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Paraben Substituted *Monospiro*-Cyclotriphosphazene Compounds: Synthesis and Characterization

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Abstract: Parabens are among the potential biologically active compounds due to their low toxicity potential for humans and their effective antibacterial and antifungal activity. The properties of cyclotriphosphazenes increase their efficiency according to the properties of the side groups to which they are attached. For this reason, scientists use it as a platform to design target molecules in particular. In this study, new types paraben substituted monospiro-cyclotriphosphazene compounds (**5-7**) were successfully synthesized and these compounds were fully characterized by MALDI-TOF mass, ^{1}H, ^{31}P and ^{13}C spectroscopy techniques. The molecular structure of compound **5** was also determined by single crystal X-ray crystallography.

Keywords: Cyclotriphosphazene, Paraben, NMR, X-Ray.

Paraben Sübstitüe *Monospiro*-Siklotrifosfazen Bileşikleri: Sentezi ve Karakterizasyonu

Özet: Parabenler, insanlar için düşük toksisite potansiyelleri ve etkili antibakteriyel ve antifungal aktiviteleri nedeniyle potansiyel biyolojik olarak aktif bileşikler arasındadır. Siklotrifosfazenlerin özellikleri bağlı oldukları yan grupların özelliklerine göre etkinliklerini arttırır. Siklotrifosfazenlerin göstermiş oldukları özellikler, yan gruplara bağlı olarak değişir ve etkinlikleri artar. Bu nedenle bilim adamları, özellikle hedef molekülleri tasarlamak için bir platform olarak kullanırlar. Bu çalışmada, yeni tip paraben ikameli *monospiro*-siklotrifosfazen bileşikleri (**5-7**) başarıyla sentezlendi ve bu bileşikler MALDI-TOF kütlesi, ^{1}H, ^{31}P ve ^{13}C NMR spektroskopi teknikleri ile tamamen karakterize edildi. Bileşik **5**'in moleküler yapısı da tek kristal X-ışını kristallografisi ile belirlendi.

Anahtar Kelimeler: Siklotrifosfazen, Paraben, NMR, X-Ray.

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1. INTRODUCTION

Para-hydroxy benzoate (PHB) esters and their sodium salts, often called parabens, have been used as preservatives for fifty years in the food, cosmetic and pharmaceutical industries to prevent microbe growth. For the commonly used methylparaben (MP), ethylparaben (EP), propylparaben (PP), and butylparaben (BP), antimicrobial activity increases with increasing alkyl chain length, and synergy among parabens has been reported [1]. Although parabens are frequently used against many yeast, mold and bacteria species, their mechanism of action on these organisms is still not fully elucidated [2]. In a study by Nguyen et al., it was stated that parabens interacted with mechanosensitive channels in E. coli and disrupted the bacterial osmotic gradient [3]. After the antimicrobial properties of parabens were determined, their presence in human breast cancer tissue was detected. The detection of parabens in human breast cancer tissue and its association with cancer have led researchers to this issue [4, 5]. Despite the limited epidemiological evidence linking paraben exposure with breast cancer, recent in vitro and animal studies have shed light on the endocrine-modulating effects of parabens, suggesting that parabens may be implicated in breast carcinogenesis [6]. An interesting recent study investigated the toxic effects and mechanisms of four different paraben groups (MP, EP, PP, BP) on zebrafish by Lui et al. They reported that the toxic effects of parabens on the zebrafish embryos tested increased in parallel with the carbon chain length of the paraben alkyl [7]. On the other hand, estrogenic activity of parabens was investigated by in vivo experiments in mice and rats and it was reported that especially methyl, ethyl and propyl paraben did not have a negative effect. For example, Witorsch et al. have pointed out studies that the estrogenic activity of some parabens does not threaten human health [8]. While the investigation of the potential of parabens to harm human health continues, its use in the industry continues due to its antimicrobial properties. Therefore, synthesis and research of new paraben-substituted compounds is necessary. In particular, the newly synthesized compounds should not have harmful effects on human breast tissue and should not threaten human health. Cyclotriphosphazenes an important part of inorganic chemistry and they are the most preferred platform because they can give easy substitution reactions and form stable compounds [9]. Depending on the physical and chemical properties of the substituted groups, anticancer [10-14], antimicrobial [15], antitumor [16], antifungal [17], liquid crystals [18] and chemical sensors [19], flame retardants [20] etc. The reactions of phosphazenes with parabens were first studied in our laboratories. In our first study, paraben substituted cyclotetraphosphazene compounds were synthesized and their effects on DNA (genotoxicity) were investigated. Since traditional genotoxicity test methods are laborious, time-consuming and expensive, DNA damage studies were carried out with a biosensor device in this study. Propyl and benzyl substituted cyclotetraphosphazene compounds have been shown to have more effective results [21]. In a study conducted by our research group in 2017, paraben derivatives of cyclotriphosphazene compounds were synthesized and it was determined that some derivatives could be potential anticancer agents [22]. In another study, fully paraben-substituted fluorenylidene double-bridged cyclotriphosphazenes were synthesized and their effects on DNA were evaluated by automatic biosensor device and gel electrophoresis method [23]. In our previous studies, some cyclotriphosphazene derivatives and spermine bridged cyclotriphosphazene derivatives were prepared and the in vitro cytotoxic effects (MTT) of these compounds against HT-29 (colon cancer) and Hep2 (larynx cancer) cells were investigated. As a result of studies, it was determined that some compounds showed significant effects on these cells [10, 24]. Based on these results, reactions of spermine-derived cyclotriphosphazene and parabens were carried out in 2020, and the paraben-substituted spermine-derived cyclotriphosphazene series were synthesized. DNA interactions were examined with both automatic biosensor device and gel-electrophoresis methods, and positive results were obtained [25, 26]. In recent studies by our group, new paraben-substituted compounds with mono and disipro structures were obtained and their in vitro cytotoxic activities were investigated. Some derivatives have positive results for MCF-7 and DLD-1 cells as cytotoxic agents [11,12].

All these studies encouraged us to synthesize and characterize new paraben-substituted cyclotriphosphazene compounds.

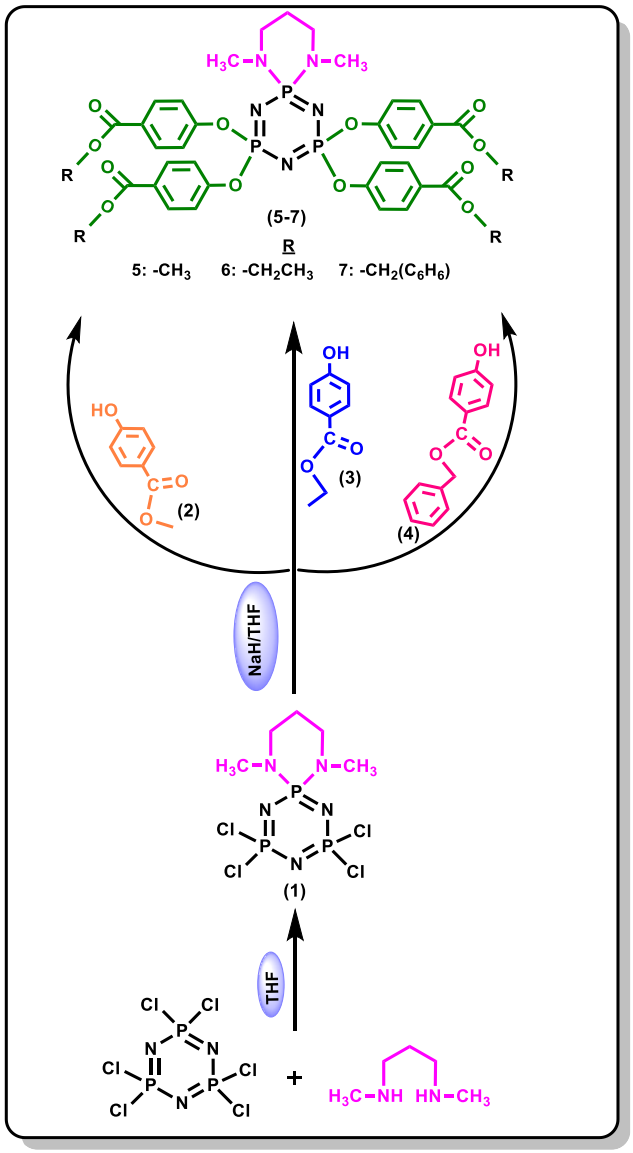
In this study *monospiro*-cyclotriphosphazene compounds decorated with different parabens that likely to show biological activity were designed and successfully synthesized for the first time (**Scheme 1**). The structures of the purified compounds **(5-7**) were elucidated by MALDI-TOF mass, ^{1}H, ^{13}C and ^{31}P NMR spectroscopic techniques. Also, the solid-state structure and geometry of compound **5** was determined by single crystal X-ray crystallography.

2. MATERIAL AND METHOD

2.1. Materials and general methods

Hexachlorocyclotriphosphazene (Otsuka Chemical Co., Ltd) was purified by fractional crystallization from n-hexane. Sodium hydride, (60% dispersion in mineral oil, Merck; prior to use the oil was removed by washing with dry heptane followed by decantation). Methyl 4-Hydroxybenzoate (99.0%), Ethyl 4-Hydroxybenzoate (99.0%) were obtained from Alfa Aesar and Benzyl 4-hydroxybenzoate (99.0%) was obtained from Aldrich. Tetrahydrofuran (99.0%), *n*-hexane (95.0%), were obtained from Merck. Silica gel 60 (230–400 mesh) for column chromatography was obtained from Merck. $CDCl_3$ for NMR spectroscopy was obtained from Merck. Mass spectra were recorded on a Bruker MALDI–TOF (Matrix-Assisted Laser Desorption/Ionization-Time-Of-Flight mass, Rheinstetten, Germany) spectrometer using DIT (1,8,9-anthrasenetriol) and DHB (2,5-Dihydroxybenzoic acid) as a matrix. All reactions were monitored using thin-layer chromatography (TLC) on Merck silica gel plates (Merck, Kieselgel 60, 0.25 mm thickness) with F_{254} indicator. Column chromatography was performed on silica gel (Merck, Kieselgel 60, 230–400 mesh; for 3 g.

crude mixture, 100 g). All reactions were carried out under an argon atmosphere. ^{1}H, ^{31}P NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions on a Varian INOVA 500 MHz spectrometer. Melting point analyses were performed on a Stuart SMP3 melting point apparatus.



Scheme 1. Synthesis routes for paraben substituted *monospiro*-cyclotriphosphazenes.

2.2. X-ray Crystallography

The structure of the compound 5 was confirmed by X-ray crystallography. The intensity data and unit cell measurements were obtained on a Bruker APEX II QUAZAR three-circle diffractometer using monochromatized Mo-Kα X–radiation (λ = 0.71073 Å). Indexing was performed using APEX2 [27]. Data integration and reduction were carried out with SAINT [28]. Absorption correction was performed by multi-scan method implemented in SADABS [29]. The structure was solved using SHELXT [30] and then refined by full-matrix least-squares refinements on F2 using the SHELXL [31] in SHELXTL Software Package [32]. All non-hydrogen atoms were refined anisotropically using all reflections with I > 2σ(I). The C-bound H atoms were positioned geometrically and refined using a riding mode. CCDC 2151053 (comp. 5) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Mercury software was used for visualization of the cif file [33].

2.3. Experimental Section

2.3.1. Syntheses of compound 1

Compound **1** was synthesized according to the literature [10].

2.3.2. Synthesis of compound 5

Methyl 4-Hydroxybenzoate (2) (0.48 g, 3.2 mmol) and NaH (0.13 g. 3.2 mmol) were dissolved in 30 mL of dry THF under an argon atmosphere in a 100 mL three-necked round-bottomed flask. The reaction mixture was cooled in an icebath and *monospiro* compound (1) (0.3 g, 0.80 mmol) in 10 mL of dry THF was dropped into the reaction medium. The reaction mixture was stirred at room temperature for 3 days, controlled by TLC. The reaction mixture was filtered to remove the formed sodium chloride and the solvent was removed under reduced pressure. The crude was subjected to column chromatography using THF:*n*-hexane (1:2) as the eluent. Compound 5 (183 mg, 28%, colorless oily, Rf = 0.32) was isolated from the crude and the product was crystallized using an *n*-hexane-THF (4:1) system (m.p:103°C). ^{1}H NMR (500 MHz, 298 K, $CDCl_3$-d1 δ, ppm): 7.96 (d, H_a/ H_a', 8H, $^{3}J_{Ha\text{-}Hb}$= 8.56 Hz), 7.26 (d, H_b/H_b', 8H, $^{3}J_{Hb\text{-}Ha}$= 8.33 Hz), 3.92 (s, -OCH_3, 12H), 2.97 (m, spiro-N-CH_2, 4H, $^{3}J_{H\text{-}H}$=5.50, $^{3}J_{H\text{-}H}$=9.15), 2.10 (d, spiro-N-CH_3, 6H), 1.84 (m, spiro-chain-CH_2- $\underline{CH_2}$-CH_2-, 2H); ^{31}P NMR-decoupled to (202 MHz, $CDCl_3$, 298 K), δ=23.88 ppm 2[PN(Spiro)] (t, 1P, $^{2}J_{AX}$=59.82 Hz); δ=9.30 [PR_2] (R=methylparaben) (d, 2P, $^{2}J_{XA}$=59.85 Hz). Spin system: AX_2. Anal. Calc. for $C_{37}H_{40}N_5O_{12}P_3$, MALDI-TOF-MS (DHB)(*m/z*) calc: 839.67 m/z, found: 840.481 m/z $[M]^+$. ^{13}C NMR ($CDCl_3$, δ, ppm) 166.23, 154.53, 131.22,126.85, 120.90, 52.16, 50.20, 34.74, 24.54.

2.3.3. Synthesis of compound 6

Ethyl 4-Hydroxybenzoate (3) (0.53 g, 3.2 mmol) and NaH (0.13 g. 3.2 mmol) were dissolved in 30 mL of dry THF under an argon atmosphere in a 100 mL three-necked round-bottomed flask. The reaction mixture was cooled in an icebath and monospiro compound (1) (0.3 g, 0.80 mmol) in 10 mL of dry THF was dropped into the reaction medium. The reaction mixture was stirred at room temperature for 4 days, controlled by TLC. The reaction mixture was filtered to remove the formed sodium chloride and the solvent was removed under reduced pressure. The crude was subjected to column chromatography using THF:n-hexane (1:2) as the eluent. Compound 8 (181 mg, 25%, colorless oily, Rf = 0.49) was isolated from the crude.^{1}H NMR (500 MHz, 298 K, $CDCl_3$-d1 δ, ppm): 7.98 (d, H_a/ H_a', 8H, $^{3}J_{Ha\text{-}Hb}$= 8.17 Hz), 7.27 (d, H_b/H_b', 8H, $^{3}J_{Hb\text{-}Ha}$= 8.50 Hz), 4.39 (s, -OCH_2-, 8H, $^{3}J_{H\text{-}H}$=6.70, $^{3}J_{H\text{-}}$

$_H$=13.51), 2.97 (m, spiro-N-CH_2, 4H, $^3J_{H-H}$=9.13, $^3J_{H-H}$=11.00), 2.10 (d, spiro-N-CH_3, 6H), 1.84 (m, spiro-chain-CH_2- $\underline{CH_2}$- CH_2-, 2H), 1.41 (t, -O-CH_2-$\underline{CH_3}$, $^3J_{H-H}$=6.81); ^{31}P NMR-decoupled to (202 MHz, $CDCl_3$, 298 K), δ=23.31 ppm [PN(Spiro)] (t, 1P, $^2J_{AX}$=58.41 Hz); δ=9.23 [PR_2] (R=ethylparaben) (d, 2P, $^2J_{XA}$=59.04 Hz). Spin system: AX_2. Anal. Calc. for $C_{41}H_{48}N_5O_{12}P_3$, MALDI-TOF-MS (DHB)(*m/z*) calc. 895.78, found: 896.367 $[M]^+$. ^{13}C NMR ($CDCl_3$, δ, ppm) 166.18, 154.45, 131.89,127.25, 120.90, 60.96, 50.23, 34.73, 24.68, 14.38.

2.3.4. Syntheses of compounds 7

Benzyl 4-Hydroxybenzoate (4) (0.73 g, 3.2 mmol) and NaH (0.13 g. 3.2 mmol) were dissolved in 30 mL of dry THF under an argon atmosphere in a 100 mL three-necked round-bottomed flask. The reaction mixture was cooled in an icebath and *monospiro* compound (1) (0.3 g, 0.80 mmol) in 10 mL of dry THF was dropped into the reaction medium. The reaction mixture was stirred at room temperature for 6 days, controlled by TLC. The reaction mixture was filtered to remove the formed sodium chloride and the solvent was removed under reduced pressure. The crude was subjected to column chromatography using THF:n-hexane (1:3) as the eluent. Compound 7 (138 mg, 15%, colorless oily, Rf = 0.17) was isolated from the crude. ^{1}H NMR (500 MHz, 298 K, $CDCl_3$-d1 δ, ppm): 8.05 (d, H_a/ H_a', 8H, $^3J_{Ha-Hb}$= 8.39 Hz), 7.51-7.34 (m, -H_d/-H_c/-H_e, 20H), 7.30 (d, H_b/H_b', 8H, $^3J_{Hb-Ha}$= 8.24 Hz), 5.38 (s, -OCH_2, 8H), 2.99 (m, spiro-N-CH_2, 4H, $^3J_{H-H}$=5.22, $^3J_{H-H}$=9.55), 2.13 (d, spiro-N-CH_3, 6H), 1.86 (m, spiro-chain-CH_2- $\underline{CH_2}$- CH_2-, 2H); ^{31}P NMR- decoupled to (202 MHz, $CDCl_3$, 298 K), δ=23.66 ppm [PN(Spiro)] (t, 1P, $^2J_{AX}$=59.64 Hz); δ=9.17 [PR_2] (R=benzylparaben) (d, 2P, $^2J_{XA}$=59.71 Hz). Spin system: AX_2. Anal. Calc. for $C_{61}H_{56}N_5O_{12}P_3$, MALDI-TOF-MS (DIT)(*m/z*) calc. 1144.06, found: 1144.182 $[M]^+$. ^{13}C NMR ($CDCl_3$, δ, ppm) 165.59, 154.71, 135.97, 131.42, 128.63, 128.30, 128.19, 126.87, 120.97, 66.82, 50.23, 34.79, 24.55.

3. RESULTS AND DISCUSSION

3.1. Synthesis and characterization of paraben substituted cyclotriphosphazenes

In the present study, hexachlorocyclotriphosphazene was reacted with N,N' -dimethyl 1,3-propane diamine under an argon atmosphere at room temperature to yield *monospiro* compound (1) according to the literature [10]. Compound **1** was reacted with methyl 4-hydroxybenzoate, ethyl 4-hydroxybenzoate and benzyl 4-hydroxybenzoate at room temperature in a ratio of 1:4 to give compounds 5-7, respectively. The final compounds (5–7) were characterized by MALDI-TOF MS, NMR (^{1}H, ^{31}P, ^{13}C) spectroscopy techniques. Also, the molecular structure of the 5 compound was also elucidated by single crystal X-ray crystallography. The spectral data of compounds 5–7 were given in the supporting information file (Fig. S1-S15). The molecular ion peaks for compounds 5–7 were measured using MALDI-TOF MS as 840.481, 896.367 and 1144.182, respectively (Table 1, Fig. S1, S6, and S11, ESI†), which are all consistent with the proposed structures. The ^{31}P (decoupled/coupled) and ^{1}H NMR spectra of compound 5 are shown in Fig. 1a, b and c, respectively. All of the compounds showed similar signals for aromatic protons at around δ=8.05–7.26 ppm range and the aliphatic protons of the spiro groups were observed at around δ=5.38–1.84 ppm range (Fig. S2, S7, and S12, ESI†). The products formed in each reaction mixture were checked using thin-layer chromatography (TLC), proton-decoupled and proton-coupled ^{31}P NMR spectroscopy. The ^{31}P NMR chemical shifts and phosphorus-phosphorus coupling constants of the pure compounds are given in the experimental section and Table 1. The proton decoupled ^{31}P NMR spectra of compounds 5–7, as expected, were observed as AX_2 spin systems, due to the two different phosphorus nuclei present in the cyclotriphosphazene rings (Table 1). All of the compounds similar signals consisted of one triplet for the [PN(Spiro)] group (δ=23.88-23.31 ppm range) and one dublet for the [PR_2] group (δ=9.30-9.17 ppm range) (Fig. S3, S8 and S13 ESI†). Also, the multiple peak resonating at δ=23.88-23.66 ppm range in the proton-coupled ^{31}P NMR spectra of all compounds belong to the [PN(Spiro)] group and are cleaved due to protons located beyond two bonds (Fig. S4, S9 and S14 ESI†). In the ^{13}C NMR spectra of the compounds (5–7), carbonyl (C=O) carbon peaks were observed in the δ=166.23–165.59 ppm range, aromatic carbon peaks in the δ=154.71–120.90 ppm range, and aliphatic carbon peaks in the δ=66.82–14.38 ppm range (Fig. S5, S10 and S15 ESI†).

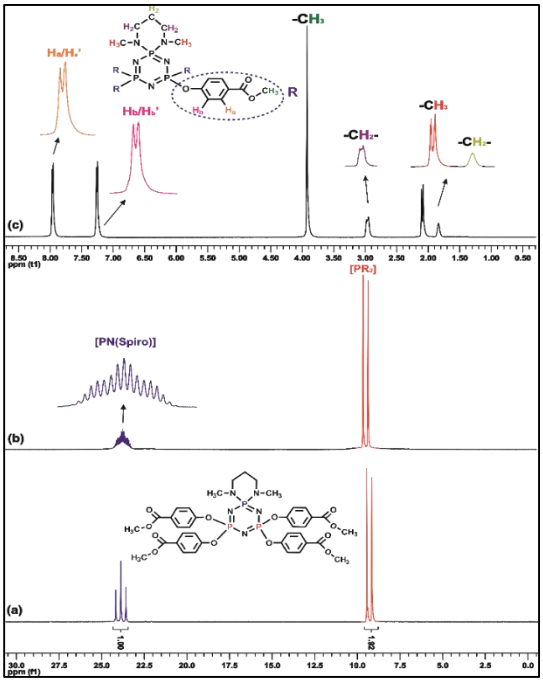


Fig. 1. **(a)** ^{31}P decoupled NMR **(b)** ^{31}P {^{1}H} NMR **(c)** ^{1}H NMR spectrum in $CDCl_3$ of compound 5.

Table 1. ^{31}P NMR and Mass Parameters for Compounds 3[a] and 5−7[a].

	^{31}P NMR (δ, ppm)				$^{2}J_{P-P}$ [Hz]	Mass (m/z)
Compd.	$[PCl_2]$	$[PR_2]$	[PN(Spiro)]	spin system	$^{2}J_{P-P}$	$[M]^+$
3[b]	22.80	-	16.00	A_2X	35.04	376.137
5	-	9.30	23.88	AX_2	59.82	840.481
6	-	9.23	23.31	AX_2	58.41	896.367
7	-	9.17	23.60	AX_2	59.64	1144.182

[a]$CDCl_3$, [b]Reference [10].

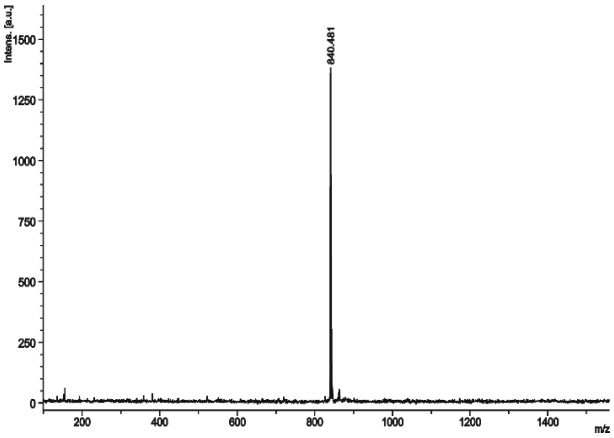


Fig. 2. Mass spectrum of compound 5.

3.2 X-Ray crystallography

The newly synthesized paraben-substituted cyclotriphosphazene (5) was crystallized in the *n*-hexane:THF solvent system, and single crystals were grown by recrystallization in the same solvent system. The solid state structure and geometry of Compound 5 was determined using single-crystal X-ray structural analysis (Fig. 3, S16). Crystallographic data and refinement details of the data collection for compound 5 is summarized in Table 2. The bond lengths and bond angles of compound **5** was given in Supplamentary Materials. Compound **5** has the triclinic crystal system with *P-1* space group. The P–N bonds in the cyclotriphosphazene ring (N_3P_3) range from 1.5674(19) Å to 1.650(2) Å and show double bond character. The P-N-P angles in the compound change range from 118.45(11)° to 123.14(12)°, and N–P–N bond angles vary range from 114.19(10)° to 118.13(10)°. The bond parameters of compound 5 are consistent with the crystallographic data of cyclotriphosphazene derivatives reported in the literatures [26, 11].

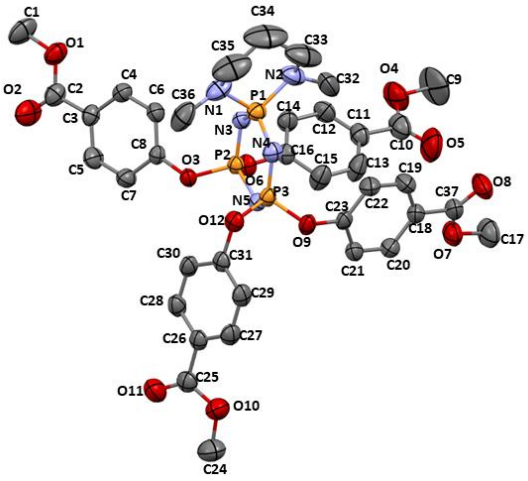


Fig. 3. The ball-stick drawings of the molecular structure of compound 5. The gray, gold, blue, and red colored atoms represent C, P, N, and O atoms, respectively. All hydrogen atoms have been omitted for clarity.

Table 2. Crystal data and refinement parameters for compound 5.

CCDC	2151053
Empirical Formula	$C_{37}H_{40}N_5O_{12}P_3$
Formula weight (g. mol^{-1})	839.65
Temperature (K)	296
Radiation	MoK_α (λ = 0.71073)
Crystal system	Triclinic
Space group	P-1
a (Å), b (Å), c (Å)	10.9405(14), 11.4582(15), 17.099(2)
α(°),β(°), γ(°)	74.851(2), 85.012(2), 75.717(2)
Crystal size (mm)	0.28 × 0.13 × 0.09
V ($Å^3$)	2004.5 (4)
Z	2
ρ_{calcd} (g. cm^{-3})	1.391
μ (mm^{-1})	0.22
F(000)	876
h, k, l max.	14,14,22
Reflections collected	9189
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.048, 0.131, 1.03

4. CONCLUSIONS

Although parabens show antibacterial and antifungal activity properties, their toxic effects to human health research and discussions still continue. In this case, scientists are in an effort to obtain new paraben-substituted compounds that have no toxicity effect. It is essential to synthesize and research new paraben-substituted compounds that do not have side effects on, especially human breast tissue etc. In this direction, studies continue in our laboratory. For this purpose, a series of paraben substituted *monospiro*-cyclotriphosphazene compounds have been successfully synthesized. The structural properties of all synthesized compounds (5-7) were examined by MALDI-TOF spectrometer, X-Ray (for compound 5), ^{1}H, ^{31}P and ^{13}C NMR spectroscopy. Biological activity and application studies will be continued in our laboratory in the future.

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5. CONFLICT OF INTEREST

The authors declare no competing financial interest.

Ethical Approval: Ethics Approval is not required for this study.

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Supplamentery Materials

Contents of Figures

COMPOUND 5

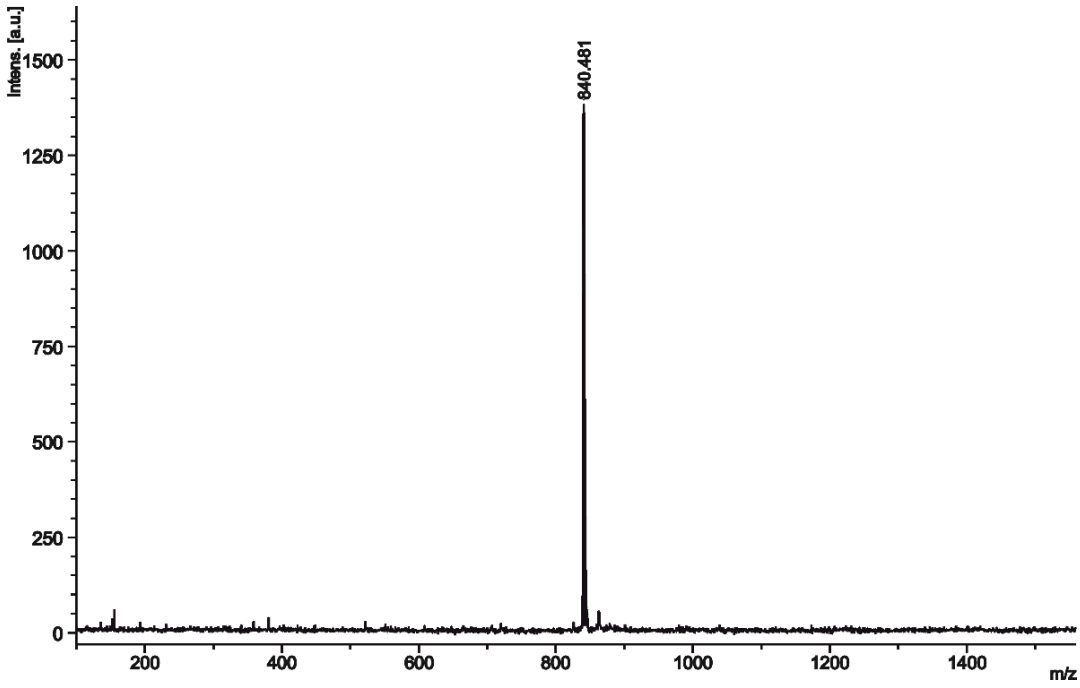

Figure S1. MALDI-MS spectrum of Compound 5

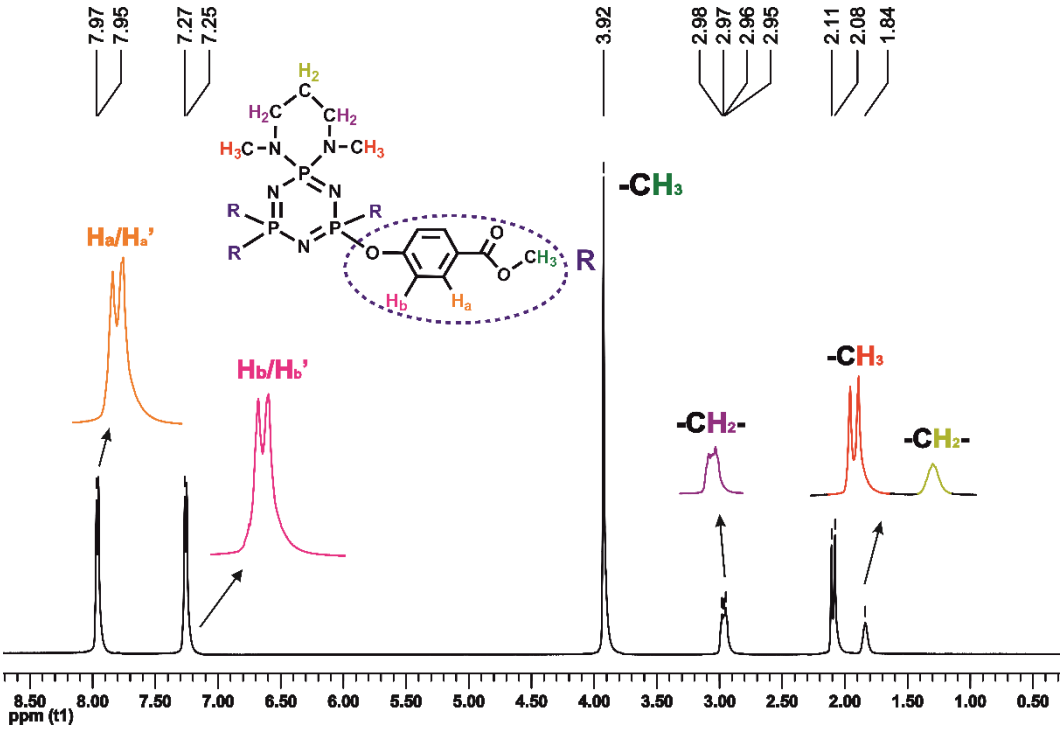

Figure S2. ^{1}H NMR spectrum of Compound 5 in $CDCl_3$

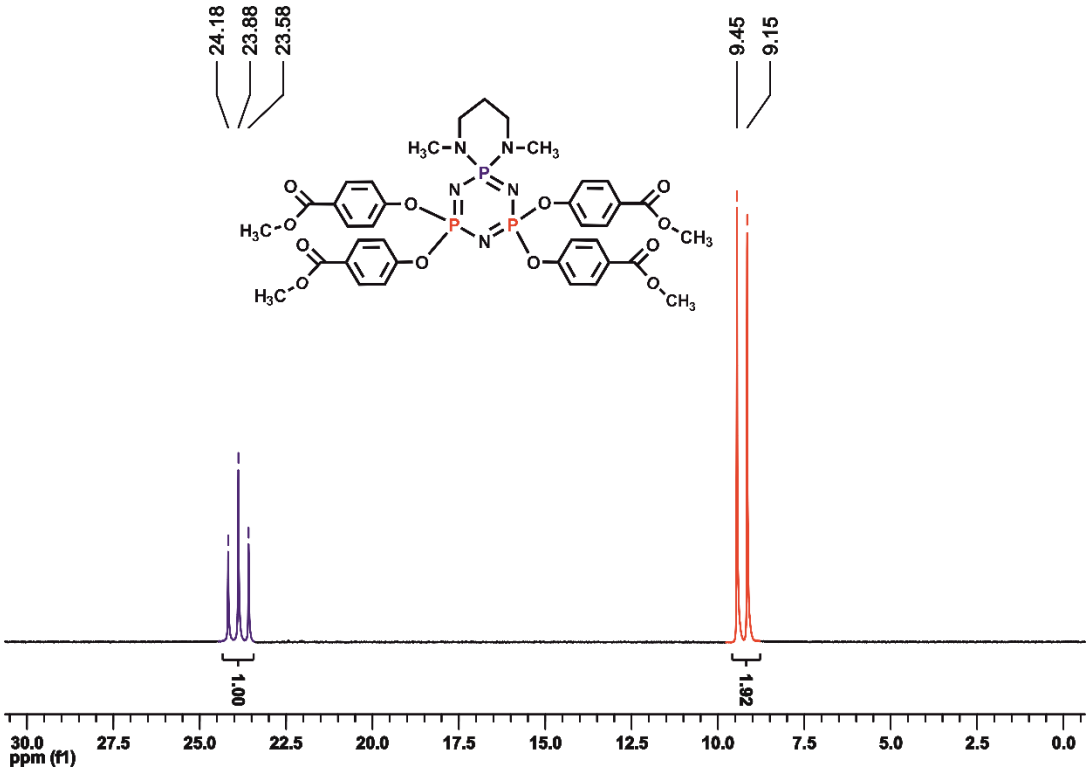

Figure S3. ^{31}P NMR decoupled spectrum of Compound 5 in $CDCl_3$

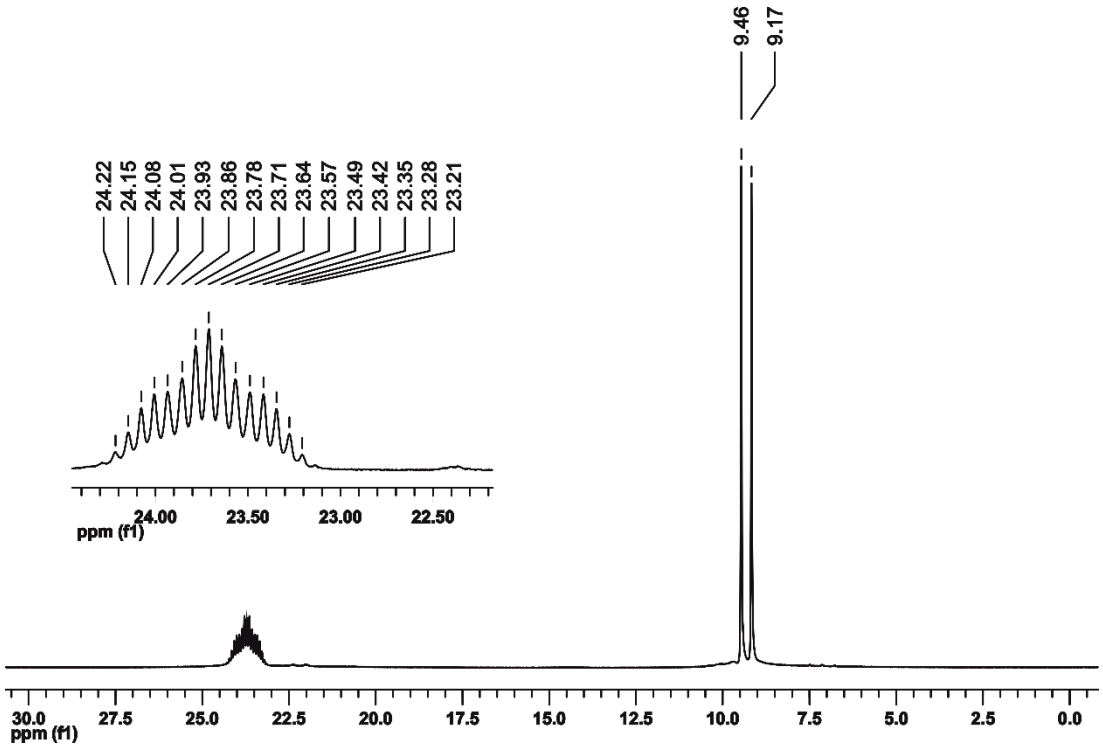

Figure S4. ^{31}P NMR coupled spectrum of Compound 5 in $CDCl_3$

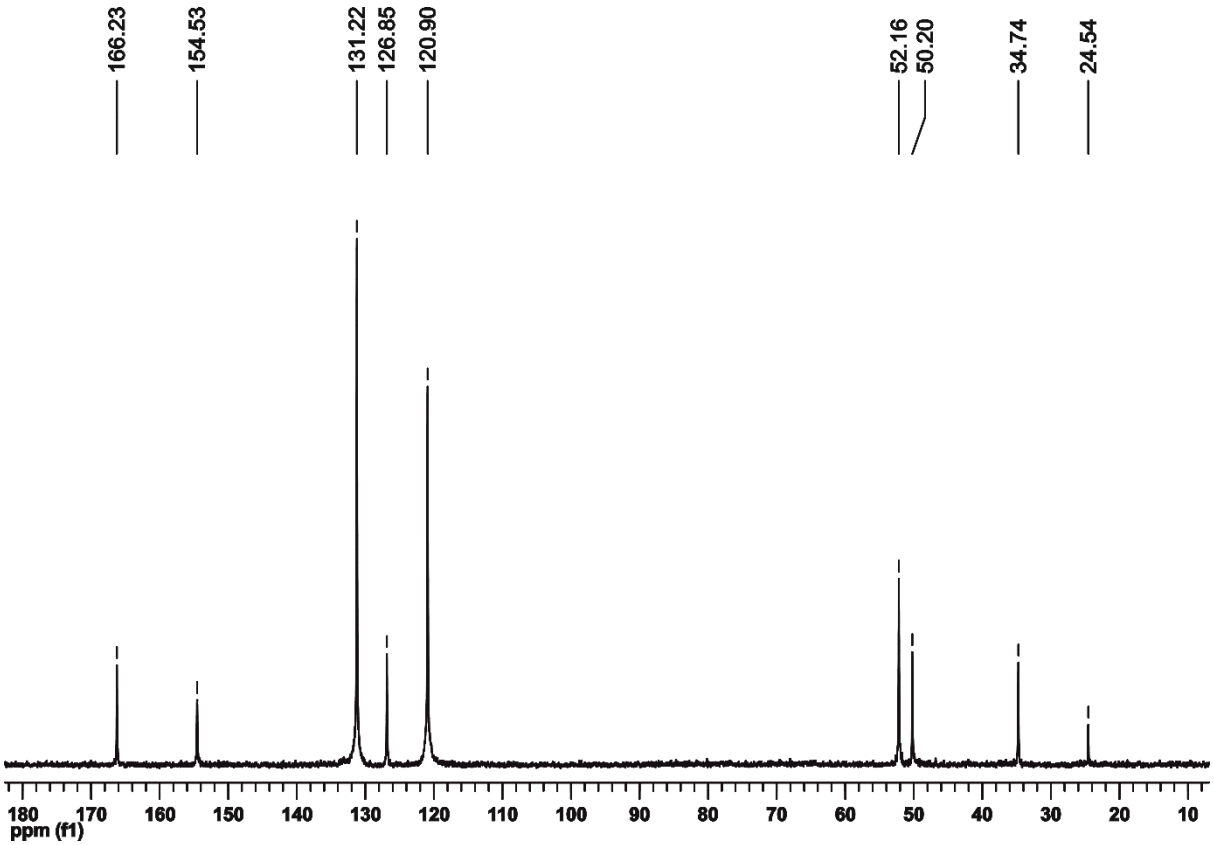

Figure S5. ^{13}C NMR spectrum of Compound **5** in $CDCl_3$

COMPOUND 6

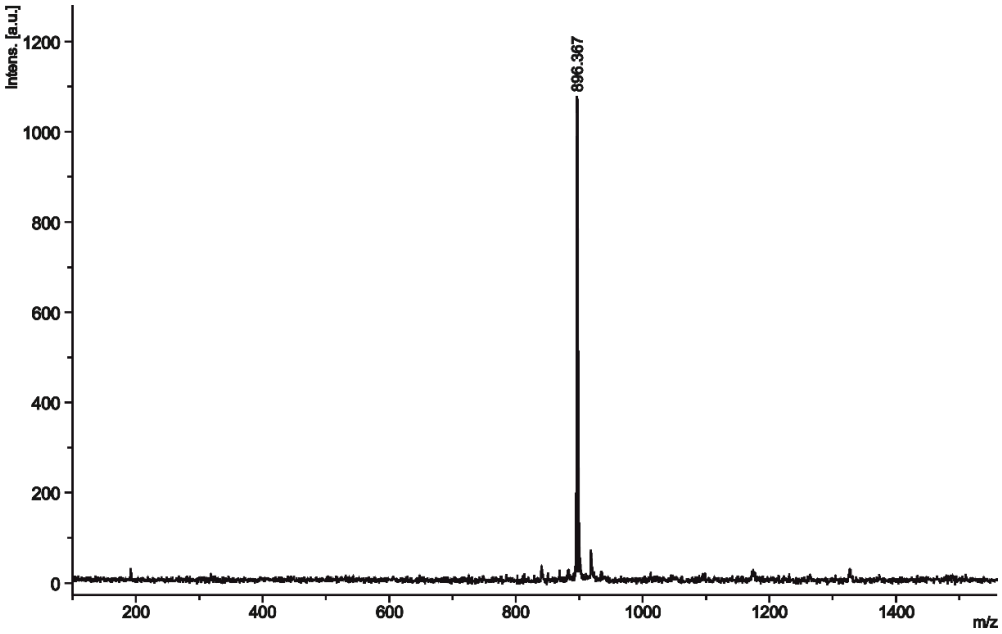

Figure S6. MALDI-MS spectrum of Compound 6

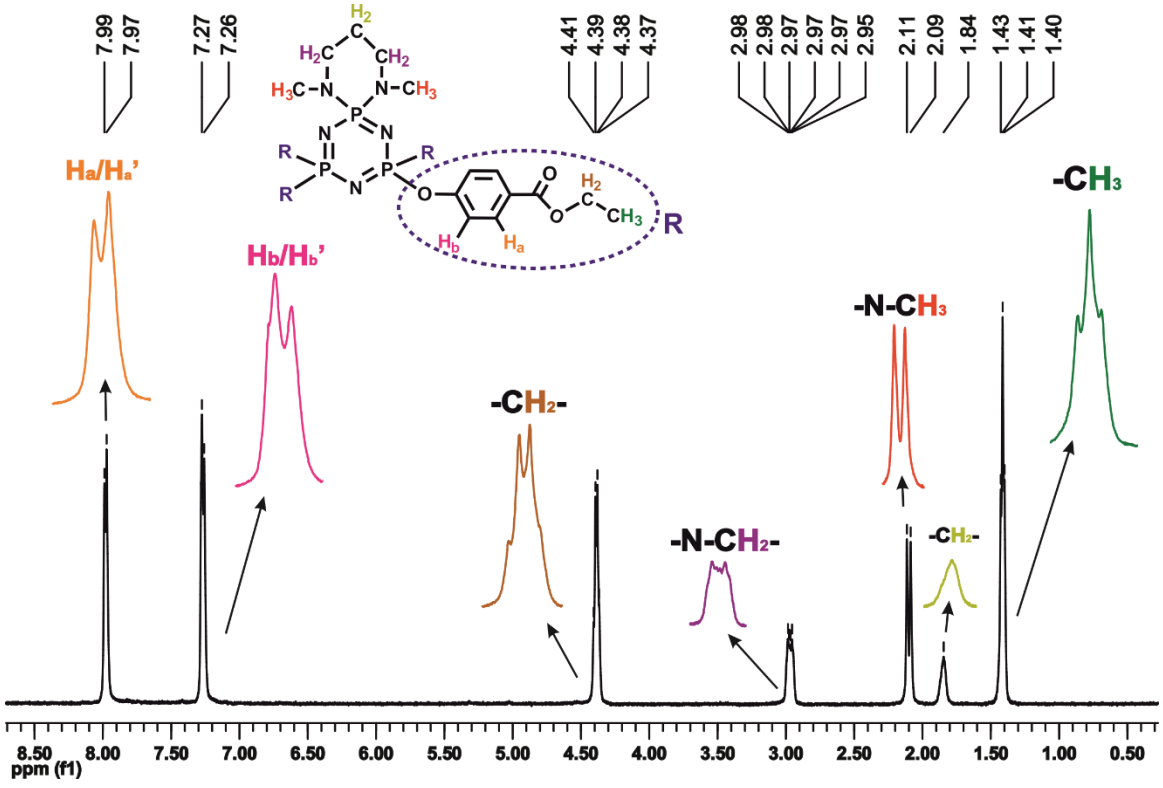

Figure S7. ^{1}H NMR spectrum of Compound 6 in $CDCl_3$

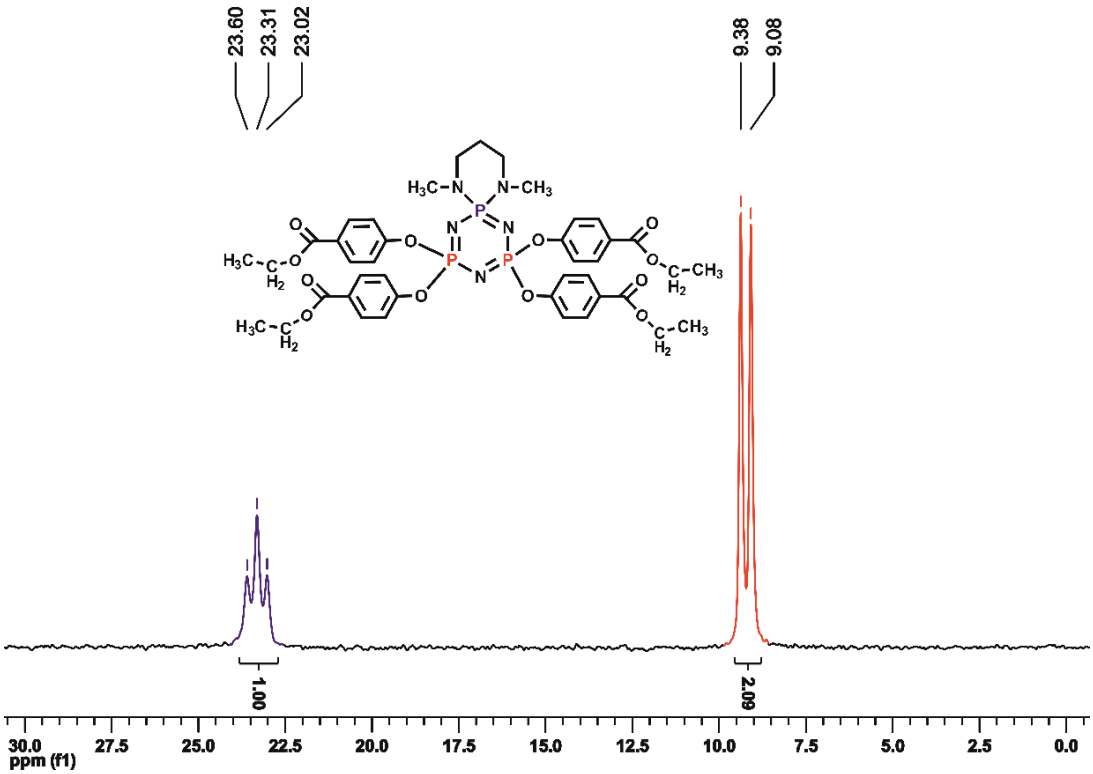

Figure S8. ^{31}P NMR decoupled spectrum of Compound 6 in $CDCl_3$

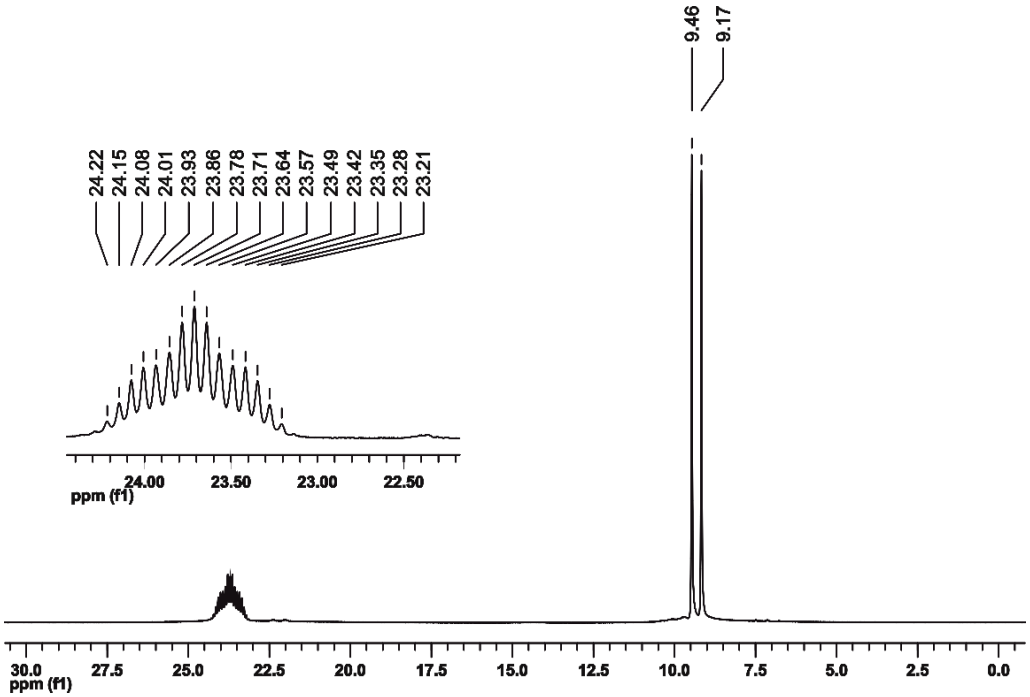

Figure S9. ^{31}P NMR coupled spectrum of Compound 6 in $CDCl_3$

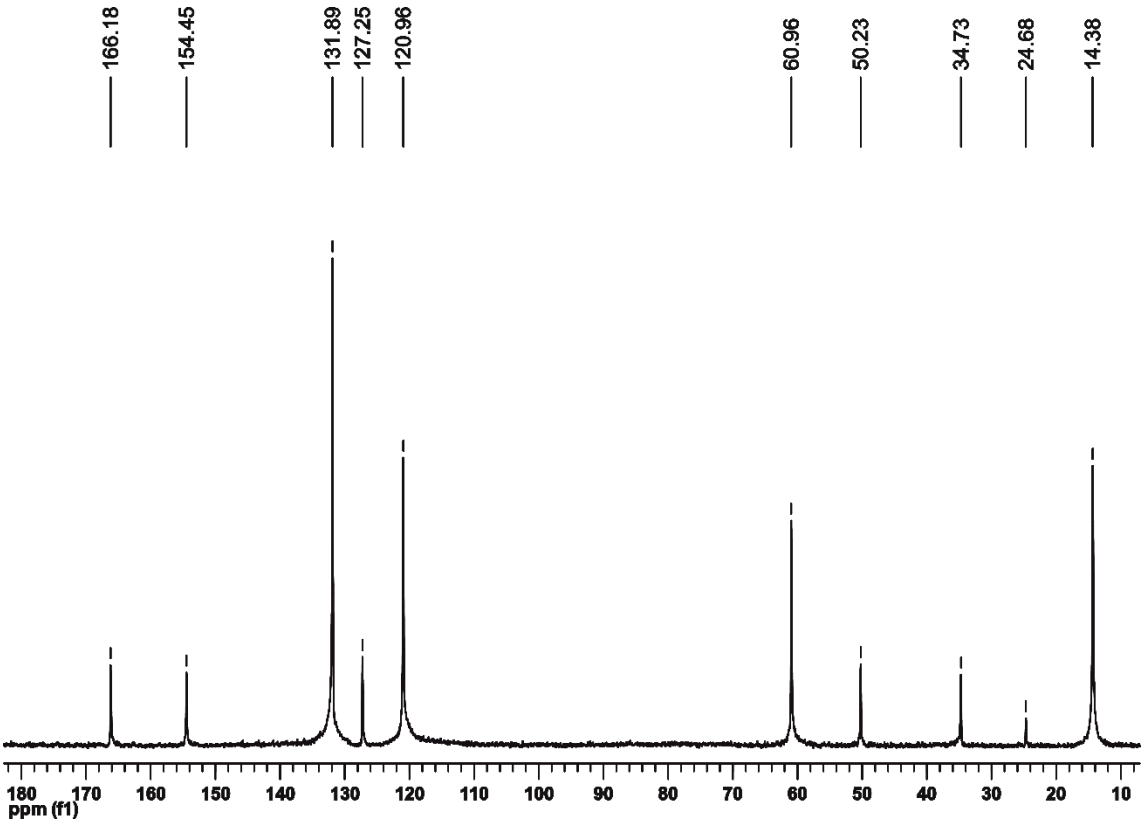

Figure S10. ^{13}C NMR spectrum of Compound 6 in $CDCl_3$

COMPOUND 7

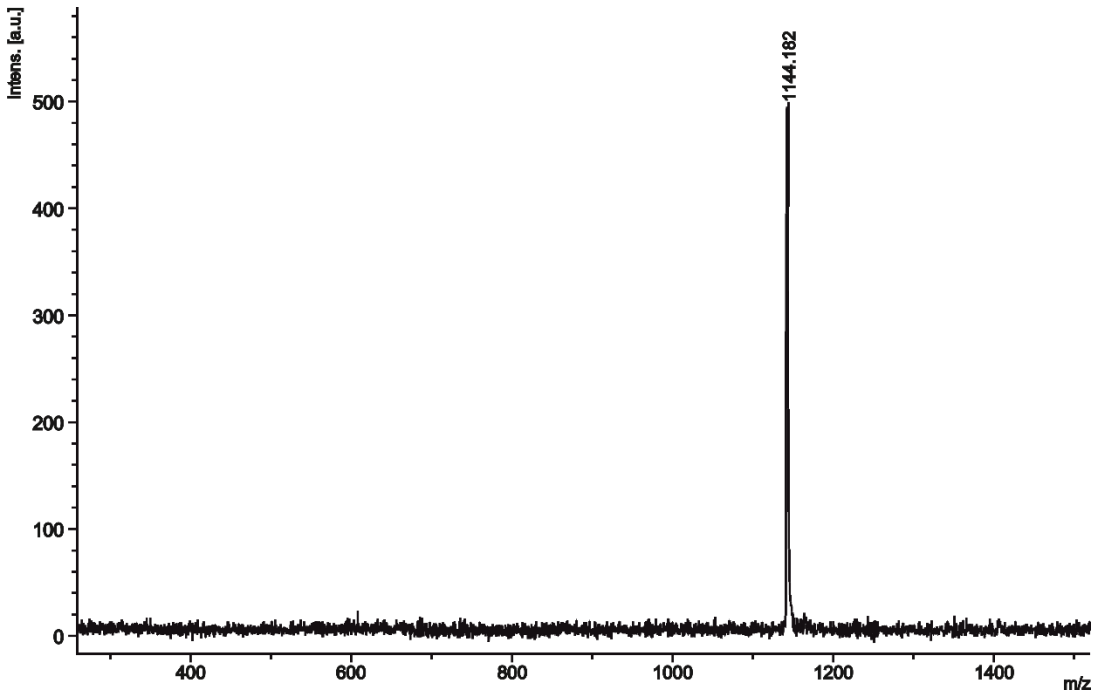

Figure S11. MALDI-MS spectrum of Compound 7

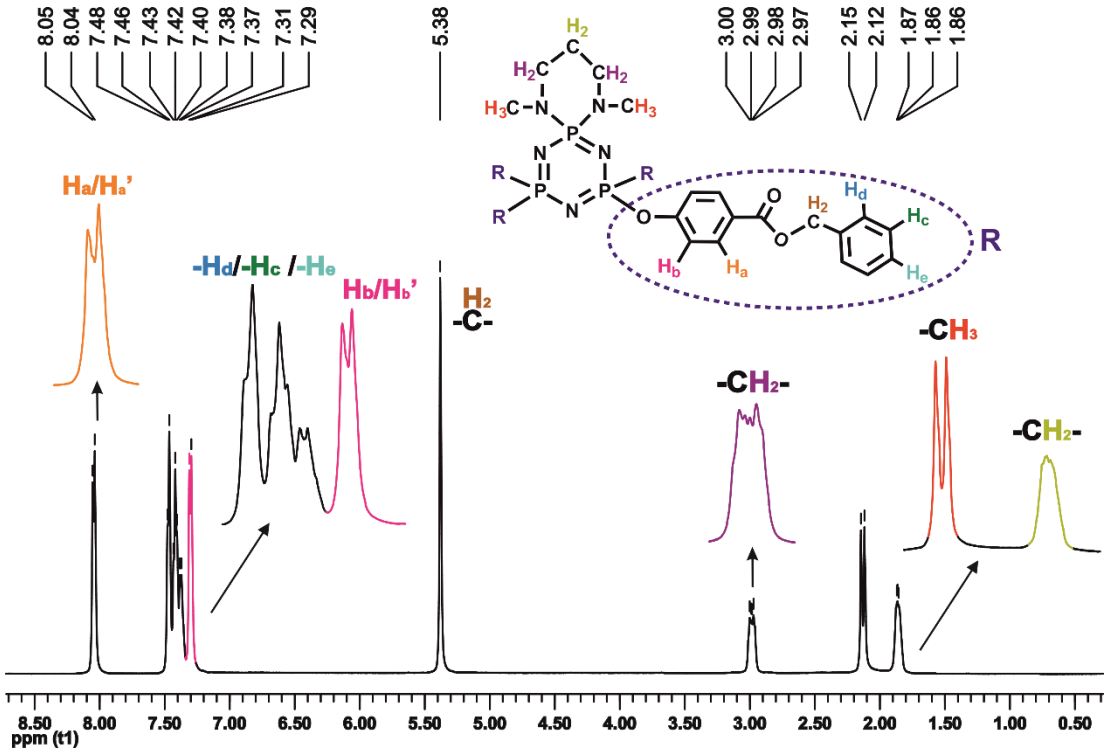

Figure S12. ^{1}H NMR spectrum of Compound 7 in $CDCl_3$

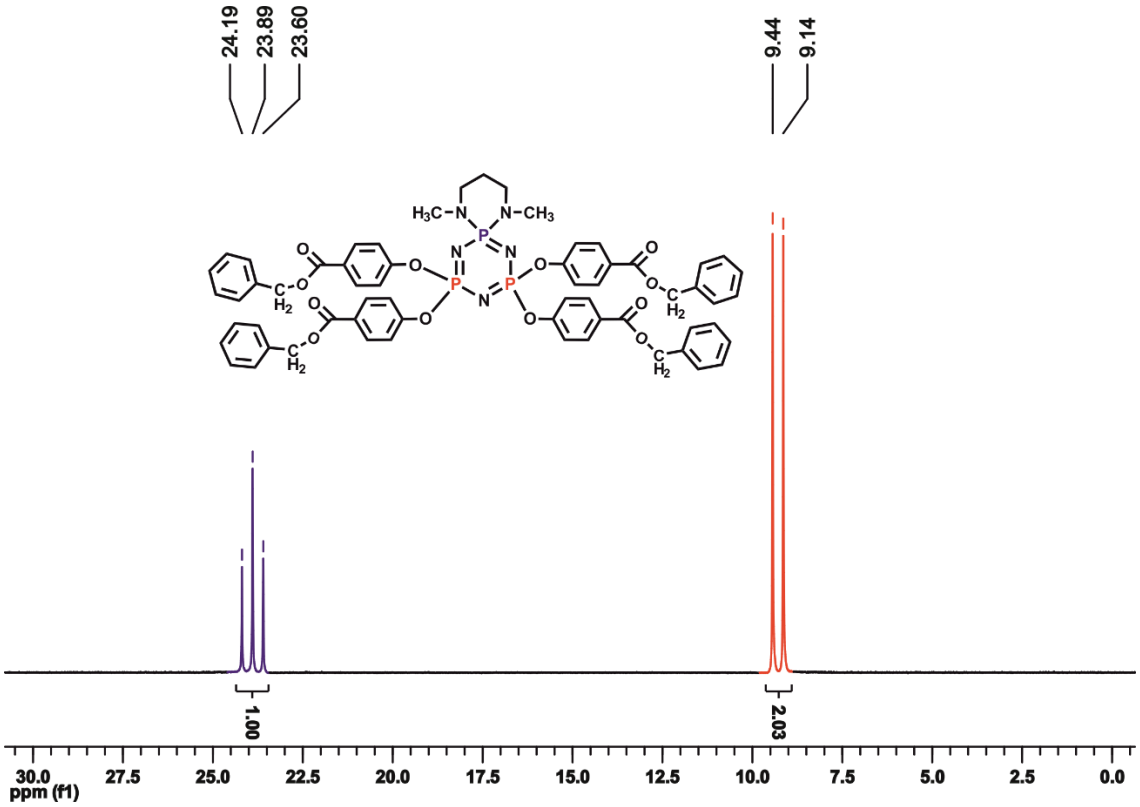

Figure S13. ^{31}P NMR decoupled spectrum of Compound 7 in $CDCl_3$

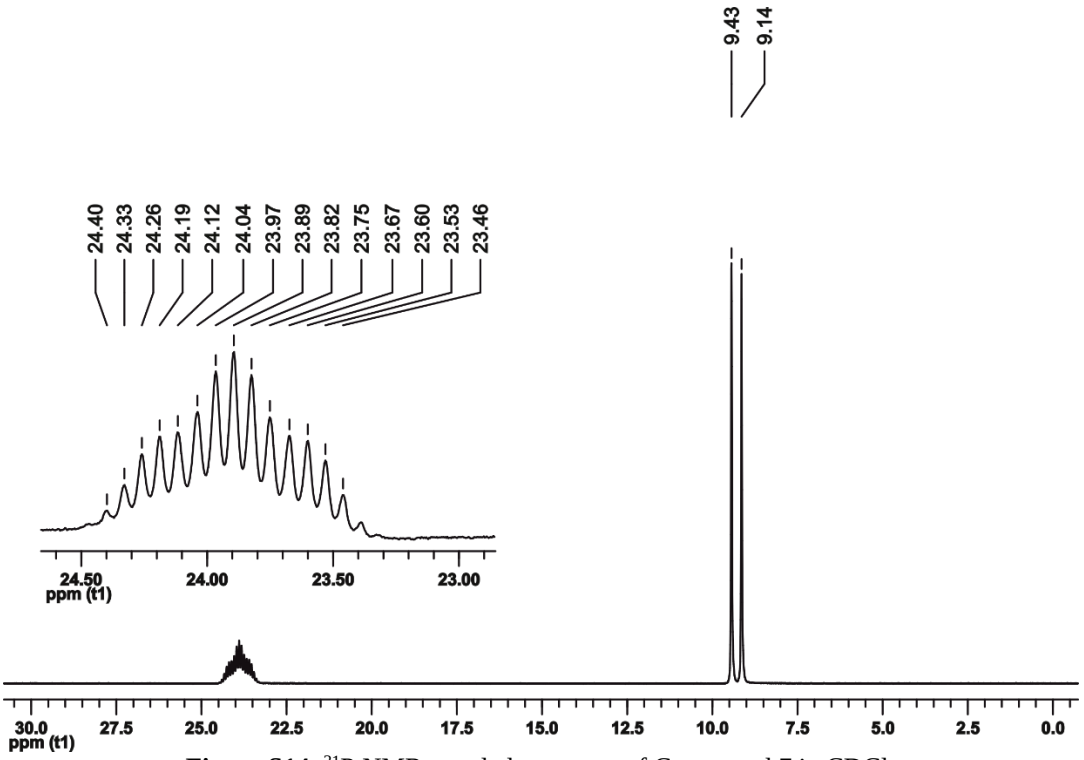

Figure S14. ^{31}P NMR coupled spectrum of Compound 7 in $CDCl_3$

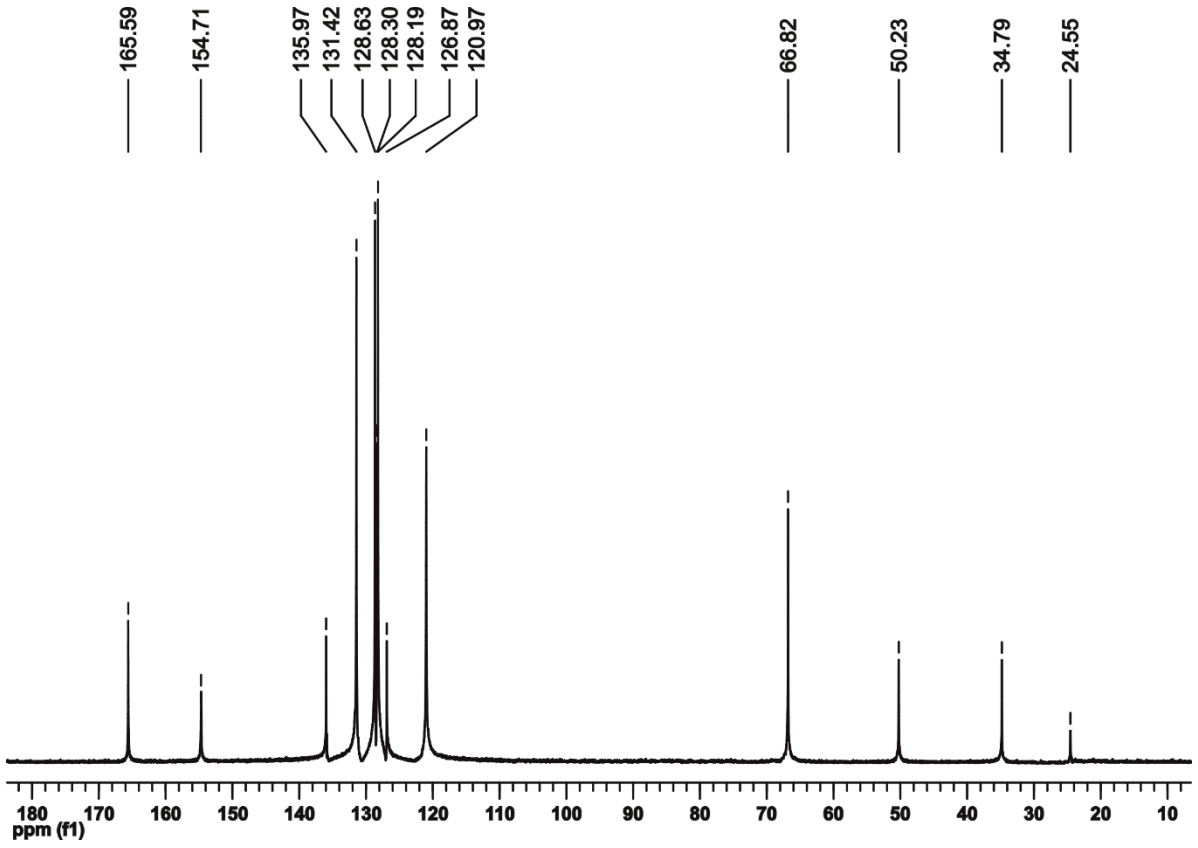

Figure S15. ^{13}C NMR spectrum of Compound 7 in $CDCl_3$

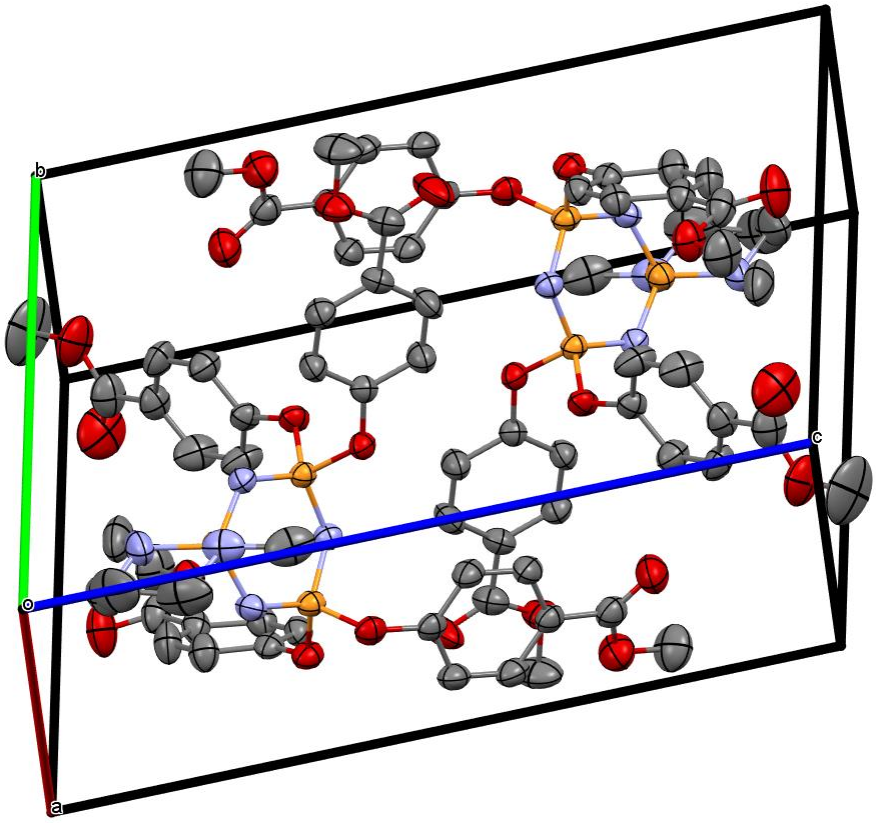

Figure S16. Perspective view of crystal packing of compound **5**

checkCIF (basic structural check) running

Checking for embedded fcf data in CIF ...
Found embedded fcf data in CIF. Extracting fcf data from uploaded CIF, please wait ...

checkCIF/PLATON (basic structural check)

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

You have not supplied any structure factors. As a result the full set of tests cannot be run.

No syntax errors found.
Please wait while processing ....

CIF dictionary
Interpreting this report

Structure factor report

Datablock: 20gtu73_20_nb_01

Bond precision: C-C = 0.0040 A Wavelength=0.71073
Cell: a=10.9405(14) b=11.4582(15) c=17.099(2)
alpha=74.851(2) beta=85.012(2) gamma=75.717(2)
Temperature: 273 K

	Calculated	Reported
Volume	2004.5(4)	2004.5(4)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C37 H40 N5 O12 P3	C37 H40 N5 O12 P3
Sum formula	C37 H40 N5 O12 P3	C37 H40 N5 O12 P3
Mr	839.65	839.65
Dx,g cm-3	1.391	1.391
Z	2	2
Mu (mm-1)	0.216	0.216
F000	876.0	876.0
F000'	877.04	
h,k,lmax	14,14,22	14,14,22
Nref	9198	9189
Tmin,Tmax	0.967,0.982	
Tmin'	0.942	

Correction method= Not given
Data completeness= 0.999 Theta(max)= 27.485
R(reflections)= 0.0483(5796) wR2(reflections)= 0.1311(9189)
S = 1.026 Npar= 520

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT220_ALERT_2_C NonSolvent Resd 1 C Ueq(max)/Ueq(min) Range 4.3 Ratio
PLAT222_ALERT_3_C NonSolvent Resd 1 H Uiso(max)/Uiso(min) Range 4.2 Ratio
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C34 Check
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C35 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of O4 Check
And 2 other PLAT242 Alerts

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PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of         N1 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of        C10 Check

PLAT334_ALERT_2_C Small Aver. Benzene C-C Dist C11      -C13            1.37 Ang.
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Alert level G

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PLAT199_ALERT_1_G Reported _cell_measurement_temperature ..... (K)        273 Check
PLAT200_ALERT_1_G Reported   _diffrn_ambient_temperature ..... (K)        273 Check
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ...........        3.3 Low
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   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   8 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   4 ALERT level G = General information/check it is not something unexpected

   3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   7 ALERT type 2 Indicator that the structure model may be wrong or deficient
   2 ALERT type 3 Indicator that the structure quality may be low
   0 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
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It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

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PLATON version of 18/09/2020; check.def file version of 20/08/2020

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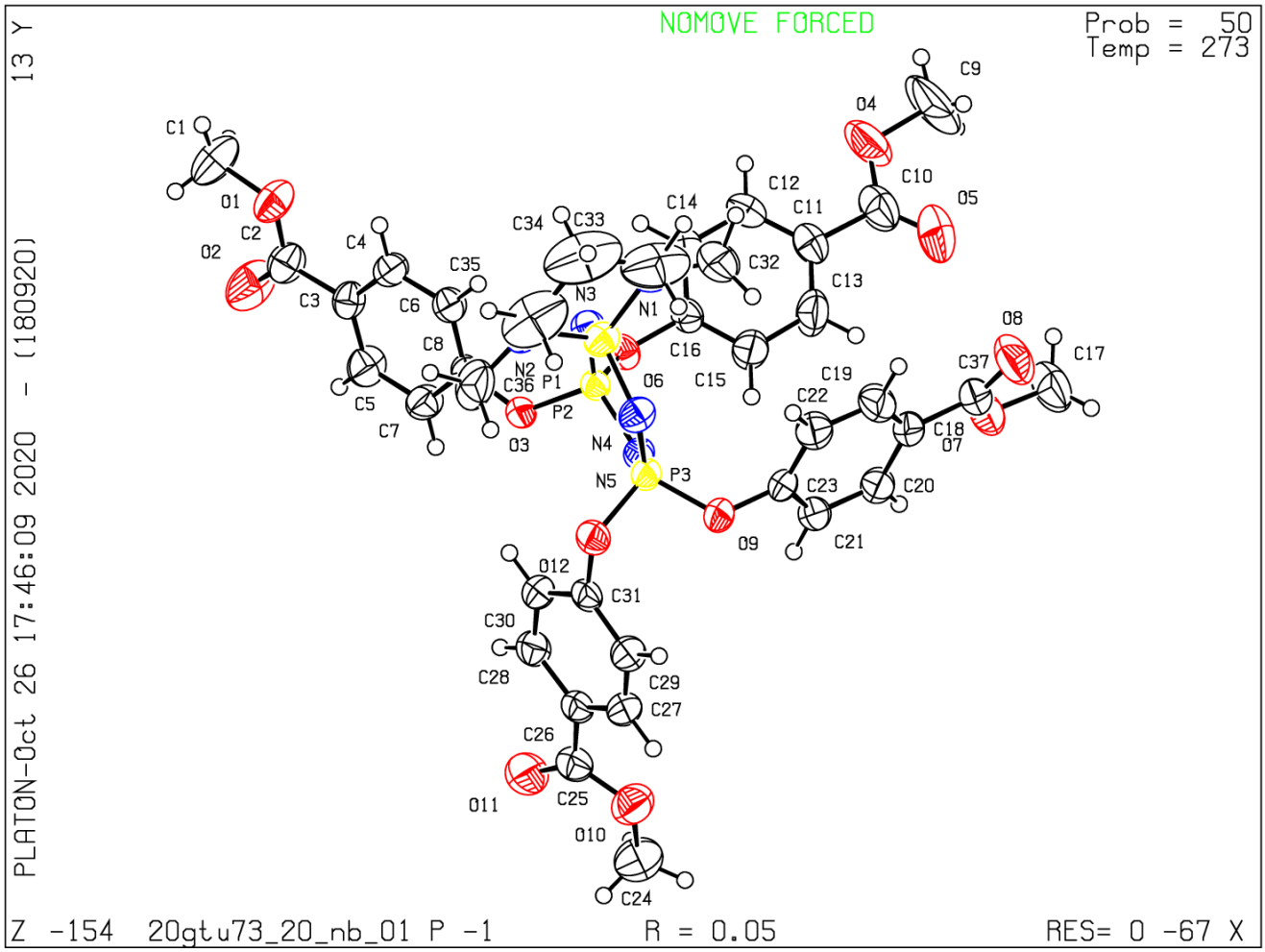

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Title

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Abstract

Table 1

Experimental details

Crystal data	
Chemical formula	$C_{37}H_{40}N_5O_{12}P_3$
M_r	839.65
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	273
a, b, c (Å)	10.9405 (14), 11.4582 (15), 17.099 (2)
α, β, γ (°)	74.851 (2), 85.012 (2), 75.717 (2)
V (Å^3)	2004.5 (4)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.22
Crystal size (mm)	0.28 × 0.13 × 0.09
Data collection	
Diffractometer	Bruker APEXII Quazer
Absorption correction	–
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	30322, 9189, 5796
R_{int}	0.049
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.048, 0.131, 1.03
No. of reflections	9189
No. of parameters	520
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.19, −0.29

Computer programs: *SHELXT* 2018/2 (Sheldrick, 2018), *SHELXL* 2018/3 (Sheldrick, 2015), Olex2 1.3 (Dolomanov *et al.*, 2009).

Acknowledgements

Funding information

References

Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). J. Appl. Cryst. 42, 339-341.

Sheldrick, G. M. (2015). Acta Cryst. A71, 3-8.

Sheldrick, G. M. (2015). Acta Cryst. C71, 3-8.

Figure 1

supporting information

Title

Computing details

Program(s) used to solve structure: *SHELXT* 2018/2 (Sheldrick, 2018); program(s) used to refine structure: *SHELXL* 2018/3 (Sheldrick, 2015); molecular graphics: Olex2 1.3 (Dolomanov *et al.*, 2009); software used to prepare material for publication: Olex2 1.3 (Dolomanov *et al.*, 2009).

(20gtu73_20_nb_01)

Crystal data

$C_{37}H_{40}N_5O_{12}P_3$
$M_r = 839.65$
Triclinic, $P\overline{1}$
$a = 10.9405$ (14) Å
$b = 11.4582$ (15) Å
$c = 17.099$ (2) Å
$\alpha = 74.851$ (2)°
$\beta = 85.012$ (2)°
$\gamma = 75.717$ (2)°
$V = 2004.5$ (4) Å^3
$Z = 2$
$F(000) = 876$
$D_x = 1.391$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5859 reflections
$\theta = 2.3$–$23.7°$
$\mu = 0.22$ mm^{-1}
$T = 273$ K
Plate, clear colourless
0.28 × 0.13 × 0.09 mm

Data collection

Bruker APEXII Quazer diffractometer
Detector resolution: 8.3333 pixels mm^{-1}
φ and ω scans
30322 measured reflections
9189 independent reflections
5796 reflections with $I > 2\sigma(I)$
$R_{int} = 0.049$
$\theta_{max} = 27.5°$, $\theta_{min} = 1.2°$
$h = -14 \rightarrow 14$
$k = -14 \rightarrow 14$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.131$
$S = 1.03$
9189 reflections
520 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0532P)^2 + 0.6682P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.19$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
P2	0.46982 (5)	0.56738 (5)	0.67167 (4)	0.03449 (15)

P3	0.30932 (6)	0.79245 (5)	0.66362 (4)	0.03764 (16)
P1	0.49931 (6)	0.70515 (6)	0.77738 (4)	0.04412 (17)
O3	0.55948 (14)	0.57249 (14)	0.59309 (9)	0.0393 (4)
O12	0.33325 (15)	0.89642 (14)	0.58539 (10)	0.0445 (4)
O6	0.45837 (15)	0.42760 (14)	0.68555 (9)	0.0430 (4)
O9	0.16054 (14)	0.83871 (15)	0.67240 (10)	0.0459 (4)
O1	1.13081 (17)	0.28201 (18)	0.61162 (12)	0.0630 (5)
N5	0.34068 (17)	0.66076 (17)	0.64319 (11)	0.0372 (4)
O7	−0.15543 (19)	0.45380 (19)	0.84150 (11)	0.0655 (5)
N3	0.53438 (18)	0.58162 (17)	0.74589 (11)	0.0395 (5)
O10	0.03480 (19)	0.9225 (2)	0.28410 (12)	0.0688 (6)
N4	0.37631 (19)	0.80507 (18)	0.73683 (12)	0.0452 (5)
O11	0.2252 (2)	0.8505 (2)	0.23354 (12)	0.0744 (6)
O8	−0.1507 (2)	0.5285 (2)	0.94963 (12)	0.0867 (7)
O2	1.0919 (2)	0.2716 (2)	0.48846 (14)	0.0865 (7)
C8	0.6826 (2)	0.5016 (2)	0.58781 (14)	0.0364 (5)
N2	0.6213 (2)	0.7695 (2)	0.76306 (17)	0.0643 (7)
C26	0.2068 (2)	0.8952 (2)	0.36326 (15)	0.0436 (6)
C16	0.3929 (2)	0.3667 (2)	0.75100 (14)	0.0407 (5)
O4	0.2721 (3)	0.0488 (2)	0.97601 (13)	0.0941 (8)
C3	0.9263 (2)	0.3743 (2)	0.56373 (15)	0.0435 (6)
N1	0.4825 (2)	0.6636 (2)	0.87694 (14)	0.0657 (7)
C31	0.2917 (2)	0.8974 (2)	0.50938 (14)	0.0409 (6)
C6	0.7664 (2)	0.4660 (2)	0.64938 (15)	0.0457 (6)
H6	0.741181	0.483904	0.699144	0.055*
C23	0.0899 (2)	0.7633 (2)	0.72509 (14)	0.0419 (6)
C29	0.1750 (2)	0.9677 (2)	0.48444 (16)	0.0502 (6)
H29	0.125198	1.016635	0.516301	0.060*
C21	0.0166 (2)	0.7087 (2)	0.69138 (15)	0.0465 (6)
H21	0.014492	0.722029	0.635423	0.056*
C18	−0.0516 (2)	0.6140 (3)	0.82533 (15)	0.0487 (6)
C4	0.8886 (2)	0.4031 (2)	0.63699 (15)	0.0470 (6)
H4	0.946115	0.379947	0.678409	0.056*
C28	0.3271 (2)	0.8296 (2)	0.38794 (16)	0.0514 (7)
H28	0.379625	0.785221	0.354575	0.062*
C30	0.3696 (2)	0.8295 (2)	0.46142 (16)	0.0507 (6)
H30	0.449866	0.784181	0.478342	0.061*
C7	0.7180 (2)	0.4732 (2)	0.51438 (15)	0.0505 (6)
H7	0.660488	0.497006	0.472933	0.061*
C11	0.2690 (3)	0.2279 (3)	0.87234 (16)	0.0532 (7)
C20	−0.0538 (2)	0.6339 (2)	0.74169 (15)	0.0484 (6)
H20	−0.103528	0.596154	0.719448	0.058*
C27	0.1318 (2)	0.9654 (2)	0.41171 (16)	0.0512 (7)
H27	0.051603	1.011420	0.395065	0.061*
C2	1.0561 (3)	0.3045 (2)	0.54925 (18)	0.0544 (7)
O5	0.0852 (3)	0.1822 (3)	0.94749 (17)	0.1124 (10)
C25	0.1603 (3)	0.8869 (2)	0.28700 (17)	0.0524 (7)
C5	0.8396 (3)	0.4092 (3)	0.50322 (17)	0.0568 (7)
H5	0.863658	0.389006	0.453968	0.068*
C37	−0.1245 (3)	0.5301 (3)	0.87977 (17)	0.0583 (7)
C22	0.0907 (3)	0.7480 (3)	0.80785 (16)	0.0563 (7)
H22	0.138839	0.787557	0.829802	0.068*

C14	0.4609 (3)	0.2619 (2)	0.80209 (16)	0.0530 (7)
H14	0.548143	0.238064	0.795967	0.064*
C19	0.0197 (3)	0.6735 (3)	0.85737 (16)	0.0622 (8)
H19	0.019517	0.662991	0.913179	0.075*
C12	0.3975 (3)	0.1925 (3)	0.86275 (16)	0.0598 (7)
H12	0.442405	0.120963	0.897532	0.072*
C15	0.2652 (3)	0.4042 (3)	0.75908 (19)	0.0643 (8)
H15	0.220445	0.475423	0.723904	0.077*
C10	0.1963 (4)	0.1539 (3)	0.93527 (19)	0.0709 (9)
C13	0.2034 (3)	0.3339 (3)	0.8209 (2)	0.0708 (9)
H13	0.116357	0.358832	0.827536	0.085*
C36	0.6520 (3)	0.8161 (3)	0.6777 (2)	0.0823 (10)
H36A	0.657661	0.752385	0.649724	0.123*
H36B	0.731441	0.839306	0.672839	0.123*
H36C	0.587300	0.887402	0.654325	0.123*
C17	−0.2304 (3)	0.3713 (3)	0.8877 (2)	0.0834 (10)
H17A	−0.242511	0.317199	0.856088	0.125*
H17B	−0.310849	0.419134	0.901190	0.125*
H17C	−0.187812	0.322586	0.936488	0.125*
C32	0.3905 (3)	0.5873 (4)	0.90837 (18)	0.0900 (12)
H32A	0.306705	0.639424	0.902785	0.135*
H32B	0.405686	0.547034	0.964549	0.135*
H32C	0.399019	0.525634	0.878288	0.135*
C1	1.2583 (3)	0.2114 (3)	0.6036 (2)	0.0848 (11)
H1A	1.291535	0.241867	0.550324	0.127*
H1B	1.258290	0.125273	0.611636	0.127*
H1C	1.309885	0.220089	0.643377	0.127*
C24	−0.0235 (3)	0.9119 (4)	0.2150 (2)	0.0873 (11)
H24A	−0.002722	0.970621	0.167465	0.131*
H24B	−0.113431	0.928843	0.223451	0.131*
H24C	0.006542	0.829220	0.207746	0.131*
C33	0.4820 (5)	0.7581 (4)	0.9199 (2)	0.1108 (16)
H33A	0.475920	0.722809	0.977772	0.133*
H33B	0.408658	0.826230	0.904680	0.133*
C35	0.6178 (4)	0.8611 (4)	0.8114 (3)	0.1121 (16)
H35A	0.549466	0.933281	0.793005	0.135*
H35B	0.696173	0.888388	0.802422	0.135*
C34	0.5993 (5)	0.8069 (5)	0.9006 (3)	0.128 (2)
H34A	0.671826	0.739711	0.919779	0.154*
H34B	0.595139	0.870339	0.929409	0.154*
C9	0.2079 (5)	−0.0286 (5)	1.0390 (3)	0.155 (2)
H9A	0.151069	−0.059783	1.014533	0.233*
H9B	0.161211	0.019923	1.074512	0.233*
H9C	0.269006	−0.097037	1.069430	0.233*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P2	0.0344 (3)	0.0316 (3)	0.0351 (3)	−0.0075 (2)	0.0019 (2)	−0.0053 (2)
P3	0.0324 (3)	0.0354 (3)	0.0418 (4)	−0.0052 (2)	0.0015 (3)	−0.0070 (3)
P1	0.0413 (4)	0.0488 (4)	0.0435 (4)	−0.0061 (3)	−0.0036 (3)	−0.0169 (3)
O3	0.0364 (9)	0.0410 (9)	0.0351 (9)	−0.0054 (7)	0.0030 (7)	−0.0045 (7)

O12	0.0467 (10)	0.0364 (9)	0.0484 (10)	−0.0126 (7)	0.0009 (8)	−0.0049 (7)
O6	0.0500 (10)	0.0313 (8)	0.0455 (10)	−0.0104 (7)	0.0066 (8)	−0.0071 (7)
O9	0.0334 (9)	0.0463 (9)	0.0497 (10)	−0.0027 (7)	0.0046 (7)	−0.0055 (8)
O1	0.0418 (11)	0.0682 (13)	0.0779 (14)	0.0023 (9)	−0.0042 (10)	−0.0294 (11)
N5	0.0336 (11)	0.0372 (10)	0.0400 (11)	−0.0079 (8)	−0.0011 (8)	−0.0088 (8)
O7	0.0691 (14)	0.0768 (14)	0.0533 (12)	−0.0336 (11)	0.0130 (10)	−0.0096 (10)
N3	0.0376 (11)	0.0400 (11)	0.0376 (11)	−0.0040 (9)	−0.0033 (9)	−0.0080 (9)
O10	0.0560 (13)	0.0824 (15)	0.0671 (13)	−0.0103 (11)	−0.0086 (10)	−0.0204 (11)
N4	0.0434 (12)	0.0420 (11)	0.0501 (12)	−0.0027 (9)	−0.0021 (10)	−0.0176 (10)
O11	0.0723 (15)	0.0930 (16)	0.0517 (12)	−0.0078 (12)	0.0034 (11)	−0.0197 (11)
O8	0.0926 (18)	0.131 (2)	0.0459 (13)	−0.0560 (16)	0.0165 (11)	−0.0165 (13)
O2	0.0649 (14)	0.1080 (18)	0.0882 (16)	0.0164 (12)	−0.0012 (12)	−0.0621 (15)
C8	0.0344 (13)	0.0351 (12)	0.0389 (13)	−0.0099 (10)	0.0037 (10)	−0.0077 (10)
N2	0.0507 (15)	0.0596 (15)	0.093 (2)	−0.0167 (12)	−0.0140 (13)	−0.0289 (14)
C26	0.0431 (15)	0.0377 (13)	0.0419 (14)	−0.0067 (11)	0.0035 (11)	0.0002 (11)
C16	0.0442 (14)	0.0329 (12)	0.0445 (14)	−0.0123 (11)	0.0033 (11)	−0.0071 (10)
O4	0.117 (2)	0.0920 (18)	0.0637 (14)	−0.0503 (16)	0.0075 (14)	0.0187 (13)
C3	0.0397 (14)	0.0400 (13)	0.0517 (15)	−0.0064 (11)	0.0050 (11)	−0.0178 (11)
N1	0.0713 (17)	0.0790 (17)	0.0439 (13)	0.0025 (14)	−0.0102 (12)	−0.0261 (13)
C31	0.0422 (14)	0.0329 (12)	0.0417 (14)	−0.0103 (10)	0.0044 (11)	0.0006 (10)
C6	0.0442 (15)	0.0541 (15)	0.0380 (14)	−0.0074 (12)	0.0030 (11)	−0.0151 (12)
C23	0.0288 (12)	0.0456 (14)	0.0436 (14)	0.0002 (10)	0.0023 (10)	−0.0068 (11)
C29	0.0458 (16)	0.0409 (14)	0.0536 (16)	0.0024 (12)	0.0053 (12)	−0.0075 (12)
C21	0.0412 (14)	0.0561 (15)	0.0375 (14)	−0.0049 (12)	0.0025 (11)	−0.0105 (12)
C18	0.0376 (14)	0.0645 (17)	0.0396 (14)	−0.0094 (12)	0.0026 (11)	−0.0089 (12)
C4	0.0401 (14)	0.0514 (15)	0.0473 (15)	−0.0062 (12)	−0.0048 (11)	−0.0115 (12)
C28	0.0480 (16)	0.0506 (15)	0.0448 (15)	0.0012 (12)	0.0078 (12)	−0.0078 (12)
C30	0.0374 (14)	0.0522 (15)	0.0501 (16)	0.0013 (12)	0.0036 (12)	−0.0036 (12)
C7	0.0459 (16)	0.0612 (16)	0.0430 (15)	−0.0029 (13)	−0.0041 (12)	−0.0185 (13)
C11	0.0615 (19)	0.0522 (16)	0.0492 (16)	−0.0254 (14)	0.0081 (13)	−0.0097 (13)
C20	0.0422 (15)	0.0586 (16)	0.0453 (15)	−0.0118 (12)	−0.0004 (11)	−0.0147 (13)
C27	0.0417 (15)	0.0455 (14)	0.0545 (17)	0.0007 (12)	−0.0004 (12)	−0.0023 (12)
C2	0.0476 (16)	0.0496 (15)	0.0664 (19)	−0.0051 (12)	0.0005 (14)	−0.0215 (14)
O5	0.086 (2)	0.128 (2)	0.114 (2)	−0.0534 (18)	0.0305 (16)	0.0021 (17)
C25	0.0541 (18)	0.0463 (15)	0.0494 (17)	−0.0095 (13)	0.0004 (14)	−0.0016 (12)
C5	0.0537 (17)	0.0696 (18)	0.0494 (16)	−0.0028 (14)	0.0044 (13)	−0.0316 (14)
C37	0.0460 (16)	0.079 (2)	0.0440 (17)	−0.0177 (15)	0.0035 (13)	−0.0037 (15)
C22	0.0506 (17)	0.0760 (19)	0.0465 (16)	−0.0211 (15)	−0.0046 (13)	−0.0153 (14)
C14	0.0462 (16)	0.0511 (15)	0.0539 (16)	−0.0076 (12)	0.0007 (13)	−0.0036 (13)
C19	0.0599 (19)	0.092 (2)	0.0368 (15)	−0.0247 (17)	0.0001 (13)	−0.0126 (15)
C12	0.066 (2)	0.0547 (17)	0.0475 (16)	−0.0156 (14)	−0.0028 (14)	0.0087 (13)
C15	0.0466 (17)	0.0466 (15)	0.084 (2)	−0.0071 (13)	0.0031 (15)	0.0068 (15)
C10	0.084 (3)	0.076 (2)	0.060 (2)	−0.045 (2)	0.0079 (18)	−0.0090 (17)
C13	0.0449 (17)	0.0634 (19)	0.096 (2)	−0.0189 (15)	0.0148 (16)	−0.0048 (17)
C36	0.054 (2)	0.066 (2)	0.123 (3)	−0.0277 (16)	0.0040 (19)	−0.007 (2)
C17	0.093 (3)	0.088 (2)	0.073 (2)	−0.050 (2)	0.0168 (19)	−0.0055 (18)
C32	0.077 (2)	0.126 (3)	0.0452 (18)	−0.006 (2)	0.0081 (16)	−0.0017 (19)
C1	0.0470 (19)	0.082 (2)	0.122 (3)	0.0119 (16)	−0.0120 (19)	−0.041 (2)
C24	0.077 (2)	0.111 (3)	0.077 (2)	−0.028 (2)	−0.0203 (19)	−0.019 (2)
C33	0.139 (4)	0.115 (3)	0.074 (3)	0.026 (3)	−0.038 (3)	−0.058 (2)
C35	0.111 (3)	0.082 (3)	0.167 (5)	−0.019 (2)	−0.049 (3)	−0.060 (3)
C34	0.157 (5)	0.115 (4)	0.136 (4)	0.004 (3)	−0.075 (4)	−0.081 (3)

C9	0.186 (5)	0.159 (5)	0.102 (3)	−0.102 (4)	0.022 (3)	0.051 (3)

Geometric parameters (Å, º)

P2—O3	1.5904 (16)	C18—C20	1.390 (3)
P2—O6	1.5913 (16)	C18—C37	1.486 (4)
P2—N5	1.5747 (19)	C18—C19	1.380 (4)
P2—N3	1.5674 (19)	C4—H4	0.9300
P3—O12	1.5928 (17)	C28—H28	0.9300
P3—O9	1.5895 (16)	C28—C30	1.377 (4)
P3—N5	1.5861 (19)	C30—H30	0.9300
P3—N4	1.559 (2)	C7—H7	0.9300
P1—N3	1.592 (2)	C7—C5	1.375 (4)
P1—N4	1.609 (2)	C11—C12	1.371 (4)
P1—N2	1.649 (2)	C11—C10	1.488 (4)
P1—N1	1.650 (2)	C11—C13	1.374 (4)
O3—C8	1.400 (3)	C20—H20	0.9300
O12—C31	1.410 (3)	C27—H27	0.9300
O6—C16	1.397 (3)	O5—C10	1.194 (4)
O9—C23	1.399 (3)	C5—H5	0.9300
O1—C2	1.333 (3)	C22—H22	0.9300
O1—C1	1.445 (3)	C22—C19	1.373 (4)
O7—C37	1.338 (3)	C14—H14	0.9300
O7—C17	1.438 (3)	C14—C12	1.381 (4)
O10—C25	1.334 (3)	C19—H19	0.9300
O10—C24	1.437 (4)	C12—H12	0.9300
O11—C25	1.206 (3)	C15—H15	0.9300
O8—C37	1.201 (3)	C15—C13	1.386 (4)
O2—C2	1.198 (3)	C13—H13	0.9300
C8—C6	1.369 (3)	C36—H36A	0.9600
C8—C7	1.378 (3)	C36—H36B	0.9600
N2—C36	1.458 (4)	C36—H36C	0.9600
N2—C35	1.487 (4)	C17—H17A	0.9600
C26—C28	1.385 (3)	C17—H17B	0.9600
C26—C27	1.382 (3)	C17—H17C	0.9600
C26—C25	1.474 (4)	C32—H32A	0.9600
C16—C14	1.372 (3)	C32—H32B	0.9600
C16—C15	1.363 (4)	C32—H32C	0.9600
O4—C10	1.338 (4)	C1—H1A	0.9600
O4—C9	1.455 (4)	C1—H1B	0.9600
C3—C4	1.381 (3)	C1—H1C	0.9600
C3—C2	1.483 (3)	C24—H24A	0.9600
C3—C5	1.378 (4)	C24—H24B	0.9600
N1—C32	1.470 (4)	C24—H24C	0.9600
N1—C33	1.458 (4)	C33—H33A	0.9700
C31—C29	1.368 (3)	C33—H33B	0.9700
C31—C30	1.374 (3)	C33—C34	1.501 (7)
C6—H6	0.9300	C35—H35A	0.9700
C6—C4	1.381 (3)	C35—H35B	0.9700
C23—C21	1.373 (3)	C35—C34	1.506 (6)
C23—C22	1.380 (3)	C34—H34A	0.9700
C29—H29	0.9300	C34—H34B	0.9700

C29—C27	1.377 (4)	C9—H9A	0.9600
C21—H21	0.9300	C9—H9B	0.9600
C21—C20	1.376 (3)	C9—H9C	0.9600

O3—P2—O6	97.35 (8)	O2—C2—O1	122.8 (3)
N5—P2—O3	106.00 (9)	O2—C2—C3	124.6 (3)
N5—P2—O6	110.58 (9)	O10—C25—C26	111.6 (2)
N3—P2—O3	112.78 (10)	O11—C25—O10	122.9 (3)
N3—P2—O6	109.99 (9)	O11—C25—C26	125.5 (3)
N3—P2—N5	118.13 (10)	C3—C5—H5	119.4
O9—P3—O12	98.76 (9)	C7—C5—C3	121.1 (2)
N5—P3—O12	110.06 (9)	C7—C5—H5	119.4
N5—P3—O9	108.83 (10)	O7—C37—C18	111.3 (2)
N4—P3—O12	108.86 (10)	O8—C37—O7	123.8 (3)
N4—P3—O9	110.77 (10)	O8—C37—C18	124.9 (3)
N4—P3—N5	117.88 (10)	C23—C22—H22	120.4
N3—P1—N4	114.19 (10)	C19—C22—C23	119.2 (3)
N3—P1—N2	109.59 (12)	C19—C22—H22	120.4
N3—P1—N1	107.52 (12)	C16—C14—H14	120.6
N4—P1—N2	110.01 (12)	C16—C14—C12	118.8 (3)
N4—P1—N1	111.31 (12)	C12—C14—H14	120.6
N2—P1—N1	103.68 (14)	C18—C19—H19	119.6
C8—O3—P2	126.90 (14)	C22—C19—C18	120.8 (2)
C31—O12—P3	119.74 (13)	C22—C19—H19	119.6
C16—O6—P2	123.85 (14)	C11—C12—C14	120.8 (3)
C23—O9—P3	120.67 (14)	C11—C12—H12	119.6
C2—O1—C1	116.3 (2)	C14—C12—H12	119.6
P2—N5—P3	118.45 (11)	C16—C15—H15	120.7
C37—O7—C17	116.1 (2)	C16—C15—C13	118.6 (3)
P2—N3—P1	122.95 (12)	C13—C15—H15	120.7
C25—O10—C24	117.4 (2)	O4—C10—C11	110.9 (3)
P3—N4—P1	123.14 (12)	O5—C10—O4	123.9 (3)
C6—C8—O3	123.4 (2)	O5—C10—C11	125.2 (3)
C6—C8—C7	120.8 (2)	C11—C13—C15	120.9 (3)
C7—C8—O3	115.8 (2)	C11—C13—H13	119.6
C36—N2—P1	113.16 (19)	C15—C13—H13	119.6
C36—N2—C35	112.6 (3)	N2—C36—H36A	109.5
C35—N2—P1	115.3 (2)	N2—C36—H36B	109.5
C28—C26—C25	119.5 (2)	N2—C36—H36C	109.5
C27—C26—C28	119.1 (2)	H36A—C36—H36B	109.5
C27—C26—C25	121.3 (2)	H36A—C36—H36C	109.5
C14—C16—O6	117.1 (2)	H36B—C36—H36C	109.5
C15—C16—O6	120.9 (2)	O7—C17—H17A	109.5
C15—C16—C14	121.8 (2)	O7—C17—H17B	109.5
C10—O4—C9	114.2 (3)	O7—C17—H17C	109.5
C4—C3—C2	121.9 (2)	H17A—C17—H17B	109.5
C5—C3—C4	118.8 (2)	H17A—C17—H17C	109.5
C5—C3—C2	119.3 (2)	H17B—C17—H17C	109.5
C32—N1—P1	115.9 (2)	N1—C32—H32A	109.5
C33—N1—P1	116.3 (3)	N1—C32—H32B	109.5
C33—N1—C32	114.7 (3)	N1—C32—H32C	109.5
C29—C31—O12	119.0 (2)	H32A—C32—H32B	109.5

C29—C31—C30	121.4 (2)	H32A—C32—H32C	109.5
C30—C31—O12	119.6 (2)	H32B—C32—H32C	109.5
C8—C6—H6	120.3	O1—C1—H1A	109.5
C8—C6—C4	119.4 (2)	O1—C1—H1B	109.5
C4—C6—H6	120.3	O1—C1—H1C	109.5
C21—C23—O9	117.6 (2)	H1A—C1—H1B	109.5
C21—C23—C22	121.3 (2)	H1A—C1—H1C	109.5
C22—C23—O9	121.1 (2)	H1B—C1—H1C	109.5
C31—C29—H29	120.3	O10—C24—H24A	109.5
C31—C29—C27	119.4 (2)	O10—C24—H24B	109.5
C27—C29—H29	120.3	O10—C24—H24C	109.5
C23—C21—H21	120.5	H24A—C24—H24B	109.5
C23—C21—C20	118.9 (2)	H24A—C24—H24C	109.5
C20—C21—H21	120.5	H24B—C24—H24C	109.5
C20—C18—C37	120.8 (2)	N1—C33—H33A	109.4
C19—C18—C20	118.9 (2)	N1—C33—H33B	109.4
C19—C18—C37	120.2 (2)	N1—C33—C34	111.3 (3)
C3—C4—H4	119.7	H33A—C33—H33B	108.0
C6—C4—C3	120.7 (2)	C34—C33—H33A	109.4
C6—C4—H4	119.7	C34—C33—H33B	109.4
C26—C28—H28	119.7	N2—C35—H35A	109.2
C30—C28—C26	120.6 (2)	N2—C35—H35B	109.2
C30—C28—H28	119.7	N2—C35—C34	111.9 (3)
C31—C30—C28	119.0 (2)	H35A—C35—H35B	107.9
C31—C30—H30	120.5	C34—C35—H35A	109.2
C28—C30—H30	120.5	C34—C35—H35B	109.2
C8—C7—H7	120.4	C33—C34—C35	113.0 (3)
C5—C7—C8	119.1 (2)	C33—C34—H34A	109.0
C5—C7—H7	120.4	C33—C34—H34B	109.0
C12—C11—C10	122.6 (3)	C35—C34—H34A	109.0
C12—C11—C13	119.2 (2)	C35—C34—H34B	109.0
C13—C11—C10	118.2 (3)	H34A—C34—H34B	107.8
C21—C20—C18	120.8 (2)	O4—C9—H9A	109.5
C21—C20—H20	119.6	O4—C9—H9B	109.5
C18—C20—H20	119.6	O4—C9—H9C	109.5
C26—C27—H27	119.8	H9A—C9—H9B	109.5
C29—C27—C26	120.4 (2)	H9A—C9—H9C	109.5
C29—C27—H27	119.8	H9B—C9—H9C	109.5
O1—C2—C3	112.6 (2)		

P2—O3—C8—C6	−34.2 (3)	C16—C14—C12—C11	−0.5 (4)
P2—O3—C8—C7	148.50 (18)	C16—C15—C13—C11	−0.8 (5)
P2—O6—C16—C14	−119.4 (2)	N1—P1—N3—P2	134.00 (15)
P2—O6—C16—C15	66.3 (3)	N1—P1—N4—P3	−131.14 (16)
P3—O12—C31—C29	92.5 (2)	N1—P1—N2—C36	−178.9 (2)
P3—O12—C31—C30	−88.5 (2)	N1—P1—N2—C35	−47.3 (3)
P3—O9—C23—C21	−107.0 (2)	N1—C33—C34—C35	57.8 (5)
P3—O9—C23—C22	75.2 (3)	C31—C29—C27—C26	−1.6 (4)
P1—N2—C35—C34	54.1 (4)	C6—C8—C7—C5	−0.6 (4)
P1—N1—C33—C34	−56.2 (4)	C23—C21—C20—C18	0.3 (4)
O3—P2—O6—C16	176.80 (17)	C23—C22—C19—C18	0.3 (4)
O3—P2—N5—P3	−103.03 (13)	C29—C31—C30—C28	−2.1 (4)

O3—P2—N3—P1	106.15 (14)	C21—C23—C22—C19	2.0 (4)
O3—C8—C6—C4	−175.7 (2)	C4—C3—C2—O1	−4.4 (3)
O3—C8—C7—C5	176.8 (2)	C4—C3—C2—O2	176.1 (3)
O12—P3—O9—C23	168.15 (17)	C4—C3—C5—C7	1.0 (4)
O12—P3—N5—P2	101.92 (13)	C28—C26—C27—C29	−1.5 (4)
O12—P3—N4—P1	−109.84 (15)	C28—C26—C25—O10	161.1 (2)
O12—C31—C29—C27	−177.6 (2)	C28—C26—C25—O11	−17.6 (4)
O12—C31—C30—C28	179.0 (2)	C30—C31—C29—C27	3.5 (4)
O6—P2—O3—C8	−63.41 (18)	C7—C8—C6—C4	1.4 (4)
O6—P2—N5—P3	152.50 (11)	C20—C18—C37—O7	18.7 (4)
O6—P2—N3—P1	−146.36 (13)	C20—C18—C37—O8	−162.6 (3)
O6—C16—C14—C12	−173.8 (2)	C20—C18—C19—C22	−2.2 (4)
O6—C16—C15—C13	174.2 (3)	C27—C26—C28—C30	2.9 (4)
O9—P3—O12—C31	−70.12 (17)	C27—C26—C25—O10	−17.6 (3)
O9—P3—N5—P2	−150.88 (11)	C27—C26—C25—O11	163.7 (3)
O9—P3—N4—P1	142.61 (14)	C2—C3—C4—C6	−178.6 (2)
O9—C23—C21—C20	179.9 (2)	C2—C3—C5—C7	179.5 (2)
O9—C23—C22—C19	179.7 (2)	C25—C26—C28—C30	−175.8 (2)
N5—P2—O3—C8	−177.34 (16)	C25—C26—C27—C29	177.2 (2)
N5—P2—O6—C16	−73.00 (19)	C5—C3—C4—C6	−0.2 (4)
N5—P2—N3—P1	−18.15 (18)	C5—C3—C2—O1	177.2 (2)
N5—P3—O12—C31	43.70 (19)	C5—C3—C2—O2	−2.3 (4)
N5—P3—O9—C23	53.37 (19)	C37—C18—C20—C21	−178.1 (2)
N5—P3—N4—P1	16.4 (2)	C37—C18—C19—C22	177.8 (3)
N3—P2—O3—C8	51.94 (19)	C22—C23—C21—C20	−2.3 (4)
N3—P2—O6—C16	59.3 (2)	C14—C16—C15—C13	0.1 (4)
N3—P2—N5—P3	24.56 (17)	C19—C18—C20—C21	1.9 (4)
N3—P1—N4—P3	−9.17 (19)	C19—C18—C37—O7	−161.3 (3)
N3—P1—N2—C36	66.6 (2)	C19—C18—C37—O8	17.4 (5)
N3—P1—N2—C35	−161.8 (2)	C12—C11—C10—O4	−3.3 (4)
N3—P1—N1—C32	−55.8 (2)	C12—C11—C10—O5	177.9 (3)
N3—P1—N1—C33	165.0 (3)	C12—C11—C13—C15	0.8 (5)
N4—P3—O12—C31	174.30 (16)	C15—C16—C14—C12	0.5 (4)
N4—P3—O9—C23	−77.75 (19)	C10—C11—C12—C14	178.1 (3)
N4—P3—N5—P2	−23.71 (17)	C10—C11—C13—C15	−177.6 (3)
N4—P1—N3—P2	9.97 (18)	C13—C11—C12—C14	−0.2 (4)
N4—P1—N2—C36	−59.7 (2)	C13—C11—C10—O4	175.0 (3)
N4—P1—N2—C35	71.8 (3)	C13—C11—C10—O5	−3.8 (5)
N4—P1—N1—C32	69.9 (2)	C36—N2—C35—C34	−174.0 (3)
N4—P1—N1—C33	−69.3 (3)	C17—O7—C37—O8	3.5 (4)
C8—C6—C4—C3	−1.0 (4)	C17—O7—C37—C18	−177.8 (2)
C8—C7—C5—C3	−0.7 (4)	C32—N1—C33—C34	164.1 (3)
N2—P1—N3—P2	−113.94 (16)	C1—O1—C2—O2	−2.0 (4)
N2—P1—N4—P3	114.52 (17)	C1—O1—C2—C3	178.4 (2)
N2—P1—N1—C32	−171.9 (2)	C24—O10—C25—O11	2.3 (4)
N2—P1—N1—C33	48.9 (3)	C24—O10—C25—C26	−176.4 (2)
N2—C35—C34—C33	−57.0 (5)	C9—O4—C10—C11	179.8 (3)
C26—C28—C30—C31	−1.2 (4)	C9—O4—C10—O5	−1.3 (5)