Synthesis and characterization number of amino phosphazne compounds.

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Abstract

The reaction of hexachloro cyclo triphosphazene (**A**) with 4-aminoantipyrine (**B**), 4-aminophenyl sulfone (**C**) and sulfamethoxazole (**D**) in mole ratio (1:1), in the presence of triethylamine at -80°C as HCl acceptor, provided compounds **1**, **2** and **3**. The synthesized compounds were characterized by FT-IR, ^{1}H and ^{31}P NMR specroscopic techniques.
Keywords: Amino phosphazene compounds , Hexachlorocyclotriphosphazene , 4-Aminoantipyrine , 4-aminophenyl sulfone, sulfamethoxazole, FT-IR Spectra, ^{1}H- ^{31}PNMR Spectra.

تحضير وتشخيص عدد من المركبات الامينية للفوسفازين

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الخلاصة

تتضمن الدراسة تحضير ثلاث مشتقات للفوسفازين من تفاعل سداسي كلوروتراي فوسفازين الحلقي (**A**) مع كل من 4-امينو انتي بايرين (**B**)، 4 -امينو فنايل سلفون (**C**) و سلفاميثوكسزول (**D**) بنسبة مولية (1:1) في الاسيتون وبدرجة حرارة (-80°C) بواسطة النتروجين السائل وباستعمال ثلاثي اثيل امين كمستقبل ل HCl ليعطي المركبات 3,2,1 وشخصت هذة المركبات بواسطة طيف الاشعة تحت الحمراء FT-IR وطيف الرنين النووي المغناطيسي ^{1}H - ^{31}P NMR فضلا عن قياس درجة الانصهار.
الكلمات المفتاحية: مركبات الفوسفازين الامينية، سداسي كلوروتراي فوسفازين الحلقي، 4-امينو انتي بايرين، 4-امينو فنايل سلفون، سلفاميثوكسزول.

Introduction

Phosphazenes are a class of compounds having –P=N- group in their molecules and constitutes one of the important class of phosphorous and nitrogen chemistry [1-4]. Several types of cyclotriphosphazenes have been synthesized so far (Chart 1). Hexachlorocyclotriphosphazene is significant because of its interesting structure where halides can be replaced with the substituents of interests[5-7].

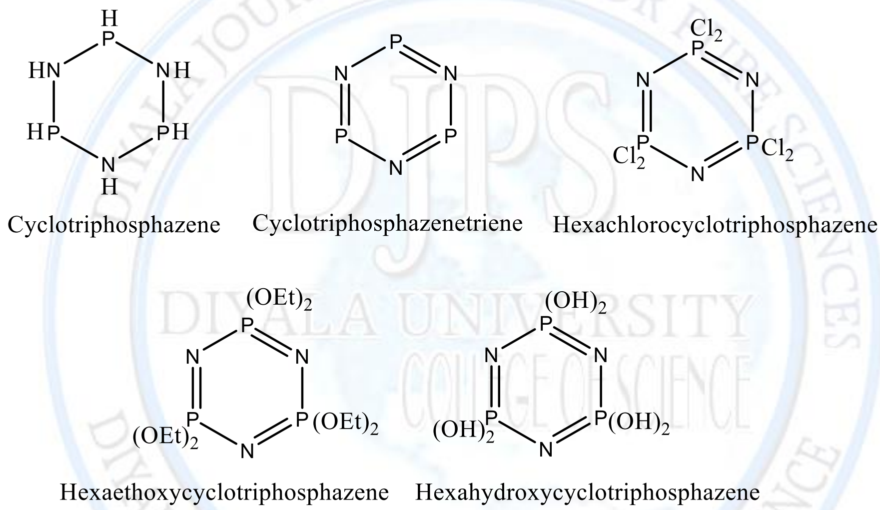
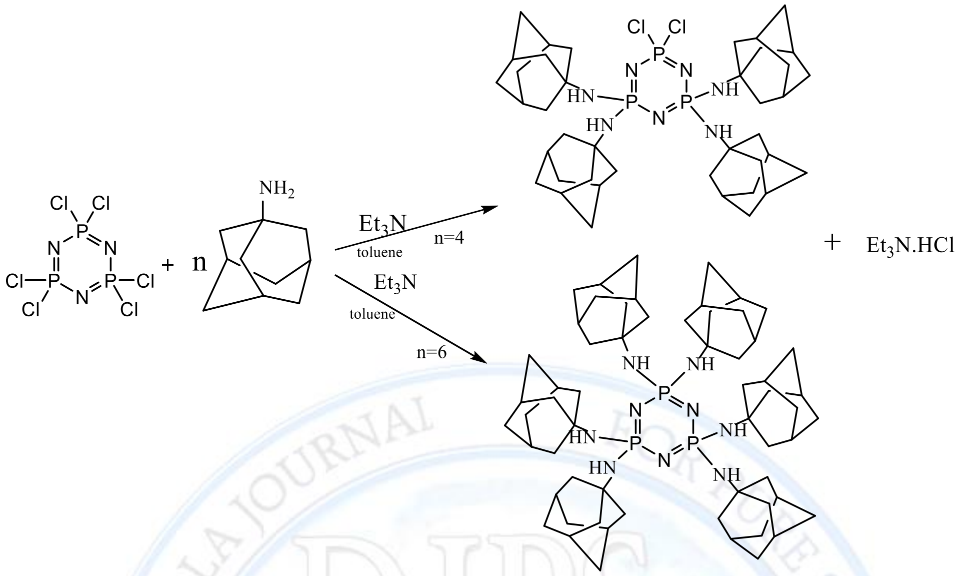


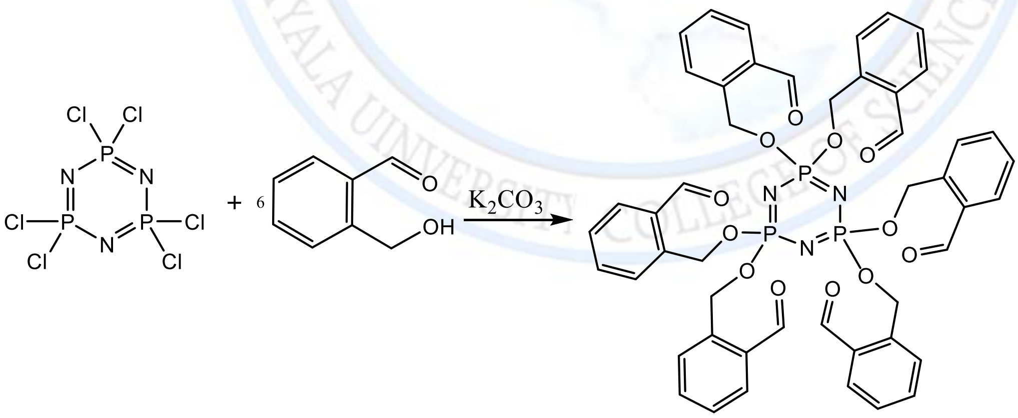
Chart 1: Examples of some cyclotriphosphazene derivatives.

Hexachlorocyclotriphosphazene ($P_3N_3Cl_6$), can be synthesized easily and are commonly used as starting material for the syntheses of new derivatives of interest[8,9]. A number of its derivatives have been found to reflect divrese biological and pharmacological properties [10,11]. Recently, some interesting derivatives of $P_3N_3Cl_6$ have been reported as significant biopharmacores [12]. However, the structural diverity of these compounds have also been studied and found interesting. For example, Vozicova and co-workers recently synthesized new derivatives (scheme 1) of $P_3N_3Cl_6$ and their crystal structres were reported [13-15]. The compounds were synthesized by reacting $P_3N_3Cl_6$ with amines in the resence of triethyl amine in toluene[16].



Scheme 1: Reported synthesis of some $P_3N_3Cl_6$ derivatives bearing aminoadamantane.

Aslan and co-workers, recently reported the synthesis of several new cyclotriphosphazene derivatives bearing Schiff base (scheme 2). Furthermore their photophysical properties were studied(17-19). Some of these compounds exhibited significant fluorescence properties in the visible region(20,21).



Scheme 2: Reported synthesis of some $P_3N_3Cl_6$ derivatives bearing Schiff base.

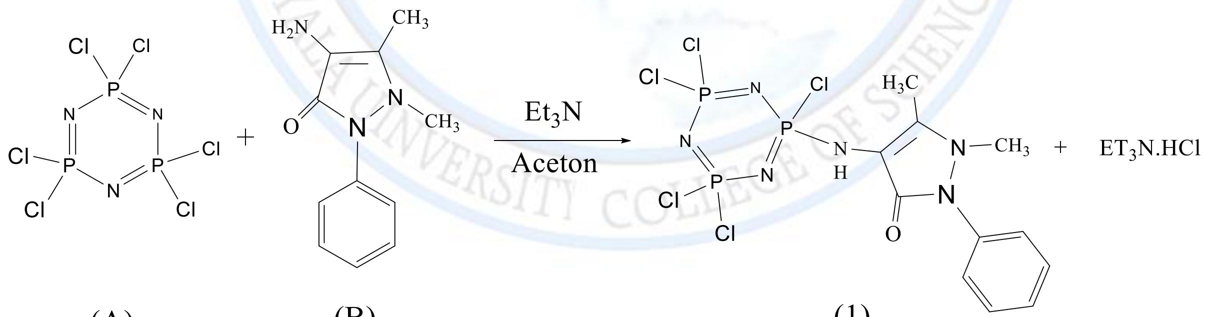
Instrumentation:

^{1}H and ^{31}PNMR spectra was recorded on a Bruker Avance III 500 MHz spectrometer and was referenced to H_3PO_4 85% (external standard). The sample was dissolved in deuterated aceton. FT-IR spectra was measured by Shimadzu FT-IR 8300 in KBr disk containing 1.2–1.7 mg of the sample and 100 mg KBr. The melting point measurment was by using Büchi melting point M-565.

Synthesis:

1. Synthesis of compound (1) PcaaP.

The reaction of $P_3N_3Cl_6$ (**A**) with 4-aminoantipyrine (**B**) was carried out simply by mixing the solution of $P_3N_3Cl_6$ in dry acetone under permanent strring in 1:1 mole ratio. The reaction mixture was placed in locked flask and cooled on liquid nitrogen bath for several hours. The product of this reaction, compound (1), was obtained after filteration and solvent evaporation, (0.431g, yield 83.7%), mp. 159-162C^{o}. FT-IR (KBr, V_{max}, cm^{-1}): 3360 (NH stretch), 3053 (aromatic C-H stretch), 1577, 1500 (aromatic C=C stretch), 1296 (C-N stretch), 1184 (P=N stretch), 823 (P-N stretch). ^{31}P NMR (202.4 MHz, DMSO-*d*$_6$): δ ppm 5.527(2P, d, PCl_2), -3.26 (1P, t, P($N_3C_{11}H_{12}O_1$)). ^{1}H NMR (50.6 MHz, DMSO-*d*$_6$): δ ppm 7.08 (2H, t), 6.59 (3H, t), 4.51 (1H, s), 3.09 (3H, s), 2.75(3H, s) scheme 3.

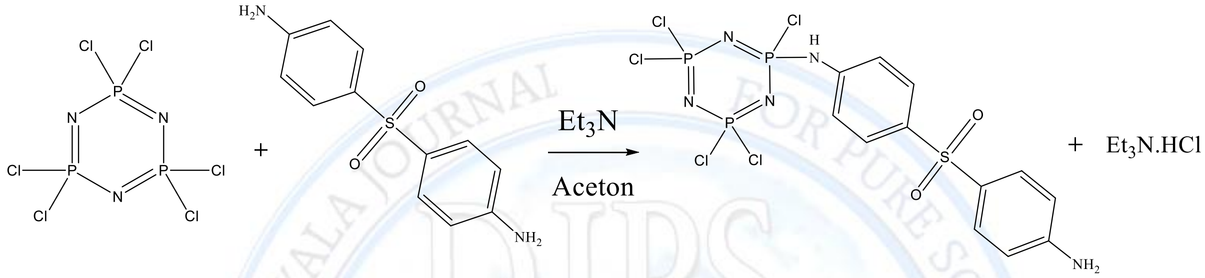


(A) (B) (1)

Scheme 3: Synthesis of compound (**1**).

2. Synthesis of compound (2) PcasP.

The reaction of $P_3N_3Cl_6$ (**A**) with 4-aminophenyl sulfone (**C**) was carried out simply by mixing the solution of $P_3N_3Cl_6$ in dry acetone under permanent strring in 1:1 mole ratio. The reaction mixture was placed in locked flask and cooled on liquid nitrogen bath for several hours. The product of this reaction, compound (2), was obtained after filteration and solvent evaporation, (0.39g, yield 69.2%), mp. 97.2C°. FT-IR (KBr, V_{max}, cm^{-1}): 3375 (NH_2 stretch), 3303 (NH stretch), 3064 (aromatic C-H stretch), 1595،1495 (aromatic C=C stretch), 1296 (C-N stretch), 1183 (P=N stretch), 835 (P-N stretch). ^{31}P NMR (202.4 MHz, DMSO-d_6): δ ppm 12.87 (2P, d, PCl_2), -3.206 (1P, t, $P(N_2C_{10}H_{11}O_2S)$). ^1H NMR (50.6 MHz, DMSO-d_6): δ ppm 7.43 (4H, d), 6.60 (4H, d), 4.43 (1H, s), 3.50 (2H, s) scheme 4.

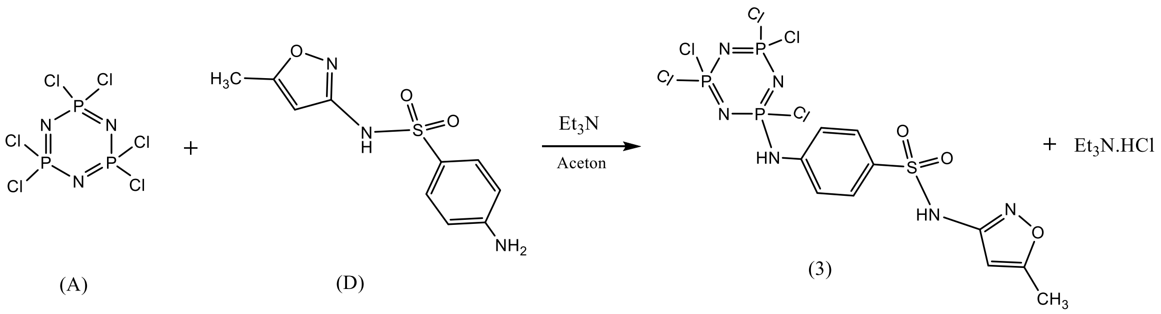


(A) (C) (2)

Scheme 4: Synthesis of compound (2).

3. Synthesis of compound (3) PcabsP.

The reaction of $P_3N_3Cl_6$ (**A**) with sulfamethoxazole (**D**) was carried out simply by mixing the solution of $P_3N_3Cl_6$ in dry acetone under permanent strring in 1:1 mole ratio. The reaction mixture was placed in locked flask and cooled on liquid nitrogen bath for several hours. The product of this reaction, compound 3, was obtained after filteration and solvent evaporation, (0.458g, yield 82.1%), mp. 171C°. FT-IR (KBr, V_{max}, cm^{-1}): 3369, 3336 ($NH_{asy,sy}$ stretch), 3218 (NH stretch), 3091, 2933 (C-H ar, alp stretch), 1570، 1495 (aromatic C=C stretch), 1319 (C-N stretch), 1201 (P=N stretch), 835 (P-N stretch). ^{31}P NMR (202.4 MHz, DMSO-d_6): δ ppm 13.62 (2P, d, PCl_2), -3.501 (1P, t, $P(N_3C_{10}H_{10}O_3S)$). ^1H NMR (50.6 MHz, DMSO-d_6): δ ppm 10.93(1H, s), 7.56 (2H, d). 6.57 (2H, d), 6.20 (1H, s), 5.62 (1H, s), 3.39 (3H, s) scheme 5.



Scheme 5: Synthesis of compound (3).

Discussions

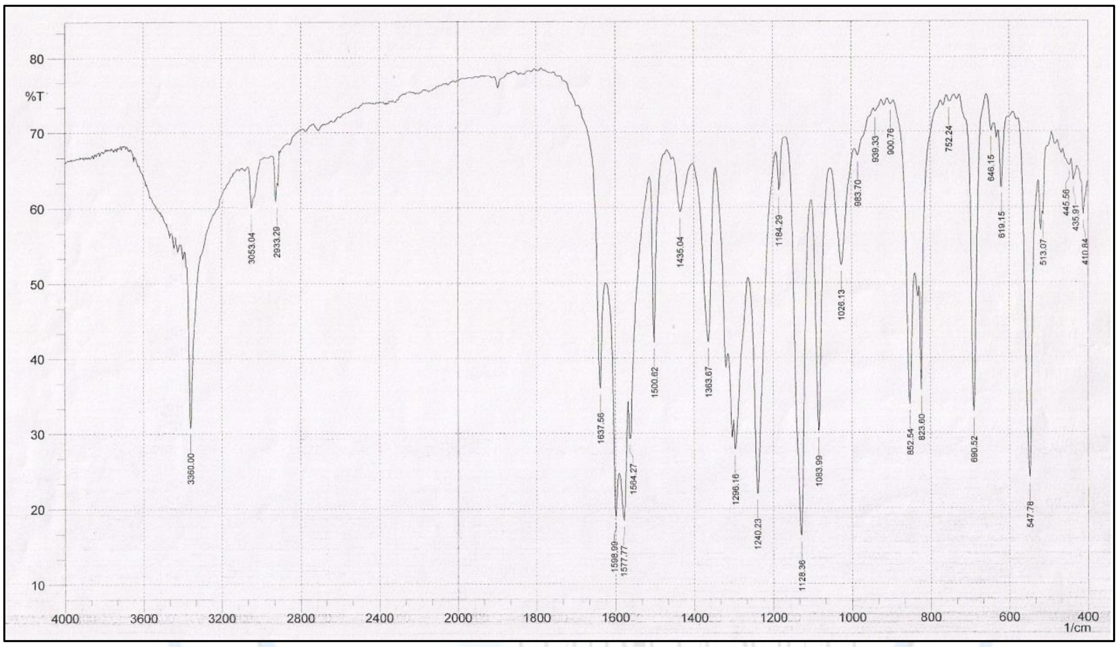
1. Characterization by FT-IR.

On comparing the FT-IR features of **B** with the FT-IR patterns of compound **1**, it was observed that a sharp stretching vibration at around 3435 cm^{-1} in **B**, due to NH_2, shifted to 3360 cm^{-1} in **1 (**Scheme 6). This might be due to replacement of one of the NH_2 proton with reactant **A**, as shown in scheme **3**. In similar fashion, on comparing the FT-IR features of **C** with the FT-IR patterns of compound **2**, it was observed that a sharp stretching vibration at around 3365 cm^{-1} in **C**, due to NH_2, shifted to 3303 cm^{-1} in **2**. This might also be due to replacement of one of the NH_2 protons with reactant **A**, as shown in scheme 4. In similar fashion, on comparing the FT-IR features of **D** with the FT-IR patterns of compound **3**, it was observed that a sharp stretching vibration at around 3468 cm^{-1} in **D**, due to NH_2, shifted to 3369 cm^{-1} in **3**. This might also be due to replacement of one of the NH_2 protons with reactant **A**, as shown in scheme 5.

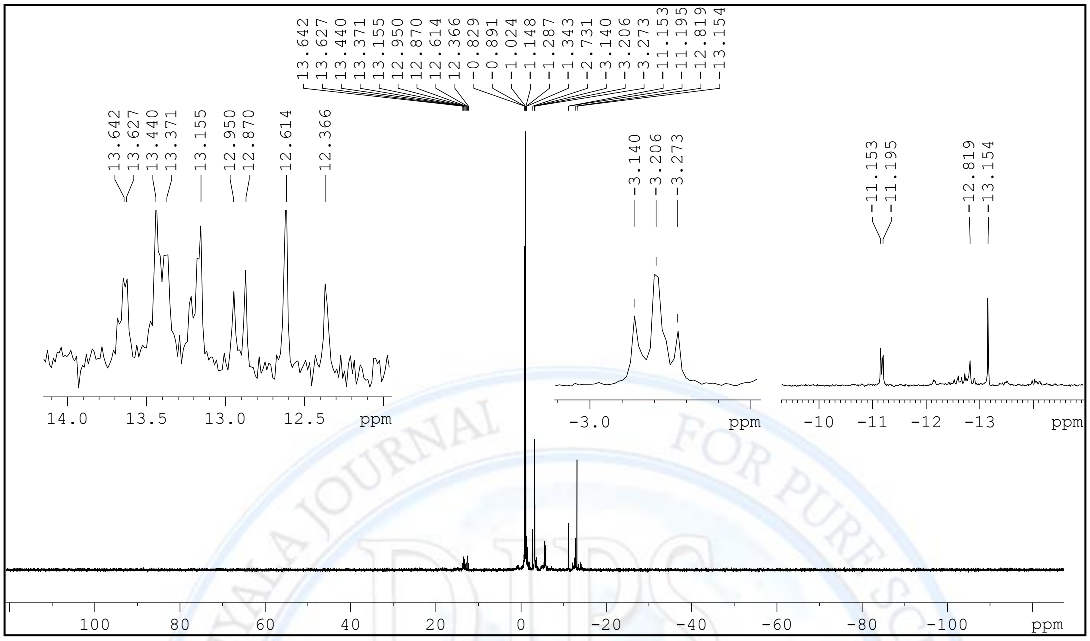
2. Characterization by NMR.

Synthesis of **1** was further characterized by ^{31}PNMR. Appearance of two signals 5.52, and -3.26 ppm represent the presence of two sets of P-Cl_2 in **1**. In synthesis of **2** appearance of two signals 12.87, and -3.20 ppm represent the presence of two sets of P-Cl_2 in **2 (**Scheme 7). Synthesis of **3** appearance of two signals 13.62, and -3.50 ppm represent the presence of two sets of P-Cl_2 in **3**.

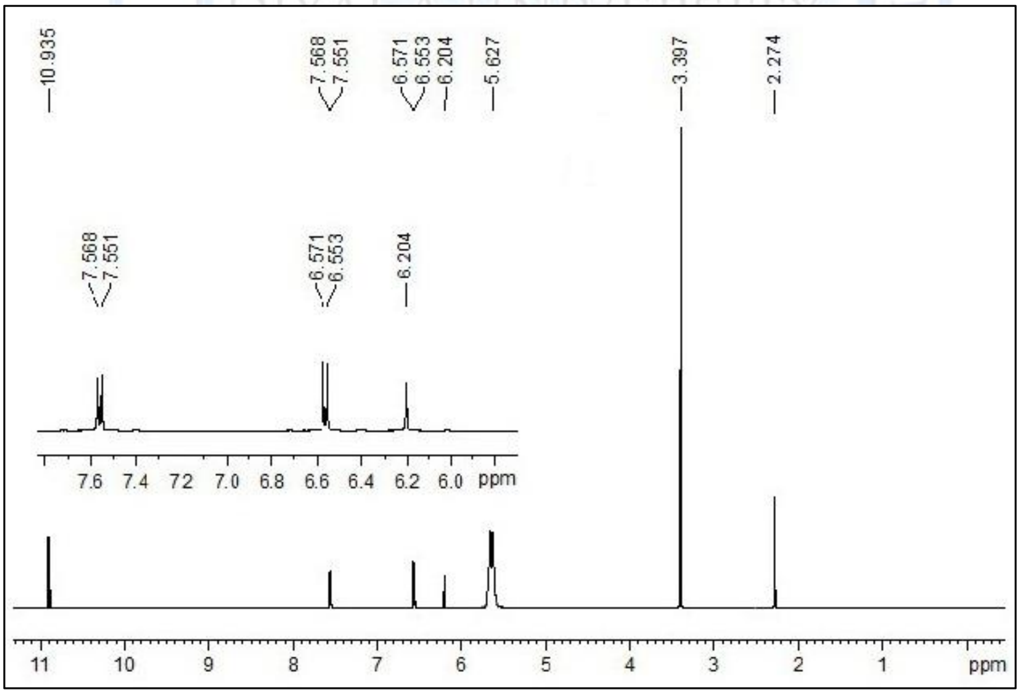
For compound **1** [1]HNMR spectrum showed a singlet at 4.51 ppm representing the NH group, in compound **2** a singlet at 4.43 ppm representing the NH group and compound **3** a singlet at 5.62 ppm representing the NH group (Scheme 8).



Scheme 6: FT-IR of compound (1).



Scheme 7: ^{31}PNMR of compound (2).



Scheme 8: ^{1}HNMR of compound (3).

Table 1: FT-IR data (cm^{-1}) for the prepared compounds

Seq.	Comp.	ν(N-H)	$\nu(C\text{-}H)_{Ar.}$	ν(C=C)	ν(C-N)	ν(P=N)	ν(P-N)
1	PcaaP	3360	3053	1500	1297	1184	823
2	PcasP	3303	3064	1497	1296	1183	835
3	PcabsP	3369	3091	1494	1319	1201	835

Table 2: ^{31}PNMR and ^{1}HNMR (δ ppm) spectral values (selected) of the synthesized compounds

Seq.	Comp.	^{31}P (d)	^{31}P (t)	^{1}H (NH)
1	PcaaP	5.52 5.58	-3.19 -3.26 -3.33	4.51
2	PcasP	12.87 12.95	-3.14 -3.20 -3.27	4.43
3	PcabsP	13.34 13.62	-3.43 -3.50 -3.56	5.62

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