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Protonation of Some Cyclic Triphosphenium Ions

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ABSTRACT: *Several cyclic triphosphenium ions of various ring sizes have been successfully protonated to form the corresponding triphosphane di-ium dications, either by a ^{t}BuCl/AlCl$_3$ mixture and/or by triflic acid. The latter reagent appears to be harsher, however, sometimes leading to decomposition. The new dications have been identified in solution by ^{31}P NMR spectroscopy; recording the spectra proton coupled as well as decoupled has enabled $^1J_{PH}$ as well as $^1J_{PP}$ to be evaluated in most cases. The protonated derivatives of three compounds could not be observed, with only decomposition products being detected. In the case of the triphosphenium ion derived from bis-1,4-diphenylphosphinobutane (dppb), clear spectroscopic evidence for an intermediate in the decomposition process of the di-ium dication has been obtained, enabling a plausible mechanism to be proposed. In addition, a novel triphosphorus-containing trication with a norbornane-like structure has been detected, and characterized by single crystal X-ray diffraction, as a minor product from the protonation of the triphosphenium ion derived from cis-bis-1,2-diphenylphosphinoethene (dppE).* © 2005 Wiley Periodicals, Inc. Heteroatom Chem 16:447–452, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20124

INTRODUCTION

Since the first cyclic triphosphenium ion **1** (Scheme 1) was characterized by Schmidpeter et al. in 1982 [1], several of these species, with three linked phosphorus atoms in a cyclic structure and an overall positive charge, have been prepared [2–9]. These include examples with five-, six-, or seven-membered rings, or with two linked six-membered rings, each containing three phosphorus atoms. Very recently we have reported the first syntheses of four-membered ring examples with carbon substituents on the outer phosphorus atoms [10]. Comparatively little investigation has been carried out into the chemistry of these species, however. Alkylation of the dication derived from tetraphos by a mixture of CH$_2$Cl$_2$ and AlCl$_3$ was demonstrated by Schmidpeter and Lochschmidt to give a tetracation with —CH$_2$Cl substituents on both central phosphorus atoms [4]. Subsequently we have shown that a number of cyclic triphosphenium ions can be methylated, by using excess methyl triflate [10,11]. Schmidpeter et al. also demonstrated that the cation **1** (Scheme 1) derived from bis-diphenylphosphinoethane (dppe) and the dication derived from tetraphos, (as well as several noncyclic species), could be protonated by a 1:1 mixture of ^{t}BuCl and AlCl$_3$ to give the corresponding triphosphane-1,3-di-ium dication **2** and tetracation respectively [4,12]. We have extended this work considerably, to include other cyclic triphosphenium ions of various ring sizes, and have investigated both ^{t}BuCl/AlCl$_3$ and triflic acid as potential protonating agents. Newly protonated species have been identified via their ^{31}P NMR spectra, which have been

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Dedicated to Prof. Dr. Alfred Schmidpeter on the occasion of his 75th birthday.

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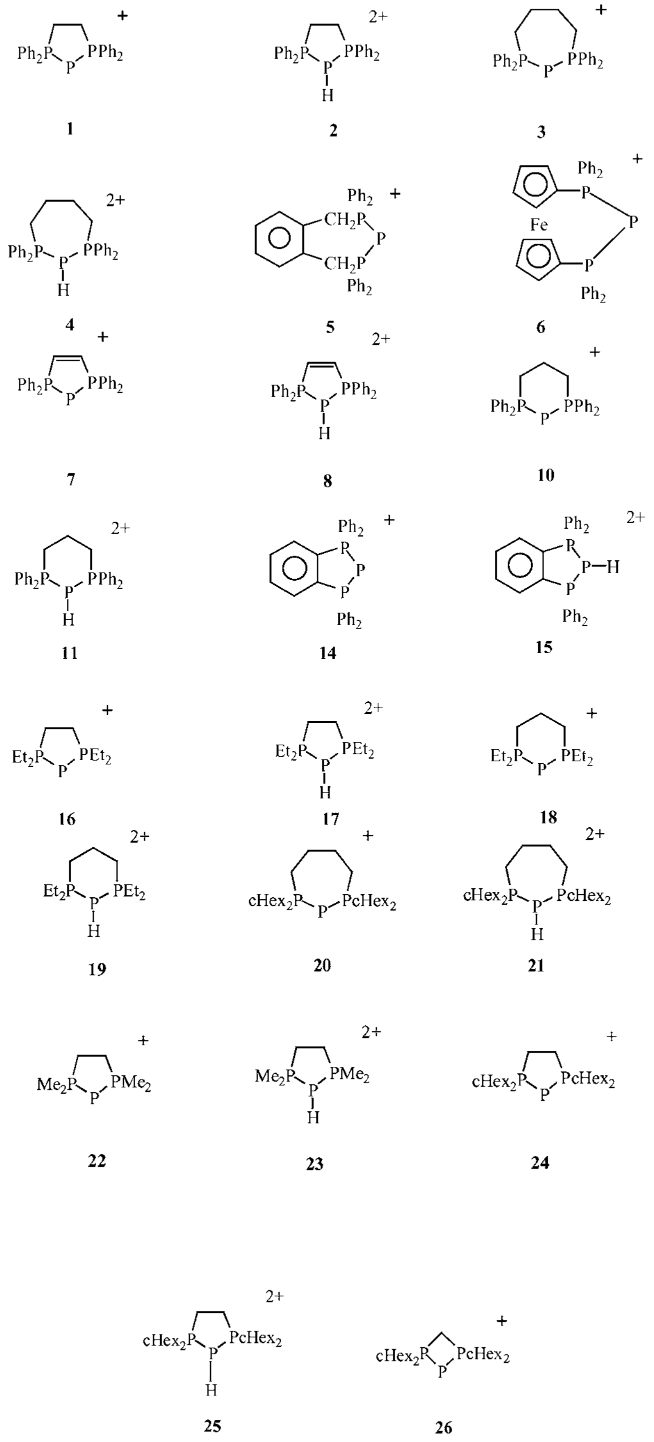


SCHEME 1

recorded both proton decoupled and proton coupled, in order to obtain ${}^1J_{PP}$ and ${}^1J_{PH}$. From spectroscopic observation of a key intermediate in the decomposition of the protonated species **4**, obtained from the bis-1,4-diphenylphosphinobutane derivative **3** (Scheme 1), we have been able to propose a mechanism for the decomposition. No evidence was found for protonation of cyclic triphosphenium ions **5** and **6**, with only decomposition products being detected.

RESULTS AND DISCUSSION

Protonations with $AlCl_3$ and ${}^tBuCl$ (1:1)

As mentioned above, two cyclic triphosphenium ions were successfully protonated by Schmidpeter et al., using a 1:1 mixture of $AlCl_3$ and ${}^tBuCl$, including **1** (Scheme 1), the ion derived from dppe [4]. On protonation, the ${}^{31}P$ chemical shift of the central phosphorus atom in **1** changed from −232.0 to −157.1 ppm, and ${}^1J_{PP}$ decreased substantially from 451.5 to 238.7 Hz [4]. In addition, ${}^1J_{PH}$ was obtained as 217.5 Hz. There are two possible sources for the proton required to cause protonation in this system. $AlCl_3$ hydrolyses very easily, and frequently is found in an impure state; the presence of —OH groups or even H_2O molecules on the surface can readily provide protons. Alternatively, a proton can be abstracted from the ^{t}butyl group to form an alkene, Eq. (1).

$$ {}^tBuCl + AlCl_3 \rightarrow H^+ + AlCl_4^- + Me_2C{=}CH_2 \qquad (1) $$

In our experiments, we initially tried to protonate the same cyclic triphosphenium ion **1** as Schmidpeter and co-workers, as a test of the method, and obtained very similar NMR parameters, with δ P_B 53.5 (d), δ P_A–154.5 (t) ppm, ${}^1J_{PP}$ 240.1 Hz (Table 1). The spectrum was not recorded proton coupled, since ${}^1J_{PH}$ had already been reported in the literature, as described above [4]. Attempts were then made to protonate other cyclic triphosphenium ions with various ring sizes, using a mixture of these reagents. The ${}^{31}P$ NMR results are collected in Table 1, together with the data for the precursor ions (Scheme 1), which in all cases were in good agreement with either literature results [2–9] or previous measurements made in our group. By chance we had a reasonably pure sample of $AlCl_3$ (a commercial product), and occasionally found it necessary to add a very small quantity of water by syringe in order to facilitate reaction, suggesting that the former route of those described above is followed. For all successful protonations, there was a marked shift of the central phosphorus resonance P_A to higher frequency, and a large decrease in ${}^1J_{PP}$, indicating less s character in the hybrid orbitals of the protonated species. By running the spectra proton coupled, it was also possible to obtain ${}^1J_{PH}$ in most cases, the value of which was slightly lower than ${}^1J_{PP}$.

Some of the systems studied merit particular mention. With the derivative **7** of the unsaturated

TABLE 1 ^{31}P NMR Data for Some Cyclic Triphosphenium Ions and Their Protonated Derivatives Using $AlCl_3$/^{t}BuCl

Precursor				*Protonated Derivative*				
No.	δP_B	δP_A	$^1J_{PP}$	*No.*	δP_B	δP_A	$^1J_{PP}$	$^1J_{PH}$
1	65.3	−231.6	451.5	**2**	53.5	−154.5	240.0	Not recorded
3	34.1	−211.2	456.1	**4**	28.6	−134.4	255.0	236.0
5	25.2	−215.0	438.0	–	–	–	–	–
6	33.2	−135.4	496.8	–	–	–	–	–
7	72.1	−248.6	473.8	**8**	58.1	−157.2	258.4	230.9
10	23.3	−209.1	423.4	**11**	13.8	−156.2	226.0	223.0
14	57.6	−212.9	453.2	**15**	42.7	−133.0	240.6	218.5
16	81.4	−269.9	441.3	**17**	68.0	−183.9	254.6	Not recorded

Chemical shifts in ppm; coupling constants in Hz.

ligand *cis*-bis-diphenylphosphinoethene (dppE), in addition to the expected signals for the protonated ion **8**, a small doublet and triplet were observed in the NMR spectrum, δ ^{31}P 29.9 (d), 2P, and 54.9 (t), 1P ppm, $^2J_{PP}$ 25.1 Hz. Crystals formed in the NMR tube, and single crystal X-ray diffraction at 120 K showed that these arose from the novel trication [1,4,7-tris(diphenylphosphonium)-norbornane] **9** as its tris(tetrachloroaluminate) salt, Fig. 1 and Scheme 2. Some solvent of crystallization, consisting of a mixture of CH_2Cl_2 and $CHCl_3$ (the latter from the $CDCl_3$ used to provide the deuterium lock for NMR spectroscopy) was also present, modeled as $CH_{1.14}Cl_{2.86}$; a full account of this structure has already been published [13]. The mechanism of its formation is not clear, but it must involve the cleavage of a P—C bond to generate one of the three diphenylphosphonium groups. It is also worth pointing out that the two C—C bonds in the trication are both single, with lengths of 1.565(10) and 1.541(10) Å. Crystals were also obtained by cooling the reaction mixture from protonation of the dppp derivative **10**, but low temperature X-ray diffraction proved that these were from the cation **10** as its tetrachloroaluminate(III) salt, rather than of the protonated species **11**. This structure is very similar to that of the corresponding cation as its hexachlorostannate(IV) [7], and is described fully elsewhere [14].

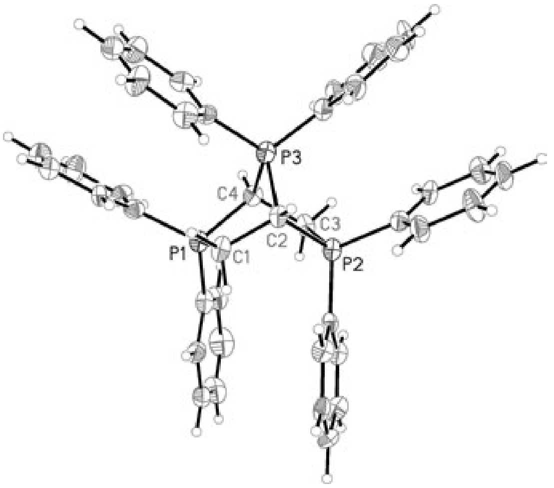
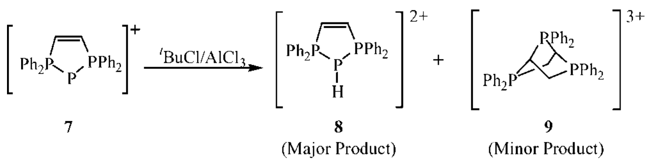


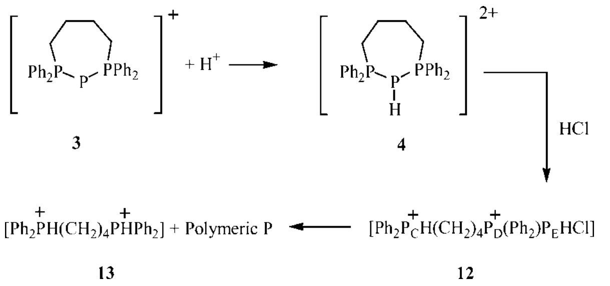
FIGURE 1 Thermal ellipsoid plot of the molecular structure of **9**, showing 50% probability displacement ellipsoids, with selected atoms labeled.

One of the most interesting systems studied was that of the 1,4-bis(diphenylphosphino)butane derivative **3**; protonation was achieved (Table 1), but the dication did not appear to be very stable. Two new equally intense doublets became apparent in the proton-decoupled ^{31}P spectrum, at 27.6 and −16.9 ppm, $^1J_{PP}$ 277.6 Hz, together with an equally intense singlet at 10.5 ppm. This implies the scission of one of the P—P bonds, resulting in a noncyclic dication **12** (Eq. (2)). The signals may then be assigned to P_D (27.6 ppm), P_E (−16.9 ppm), and P_C (10.5 ppm). The doublets were confirmed by recording the spectra at two different frequencies. Unfortunately the new signals had disappeared when the spectrum was recorded proton coupled, but singlets at 10.2 (vs) and 9.4 (s) ppm now apparent in the proton-decoupled spectrum were split into doublets, $^1J_{PH}$ 497.7 and 494.8 Hz, respectively. The intense signal is attributed to the protonated diphosphane **13**, while an orange deposit was seen in the tube, so the other



SCHEME 2

decomposition product is almost certainly polymeric phosphorus [15]. A control experiment on protonating 1,4-bis(diphenylphosphino)butane (dppb) with $AlCl_3$/^{t}BuCl produced a singlet at δ 10.1 ppm in the proton-decoupled ^{31}P NMR spectrum, which became a doublet, $^1J_{PH}$ 499 Hz, when recorded proton coupled, assigned to **13**. The second doublet described above could arise from the same cation with a different counterion, such as Cl^- [11,16,17]. It was not present in the control experiment, where the only anion should be $[AlCl_4]^-$. Hence a reasonable decomposition mechanism for the protonated cyclic triphosphenium ion may be deduced, as shown in Eq. (2).



(2)

There was no evidence of protonation by $AlCl_3$/^{t}BuCl of cyclic triphosphenium ions **5** or **6**, although the rings themselves were readily observable (Table 1). **5** is another seven-membered ring system, while the ferrocenium derivative **6** is of a different type, where ring size is rather problematic.

Protonations with Triflic Acid

It would clearly be more convenient to carry out protonations with a single reagent rather than a mixture, so the suitability of triflic acid for this purpose was investigated. As a test sample, protonation of **1** was attempted by direct addition of an equimolar quantity of triflic acid to a solution of the ring in CH_2Cl_2, and similar results were obtained (Table 2) to those from $AlCl_3$/^{t}BuCl. The difference was that the proton-coupled spectrum was broader, and the proton-phosphorus coupling could not be resolved, possibly because of exchange processes occurring in solution.

Interesting results were obtained from **7**, which was studied to see whether the trication **9** as well as the protonated species **8** would be formed. The initial spectrum after addition of one equivalent of triflic acid showed no evidence of protonation. When a second equivalent was added, the doublet from P_B in the proton-decoupled spectrum moved to an intermediate position with an intermediate $^1J_{PP}$ (δ 65.8 ppm, $^1J_{PP}$ 387.8 Hz), suggesting exchange between **7** and **8**. When the proton-coupled spectrum was subsequently recorded, these values had changed to δ 64.7 ppm, $^1J_{PP}$ 365.3 Hz. Addition of a further equivalent of triflic acid resulted in values of δ 58.1 (d) 2P, −159.2 (t) 1P ppm, $^1J_{PP}$ 272.5 Hz (Table 2). The shifts are now very similar to those found with $AlCl_3$/^{t}BuCl (Table 1), although $^1J_{PP}$ is slightly higher. As in the previous system, there was too much broadening in the proton-coupled spectrum for $^1J_{PH}$ to be obtained. A very small doublet at 29.9 ppm, $^2J_{PP}$ 26.4 Hz, was found in the spectrum after addition of the second equivalent of triflic acid, possibly from the trication **9**, but the corresponding triplet could not be detected with certainty, since other resonances were present in the same region.

Attempts were also made to protonate the ions **5** and **6**, where $AlCl_3$/^{t}BuCl had been unsuccessful. With **5**, addition of an equimolar quantity of triflic acid caused the solution to turn yellow, and eventually to deposit an orange solid, believed to be polymeric phosphorus [15]. No evidence was found for protonation of the ring, but its signals diminished in intensity and a new strong singlet appeared at 9.3 ppm, which split into a doublet when proton coupled, $^1J_{PH}$ 517.1 Hz, ascribed to the diprotonated diphosphane dppox H_2^{2+}. These results suggest that triflic acid is a harsh reagent which causes the seven-membered ring **5** to break up; this reaction may proceed via a protonated intermediate, as in the mechanism proposed for the decomposition of **4** with $AlCl_3$/^{t}BuCl, but direct evidence is lacking. Similar results were obtained with **6**. An orange solid was again deposited, and the ring signals disappeared. A new strong singlet at 6.7 ppm in the proton-decoupled spectrum became a doublet, $^1J_{PH}$ 528.2 Hz, when recorded proton coupled, indicating breakup of the ring, with formation of polymeric phosphorus and the diprotonated diphosphane.

In contrast, other cyclic triphosphenium ions could be protonated directly with triflic acid, and resolution of the proton-phosphorus coupling was possible for the derivatives **17, 19, 21, 23,** and **25** (Table 2).

Protonation of the four-membered ring with *cyclo*-hexyl substituents **26** (described very recently by us [10]) was also attempted. In this case the ring was freshly prepared from the diphosphane, $SnCl_2$, and PCl_3; NMR spectroscopy confirmed that it had formed (δ ^{31}P P_B 45.4 (d) 2P, P_A −216.1 (t) 1P ppm, $^1J_{PP}$ 330.9 Hz). An equimolar quantity of triflic acid was added, but the ring signals had disappeared even after 30 min, suggesting that it was unstable to triflic acid. A fresh solution of the ring (δ ^{31}P P_B 45.2 (d) 2P ppm, $^1J_{PP}$ 335.7 Hz) was prepared and treated with an equimolar quantity of $AlCl_3$ and ^{t}BuCl (1:1). There

TABLE 2 ^{31}P NMR Data for Some Cyclic Triphosphenium Ions and Their Protonated Derivatives Using Triflic Acid

Precursor				*Protonated Derivative*				
No.	δP_B	δP_A	$^1J_{PP}$	*No.*	δP_B	δP_A	$^1J_{PP}$	$^1J_{PH}$
1	65.1	Not recorded	450.9	**2**	53.4	−153.1	240.9	NR
7	72.0	Not recorded	469.8	**8**[a]	58.1	−159.2	272.5	NR
16	81.6	−269.9	441.4	**17**	72.3	−180.7	243.1	230.2
18	31.1	−253.3	416.7	**19**	29.0	−182.0	232.3	223.4
20	48.3	−262.5	472.0	**21**	49.3	−166.5	275.6	267.1
22	60.4	−212.9	430.0	**23**	55.7	−148.6	239.5	218.2
24	87.3	−289.3	456.8	**25**	77.6	−203.1	258.8	228.1
26	45.4	−216.1	331.0	–	–	–	–	–

Chemical shifts in ppm; coupling constants in Hz.
NR not resolved (see text).
[a] See text.

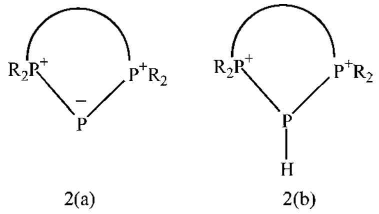
was no change in the spectrum after 30 min. On leaving the solution overnight, however, the doublet had diminished considerably in intensity, although with the same δ and J values, suggesting that slow decomposition was occurring. No evidence for the protonated dication was found.

Our results thus indicate that protonation of a number of cyclic triphosphenium ions is possible, using either $AlCl_3/^tBuCl$ and/or triflic acid. The stability of the seven-membered rings appears to be lower than that of their five- or six-membered analogues, and clear spectroscopic evidence has been found for the probable decomposition mechanism. This involves scission of one of the P—P bonds with formation of a noncyclic dication, which then suffers further P—P bond rupture with the formation of polymeric phosphorus and the diprotonated parent diphosphane. Triflic acid appears to be a harsher reagent than $AlCl_3/^tBuCl$, and its use is more likely to cause decomposition where the stability of the ring is suspect. Exchange reactions between the protonated and nonprotonated species have also been observed for one system (cations **7** and **8**) in this solvent. Attempts to protonate the four-membered ring **26**, the seven-membered ring **5**, and the ferrocenium derivative **6** were unsuccessful, although the unprotonated rings could be formed in each case. These results suggest that the dications are in general less stable than their monocationic precursors. A novel triphosphorus-containing trication **9** has been fully characterized by single-crystal X-ray diffraction at low temperature, as a minor product from the reaction of **7** with $AlCl_3/^tBuCl$, and may well be present in low concentration in the corresponding reaction mixture with triflic acid.

The charge distribution in a cyclic triphosphenium ion is usually regarded as shown in Fig. 2(a), although the system is delocalized [6,7,18–21]. In the protonated derivative, the middle phosphorus P_A is expected to become effectively a neutral P(III) species coordinated by two positively charged P_B atoms, Fig. 2(b). The P—P bond distance is thus expected to increase to a normal single bond length, instead of being intermediate between P—P single and P=P double bond lengths, as found in all crystal structures of cyclic triphosphenium ions ascertained to date [1,7,8]. None of the protonated derivatives has yet been isolated in a crystalline state, so this prediction remains unconfirmed at present. It has, however, been demonstrated by Schmidpeter et al. for the noncyclic species $[Ph_3PPPPh_3]^+$, with a P—P bond length of 2.133(6) Å, and its protonated form $[Ph_3PPHPPh_3]^{2+}$, with P—P bond lengths of 2.205(1) and 2.224(1) Å [12].

EXPERIMENTAL

All manipulations, including NMR sample preparation, were carried out either under an inert atmosphere of dry nitrogen or in vacuo, using standard Schlenk or vacuum line techniques. Chemicals of the best available commercial grade were used, in general without further purification. The ^{31}P NMR



2(a) 2(b)

FIGURE 2 Charge distribution in a cyclic triphosphenium ion (a) and its protonated derivative (b).

spectra of all starting materials were recorded, to check for the absence of any major phosphorus-containing impurities. Small amounts of oxidation products such as the diphosphane monoxide, which gives rise to two doublets, or the diphosphane dioxide, which gives a single resonance, were occasionally detected, particularly for diphosphanes with alkyl substituents, but these did not interfere with formation of the cyclic triphosphenium ions. These were prepared quantitatively in CH_2Cl_2 solution as described previously [7,8,10,11], from either a 3:2 mixture of the diphosphane and PCl_3, or a 1:1:1 mixture of the diphosphane, PCl_3, and $SnCl_2$, where the hexachlorostannate(IV) was required. The calculated quantity of a solution of $AlCl_3$ and ^tBuCl (1:1) in CH_2Cl_2 or of triflic acid was added by microsyringe, once formation of the ring had been confirmed spectroscopically. Where protonation was not achieved by direct addition of the $AlCl_3/^tBuCl$ mixture, a very small quantity of water was added to the mixture by microsyringe. Protonation was still not achieved for **5** or **6** even by this means, however. $CDCl_3$ was added to NMR samples to provide the deuterium lock. ^{31}P NMR spectra were recorded on Varian Mercury 200, Varian Unity 300, or Varian VXR 400 Fourier-transform spectrometers at 80.96, 121.40, or 161.91 MHz respectively; chemical shifts were measured relative to external 85% H_3PO_4.

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