Supporting Information

1-PHOSPHA-2-AZANORBORNENE AS PRECURSOR FOR 1-PHOSPHA-BICYCLO[3.2.1]OCTA-2,5-DIENE

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

Empirical formula	$C_{15}H_{20}NOP$	
Formula weight	261.29	
Temperature	130(2) K	
Wavelength	71.073 pm	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 812.02(4) pm	a= 103.699(4)°
	b = 995.95(4) pm	b= 111.168(4)°
	c = 1002.79(4) pm	g= 108.539(4)°
Volume	0.65787(6) nm^3	
Z	2	
Density (calculated)	1.319 Mg/m^3	
Absorption coefficient	0.197 mm^{-1}	
F(000)	280	
Crystal size	0.36 · 0.26 · 0.18 mm^3	
Theta range for data collection	2.351 to 32.390°.	
Index ranges	$-12 \le h \le 11$	
	$-14 \le k \le 14$	
	$-15 \le l \le 14$	
Reflections collected	13522	
Independent reflections	4381 [R(int) = 0.0305]	
Completeness to theta = 30.510°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.99371	
Refinement method	Full-matrix least-squares on F^2	
Restraints / parameters	0 / 243	
Goodness-of-fit on F^2	1.031	
Final R indices [I>2sigma(I)]	R1 = 0.0413, wR2 = 0.0977	
R indices (all data)	R1 = 0.0525, wR2 = 0.1044	
Residual electron density	0.376 and -0.244 $e \cdot Å^{-3}$	
CCDC-number	2490394	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (pm^2x 10^{-1}) for **2b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	2031(1)	4169(1)	7267(1)	18(1)
O(1)	4431(1)	1100(1)	3538(1)	19(1)
N(1)	3080(2)	306(1)	5516(1)	16(1)
C(1)	4457(2)	5412(1)	7571(1)	18(1)
C(2)	5622(2)	4712(1)	7651(1)	18(1)
C(3)	4647(2)	3009(1)	7413(1)	15(1)
C(4)	3579(2)	1912(1)	5634(1)	14(1)
C(5)	1692(2)	2015(1)	4624(1)	13(1)
C(6)	642(2)	1060(1)	3033(1)	15(1)
C(7)	-1074(2)	1049(1)	2004(1)	15(1)
C(8)	-1770(2)	2029(1)	2591(2)	17(1)
C(9)	-788(2)	2958(1)	4169(2)	17(1)
C(10)	934(2)	2974(1)	5199(1)	15(1)
C(11)	3088(2)	2936(1)	7961(1)	18(1)
C(12)	7742(2)	5526(2)	8031(2)	27(1)
C(13)	6128(2)	2560(2)	8426(2)	21(1)
C(14)	5040(2)	2288(1)	4969(1)	16(1)
C(15)	-2134(2)	18(2)	301(2)	22(1)

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

P(1)-C(10)	182.57(12)
P(1)-C(1)	182.87(14)
P(1)-C(11)	183.63(13)
O(1)-C(14)	141.90(14)
O(1)-H(1O)	83(2)
N(1)-C(4)	148.34(15)
N(1)-H(1N)	86.7(19)
N(1)-H(2N)	89.0(19)
C(1)-C(2)	133.32(18)
C(1)-H(1)	97.8(17)
C(2)-C(12)	150.27(19)
C(2)-C(3)	154.24(17)
C(3)-C(13)	153.39(17)
C(3)-C(11)	154.04(17)
C(3)-C(4)	157.71(16)
C(4)-C(14)	154.83(17)
C(4)-C(5)	155.39(15)
C(5)-C(6)	140.06(16)
C(5)-C(10)	141.12(15)
C(6)-C(7)	139.72(16)
C(6)-H(6)	96.4(16)
C(7)-C(8)	139.24(17)
C(7)-C(15)	150.23(17)
C(8)-C(9)	138.60(17)
C(8)-H(8)	98.1(16)
C(9)-C(10)	139.91(16)
C(9)-H(9)	96.4(17)
C(11)-H(11A)	97.7(17)
C(11)-H(11B)	96.8(18)
C(12)-H(12A)	93(2)
C(12)-H(12B)	94(2)
C(12)-H(12C)	98(3)
C(13)-H(13A)	99.0(19)
C(13)-H(13B)	96.1(18)

C(13)-H(13C)	100(2)
C(14)-H(14A)	98.8(16)
C(14)-H(14B)	100.9(16)
C(15)-H(15A)	96(2)
C(15)-H(15B)	97.4(19)
C(15)-H(15C)	98(2)

C(10)-P(1)-C(1)	98.55(5)
C(10)-P(1)-C(11)	95.32(5)
C(1)-P(1)-C(11)	88.15(6)
C(14)-O(1)-H(1O)	109.3(14)
C(4)-N(1)-H(1N)	111.4(11)
C(4)-N(1)-H(2N)	108.8(12)
H(1N)-N(1)-H(2N)	107.7(16)
C(2)-C(1)-P(1)	113.07(10)
C(2)-C(1)-H(1)	123.4(10)
P(1)-C(1)-H(1)	123.5(10)
C(1)-C(2)-C(12)	123.26(12)
C(1)-C(2)-C(3)	114.26(11)
C(12)-C(2)-C(3)	122.39(11)
C(13)-C(3)-C(11)	109.37(10)
C(13)-C(3)-C(2)	111.74(10)
C(11)-C(3)-C(2)	103.62(10)
C(13)-C(3)-C(4)	111.94(10)
C(11)-C(3)-C(4)	109.14(9)
C(2)-C(3)-C(4)	110.67(9)
N(1)-C(4)-C(14)	106.16(9)
N(1)-C(4)-C(5)	109.89(9)
C(14)-C(4)-C(5)	109.20(9)
N(1)-C(4)-C(3)	108.00(9)
C(14)-C(4)-C(3)	109.35(9)
C(5)-C(4)-C(3)	113.95(9)
C(6)-C(5)-C(10)	117.65(10)
C(6)-C(5)-C(4)	117.48(10)
C(10)-C(5)-C(4)	124.85(10)
C(7)-C(6)-C(5)	122.90(11)

C(7)-C(6)-H(6)	117.2(10)
C(5)-C(6)-H(6)	119.9(10)
C(8)-C(7)-C(6)	118.42(11)
C(8)-C(7)-C(15)	120.64(11)
C(6)-C(7)-C(15)	120.94(11)
C(9)-C(8)-C(7)	119.87(11)
C(9)-C(8)-H(8)	120.8(9)
C(7)-C(8)-H(8)	119.3(9)
C(8)-C(9)-C(10)	121.74(11)
C(8)-C(9)-H(9)	119.1(10)
C(10)-C(9)-H(9)	119.2(10)
C(9)-C(10)-C(5)	119.38(11)
C(9)-C(10)-P(1)	117.89(9)
C(5)-C(10)-P(1)	122.63(9)
C(3)-C(11)-P(1)	105.77(8)
C(3)-C(11)-H(11A)	110.7(10)
P(1)-C(11)-H(11A)	107.6(10)
C(3)-C(11)-H(11B)	113.0(10)
P(1)-C(11)-H(11B)	113.2(10)
H(11A)-C(11)-H(11B)	106.5(14)
C(2)-C(12)-H(12A)	114.2(14)
C(2)-C(12)-H(12B)	110.4(13)
H(12A)-C(12)-H(12B)	109.3(19)
C(2)-C(12)-H(12C)	111.3(14)
H(12A)-C(12)-H(12C)	105.4(18)
H(12B)-C(12)-H(12C)	105.9(18)
C(3)-C(13)-H(13A)	111.4(11)
C(3)-C(13)-H(13B)	110.3(11)
H(13A)-C(13)-H(13B)	105.6(15)
C(3)-C(13)-H(13C)	114.0(11)
H(13A)-C(13)-H(13C)	106.5(15)
H(13B)-C(13)-H(13C)	108.6(15)
O(1)-C(14)-C(4)	113.25(10)
O(1)-C(14)-H(14A)	109.3(9)
C(4)-C(14)-H(14A)	107.6(9)
O(1)-C(14)-H(14B)	109.5(9)

C(4)-C(14)-H(14B)	108.0(9)
H(14A)-C(14)-H(14B)	109.0(13)
C(7)-C(15)-H(15A)	112.2(12)
C(7)-C(15)-H(15B)	110.4(11)
H(15A)-C(15)-H(15B)	107.3(16)
C(7)-C(15)-H(15C)	111.2(12)
H(15A)-C(15)-H(15C)	106.8(17)
H(15B)-C(15)-H(15C)	108.8(17)

Table S4. Anisotropic displacement parameters ($pm^2 \times 10^{-1}$) for **2b**.

The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	20(1)	17(1)	17(1)	4(1)	10(1)	10(1)
O(1)	19(1)	27(1)	14(1)	6(1)	8(1)	14(1)
N(1)	17(1)	13(1)	16(1)	5(1)	8(1)	7(1)
C(1)	22(1)	14(1)	15(1)	3(1)	7(1)	7(1)
C(2)	18(1)	15(1)	14(1)	3(1)	6(1)	5(1)
C(3)	15(1)	15(1)	13(1)	5(1)	5(1)	6(1)
C(4)	13(1)	14(1)	13(1)	5(1)	6(1)	7(1)
C(5)	12(1)	13(1)	14(1)	6(1)	6(1)	6(1)
C(6)	14(1)	15(1)	15(1)	6(1)	7(1)	7(1)
C(7)	13(1)	16(1)	14(1)	7(1)	5(1)	5(1)
C(8)	13(1)	18(1)	21(1)	9(1)	7(1)	8(1)
C(9)	14(1)	15(1)	22(1)	8(1)	9(1)	8(1)
C(10)	14(1)	13(1)	18(1)	6(1)	8(1)	6(1)
C(11)	22(1)	17(1)	15(1)	6(1)	10(1)	7(1)
C(12)	19(1)	20(1)	33(1)	4(1)	10(1)	3(1)
C(13)	23(1)	23(1)	15(1)	7(1)	4(1)	12(1)
C(14)	16(1)	19(1)	16(1)	7(1)	8(1)	9(1)
C(15)	18(1)	28(1)	15(1)	6(1)	4(1)	10(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (pm^2x 10^{-1}) for **2b**.

	x	y	z	U(eq)
H(1N)	2260(30)	10(20)	5870(20)	25(4)
H(2N)	2510(30)	-320(20)	4520(20)	30(5)
H(1O)	5060(30)	590(20)	3710(20)	44(6)
H(1)	4880(30)	6490(20)	7700(20)	26(4)
H(6)	1100(20)	368(18)	2606(18)	20(4)
H(8)	-2980(20)	2029(18)	1884(19)	20(4)
H(9)	-1310(30)	3600(20)	4570(20)	28(4)
H(11A)	3700(20)	3376(19)	9100(20)	25(4)
H(11B)	2110(30)	1890(20)	7614(19)	25(4)
H(12A)	8060(30)	5050(30)	7310(30)	50(6)
H(12B)	8080(30)	6560(30)	8140(20)	49(6)
H(12C)	8630(40)	5580(30)	9030(30)	60(7)
H(13A)	5450(30)	1550(20)	8450(20)	32(5)
H(13B)	6830(30)	3290(20)	9490(20)	30(5)
H(13C)	7100(30)	2470(20)	8070(20)	34(5)
H(14A)	5160(20)	3249(18)	4811(18)	19(4)
H(14B)	6360(20)	2468(18)	5770(18)	19(4)
H(15A)	-3530(30)	-450(20)	-110(20)	39(5)
H(15B)	-1750(30)	-810(20)	130(20)	35(5)
H(15C)	-1840(30)	600(20)	-320(30)	50(6)

Table S6. Hydrogen bonds for **2b** [pm and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1O)...N(1)#1	83(2)	200(2)	282.69(14)	169(2)

Symmetry transformations used to generate equivalent atoms:

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

NMR Spectra of 2b

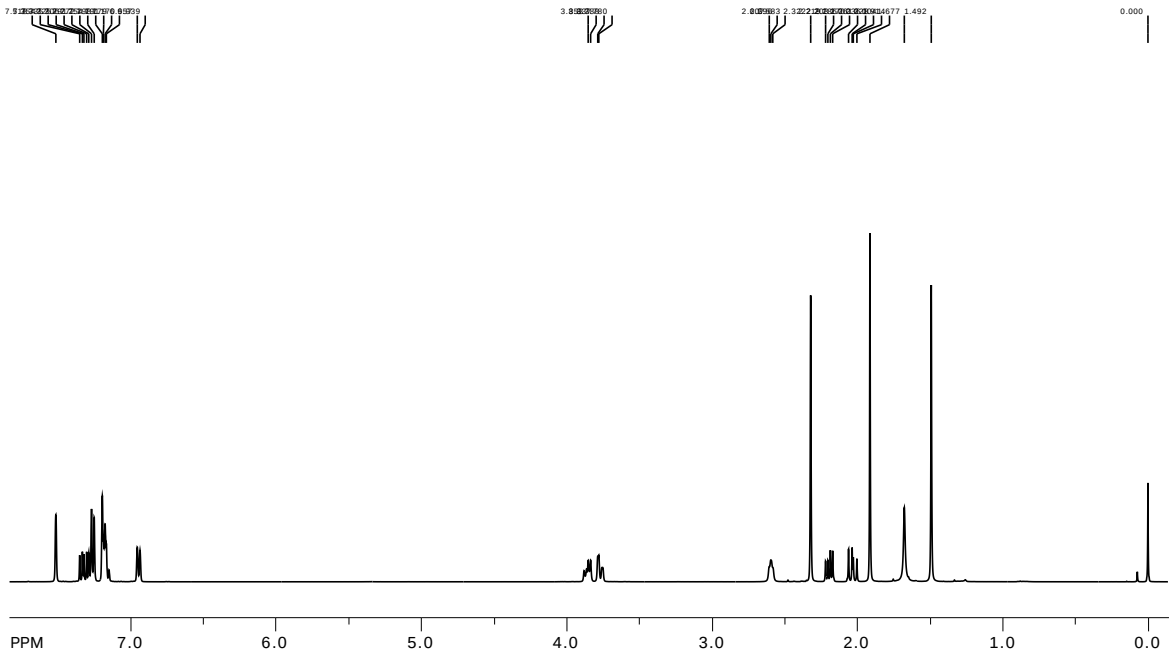

Figure S1. ^{1}H NMR spectrum of **2b** (in $CDCl_3$).

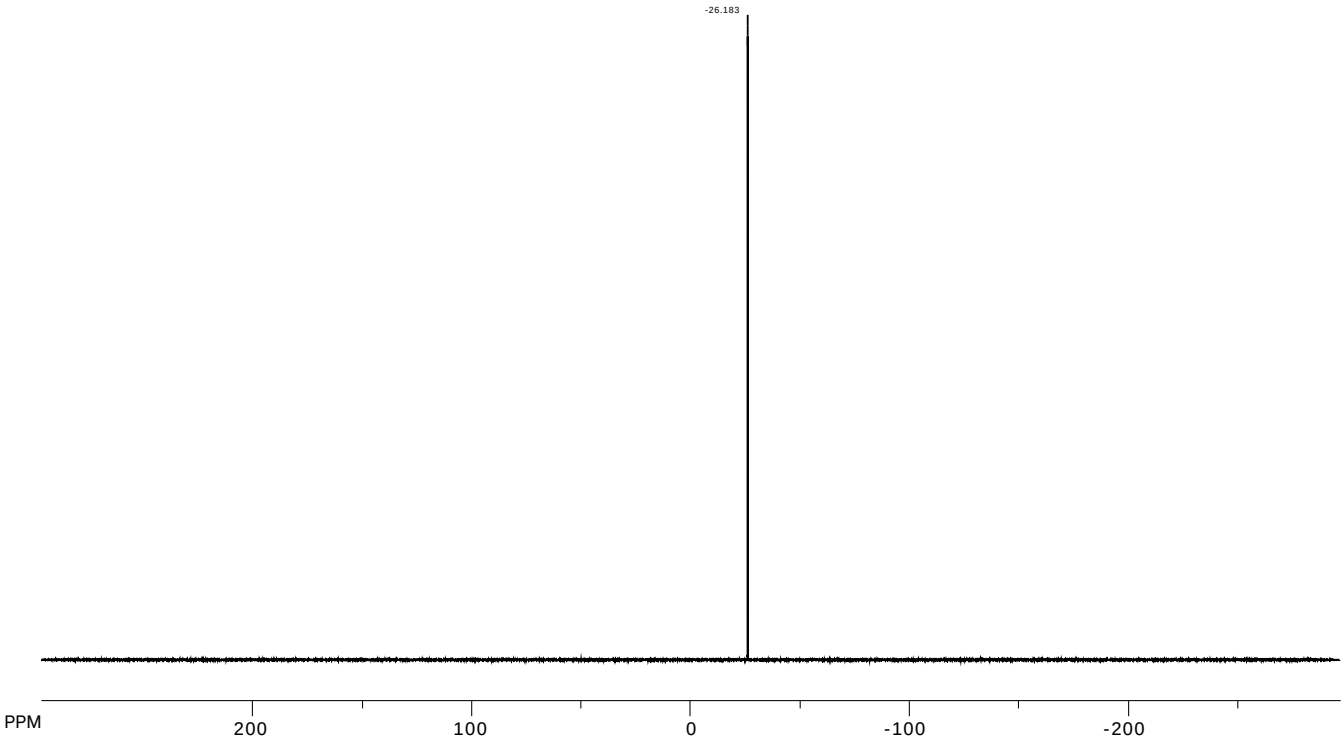

Figure S2. $^{31}P\{^{1}H\}$ NMR spectrum of **2b** (in $CDCl_3$).

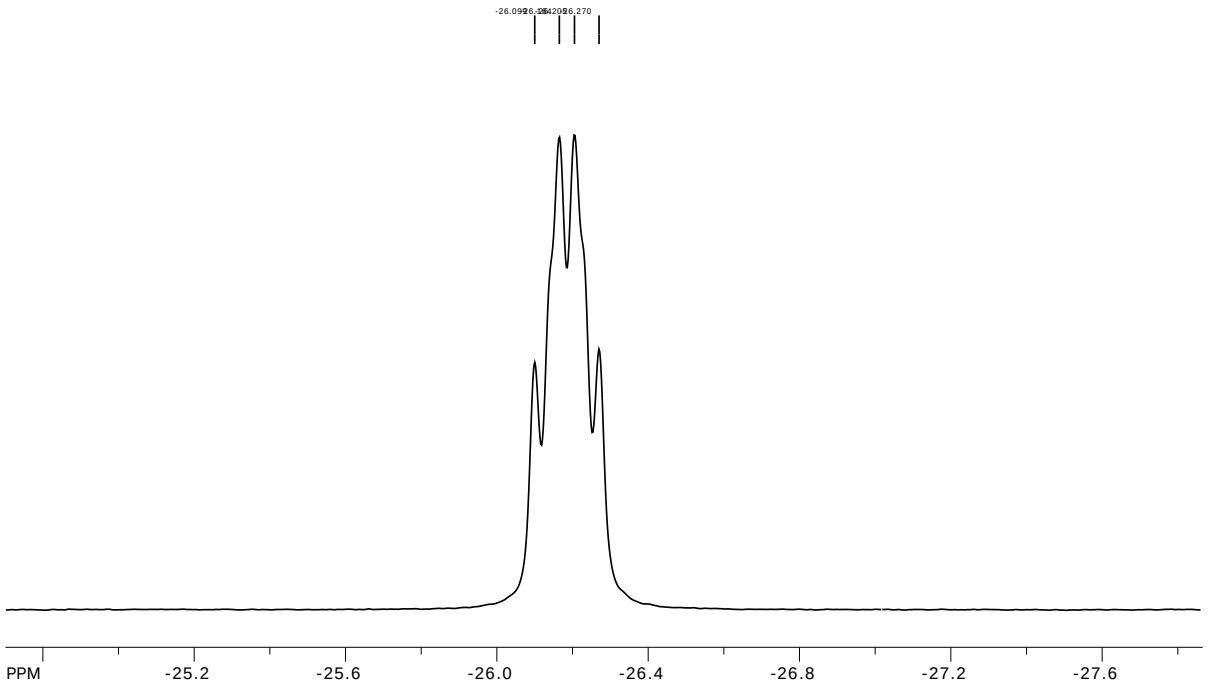

Figure S3. ^{31}P-^{1}H NMR spectrum of **2b** (in $CDCl_3$).

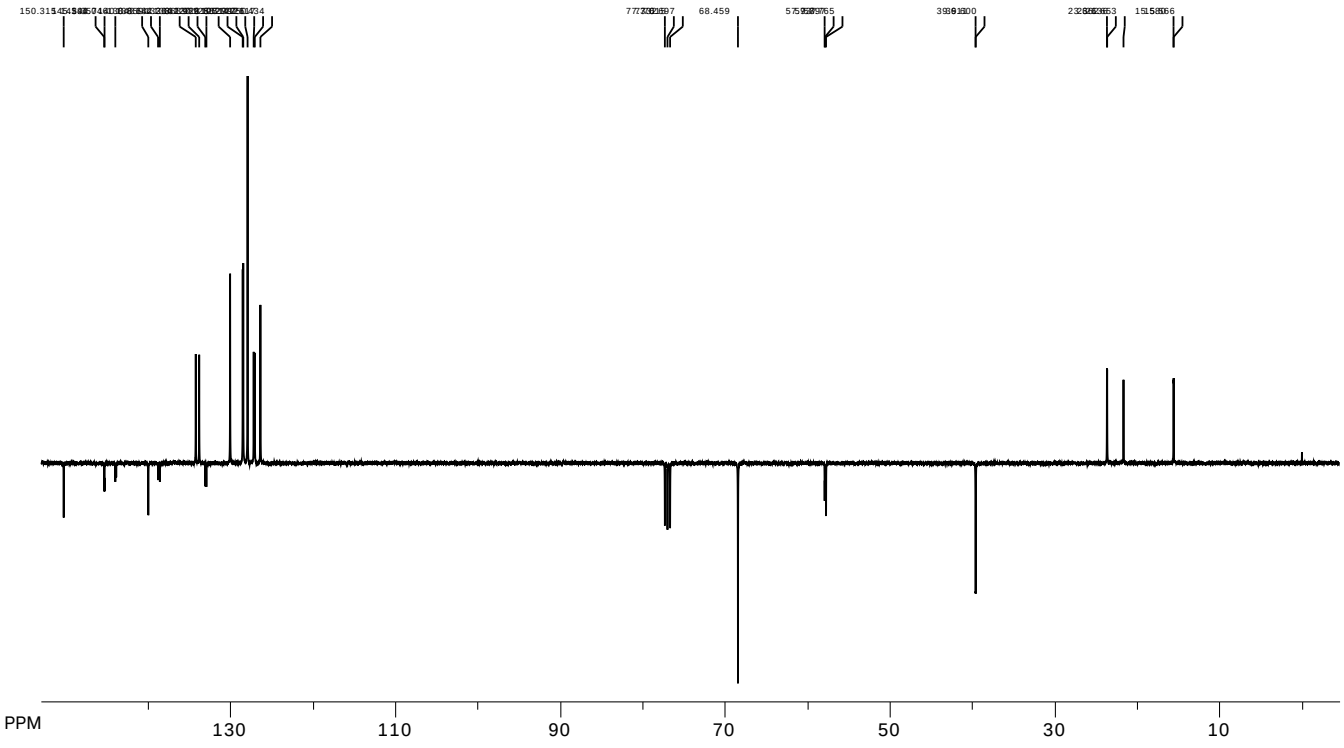

Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of **2b** (in $CDCl_3$).