) 109.5

 C(9)-C(12)-H(12B) 109.5

 H(12A)-C(12)-H(12B) 109.5

 C(9)-C(12)-H(12C) 109.5

 H(12A)-C(12)-H(12C) 109.5

 H(12B)-C(12)-H(12C) 109.5

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 Symmetry transformations used to generate equivalent atoms:

 Table S 4. Anisotropic displacement parameters (A^2 x 10^3) for 3a. The anisotropic displacement factor exponent takes the form: -2 pi^2 [ h^2 a\*^2 U11 + ... + 2 h k a\* b\* U12 ]

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 U11 U22 U33 U23 U13 U12

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 P(1) 79(1) 41(1) 90(1) 7(1) 40(1) 10(1)

 N(1) 84(3) 55(3) 70(3) -4(2) 35(2) 16(2)

 N(2) 68(3) 45(2) 64(2) -1(2) 30(2) 7(2)

 C(1) 68(3) 60(3) 101(4) -11(3) 32(3) 5(3)

 C(2) 68(3) 46(2) 60(3) -5(2) 35(2) -3(2)

 C(3) 69(3) 99(4) 75(3) -5(3) 37(3) 8(3)

 C(4) 80(4) 156(6) 111(5) 1(4) 42(4) 5(4)

 C(5) 104(5) 136(6) 102(5) 32(4) 25(4) 11(4)

 C(6) 98(5) 129(6) 134(5) -45(5) 6(4) 7(4)

 P(2) 77(1) 49(1) 111(1) -20(1) 25(1) 7(1)

 N(3) 75(3) 51(2) 84(3) -16(2) 37(3) -13(2)

 N(4) 68(3) 49(2) 74(3) -7(2) 38(2) -2(2)

 C(7) 76(3) 64(3) 68(3) 12(3) 32(3) 11(3)

 C(8) 42(2) 44(2) 65(3) -4(2) 20(2) 0(2)

 C(9) 89(3) 79(3) 92(3) -6(3) 60(3) -3(3)

 C(10) 99(4) 126(5) 116(5) 3(4) 56(4) -32(4)

 C(11) 115(5) 170(6) 75(4) -7(4) 44(4) -2(5)

 C(12) 159(6) 109(5) 156(6) -9(5) 109(5) 20(5)

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Table S 5. Hydrogen coordinates ( x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 3a.

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 x y z U(eq)

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 H(2) 690 6888 3532 84

 H(1) -1062 10564 2824 95

 H(4A) 1772 8930 3940 175

 H(4B) 2407 9738 4649 175

 H(4C) 1797 10513 3895 175

 H(5A) 1360 8721 5586 185

 H(5B) 2126 8577 5625 185

 H(5C) 1450 7837 4928 185

 H(6A) 1564 11915 4855 209

 H(6B) 2180 11127 5596 209

 H(6C) 1398 11224 5519 209

 H(3) -662 8406 2825 84

 H(7) 806 4681 3971 84

 H(10A) 2408 6275 2502 167

 H(10B) 1804 7361 2029 167

 H(10C) 2132 6519 1556 167

 H(11A) 886 5961 551 181

 H(11B) 574 6729 1066 181

 H(11C) 370 5207 825 181

 H(12A) 2119 3831 2173 191

 H(12B) 1805 4120 1225 191

 H(12C) 1321 3395 1556 191

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ Table S 6. Torsion angles [deg] for 3a.

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 C(7)-N(1)-N(2)-C(8) -0.5(6)

 N(4)-C(2)-C(3)-C(4) 70.6(7)

 P(2)-C(2)-C(3)-C(4) -107.1(6)

 N(4)-C(2)-C(3)-C(6) -170.3(6)

 P(2)-C(2)-C(3)-C(6) 12.0(8)

 N(4)-C(2)-C(3)-C(5) -48.4(7)

 P(2)-C(2)-C(3)-C(5) 133.9(5)

 N(3)-C(1)-P(2)-C(2) -0.4(5)

 N(4)-C(2)-P(2)-C(1) 0.4(4)

 C(3)-C(2)-P(2)-C(1) 178.3(5)

 P(2)-C(1)-N(3)-N(4) 0.3(7)

 C(1)-N(3)-N(4)-C(2) 0.0(7)

 C(3)-C(2)-N(4)-N(3) -178.4(4)

 P(2)-C(2)-N(4)-N(3) -0.4(5)

 N(2)-N(1)-C(7)-P(1) 0.2(6)

 C(8)-P(1)-C(7)-N(1) 0.1(4)

 N(1)-N(2)-C(8)-C(9) -179.8(4)

 N(1)-N(2)-C(8)-P(1) 0.5(5)

 C(7)-P(1)-C(8)-N(2) -0.3(4)

 C(7)-P(1)-C(8)-C(9) -179.9(5)

 N(2)-C(8)-C(9)-C(10) 54.3(7)

 P(1)-C(8)-C(9)-C(10) -126.1(5)

 N(2)-C(8)-C(9)-C(12) 175.3(6)

 P(1)-C(8)-C(9)-C(12) -5.1(8)

 N(2)-C(8)-C(9)-C(11) -63.0(7)

 P(1)-C(8)-C(9)-C(11) 116.6(6)

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 Symmetry transformations used to generate equivalent atoms:

 Table S 7. Hydrogen bonds for 3a [A and deg.].

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 D-H...A d(D-H) d(H...A) d(D...A) <(DHA)

 N(1)-H(2)...N(4) 0.86 2.11 2.930(6) 158.4

 N(3)-H(3)...N(2)#1 0.86 2.11 2.924(6) 158.4

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 Symmetry transformations used to generate equivalent atoms:

 #1 -x,y,-z+1/2

Crystallographic data for **3b**

 Table S 8. Crystal data and structure refinement for 3b.

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 Identification code L4

 Empirical formula C7 H13 N2 P

 Formula weight 156.16

 Temperature 296(2) K

 Wavelength 0.71073 A

 Crystal system, space group Monoclinic, C2/c

 Unit cell dimensions a = 12.260(17) A alpha = 90 deg.

 b = 22.05(3) A beta = 94.24(2) deg.

 c = 14.10(2) A gamma = 90 deg.

 Volume 3802(9) A^3

 Z, Calculated density 16, 1.091 Mg/m^3

 Absorption coefficient 0.226 mm^-1

 F(000) 1344

 Crystal size 0.30 x 0.20 x 0.20 mm

 Theta range for data collection 1.85 to 24.99 deg.

 Limiting indices -14<=h<=14, -25<=k<=24, -16<=l<=16

 Reflections collected / unique 9803 / 3336 [R(int) = 0.0346]

 Completeness to theta = 24.99 99.6 %

 Absorption correction Semi-empirical from equivalents

 Max. and min. transmission 0.9561 and 0.9352

 Refinement method Full-matrix least-squares on F^2

 Data / restraints / parameters 3336 / 60 / 189

 Goodness-of-fit on F^2 1.075

 Final R indices [I>2sigma(I)] R1 = 0.0567, wR2 = 0.1489

 R indices (all data) R1 = 0.0835, wR2 = 0.1687

 Largest diff. peak and hole 0.435 and -0.255 e.A^-3

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

Table S 9. Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 3b. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 x y z U(eq)

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 P(1) 3604(1) 4565(1) 818(1) 63(1)

 N(1) 3572(2) 3676(1) 1992(2) 51(1)

 N(2) 4093(2) 3446(1) 1250(2) 54(1)

 C(1) 3257(3) 4254(2) 1905(2) 49(1)

 C(2) 2669(3) 4573(2) 2679(3) 62(1)

 C(3) 1517(4) 4711(3) 2314(4) 130(2)

 C(4) 2776(5) 4230(2) 3622(4) 112(2)

 C(5) 3238(5) 5193(2) 2900(4) 107(2)

 C(6) 4175(3) 3864(2) 570(2) 54(1)

 C(7) 4752(4) 3688(2) -312(3) 74(1)

 P(2) 6889(1) 1565(1) 959(1) 68(1)

 N(3) 5531(2) 2402(1) 1313(2) 51(1)

 N(4) 6509(2) 2627(1) 1677(2) 54(1)

 C(8) 5561(3) 1855(2) 913(2) 48(1)

 C(9) 4510(3) 1560(2) 505(3) 59(1)

 C(10) 3586(5) 1643(3) 1172(4) 121(2)

 C(11) 4672(5) 880(2) 364(5) 119(2)

 C(12) 4131(5) 1842(3) -447(4) 120(2)

 C(13) 7310(3) 2236(2) 1550(3) 59(1)

 C(14) 8457(3) 2395(2) 1933(4) 96(2)

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 Table S 10. Bond lengths [A] and angles [deg] for 3b.

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 P(1)-C(6) 1.745(4)

 P(1)-C(1) 1.760(4)

 N(1)-C(1) 1.336(4)

 N(1)-N(2) 1.363(4)

 N(1)-H(1) 0.8600

 N(2)-C(6) 1.338(5)

 C(1)-C(2) 1.524(5)

 C(2)-C(3) 1.498(6)

 C(2)-C(4) 1.527(6)

 C(2)-C(5) 1.557(6)

 C(3)-H(3A) 0.9600

 C(3)-H(3B) 0.9600

 C(3)-H(3C) 0.9600

 C(4)-H(4A) 0.9600

 C(4)-H(4B) 0.9600

 C(4)-H(4C) 0.9600

 C(5)-H(5A) 0.9600

 C(5)-H(5B) 0.9600

 C(5)-H(5C) 0.9600

 C(6)-C(7) 1.525(5)

 C(7)-H(7A) 0.9600

 C(7)-H(7B) 0.9600

 C(7)-H(7C) 0.9600

 P(2)-C(8) 1.747(4)

 P(2)-C(13) 1.758(4)

 N(3)-C(8) 1.335(4)

 N(3)-N(4) 1.362(4)

 N(3)-H(3) 0.8600

 N(4)-C(13) 1.330(5)

 C(8)-C(9) 1.518(5)

 C(9)-C(12) 1.520(6)

 C(9)-C(11) 1.527(6)

 C(9)-C(10) 1.536(6)

 C(10)-H(10A) 0.9600

 C(10)-H(10B) 0.9600

 C(10)-H(10C) 0.9600

 C(11)-H(11A) 0.9600

 C(11)-H(11B) 0.9600

 C(11)-H(11C) 0.9600

 C(12)-H(12A) 0.9600

 C(12)-H(12B) 0.9600

 C(12)-H(12C) 0.9600

 C(13)-C(14) 1.510(6)

 C(14)-H(14A) 0.9600

 C(14)-H(14B) 0.9600

 C(14)-H(14C) 0.9600

 C(6)-P(1)-C(1) 87.42(17)

 C(1)-N(1)-N(2) 115.6(3)

 C(1)-N(1)-H(1) 122.2

 N(2)-N(1)-H(1) 122.2

 C(6)-N(2)-N(1) 111.0(3)

 N(1)-C(1)-C(2) 121.5(3)

 N(1)-C(1)-P(1) 111.5(2)

 C(2)-C(1)-P(1) 127.0(3)

 C(3)-C(2)-C(1) 109.3(3)

 C(3)-C(2)-C(4) 114.7(5)

 C(1)-C(2)-C(4) 112.4(3)

 C(3)-C(2)-C(5) 106.7(4)

 C(1)-C(2)-C(5) 108.6(3)

 C(4)-C(2)-C(5) 104.7(4)

 C(2)-C(3)-H(3A) 109.5

 C(2)-C(3)-H(3B) 109.5

 H(3A)-C(3)-H(3B) 109.5

 C(2)-C(3)-H(3C) 109.5

 H(3A)-C(3)-H(3C) 109.5

 H(3B)-C(3)-H(3C) 109.5

 C(2)-C(4)-H(4A) 109.5

 C(2)-C(4)-H(4B) 109.5

 H(4A)-C(4)-H(4B) 109.5

 C(2)-C(4)-H(4C) 109.5

 H(4A)-C(4)-H(4C) 109.5

 H(4B)-C(4)-H(4C) 109.5

 C(2)-C(5)-H(5A) 109.5

 C(2)-C(5)-H(5B) 109.5

 H(5A)-C(5)-H(5B) 109.5

 C(2)-C(5)-H(5C) 109.5

 H(5A)-C(5)-H(5C) 109.5

 H(5B)-C(5)-H(5C) 109.5

 N(2)-C(6)-C(7) 118.3(3)

 N(2)-C(6)-P(1) 114.4(3)

 C(7)-C(6)-P(1) 127.3(3)

 C(6)-C(7)-H(7A) 109.5

 C(6)-C(7)-H(7B) 109.5

 H(7A)-C(7)-H(7B) 109.5

 C(6)-C(7)-H(7C) 109.5

 H(7A)-C(7)-H(7C) 109.5

 H(7B)-C(7)-H(7C) 109.5

 C(8)-P(2)-C(13) 87.13(18)

 C(8)-N(3)-N(4) 116.0(3)

 C(8)-N(3)-H(3) 122.0

 N(4)-N(3)-H(3) 122.0

 C(13)-N(4)-N(3) 110.6(3)

 N(3)-C(8)-C(9) 119.9(3)

 N(3)-C(8)-P(2) 111.7(2)

 C(9)-C(8)-P(2) 128.4(3)

 C(8)-C(9)-C(12) 110.8(3)

 C(8)-C(9)-C(11) 110.8(4)

 C(12)-C(9)-C(11) 108.7(4)

 C(8)-C(9)-C(10) 111.1(3)

 C(12)-C(9)-C(10) 107.5(5)

 C(11)-C(9)-C(10) 107.8(4)

 C(9)-C(10)-H(10A) 109.5

 C(9)-C(10)-H(10B) 109.5

 H(10A)-C(10)-H(10B) 109.5

 C(9)-C(10)-H(10C) 109.5

 H(10A)-C(10)-H(10C) 109.5

 H(10B)-C(10)-H(10C) 109.5

 C(9)-C(11)-H(11A) 109.5

 C(9)-C(11)-H(11B) 109.5

 H(11A)-C(11)-H(11B) 109.5

 C(9)-C(11)-H(11C) 109.5

 H(11A)-C(11)-H(11C) 109.5

 H(11B)-C(11)-H(11C) 109.5

 C(9)-C(12)-H(12A) 109.5

 C(9)-C(12)-H(12B) 109.5

 H(12A)-C(12)-H(12B) 109.5

 C(9)-C(12)-H(12C) 109.5

 H(12A)-C(12)-H(12C) 109.5

 H(12B)-C(12)-H(12C) 109.5

 N(4)-C(13)-C(14) 118.6(4)

 N(4)-C(13)-P(2) 114.6(3)

 C(14)-C(13)-P(2) 126.8(3)

 C(13)-C(14)-H(14A) 109.5

 C(13)-C(14)-H(14B) 109.5

 H(14A)-C(14)-H(14B) 109.5

 C(13)-C(14)-H(14C) 109.5

 H(14A)-C(14)-H(14C) 109.5

 H(14B)-C(14)-H(14C) 109.5

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 Symmetry transformations used to generate equivalent atoms:

 Table S 11.Anisotropic displacement parameters (A^2 x 10^3) for 3b. The anisotropic displacement factor exponent takes the form: -2 pi^2 [ h^2 a\*^2 U11 + ... + 2 h k a\* b\* U12 ]

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 U11 U22 U33 U23 U13 U12

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 P(1) 83(1) 49(1) 56(1) 10(1) 5(1) 12(1)

 N(1) 57(2) 47(2) 50(2) 9(1) 7(1) 12(1)

 N(2) 54(2) 52(2) 58(2) 3(1) 11(1) 12(1)

 C(1) 49(2) 46(2) 53(2) -1(2) -3(2) 10(2)

 C(2) 65(2) 62(2) 60(2) -8(2) 4(2) 17(2)

 C(3) 72(3) 195(6) 122(4) -68(4) -8(3) 45(4)

 C(4) 165(5) 101(4) 76(3) 3(3) 42(3) 40(4)

 C(5) 130(4) 84(3) 109(4) -37(3) 21(3) 0(3)

 C(6) 54(2) 56(2) 51(2) 2(2) 6(2) 1(2)

 C(7) 84(3) 79(3) 62(2) 1(2) 21(2) 6(2)

 P(2) 62(1) 64(1) 76(1) -20(1) 4(1) 15(1)

 N(3) 48(2) 47(2) 57(2) -5(1) 2(1) 4(1)

 N(4) 54(2) 52(2) 56(2) -8(1) 4(1) 0(2)

 C(8) 57(2) 42(2) 44(2) -5(1) 3(1) 0(2)

 C(9) 64(2) 55(2) 57(2) -6(2) 2(2) -9(2)

 C(10) 93(4) 152(5) 122(4) -47(4) 32(3) -50(3)

 C(11) 108(4) 72(3) 171(5) -22(3) -29(4) -9(3)

 C(12) 115(4) 134(4) 101(4) 36(3) -50(3) -46(4)

 C(13) 50(2) 69(2) 58(2) -7(2) 5(2) -2(2)

 C(14) 58(3) 116(4) 112(4) -29(3) -4(2) -4(3)

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 Table S 12. Hydrogen coordinates ( x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 3b.

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 x y z U(eq)

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 H(1) 3454 3462 2484 61

 H(3A) 1518 4895 1697 196

 H(3B) 1195 4984 2743 196

 H(3C) 1101 4342 2268 196

 H(4A) 2433 4459 4097 168

 H(4B) 3536 4173 3818 168

 H(4C) 2426 3842 3545 168

 H(5A) 3215 5434 2331 160

 H(5B) 3986 5126 3127 160

 H(5C) 2865 5403 3378 160

 H(7A) 5283 3378 -149 111

 H(7B) 5111 4038 -549 111

 H(7C) 4224 3539 -792 111

 H(3) 4931 2601 1339 61

 H(10A) 3770 1434 1759 182

 H(10B) 2918 1481 876 182

 H(10C) 3492 2067 1297 182

 H(11A) 5204 816 -92 179

 H(11B) 3990 699 137 179

 H(11C) 4923 698 959 179

 H(12A) 3917 2255 -352 179

 H(12B) 3519 1617 -729 179

 H(12C) 4718 1831 -861 179

 H(14A) 8844 2576 1437 143

 H(14B) 8831 2034 2155 143

 H(14C) 8426 2677 2449 143

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

Crystallographic data for **3d**

Table S 13. Crystal data and structure refinement for **3d**.

\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 Identification code L1

 Empirical formula C32 H28 N8 P4

 Formula weight 648.50

 Temperature 296(2) K

 Wavelength 0.71073 A

 Crystal system, space group Monoclinic, P2(1)/n

 Unit cell dimensions a = 15.1257(8) A alpha = 90 deg.

 b = 11.5748(6) A beta = 93.5880(10) deg.

 c = 19.0517(10) A gamma = 90 deg.

 Volume 3329.0(3) A^3

 Z, Calculated density 4, 1.294 Mg/m^3

 Absorption coefficient 0.262 mm^-1

 F(000) 1344

 Crystal size 0.30 x 0.20 x 0.20 mm

 Theta range for data collection 1.67 to 25.05 deg.

 Limiting indices -18<=h<=18, -13<=k<=13, -22<=l<=22

 Reflections collected / unique 34623 / 5885 [R(int) = 0.0360]

 Completeness to theta = 25.05 99.9 %

 Absorption correction Semi-empirical from equivalents

 Max. and min. transmission 0.9494 and 0.9255

 Refinement method Full-matrix least-squares on F^2

 Data / restraints / parameters 5885 / 0 / 397

 Goodness-of-fit on F^2 1.029

 Final R indices [I>2sigma(I)] R1 = 0.0409, wR2 = 0.0998

 R indices (all data) R1 = 0.0630, wR2 = 0.1149

 Largest diff. peak and hole 0.238 and -0.243 e.A^-3

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

Table S 14. Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for L1. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 x y z U(eq)

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 P(1) 7002(1) 2760(1) 1950(1) 69(1)

 N(1) 5587(1) 3409(2) 1248(1) 61(1)

 N(2) 5347(1) 2438(2) 1570(1) 54(1)

 C(1) 6421(2) 3697(2) 1391(1) 65(1)

 C(2) 6015(1) 1980(2) 1968(1) 48(1)

 C(3) 5850(1) 930(2) 2377(1) 49(1)

 C(4) 5133(2) 218(2) 2206(1) 64(1)

 C(5) 4971(2) -736(2) 2609(2) 78(1)

 C(6) 5516(2) -991(2) 3194(2) 80(1)

 C(7) 6227(2) -299(2) 3364(1) 75(1)

 C(8) 6405(2) 650(2) 2958(1) 63(1)

 P(2) 6172(1) 5573(1) 3453(1) 73(1)

 N(3) 5076(1) 5514(2) 2357(1) 60(1)

 N(4) 4846(1) 4634(2) 2765(1) 56(1)

 C(9) 5758(2) 6086(2) 2648(1) 65(1)

 C(10) 5342(1) 4526(2) 3363(1) 51(1)

 C(11) 5180(1) 3584(2) 3858(1) 53(1)

 C(12) 4784(2) 2554(2) 3639(1) 61(1)

 C(13) 4652(2) 1678(2) 4108(2) 74(1)

 C(14) 4911(2) 1812(3) 4804(2) 85(1)

 C(15) 5309(2) 2814(3) 5031(2) 86(1)

 C(16) 5445(2) 3699(2) 4564(1) 73(1)

 P(3) 1811(1) 2258(1) 1865(1) 88(1)

 N(5) 3330(1) 3239(2) 2145(1) 65(1)

 N(6) 3476(1) 2356(2) 1710(1) 57(1)

 C(17) 2484(2) 3299(3) 2270(1) 82(1)

 C(18) 2763(1) 1738(2) 1506(1) 51(1)

 C(19) 2835(1) 751(2) 1027(1) 50(1)

 C(20) 3551(2) 608(2) 615(1) 62(1)

 C(21) 3597(2) -326(2) 172(1) 78(1)

 C(22) 2926(2) -1130(2) 125(2) 85(1)

 C(23) 2214(2) -997(2) 523(2) 82(1)

 C(24) 2165(2) -71(2) 972(1) 66(1)

 P(4) 2418(1) 5287(1) 10390(1) 89(1)

 N(7) 3851(1) 5539(2) 11161(1) 69(1)

 N(8) 4033(1) 4674(2) 10725(1) 57(1)

 C(25) 3046(2) 5955(3) 11056(1) 81(1)

 C(26) 3344(1) 4423(2) 10283(1) 52(1)

 C(27) 3423(1) 3493(2) 9764(1) 52(1)

 C(28) 4236(2) 3144(2) 9541(1) 62(1)

 C(29) 4287(2) 2274(2) 9053(1) 74(1)

 C(30) 3532(2) 1742(2) 8778(1) 79(1)

 C(31) 2730(2) 2078(2) 8993(2) 78(1)

 C(32) 2668(2) 2944(2) 9482(1) 67(1)

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 Table S 15. Bond lengths [A] and angles [deg] for **3d**.

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 P(1)-C(1) 1.722(2)

 P(1)-C(2) 1.746(2)

 N(1)-C(1) 1.318(3)

 N(1)-N(2) 1.340(2)

 N(1)-H(1) 0.8600

 N(2)-C(2) 1.334(3)

 C(1)-H(1A) 0.9300

 C(2)-C(3) 1.474(3)

 C(3)-C(8) 1.385(3)

 C(3)-C(4) 1.385(3)

 C(4)-C(5) 1.375(3)

 C(4)-H(4) 0.9300

 C(5)-C(6) 1.376(4)

 C(5)-H(5) 0.9300

 C(6)-C(7) 1.365(4)

 C(6)-H(6) 0.9300

 C(7)-C(8) 1.378(3)

 C(7)-H(7) 0.9300

 C(8)-H(8) 0.9300

 P(2)-C(9) 1.725(2)

 P(2)-C(10) 1.745(2)

 N(3)-C(9) 1.318(3)

 N(3)-N(4) 1.341(2)

 N(4)-C(10) 1.331(3)

 N(4)-H(4A) 0.8600

 C(9)-H(9) 0.9300

 C(10)-C(11) 1.471(3)

 C(11)-C(16) 1.386(3)

 C(11)-C(12) 1.387(3)

 C(12)-C(13) 1.374(3)

 C(12)-H(12) 0.9300

 C(13)-C(14) 1.367(4)

 C(13)-H(13) 0.9300

 C(14)-C(15) 1.364(4)

 C(14)-H(14) 0.9300

 C(15)-C(16) 1.380(4)

 C(15)-H(15) 0.9300

 C(16)-H(16) 0.9300

 P(3)-C(17) 1.728(3)

 P(3)-C(18) 1.739(2)

 N(5)-C(17) 1.317(3)

 N(5)-N(6) 1.343(3)

 N(6)-C(18) 1.331(3)

 N(6)-H(6A) 0.8600

 C(17)-H(17) 0.9300

 C(18)-C(19) 1.471(3)

 C(19)-C(20) 1.386(3)

 C(19)-C(24) 1.390(3)

 C(20)-C(21) 1.375(3)

 C(20)-H(20) 0.9300

 C(21)-C(22) 1.375(4)

 C(21)-H(21) 0.9300

 C(22)-C(23) 1.365(4)

 C(22)-H(22) 0.9300

 C(23)-C(24) 1.375(4)

 C(23)-H(23) 0.9300

 C(24)-H(24) 0.9300

 P(4)-C(25) 1.719(3)

 P(4)-C(26) 1.743(2)

 N(7)-C(25) 1.313(3)

 N(7)-N(8) 1.341(3)

 N(7)-H(7A) 0.8600

 N(8)-C(26) 1.332(3)

 C(25)-H(25) 0.9300

 C(26)-C(27) 1.471(3)

 C(27)-C(32) 1.386(3)

 C(27)-C(28) 1.386(3)

 C(28)-C(29) 1.375(4)

 C(28)-H(28) 0.9300

 C(29)-C(30) 1.371(4)

 C(29)-H(29) 0.9300

 C(30)-C(31) 1.361(4)

 C(30)-H(30) 0.9300

 C(31)-C(32) 1.375(4)

 C(31)-H(31) 0.9300

 C(32)-H(32) 0.9300

 C(1)-P(1)-C(2) 86.22(10)

 C(1)-N(1)-N(2) 113.65(18)

 C(1)-N(1)-H(1) 123.2

 N(2)-N(1)-H(1) 123.2

 C(2)-N(2)-N(1) 112.10(17)

 N(1)-C(1)-P(1) 114.38(18)

 N(1)-C(1)-H(1A) 122.8

 P(1)-C(1)-H(1A) 122.8

 N(2)-C(2)-C(3) 118.80(18)

 N(2)-C(2)-P(1) 113.65(15)

 C(3)-C(2)-P(1) 127.53(16)

 C(8)-C(3)-C(4) 118.3(2)

 C(8)-C(3)-C(2) 120.2(2)

 C(4)-C(3)-C(2) 121.5(2)

 C(5)-C(4)-C(3) 120.8(2)

 C(5)-C(4)-H(4) 119.6

 C(3)-C(4)-H(4) 119.6

 C(4)-C(5)-C(6) 120.4(3)

 C(4)-C(5)-H(5) 119.8

 C(6)-C(5)-H(5) 119.8

 C(7)-C(6)-C(5) 119.3(3)

 C(7)-C(6)-H(6) 120.3

 C(5)-C(6)-H(6) 120.3

 C(6)-C(7)-C(8) 120.9(3)

 C(6)-C(7)-H(7) 119.6

 C(8)-C(7)-H(7) 119.6

 C(7)-C(8)-C(3) 120.4(2)

 C(7)-C(8)-H(8) 119.8

 C(3)-C(8)-H(8) 119.8

 C(9)-P(2)-C(10) 86.18(11)

 C(9)-N(3)-N(4) 111.19(19)

 C(10)-N(4)-N(3) 114.55(18)

 C(10)-N(4)-H(4A) 122.7

 N(3)-N(4)-H(4A) 122.7

 N(3)-C(9)-P(2) 115.64(19)

 N(3)-C(9)-H(9) 122.2

 P(2)-C(9)-H(9) 122.2

 N(4)-C(10)-C(11) 120.65(19)

 N(4)-C(10)-P(2) 112.44(16)

 C(11)-C(10)-P(2) 126.89(16)

 C(16)-C(11)-C(12) 117.8(2)

 C(16)-C(11)-C(10) 120.0(2)

 C(12)-C(11)-C(10) 122.1(2)

 C(13)-C(12)-C(11) 121.1(2)

 C(13)-C(12)-H(12) 119.4

 C(11)-C(12)-H(12) 119.4

 C(14)-C(13)-C(12) 120.2(3)

 C(14)-C(13)-H(13) 119.9

 C(12)-C(13)-H(13) 119.9

 C(15)-C(14)-C(13) 119.8(3)

 C(15)-C(14)-H(14) 120.1

 C(13)-C(14)-H(14) 120.1

 C(14)-C(15)-C(16) 120.5(3)

 C(14)-C(15)-H(15) 119.7

 C(16)-C(15)-H(15) 119.7

 C(15)-C(16)-C(11) 120.6(3)

 C(15)-C(16)-H(16) 119.7

 C(11)-C(16)-H(16) 119.7

 C(17)-P(3)-C(18) 86.41(12)

 C(17)-N(5)-N(6) 110.5(2)

 C(18)-N(6)-N(5) 115.32(19)

 C(18)-N(6)-H(6A) 122.3

 N(5)-N(6)-H(6A) 122.3

 N(5)-C(17)-P(3) 115.7(2)

 N(5)-C(17)-H(17) 122.1

 P(3)-C(17)-H(17) 122.1

 N(6)-C(18)-C(19) 120.6(2)

 N(6)-C(18)-P(3) 112.00(17)

 C(19)-C(18)-P(3) 127.40(16)

 C(20)-C(19)-C(24) 117.9(2)

 C(20)-C(19)-C(18) 122.4(2)

 C(24)-C(19)-C(18) 119.8(2)

 C(21)-C(20)-C(19) 120.8(2)

 C(21)-C(20)-H(20) 119.6

 C(19)-C(20)-H(20) 119.6

 C(20)-C(21)-C(22) 120.4(3)

 C(20)-C(21)-H(21) 119.8

 C(22)-C(21)-H(21) 119.8

 C(23)-C(22)-C(21) 119.5(3)

 C(23)-C(22)-H(22) 120.3

 C(21)-C(22)-H(22) 120.3

 C(22)-C(23)-C(24) 120.6(3)

 C(22)-C(23)-H(23) 119.7

 C(24)-C(23)-H(23) 119.7

 C(23)-C(24)-C(19) 120.8(2)

 C(23)-C(24)-H(24) 119.6

 C(19)-C(24)-H(24) 119.6

 C(25)-P(4)-C(26) 86.24(12)

 C(25)-N(7)-N(8) 113.8(2)

 C(25)-N(7)-H(7A) 123.1

 N(8)-N(7)-H(7A) 123.1

 C(26)-N(8)-N(7) 111.82(19)

 N(7)-C(25)-P(4) 114.3(2)

 N(7)-C(25)-H(25) 122.8

 P(4)-C(25)-H(25) 122.8

 N(8)-C(26)-C(27) 119.43(19)

 N(8)-C(26)-P(4) 113.79(17)

 C(27)-C(26)-P(4) 126.77(16)

 C(32)-C(27)-C(28) 118.2(2)

 C(32)-C(27)-C(26) 119.8(2)

 C(28)-C(27)-C(26) 122.0(2)

 C(29)-C(28)-C(27) 120.6(2)

 C(29)-C(28)-H(28) 119.7

 C(27)-C(28)-H(28) 119.7

 C(30)-C(29)-C(28) 120.4(3)

 C(30)-C(29)-H(29) 119.8

 C(28)-C(29)-H(29) 119.8

 C(31)-C(30)-C(29) 119.6(3)

 C(31)-C(30)-H(30) 120.2

 C(29)-C(30)-H(30) 120.2

 C(30)-C(31)-C(32) 120.7(3)

 C(30)-C(31)-H(31) 119.6

 C(32)-C(31)-H(31) 119.6

 C(31)-C(32)-C(27) 120.5(2)

 C(31)-C(32)-H(32) 119.7

 C(27)-C(32)-H(32) 119.7

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 Symmetry transformations used to generate equivalent atoms:

 Table S 16. Anisotropic displacement parameters (A^2 x 10^3) for **3d**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [ h^2 a\*^2 U11 + ... + 2 h k a\* b\* U12 ]

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 U11 U22 U33 U23 U13 U12

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 P(1) 41(1) 71(1) 94(1) 22(1) -5(1) -5(1)

 N(1) 50(1) 62(1) 69(1) 12(1) -6(1) 4(1)

 N(2) 47(1) 51(1) 64(1) 5(1) -3(1) 2(1)

 C(1) 51(1) 64(2) 80(2) 15(1) 4(1) -5(1)

 C(2) 41(1) 48(1) 54(1) -3(1) 3(1) 4(1)

 C(3) 45(1) 45(1) 58(1) -2(1) 8(1) 6(1)

 C(4) 55(1) 58(1) 79(2) 4(1) 2(1) -3(1)

 C(5) 72(2) 60(2) 103(2) 8(2) 18(2) -11(1)

 C(6) 96(2) 59(2) 90(2) 17(2) 36(2) 11(2)

 C(7) 85(2) 72(2) 68(2) 15(1) 9(1) 22(2)

 C(8) 59(1) 62(2) 68(2) 6(1) 0(1) 8(1)

 P(2) 76(1) 67(1) 72(1) 8(1) -24(1) -22(1)

 N(3) 63(1) 54(1) 62(1) 0(1) -5(1) -3(1)

 N(4) 52(1) 54(1) 60(1) -8(1) -7(1) -4(1)

 C(9) 72(2) 52(1) 71(2) 2(1) -6(1) -10(1)

 C(10) 49(1) 50(1) 52(1) -5(1) -3(1) 4(1)

 C(11) 45(1) 55(1) 57(1) 0(1) 3(1) 3(1)

 C(12) 61(1) 57(1) 64(2) -5(1) 10(1) 1(1)

 C(13) 78(2) 56(2) 91(2) 2(1) 25(2) 0(1)

 C(14) 88(2) 81(2) 88(2) 25(2) 23(2) 9(2)

 C(15) 92(2) 104(2) 62(2) 18(2) -2(2) -5(2)

 C(16) 76(2) 79(2) 61(2) 3(1) -6(1) -9(1)

 P(3) 47(1) 119(1) 99(1) -41(1) 9(1) -12(1)

 N(5) 54(1) 68(1) 71(1) -10(1) -5(1) -3(1)

 N(6) 40(1) 61(1) 69(1) 2(1) -2(1) -4(1)

 C(17) 61(2) 103(2) 83(2) -32(2) 4(1) -2(2)

 C(18) 42(1) 60(1) 49(1) 6(1) -4(1) -7(1)

 C(19) 45(1) 54(1) 48(1) 10(1) -8(1) -3(1)

 C(20) 60(2) 65(2) 61(1) 4(1) 6(1) -8(1)

 C(21) 84(2) 77(2) 73(2) -5(2) 12(2) 2(2)

 C(22) 106(2) 63(2) 84(2) -12(2) -10(2) 2(2)

 C(23) 81(2) 62(2) 102(2) -5(2) -9(2) -17(1)

 C(24) 54(1) 67(2) 76(2) 2(1) -3(1) -12(1)

 P(4) 71(1) 114(1) 79(1) -28(1) -19(1) 39(1)

 N(7) 78(1) 67(1) 59(1) 2(1) -16(1) 1(1)

 N(8) 58(1) 54(1) 56(1) 6(1) -7(1) -2(1)

 C(25) 89(2) 84(2) 68(2) -11(1) -10(2) 29(2)

 C(26) 50(1) 58(1) 49(1) 9(1) -3(1) 2(1)

 C(27) 52(1) 54(1) 51(1) 8(1) 2(1) 5(1)

 C(28) 53(1) 71(2) 64(1) 9(1) 6(1) -2(1)

 C(29) 72(2) 83(2) 70(2) 3(2) 18(1) 15(2)

 C(30) 96(2) 70(2) 70(2) -8(1) 5(2) 9(2)

 C(31) 73(2) 76(2) 84(2) -14(2) -10(2) -4(1)

 C(32) 53(1) 73(2) 73(2) -6(1) -4(1) 4(1)

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

Table S 17. Hydrogen coordinates ( x 10^4) and isotropic

 displacement parameters (A^2 x 10^3) for **3d**.

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 x y z U(eq)

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 H(1) 5229 3806 975 73

 H(1A) 6676 4352 1206 78

 H(4) 4758 386 1815 77

 H(5) 4490 -1211 2485 94

 H(6) 5400 -1629 3471 96

 H(7) 6598 -469 3758 90

 H(8) 6899 1104 3076 76

 H(4A) 4413 4177 2650 67

 H(9) 5999 6725 2434 78

 H(12) 4604 2454 3167 73

 H(13) 4386 993 3952 89

 H(14) 4817 1221 5122 102

 H(15) 5489 2902 5503 104

 H(16) 5716 4378 4725 87

 H(6A) 3993 2201 1573 69

 H(17) 2263 3866 2557 99

 H(20) 4005 1150 638 74

 H(21) 4085 -415 -96 94

 H(22) 2957 -1759 -176 102

 H(23) 1758 -1537 491 99

 H(24) 1677 5 1242 79

 H(7A) 4226 5798 11481 82

 H(25) 2833 6560 11318 97

 H(28) 4752 3502 9722 75

 H(29) 4836 2045 8909 89

 H(30) 3569 1156 8448 94

 H(31) 2218 1718 8807 94

 H(32) 2115 3163 9624 80

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

Table S 18. Torsion angles [deg] for **3d**.

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 C(1)-N(1)-N(2)-C(2) 0.2(3)

 N(2)-N(1)-C(1)-P(1) 0.3(3)

 C(2)-P(1)-C(1)-N(1) -0.5(2)

 N(1)-N(2)-C(2)-C(3) 177.78(18)

 N(1)-N(2)-C(2)-P(1) -0.6(2)

 C(1)-P(1)-C(2)-N(2) 0.61(18)

 C(1)-P(1)-C(2)-C(3) -177.6(2)

 N(2)-C(2)-C(3)-C(8) -158.4(2)

 P(1)-C(2)-C(3)-C(8) 19.8(3)

 N(2)-C(2)-C(3)-C(4) 20.0(3)

 P(1)-C(2)-C(3)-C(4) -161.82(18)

 C(8)-C(3)-C(4)-C(5) 0.8(3)

 C(2)-C(3)-C(4)-C(5) -177.6(2)

 C(3)-C(4)-C(5)-C(6) 0.6(4)

 C(4)-C(5)-C(6)-C(7) -1.1(4)

 C(5)-C(6)-C(7)-C(8) 0.1(4)

 C(6)-C(7)-C(8)-C(3) 1.3(4)

 C(4)-C(3)-C(8)-C(7) -1.8(3)

 C(2)-C(3)-C(8)-C(7) 176.7(2)

 C(9)-N(3)-N(4)-C(10) 0.0(3)

 N(4)-N(3)-C(9)-P(2) 0.3(3)

 C(10)-P(2)-C(9)-N(3) -0.3(2)

 N(3)-N(4)-C(10)-C(11) -178.69(19)

 N(3)-N(4)-C(10)-P(2) -0.2(2)

 C(9)-P(2)-C(10)-N(4) 0.27(17)

 C(9)-P(2)-C(10)-C(11) 178.7(2)

 N(4)-C(10)-C(11)-C(16) -156.0(2)

 P(2)-C(10)-C(11)-C(16) 25.7(3)

 N(4)-C(10)-C(11)-C(12) 25.6(3)

 P(2)-C(10)-C(11)-C(12) -152.71(18)

 C(16)-C(11)-C(12)-C(13) 0.4(3)

 C(10)-C(11)-C(12)-C(13) 178.9(2)

 C(11)-C(12)-C(13)-C(14) 0.1(4)

 C(12)-C(13)-C(14)-C(15) -0.6(4)

 C(13)-C(14)-C(15)-C(16) 0.6(5)

 C(14)-C(15)-C(16)-C(11) 0.0(4)

 C(12)-C(11)-C(16)-C(15) -0.5(4)

 C(10)-C(11)-C(16)-C(15) -179.0(2)

 C(17)-N(5)-N(6)-C(18) -0.6(3)

 N(6)-N(5)-C(17)-P(3) 0.6(3)

 C(18)-P(3)-C(17)-N(5) -0.4(2)

 N(5)-N(6)-C(18)-C(19) 179.68(18)

 N(5)-N(6)-C(18)-P(3) 0.3(2)

 C(17)-P(3)-C(18)-N(6) 0.07(18)

 C(17)-P(3)-C(18)-C(19) -179.3(2)

 N(6)-C(18)-C(19)-C(20) -18.5(3)

 P(3)-C(18)-C(19)-C(20) 160.75(18)

 N(6)-C(18)-C(19)-C(24) 162.1(2)

 P(3)-C(18)-C(19)-C(24) -18.6(3)

 C(24)-C(19)-C(20)-C(21) -0.7(3)

 C(18)-C(19)-C(20)-C(21) 179.9(2)

 C(19)-C(20)-C(21)-C(22) 0.8(4)

 C(20)-C(21)-C(22)-C(23) -0.3(4)

 C(21)-C(22)-C(23)-C(24) -0.3(4)

 C(22)-C(23)-C(24)-C(19) 0.4(4)

 C(20)-C(19)-C(24)-C(23) 0.1(3)

 C(18)-C(19)-C(24)-C(23) 179.5(2)

 C(25)-N(7)-N(8)-C(26) -0.6(3)

 N(8)-N(7)-C(25)-P(4) 0.4(3)

 C(26)-P(4)-C(25)-N(7) -0.1(2)

 N(7)-N(8)-C(26)-C(27) 179.98(18)

 N(7)-N(8)-C(26)-P(4) 0.5(2)

 C(25)-P(4)-C(26)-N(8) -0.22(19)

 C(25)-P(4)-C(26)-C(27) -179.7(2)

 N(8)-C(26)-C(27)-C(32) 156.9(2)

 P(4)-C(26)-C(27)-C(32) -23.7(3)

 N(8)-C(26)-C(27)-C(28) -23.5(3)

 P(4)-C(26)-C(27)-C(28) 155.96(19)

 C(32)-C(27)-C(28)-C(29) -0.2(3)

 C(26)-C(27)-C(28)-C(29) -179.8(2)

 C(27)-C(28)-C(29)-C(30) 0.3(4)

 C(28)-C(29)-C(30)-C(31) -0.3(4)

 C(29)-C(30)-C(31)-C(32) 0.0(4)

 C(30)-C(31)-C(32)-C(27) 0.2(4)

 C(28)-C(27)-C(32)-C(31) -0.1(4)

 C(26)-C(27)-C(32)-C(31) 179.6(2)

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 Symmetry transformations used to generate equivalent atoms:

Crystallographic data for **3e**

 Table S 19. Crystal data and structure refinement for 3e.

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 Identification code L5

 Empirical formula C12 H15 N2 P

 Formula weight 218.23

 Temperature 296(2) K

 Wavelength 0.71073 A

 Crystal system, space group Monoclinic, P2(1)

 Unit cell dimensions a = 11.8190(14) A alpha = 90 deg.

 b = 8.5829(9) A beta = 103.238(2) deg.

 c = 24.840(3) A gamma = 90 deg.

 Volume 2452.8(5) A^3

 Z, Calculated density 8, 1.182 Mg/m^3

 Absorption coefficient 0.195 mm^-1

 F(000) 928

 Crystal size 0.30 x 0.20 x 0.20 mm

 Theta range for data collection 1.77 to 25.05 deg.

 Limiting indices -12<=h<=14, -10<=k<=10, -29<=l<=16

 Reflections collected / unique 13876 / 8157 [R(int) = 0.0653]

 Completeness to theta = 25.05 99.9 %

 Absorption correction Semi-empirical from equivalents

 Max. and min. transmission 0.9621 and 0.9439

 Refinement method Full-matrix least-squares on F^2

 Data / restraints / parameters 8157 / 1 / 554

 Goodness-of-fit on F^2 0.981

 Final R indices [I>2sigma(I)] R1 = 0.0656, wR2 = 0.1105

 R indices (all data) R1 = 0.1643, wR2 = 0.1411

 Absolute structure parameter 0.09(13)

 Extinction coefficient 0.0018(4)

 Largest diff. peak and hole 0.185 and -0.195 e.A^-3

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Table S 20. Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 3e. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 x y z U(eq)

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 P(1) 8091(1) 2009(2) 1057(1) 58(1)

 N(1) 10207(4) 2374(6) 1036(2) 54(2)

 N(2) 10230(4) 1038(6) 1321(2) 49(1)

 C(1) 9168(5) 706(8) 1372(2) 44(2)

 C(2) 8999(5) -735(7) 1678(2) 48(2)

 C(3) 9910(6) -1330(7) 2099(2) 56(2)

 C(4) 9718(6) -2638(8) 2391(3) 68(2)

 C(5) 8655(7) -3361(8) 2281(3) 75(2)

 C(6) 7759(6) -2757(9) 1878(3) 75(2)

 C(7) 7938(6) -1455(8) 1590(3) 64(2)

 C(8) 9169(5) 3056(8) 856(2) 48(2)

 C(9) 9076(5) 4555(7) 532(3) 53(2)

 C(10) 9834(6) 5788(8) 893(3) 88(2)

 C(11) 9493(6) 4351(8) 13(2) 82(2)

 C(12) 7825(6) 5133(9) 394(3) 101(3)

 P(2) 8597(1) 8008(2) 3780(1) 63(1)

 N(3) 6430(4) 8181(7) 3717(2) 57(2)

 N(4) 6718(4) 6840(6) 4004(2) 51(1)

 C(13) 7288(5) 8958(7) 3564(2) 50(2)

 C(14) 7011(5) 10399(7) 3231(3) 49(2)

 C(15) 7680(6) 10787(9) 2866(3) 70(2)

 C(16) 7430(7) 12104(10) 2542(3) 78(2)

 C(17) 6509(7) 13013(10) 2570(3) 78(2)

 C(18) 5845(7) 12633(9) 2937(4) 87(3)

 C(19) 6103(6) 11325(8) 3265(3) 66(2)

 C(20) 7843(5) 6570(7) 4073(2) 48(2)

 C(21) 8383(5) 5125(7) 4383(3) 54(2)

 C(22) 9399(6) 5631(8) 4858(3) 88(2)

 C(23) 8895(6) 4155(8) 3971(3) 88(3)

 C(24) 7506(6) 4200(9) 4598(3) 105(3)

 P(3) 2022(1) 7022(2) 3910(1) 59(1)

 N(5) 3936(4) 8063(7) 3694(2) 53(1)

 N(6) 4183(4) 6715(6) 3983(2) 47(1)

 C(25) 2829(5) 8397(7) 3629(2) 42(2)

 C(26) 2358(5) 9791(7) 3320(2) 47(2)

 C(27) 2885(6) 10468(7) 2929(2) 52(2)

 C(28) 2429(6) 11795(9) 2630(3) 70(2)

 C(29) 1445(7) 12458(8) 2734(3) 76(2)

 C(30) 907(6) 11856(9) 3118(3) 77(2)

 C(31) 1369(6) 10514(7) 3405(3) 60(2)

 C(32) 3304(5) 6014(8) 4133(2) 46(2)

 C(33) 3522(5) 4498(7) 4455(3) 52(2)

 C(34) 4433(6) 4750(8) 4996(2) 85(2)

 C(35) 3965(6) 3292(8) 4099(3) 80(2)

 C(36) 2409(6) 3930(9) 4587(3) 94(3)

 P(4) 4778(2) 899(2) 1211(1) 66(1)

 N(7) 2719(4) 2137(7) 1020(2) 52(1)

 N(8) 2683(4) 791(6) 1302(2) 49(1)

 C(37) 3667(5) 18(7) 1439(2) 46(2)

 C(38) 3676(5) -1423(8) 1762(3) 50(2)

 C(39) 4701(5) -1898(8) 2127(3) 61(2)

 C(40) 4712(7) -3165(9) 2464(3) 74(2)

 C(41) 3713(8) -4025(9) 2437(3) 85(2)

 C(42) 2736(7) -3583(8) 2089(3) 73(2)

 C(43) 2697(6) -2317(8) 1738(3) 66(2)

 C(44) 3780(5) 2380(7) 936(2) 51(2)

 C(45) 4050(6) 3816(8) 641(3) 55(2)

 C(46) 4937(6) 4805(9) 1043(3) 93(3)

 C(47) 4586(6) 3327(8) 151(3) 86(2)

 C(48) 2977(6) 4796(9) 427(3) 102(3)

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 Table S 21. Bond lengths [A] and angles [deg] for 3e.

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 P(1)-C(8) 1.725(6)

 P(1)-C(1) 1.740(6)

 N(1)-C(8) 1.340(6)

 N(1)-N(2) 1.345(6)

 N(1)-H(1) 0.8600

 N(2)-C(1) 1.320(6)

 C(1)-C(2) 1.489(8)

 C(2)-C(7) 1.369(8)

 C(2)-C(3) 1.414(8)

 C(3)-C(4) 1.383(8)

 C(3)-H(3) 0.9300

 C(4)-C(5) 1.371(8)

 C(4)-H(4) 0.9300

 C(5)-C(6) 1.381(9)

 C(5)-H(5) 0.9300

 C(6)-C(7) 1.370(9)

 C(6)-H(6) 0.9300

 C(7)-H(7) 0.9300

 C(8)-C(9) 1.507(8)

 C(9)-C(11) 1.494(7)

 C(9)-C(12) 1.522(8)

 C(9)-C(10) 1.536(8)

 C(10)-H(10A) 0.9600

 C(10)-H(10B) 0.9600

 C(10)-H(10C) 0.9600

 C(11)-H(11A) 0.9600

 C(11)-H(11B) 0.9600

 C(11)-H(11C) 0.9600

 C(12)-H(12A) 0.9600

 C(12)-H(12B) 0.9600

 C(12)-H(12C) 0.9600

 P(2)-C(13) 1.722(6)

 P(2)-C(20) 1.774(6)

 N(3)-C(13) 1.340(7)

 N(3)-N(4) 1.356(7)

 N(3)-H(3A) 0.8600

 N(4)-C(20) 1.322(6)

 C(13)-C(14) 1.482(8)

 C(14)-C(19) 1.354(8)

 C(14)-C(15) 1.374(8)

 C(15)-C(16) 1.380(9)

 C(15)-H(15) 0.9300

 C(16)-C(17) 1.353(9)

 C(16)-H(16) 0.9300

 C(17)-C(18) 1.371(10)

 C(17)-H(17) 0.9300

 C(18)-C(19) 1.381(8)

 C(18)-H(18) 0.9300

 C(19)-H(19) 0.9300

 C(20)-C(21) 1.521(8)

 C(21)-C(24) 1.497(9)

 C(21)-C(22) 1.540(8)

 C(21)-C(23) 1.546(8)

 C(22)-H(22A) 0.9600

 C(22)-H(22B) 0.9600

 C(22)-H(22C) 0.9600

 C(23)-H(23A) 0.9600

 C(23)-H(23B) 0.9600

 C(23)-H(23C) 0.9600

 C(24)-H(24A) 0.9600

 C(24)-H(24B) 0.9600

 C(24)-H(24C) 0.9600

 P(3)-C(32) 1.723(6)

 P(3)-C(25) 1.758(6)

 N(5)-C(25) 1.313(7)

 N(5)-N(6) 1.358(6)

 N(6)-C(32) 1.325(6)

 N(6)-H(6A) 0.8600

 C(25)-C(26) 1.461(8)

 C(26)-C(31) 1.381(8)

 C(26)-C(27) 1.397(8)

 C(27)-C(28) 1.398(8)

 C(27)-H(27) 0.9300

 C(28)-C(29) 1.371(9)

 C(28)-H(28) 0.9300

 C(29)-C(30) 1.364(9)

 C(29)-H(29) 0.9300

 C(30)-C(31) 1.399(9)

 C(30)-H(30) 0.9300

 C(31)-H(31) 0.9300

 C(32)-C(33) 1.518(8)

 C(33)-C(36) 1.508(8)

 C(33)-C(35) 1.529(9)

 C(33)-C(34) 1.533(7)

 C(34)-H(34A) 0.9600

 C(34)-H(34B) 0.9600

 C(34)-H(34C) 0.9600

 C(35)-H(35A) 0.9600

 C(35)-H(35B) 0.9600

 C(35)-H(35C) 0.9600

 C(36)-H(36A) 0.9600

 C(36)-H(36B) 0.9600

 C(36)-H(36C) 0.9600

 P(4)-C(37) 1.719(7)

 P(4)-C(44) 1.763(6)

 N(7)-C(44) 1.334(7)

 N(7)-N(8) 1.357(7)

 N(8)-C(37) 1.314(6)

 N(8)-H(8) 0.8600

 C(37)-C(38) 1.472(8)

 C(38)-C(43) 1.378(8)

 C(38)-C(39) 1.398(8)

 C(39)-C(40) 1.370(9)

 C(39)-H(39) 0.9300

 C(40)-C(41) 1.382(9)

 C(40)-H(40) 0.9300

 C(41)-C(42) 1.329(9)

 C(41)-H(41) 0.9300

 C(42)-C(43) 1.387(8)

 C(42)-H(42) 0.9300

 C(43)-H(43) 0.9300

 C(44)-C(45) 1.505(8)

 C(45)-C(48) 1.512(9)

 C(45)-C(46) 1.529(8)

 C(45)-C(47) 1.553(8)

 C(46)-H(46A) 0.9600

 C(46)-H(46B) 0.9600

 C(46)-H(46C) 0.9600

 C(47)-H(47A) 0.9600

 C(47)-H(47B) 0.9600

 C(47)-H(47C) 0.9600

 C(48)-H(48A) 0.9600

 C(48)-H(48B) 0.9600

 C(48)-H(48C) 0.9600

 C(8)-P(1)-C(1) 87.3(3)

 C(8)-N(1)-N(2) 117.0(5)

 C(8)-N(1)-H(1) 121.5

 N(2)-N(1)-H(1) 121.5

 C(1)-N(2)-N(1) 109.2(5)

 N(2)-C(1)-C(2) 118.0(6)

 N(2)-C(1)-P(1) 115.6(5)

 C(2)-C(1)-P(1) 126.4(4)

 C(7)-C(2)-C(3) 118.0(6)

 C(7)-C(2)-C(1) 121.3(6)

 C(3)-C(2)-C(1) 120.6(6)

 C(4)-C(3)-C(2) 119.5(6)

 C(4)-C(3)-H(3) 120.3

 C(2)-C(3)-H(3) 120.3

 C(5)-C(4)-C(3) 121.1(7)

 C(5)-C(4)-H(4) 119.5

 C(3)-C(4)-H(4) 119.5

 C(4)-C(5)-C(6) 119.4(7)

 C(4)-C(5)-H(5) 120.3

 C(6)-C(5)-H(5) 120.3

 C(7)-C(6)-C(5) 120.0(7)

 C(7)-C(6)-H(6) 120.0

 C(5)-C(6)-H(6) 120.0

 C(6)-C(7)-C(2) 122.1(7)

 C(6)-C(7)-H(7) 119.0

 C(2)-C(7)-H(7) 119.0

 N(1)-C(8)-C(9) 120.0(5)

 N(1)-C(8)-P(1) 110.9(5)

 C(9)-C(8)-P(1) 129.1(4)

 C(11)-C(9)-C(8) 111.2(5)

 C(11)-C(9)-C(12) 109.8(5)

 C(8)-C(9)-C(12) 110.3(5)

 C(11)-C(9)-C(10) 108.7(6)

 C(8)-C(9)-C(10) 108.4(5)

 C(12)-C(9)-C(10) 108.3(6)

 C(9)-C(10)-H(10A) 109.5

 C(9)-C(10)-H(10B) 109.5

 H(10A)-C(10)-H(10B) 109.5

 C(9)-C(10)-H(10C) 109.5

 H(10A)-C(10)-H(10C) 109.5

 H(10B)-C(10)-H(10C) 109.5

 C(9)-C(11)-H(11A) 109.5

 C(9)-C(11)-H(11B) 109.5

 H(11A)-C(11)-H(11B) 109.5

 C(9)-C(11)-H(11C) 109.5

 H(11A)-C(11)-H(11C) 109.5

 H(11B)-C(11)-H(11C) 109.5

 C(9)-C(12)-H(12A) 109.5

 C(9)-C(12)-H(12B) 109.5

 H(12A)-C(12)-H(12B) 109.5

 C(9)-C(12)-H(12C) 109.5

 H(12A)-C(12)-H(12C) 109.5

 H(12B)-C(12)-H(12C) 109.5

 C(13)-P(2)-C(20) 87.6(3)

 C(13)-N(3)-N(4) 117.2(5)

 C(13)-N(3)-H(3A) 121.4

 N(4)-N(3)-H(3A) 121.4

 C(20)-N(4)-N(3) 109.9(5)

 N(3)-C(13)-C(14) 119.2(6)

 N(3)-C(13)-P(2) 111.1(5)

 C(14)-C(13)-P(2) 129.6(5)

 C(19)-C(14)-C(15) 118.9(6)

 C(19)-C(14)-C(13) 122.2(6)

 C(15)-C(14)-C(13) 118.9(6)

 C(14)-C(15)-C(16) 120.3(7)

 C(14)-C(15)-H(15) 119.9

 C(16)-C(15)-H(15) 119.9

 C(17)-C(16)-C(15) 120.7(7)

 C(17)-C(16)-H(16) 119.7

 C(15)-C(16)-H(16) 119.7

 C(16)-C(17)-C(18) 119.1(8)

 C(16)-C(17)-H(17) 120.5

 C(18)-C(17)-H(17) 120.5

 C(17)-C(18)-C(19) 120.3(8)

 C(17)-C(18)-H(18) 119.9

 C(19)-C(18)-H(18) 119.9

 C(14)-C(19)-C(18) 120.7(7)

 C(14)-C(19)-H(19) 119.6

 C(18)-C(19)-H(19) 119.6

 N(4)-C(20)-C(21) 120.1(6)

 N(4)-C(20)-P(2) 114.2(5)

 C(21)-C(20)-P(2) 125.7(4)

 C(24)-C(21)-C(20) 111.6(5)

 C(24)-C(21)-C(22) 111.0(6)

 C(20)-C(21)-C(22) 108.7(5)

 C(24)-C(21)-C(23) 111.0(6)

 C(20)-C(21)-C(23) 106.6(5)

 C(22)-C(21)-C(23) 107.7(6)

 C(21)-C(22)-H(22A) 109.5

 C(21)-C(22)-H(22B) 109.5

 H(22A)-C(22)-H(22B) 109.5

 C(21)-C(22)-H(22C) 109.5

 H(22A)-C(22)-H(22C) 109.5

 H(22B)-C(22)-H(22C) 109.5

 C(21)-C(23)-H(23A) 109.5

 C(21)-C(23)-H(23B) 109.5

 H(23A)-C(23)-H(23B) 109.5

 C(21)-C(23)-H(23C) 109.5

 H(23A)-C(23)-H(23C) 109.5

 H(23B)-C(23)-H(23C) 109.5

 C(21)-C(24)-H(24A) 109.5

 C(21)-C(24)-H(24B) 109.5

 H(24A)-C(24)-H(24B) 109.5

 C(21)-C(24)-H(24C) 109.5

 H(24A)-C(24)-H(24C) 109.5

 H(24B)-C(24)-H(24C) 109.5

 C(32)-P(3)-C(25) 87.0(3)

 C(25)-N(5)-N(6) 109.7(5)

 C(32)-N(6)-N(5) 116.6(5)

 C(32)-N(6)-H(6A) 121.7

 N(5)-N(6)-H(6A) 121.7

 N(5)-C(25)-C(26) 119.5(5)

 N(5)-C(25)-P(3) 114.9(5)

 C(26)-C(25)-P(3) 125.6(4)

 C(31)-C(26)-C(27) 116.6(6)

 C(31)-C(26)-C(25) 121.4(6)

 C(27)-C(26)-C(25) 122.0(6)

 C(26)-C(27)-C(28) 121.9(7)

 C(26)-C(27)-H(27) 119.1

 C(28)-C(27)-H(27) 119.1

 C(29)-C(28)-C(27) 118.7(7)

 C(29)-C(28)-H(28) 120.7

 C(27)-C(28)-H(28) 120.7

 C(28)-C(29)-C(30) 121.7(7)

 C(28)-C(29)-H(29) 119.1

 C(30)-C(29)-H(29) 119.1

 C(29)-C(30)-C(31) 118.6(7)

 C(29)-C(30)-H(30) 120.7

 C(31)-C(30)-H(30) 120.7

 C(26)-C(31)-C(30) 122.5(7)

 C(26)-C(31)-H(31) 118.8

 C(30)-C(31)-H(31) 118.8

 N(6)-C(32)-C(33) 119.2(5)

 N(6)-C(32)-P(3) 111.7(5)

 C(33)-C(32)-P(3) 129.1(4)

 C(36)-C(33)-C(32) 109.9(5)

 C(36)-C(33)-C(35) 109.8(6)

 C(32)-C(33)-C(35) 108.4(5)

 C(36)-C(33)-C(34) 109.1(5)

 C(32)-C(33)-C(34) 109.9(5)

 C(35)-C(33)-C(34) 109.7(5)

 C(33)-C(34)-H(34A) 109.5

 C(33)-C(34)-H(34B) 109.5

 H(34A)-C(34)-H(34B) 109.5

 C(33)-C(34)-H(34C) 109.5

 H(34A)-C(34)-H(34C) 109.5

 H(34B)-C(34)-H(34C) 109.5

 C(33)-C(35)-H(35A) 109.5

 C(33)-C(35)-H(35B) 109.5

 H(35A)-C(35)-H(35B) 109.5

 C(33)-C(35)-H(35C) 109.5

 H(35A)-C(35)-H(35C) 109.5

 H(35B)-C(35)-H(35C) 109.5

 C(33)-C(36)-H(36A) 109.5

 C(33)-C(36)-H(36B) 109.5

 H(36A)-C(36)-H(36B) 109.5

 C(33)-C(36)-H(36C) 109.5

 H(36A)-C(36)-H(36C) 109.5

 H(36B)-C(36)-H(36C) 109.5

 C(37)-P(4)-C(44) 87.2(3)

 C(44)-N(7)-N(8) 110.8(5)

 C(37)-N(8)-N(7) 115.7(5)

 C(37)-N(8)-H(8) 122.2

 N(7)-N(8)-H(8) 122.2

 N(8)-C(37)-C(38) 117.4(6)

 N(8)-C(37)-P(4) 112.9(5)

 C(38)-C(37)-P(4) 129.6(5)

 C(43)-C(38)-C(39) 117.4(6)

 C(43)-C(38)-C(37) 122.9(6)

 C(39)-C(38)-C(37) 119.7(6)

 C(40)-C(39)-C(38) 120.9(7)

 C(40)-C(39)-H(39) 119.6

 C(38)-C(39)-H(39) 119.6

 C(39)-C(40)-C(41) 120.4(7)

 C(39)-C(40)-H(40) 119.8

 C(41)-C(40)-H(40) 119.8

 C(42)-C(41)-C(40) 118.9(7)

 C(42)-C(41)-H(41) 120.5

 C(40)-C(41)-H(41) 120.5

 C(41)-C(42)-C(43) 122.1(7)

 C(41)-C(42)-H(42) 119.0

 C(43)-C(42)-H(42) 119.0

 C(38)-C(43)-C(42) 120.2(6)

 C(38)-C(43)-H(43) 119.9

 C(42)-C(43)-H(43) 119.9

 N(7)-C(44)-C(45) 121.1(6)

 N(7)-C(44)-P(4) 113.3(5)

 C(45)-C(44)-P(4) 125.6(5)

 C(44)-C(45)-C(48) 111.9(5)

 C(44)-C(45)-C(46) 109.1(5)

 C(48)-C(45)-C(46) 108.4(6)

 C(44)-C(45)-C(47) 109.3(5)

 C(48)-C(45)-C(47) 109.5(6)

 C(46)-C(45)-C(47) 108.7(6)

 C(45)-C(46)-H(46A) 109.5

 C(45)-C(46)-H(46B) 109.5

 H(46A)-C(46)-H(46B) 109.5

 C(45)-C(46)-H(46C) 109.5

 H(46A)-C(46)-H(46C) 109.5

 H(46B)-C(46)-H(46C) 109.5

 C(45)-C(47)-H(47A) 109.5

 C(45)-C(47)-H(47B) 109.5

 H(47A)-C(47)-H(47B) 109.5

 C(45)-C(47)-H(47C) 109.5

 H(47A)-C(47)-H(47C) 109.5

 H(47B)-C(47)-H(47C) 109.5

 C(45)-C(48)-H(48A) 109.5

 C(45)-C(48)-H(48B) 109.5

 H(48A)-C(48)-H(48B) 109.5

 C(45)-C(48)-H(48C) 109.5

 H(48A)-C(48)-H(48C) 109.5

 H(48B)-C(48)-H(48C) 109.5

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 Symmetry transformations used to generate equivalent atoms:

Table S 22. Anisotropic displacement parameters (A^2 x 10^3) for 3e. The anisotropic displacement factor exponent takes the form: -2 pi^2 [ h^2 a\*^2 U11 + ... + 2 h k a\* b\* U12 ]

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 U11 U22 U33 U23 U13 U12

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 P(1) 39(1) 66(1) 69(1) 11(1) 15(1) 5(1)

 N(1) 33(3) 70(5) 61(4) 10(3) 15(2) 0(3)

 N(2) 60(4) 39(3) 51(4) 6(3) 19(3) -2(3)

 C(1) 32(4) 63(5) 37(4) -13(3) 8(3) -3(3)

 C(2) 49(4) 46(4) 50(4) -6(3) 16(3) 1(3)

 C(3) 63(5) 58(5) 46(4) -1(4) 7(3) -9(4)

 C(4) 83(6) 62(5) 60(5) 8(4) 16(4) 4(4)

 C(5) 93(6) 54(6) 88(7) -3(4) 39(5) -20(5)

 C(6) 59(5) 71(6) 98(6) 8(5) 27(4) -17(4)

 C(7) 56(5) 54(5) 82(5) -4(4) 17(4) -11(4)

 C(8) 36(4) 59(4) 51(4) 7(4) 11(3) 18(3)

 C(9) 55(4) 42(4) 62(5) 8(4) 16(3) 9(3)

 C(10) 97(6) 52(5) 120(7) -12(5) 36(5) -5(5)

 C(11) 111(7) 86(6) 57(5) 13(4) 36(5) 29(5)

 C(12) 63(6) 104(7) 134(8) 45(5) 22(5) 31(5)

 P(2) 40(1) 69(1) 81(2) 19(1) 18(1) 8(1)

 N(3) 30(3) 70(4) 72(4) 4(3) 16(3) 8(3)

 N(4) 41(3) 47(4) 65(4) 14(3) 11(2) 12(3)

 C(13) 42(4) 61(5) 51(5) -14(4) 19(3) -2(3)

 C(14) 41(4) 53(5) 53(5) 1(3) 12(3) -2(3)

 C(15) 58(5) 77(6) 80(6) 7(5) 29(4) 10(4)

 C(16) 108(7) 76(6) 60(5) -4(5) 40(4) -10(5)

 C(17) 90(6) 73(5) 70(6) 3(5) 17(5) 16(5)

 C(18) 73(6) 83(7) 104(7) 15(5) 21(5) 18(5)

 C(19) 55(5) 65(5) 82(5) 15(4) 26(4) 9(4)

 C(20) 36(4) 54(5) 55(4) -7(3) 13(3) 5(3)

 C(21) 48(4) 60(5) 54(5) 8(4) 15(3) 17(3)

 C(22) 89(6) 74(6) 87(6) 3(5) -5(5) 31(5)

 C(23) 98(6) 53(5) 108(6) -12(4) 9(5) 32(5)

 C(24) 83(6) 82(6) 155(8) 67(6) 40(6) 17(5)

 P(3) 40(1) 68(1) 71(1) 11(1) 17(1) 0(1)

 N(5) 42(3) 54(4) 62(4) 5(3) 11(3) 0(3)

 N(6) 31(3) 52(4) 53(3) 10(3) 3(2) 5(3)

 C(25) 40(4) 47(4) 42(4) 1(3) 17(3) 4(3)

 C(26) 43(4) 51(4) 49(4) -5(3) 13(3) -4(3)

 C(27) 62(5) 40(4) 55(5) -13(3) 14(4) -4(3)

 C(28) 83(6) 62(5) 63(5) -5(4) 15(4) -10(5)

 C(29) 86(6) 48(6) 86(7) 11(4) 4(5) 9(4)

 C(30) 66(5) 70(6) 94(6) 6(5) 15(4) 16(5)

 C(31) 61(5) 54(5) 67(5) 2(4) 18(4) -4(4)

 C(32) 36(4) 60(4) 44(4) 1(3) 11(3) -17(3)

 C(33) 43(4) 55(5) 57(5) 13(4) 12(3) -1(3)

 C(34) 101(7) 78(6) 67(6) 10(4) 2(5) -8(5)

 C(35) 98(6) 49(5) 88(6) 1(4) 12(4) 6(4)

 C(36) 69(6) 92(6) 121(7) 48(5) 23(5) -7(5)

 P(4) 41(1) 72(1) 88(2) 9(1) 22(1) 7(1)

 N(7) 48(3) 47(4) 63(4) 10(3) 18(3) -6(3)

 N(8) 42(3) 50(4) 59(4) 12(3) 18(2) 1(3)

 C(37) 37(4) 50(4) 48(4) -12(3) 3(3) 13(3)

 C(38) 35(4) 62(5) 56(5) -10(4) 15(3) 5(3)

 C(39) 48(4) 64(5) 70(5) 4(4) 11(3) 4(4)

 C(40) 84(6) 68(6) 59(5) -3(4) -3(4) 19(5)

 C(41) 97(7) 60(5) 90(6) 28(5) 9(5) 10(5)

 C(42) 73(6) 65(6) 83(6) 17(4) 19(4) 7(4)

 C(43) 49(5) 64(5) 80(6) 2(4) 1(4) 10(4)

 C(44) 37(4) 57(5) 56(4) -3(3) 9(3) -7(3)

 C(45) 51(4) 64(5) 47(4) -5(4) 8(3) -15(4)

 C(46) 89(6) 86(6) 107(7) -5(5) 30(5) -37(5)

 C(47) 106(6) 88(6) 74(5) -4(5) 45(4) -36(5)

 C(48) 80(6) 86(6) 146(8) 60(6) 41(5) 5(5)

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

Table S 23. Hydrogen coordinates ( x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 3e.

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 x y z U(eq)

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 H(1) 10830 2772 971 65

 H(3) 10633 -844 2180 68

 H(4) 10319 -3034 2666 82

 H(5) 8540 -4251 2475 90

 H(6) 7033 -3235 1803 90

 H(7) 7321 -1047 1327 76

 H(10A) 9790 6749 692 132

 H(10B) 10626 5437 989 132

 H(10C) 9561 5950 1224 132

 H(11A) 9473 5335 -173 122

 H(11B) 9000 3622 -225 122

 H(11C) 10276 3963 102 122

 H(12A) 7596 5397 729 151

 H(12B) 7325 4330 203 151

 H(12C) 7766 6039 162 151

 H(3A) 5726 8519 3637 68

 H(15) 8305 10159 2838 83

 H(16) 7898 12369 2302 93

 H(17) 6330 13884 2344 93

 H(18) 5218 13259 2964 104

 H(19) 5648 11078 3513 79

 H(22A) 9098 6151 5138 131

 H(22B) 9897 6329 4717 131

 H(22C) 9833 4730 5014 131

 H(23A) 9241 3222 4149 133

 H(23B) 9475 4756 3850 133

 H(23C) 8286 3884 3658 133

 H(24A) 7180 4838 4842 157

 H(24B) 7877 3308 4796 157

 H(24C) 6899 3863 4293 157

 H(6A) 4875 6336 4065 56

 H(27) 3560 10023 2864 63

 H(28) 2786 12219 2367 84

 H(29) 1137 13341 2537 91

 H(30) 247 12329 3187 93

 H(31) 996 10092 3663 72

 H(34A) 4168 5542 5210 127

 H(34B) 5154 5071 4914 127

 H(34C) 4549 3795 5202 127

 H(35A) 4032 2297 4280 120

 H(35B) 4713 3606 4048 120

 H(35C) 3429 3214 3746 120

 H(36A) 2123 4705 4801 141

 H(36B) 2556 2980 4795 141

 H(36C) 1841 3746 4250 141

 H(8) 2057 465 1386 59

 H(39) 5385 -1347 2141 73

 H(40) 5397 -3448 2712 88

 H(41) 3723 -4899 2660 101

 H(42) 2057 -4141 2080 88

 H(43) 2009 -2071 1486 80

 H(46A) 4655 5009 1369 139

 H(46B) 5051 5774 870 139

 H(46C) 5662 4255 1143 139

 H(47A) 5264 2700 287 128

 H(47B) 4800 4241 -25 128

 H(47C) 4027 2737 -111 128

 H(48A) 2452 4239 139 152

 H(48B) 3197 5758 282 152

 H(48C) 2603 5011 723 152

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

Crystallographic data for **3g**

 Table S 24. Crystal data and structure refinement for 110925.

 Identification code 110925

 Empirical formula C10 H13 N2 P S

 Formula weight 224.25

 Temperature 296(2) K

 Wavelength 0.71073 A

 Crystal system, space group Monoclinic, P2(1)/c

 Unit cell dimensions a = 11.9543(2) A alpha = 90 deg.

 b = 8.8572(2) A beta = 115.9730(10) deg.

 c = 12.5222(2) A gamma = 90 deg.

 Volume 1191.96(4) A^3

 Z, Calculated density 4, 1.250 Mg/m^3

 Absorption coefficient 0.371 mm^-1

 F(000) 472

 Crystal size 0.21 x 0.16 x 0.12 mm

 Theta range for data collection 1.89 to 25.99 deg.

 Limiting indices -14<=h<=14, -10<=k<=10, -15<=l<=15

 Reflections collected / unique 16465 / 2340 [R(int) = 0.0203]

 Completeness to theta = 25.99 100.0 %

 Absorption correction multi-scan

 Max. and min. transmission 0.9565 and 0.9256

 Refinement method Full-matrix least-squares on F^2

 Data / restraints / parameters 2340 / 0 / 131

 Goodness-of-fit on F^2 1.022

 Final R indices [I>2sigma(I)] R1 = 0.0512, wR2 = 0.1494

 R indices (all data) R1 = 0.0596, wR2 = 0.1601

 Largest diff. peak and hole 0.567 and -0.304 e.A^-3

 Table S 26. Atomic coordinates ( x 10^4) and equivalent isotropic

 displacement parameters (A^2 x 10^3) for 110925.

 U(eq) is defined as one third of the trace of the orthogonalized

 Uij tensor.

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 x y z U(eq)

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 P(1) 3109(1) 538(1) 4669(1) 59(1)

 S(1) 2993(1) -3038(1) 7061(1) 72(1)

 N(1) 1447(2) -529(2) 5313(2) 49(1)

 N(2) 1031(2) 797(3) 4729(2) 50(1)

 C(1) 1745(2) 1522(3) 4321(2) 47(1)

 C(2) 2550(2) -817(3) 5353(2) 46(1)

 C(3) 3230(2) -2172(3) 5947(2) 51(1)

 C(4) 4148(3) -2915(3) 5750(3) 65(1)

 C(5) 4615(3) -4173(4) 6524(4) 80(1)

 C(6) 4085(3) -4367(4) 7257(3) 76(1)

 C(7) 1312(3) 3003(3) 3682(3) 57(1)

 C(8) 1062(6) 4108(5) 4497(5) 121(2)

 C(9) 2301(5) 3672(6) 3385(6) 130(2)

 C(10) 115(4) 2810(5) 2584(4) 115(2)

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 Table S 27. Bond lengths [A] and angles [deg] for 110925.

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 P(1)-C(1) 1.728(3)

 P(1)-C(2) 1.767(3)

 S(1)-C(6) 1.694(3)

 S(1)-C(3) 1.720(3)

 N(1)-C(2) 1.322(3)

 N(1)-N(2) 1.358(3)

 N(2)-C(1) 1.335(3)

 N(2)-H(1) 0.81(3)

 C(1)-C(7) 1.505(4)

 C(2)-C(3) 1.458(4)

 C(3)-C(4) 1.391(4)

 C(4)-C(5) 1.421(4)

 C(4)-H(4A) 0.9300

 C(5)-C(6) 1.335(5)

 C(5)-H(5A) 0.9300

 C(6)-H(6A) 0.9300

 C(7)-C(10) 1.498(5)

 C(7)-C(9) 1.508(5)

 C(7)-C(8) 1.535(5)

 C(8)-H(8A) 0.9600

 C(8)-H(8B) 0.9600

 C(8)-H(8C) 0.9600

 C(9)-H(9A) 0.9600

 C(9)-H(9B) 0.9600

 C(9)-H(9C) 0.9600

 C(10)-H(10A) 0.9600

 C(10)-H(10B) 0.9600

 C(10)-H(10C) 0.9600

 C(1)-P(1)-C(2) 87.08(12)

 C(6)-S(1)-C(3) 92.10(15)

 C(2)-N(1)-N(2) 108.1(2)

 C(1)-N(2)-N(1) 118.5(2)

 C(1)-N(2)-H(1) 119(2)

 N(1)-N(2)-H(1) 123(2)

 N(2)-C(1)-C(7) 119.6(2)

 N(2)-C(1)-P(1) 110.59(19)

 C(7)-C(1)-P(1) 129.8(2)

 N(1)-C(2)-C(3) 120.2(2)

 N(1)-C(2)-P(1) 115.68(19)

 C(3)-C(2)-P(1) 124.17(19)

 C(4)-C(3)-C(2) 127.3(2)

 C(4)-C(3)-S(1) 110.9(2)

 C(2)-C(3)-S(1) 121.8(2)

 C(3)-C(4)-C(5) 110.8(3)

 C(3)-C(4)-H(4A) 124.6

 C(5)-C(4)-H(4A) 124.6

 C(6)-C(5)-C(4) 114.0(3)

 C(6)-C(5)-H(5A) 123.0

 C(4)-C(5)-H(5A) 123.0

 C(5)-C(6)-S(1) 112.3(3)

 C(5)-C(6)-H(6A) 123.9

 S(1)-C(6)-H(6A) 123.9

 C(10)-C(7)-C(1) 110.9(3)

 C(10)-C(7)-C(9) 110.8(4)

 C(1)-C(7)-C(9) 110.5(3)

 C(10)-C(7)-C(8) 107.3(4)

 C(1)-C(7)-C(8) 108.9(3)

 C(9)-C(7)-C(8) 108.4(4)

 C(7)-C(8)-H(8A) 109.5

 C(7)-C(8)-H(8B) 109.5

 H(8A)-C(8)-H(8B) 109.5

 C(7)-C(8)-H(8C) 109.5

 H(8A)-C(8)-H(8C) 109.5

 H(8B)-C(8)-H(8C) 109.5

 C(7)-C(9)-H(9A) 109.5

 C(7)-C(9)-H(9B) 109.5

 H(9A)-C(9)-H(9B) 109.5

 C(7)-C(9)-H(9C) 109.5

 H(9A)-C(9)-H(9C) 109.5

 H(9B)-C(9)-H(9C) 109.5

 C(7)-C(10)-H(10A) 109.5

 C(7)-C(10)-H(10B) 109.5

 H(10A)-C(10)-H(10B) 109.5

 C(7)-C(10)-H(10C) 109.5

 H(10A)-C(10)-H(10C) 109.5

 H(10B)-C(10)-H(10C) 109.5

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 Symmetry transformations used to generate equivalent atoms:

 Table S 28. Anisotropic displacement parameters (A^2 x 10^3) for 110925.

 The anisotropic displacement factor exponent takes the form:

 -2 pi^2 [ h^2 a\*^2 U11 + ... + 2 h k a\* b\* U12 ]

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 U11 U22 U33 U23 U13 U12

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 P(1) 46(1) 65(1) 73(1) 16(1) 33(1) 4(1)

 S(1) 76(1) 80(1) 65(1) 20(1) 37(1) 15(1)

 N(1) 48(1) 51(1) 53(1) 8(1) 27(1) 3(1)

 N(2) 45(1) 51(1) 59(1) 9(1) 29(1) 6(1)

 C(1) 47(1) 50(1) 46(1) 1(1) 23(1) -3(1)

 C(2) 43(1) 52(1) 44(1) 1(1) 19(1) -1(1)

 C(3) 44(1) 53(2) 52(1) 5(1) 18(1) 0(1)

 C(4) 57(2) 61(2) 83(2) 18(2) 35(2) 13(1)

 C(5) 60(2) 75(2) 108(3) 25(2) 40(2) 21(2)

 C(6) 65(2) 73(2) 78(2) 27(2) 21(2) 12(2)

 C(7) 59(2) 49(2) 62(2) 8(1) 27(1) -2(1)

 C(8) 194(6) 64(2) 118(4) 6(2) 82(4) 26(3)

 C(9) 108(3) 106(3) 209(6) 86(4) 100(4) 24(3)

 C(10) 96(3) 91(3) 108(3) 41(3) -3(2) -8(2)

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 Table S 29. Hydrogen coordinates ( x 10^4) and isotropic

 displacement parameters (A^2 x 10^3) for 110925.

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 x y z U(eq)

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 H(4A) 4418 -2627 5188 78

 H(5A) 5234 -4805 6520 96

 H(6A) 4292 -5143 7811 91

 H(8A) 434 3698 4696 181

 H(8B) 782 5055 4094 181

 H(8C) 1815 4262 5210 181

 H(9A) 2471 2993 2876 195

 H(9B) 3047 3830 4103 195

 H(9C) 2015 4620 2986 195

 H(10A) 241 2128 2050 173

 H(10B) -155 3771 2203 173

 H(10C) -507 2407 2795 173

 H(1) 350(30) 1140(40) 4580(30) 61(9)

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 Table S 30. Torsion angles [deg] for 110925.

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 C(2)-N(1)-N(2)-C(1) 0.4(3)

 N(1)-N(2)-C(1)-C(7) -179.4(2)

 N(1)-N(2)-C(1)-P(1) -0.4(3)

 C(2)-P(1)-C(1)-N(2) 0.3(2)

 C(2)-P(1)-C(1)-C(7) 179.1(3)

 N(2)-N(1)-C(2)-C(3) 179.2(2)

 N(2)-N(1)-C(2)-P(1) -0.1(3)

 C(1)-P(1)-C(2)-N(1) -0.1(2)

 C(1)-P(1)-C(2)-C(3) -179.4(2)

 N(1)-C(2)-C(3)-C(4) 156.5(3)

 P(1)-C(2)-C(3)-C(4) -24.2(4)

 N(1)-C(2)-C(3)-S(1) -25.4(3)

 P(1)-C(2)-C(3)-S(1) 153.86(16)

 C(6)-S(1)-C(3)-C(4) -0.3(3)

 C(6)-S(1)-C(3)-C(2) -178.7(2)

 C(2)-C(3)-C(4)-C(5) 178.5(3)

 S(1)-C(3)-C(4)-C(5) 0.2(4)

 C(3)-C(4)-C(5)-C(6) 0.0(5)

 C(4)-C(5)-C(6)-S(1) -0.2(5)

 C(3)-S(1)-C(6)-C(5) 0.3(3)

 N(2)-C(1)-C(7)-C(10) -61.0(4)

 P(1)-C(1)-C(7)-C(10) 120.3(3)

 N(2)-C(1)-C(7)-C(9) 175.7(3)

 P(1)-C(1)-C(7)-C(9) -3.0(5)

 N(2)-C(1)-C(7)-C(8) 56.8(4)

 P(1)-C(1)-C(7)-C(8) -121.8(3)

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 Symmetry transformations used to generate equivalent atoms:

 Table S 31. Hydrogen bonds for 110925 [A and deg.].

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 D-H...A d(D-H) d(H...A) d(D...A) <(DHA)

 N(2)-H(1)...N(1)#1 0.81(3) 2.28(3) 2.950(3) 141(3)

 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 Symmetry transformations used to generate equivalent atoms:

 #1 -x,-y,-z+1

NMR spectra of compounds **3a – 3g**

**Figure S 1**.31P{1H}NMR spectrum of **3a**



**Figure S 2**. 31P{1H} NMR spectrum of of **3b**



**Figure S 3**. 1H NMR spectra of **3c**

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**Figure S 4**. 31P NMR spectra of **3c**



**Figure S 5**. 13C NMR spectra of **3c**



**Figure S 6**. 31P{1H} NMR spectrum of **3d**



**Figure S 7**. 1H NMR spectrum of **3e**



**Figure S 8**. 31P NMR spectrum of **3e**

