**Supporting Information**

# Synthesis and structural characterization of a dendrimer model compound based on a cyclotriphosphazene core with TEMPO radicals as substituents.

*Elena Badetti,*[†,□] *Vega Lloveras,*[†,□] *Klaus Wurs,t*[⊥] *Rosa María Sebastián,*[‡] *Anne-Marie Caminade,*[§] *Jean-Pierre Majoral,*[§] *Jaume Veciana*[†,□] *and José Vidal-Gancedo.**[†,□]

[†]Institut de Ciència de Materials de Barcelona ICMAB–CSIC; Campus UAB, 08193 Bellaterra, Barcelona (Spain).

[□] CIBER de Bioingeniería, Biomateriales y Nanomedicina, CIBER-BBN, Barcelona (Spain).

[‡]Universitat Autònoma de Barcelona; Campus UAB, 08193 Bellaterra, Barcelona. (Spain)

[§]Laboratoire de Chimmie de la Coordination – CNRS, Route de Narbonne 205, 31077 Toulouse cedex 4 (France).

[⊥]Institut für Allgemeine Anorganische und Teoretische Chemie, Universität Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria.

**Table of Contents**

## 1. Experimental Procedure

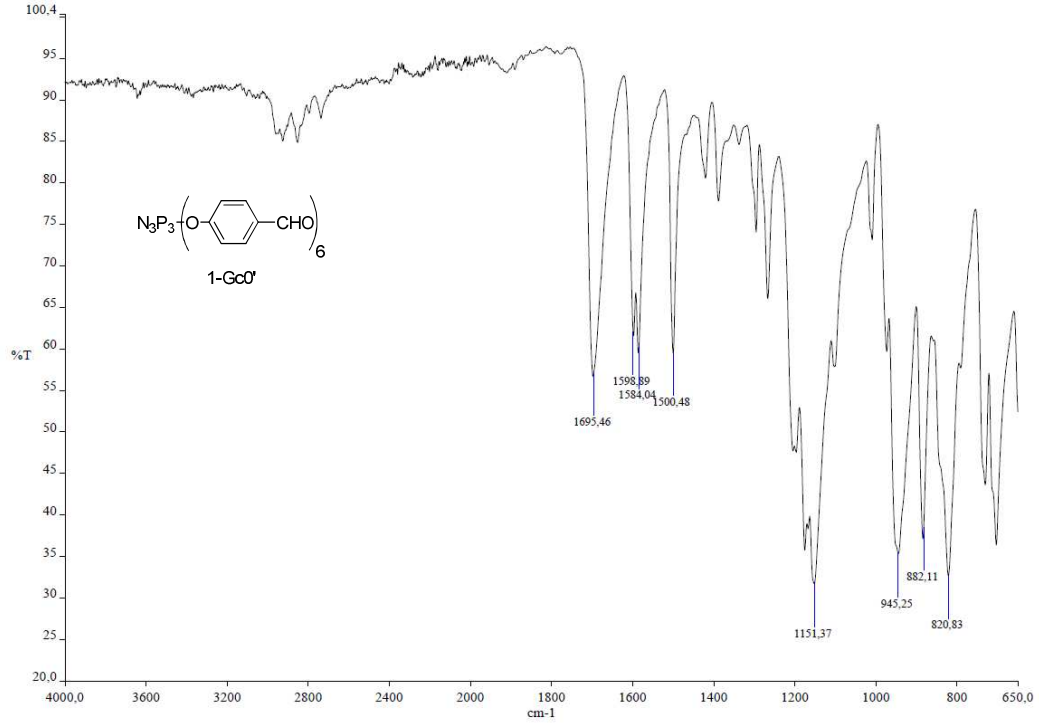
**General.** Compound **3-Gc$_0$T** was synthesized according to published procedures.[1] The preparation of dendrimer was performed under inert atmosphere with Schlenk type glassware and under dark conditions. Anhydrous solvents were used thoroughly.

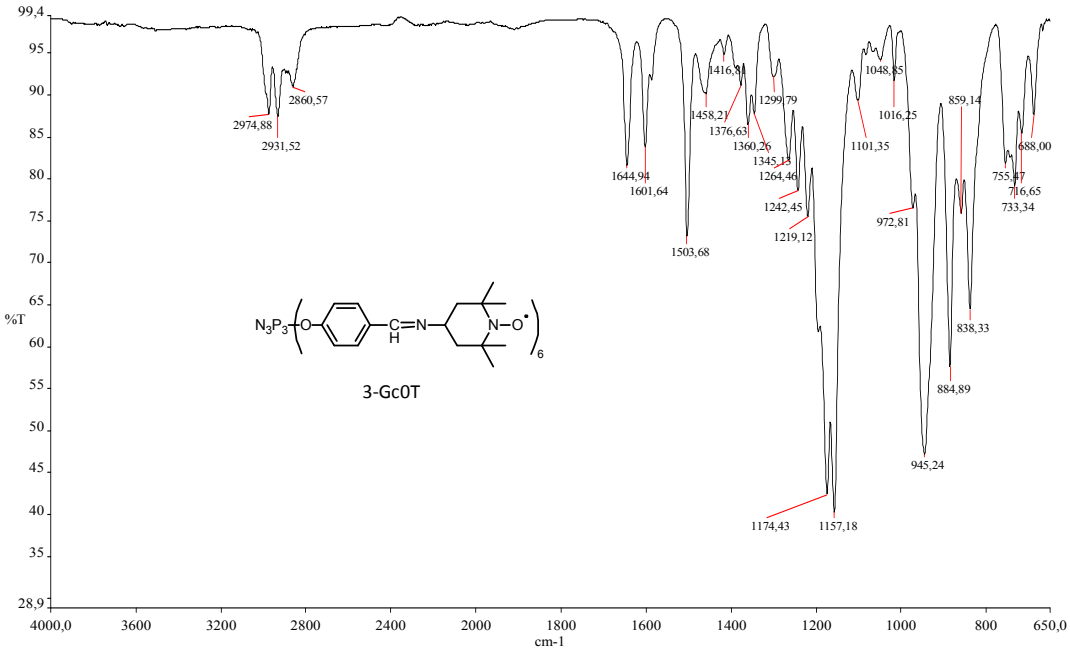
IR spectra were recorded in an attenuated total reflectance mode (ATR) in a Perkin Elmer Spectrum One Fourier transform spectrometer. NMR spectra were recorded in a Bruker AC250 instrument. $^{31}P\{^1H\}$ NMR (101.3 MHz) spectra were reported relative to $H_3PO_4$ 85% in water. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) spectra were recorded on a BIFLEX spectrometer (Bruker-Franzen Analytik) equipped with a pulsed nitrogen laser (337 nm), operating in positive-ion reflector mode, using 19 kV acceleration voltage. Matrices (4-Hydroxy-3,5-dimethoxycinnamic acid) were prepared at 5 mg/mL in tetrahydrofuran (THF). Analytes were dissolved at concentrations between 0.1 and 5 mg/mL in THF. EPR spectra were obtained in an X-Band Bruker ELEXYS 500 spectrometer equipped with a TE102 microwave cavity, a Bruker variable temperature unit, a field frequency lock system Bruker ER 033 M. Line positions were determined with an NMR Gaussmeter Bruker ER 035 M. The modulation amplitude was kept well below the line width, and the microwave power was well below saturation. Crystal structure was determined in a difractometer Nonius Kappa CCD diffractometer with an area detector and graphite-monochromized MoK$\alpha$ radiation ($\lambda$ = 0.71074 Å). The structure of the crystal was solved by direct methods and refined by full-matrix least squares method with SHELXTL software. CCDC-894232 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.

**Synthesis of 3-Gc$_0$T.** Dendrimer **1-Gc'$_0$** (0.05 g, 0.06 mmol) and free radical 4-amino-TEMPO **2** (0.08 g, 0.43 mmol) were dissolved in THF (1 mL). The mixture was stirred overnight. Pentane was added to the solution until the formation of an orange precipitate. The mixture was stirred for 10 min and filtered via cannula. The solid was washed with THF:pentane (1:10) several times and dried to afford 0.10 g of the hexaimine (97% yield) as an orange solid. IR (ATR) 2975, 2932, 2861, 1645, 1602, 1504, 1458, 1360, 1174, 1157, 945 cm$^{-1}$. $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$) $\delta$ 5.6 ppm. $^1$H-NMR (250 MHz, $CDCl_3$) See pag. S5. MALDI-TOF MS (matrix of 4-hydroxy-3,5-dimethoxycinnamic acid): *m/z* calcd for $C_{96}H_{132}N_{15}O_{12}P_3$, 1781 [M]; found, 1783 [M$^+$].

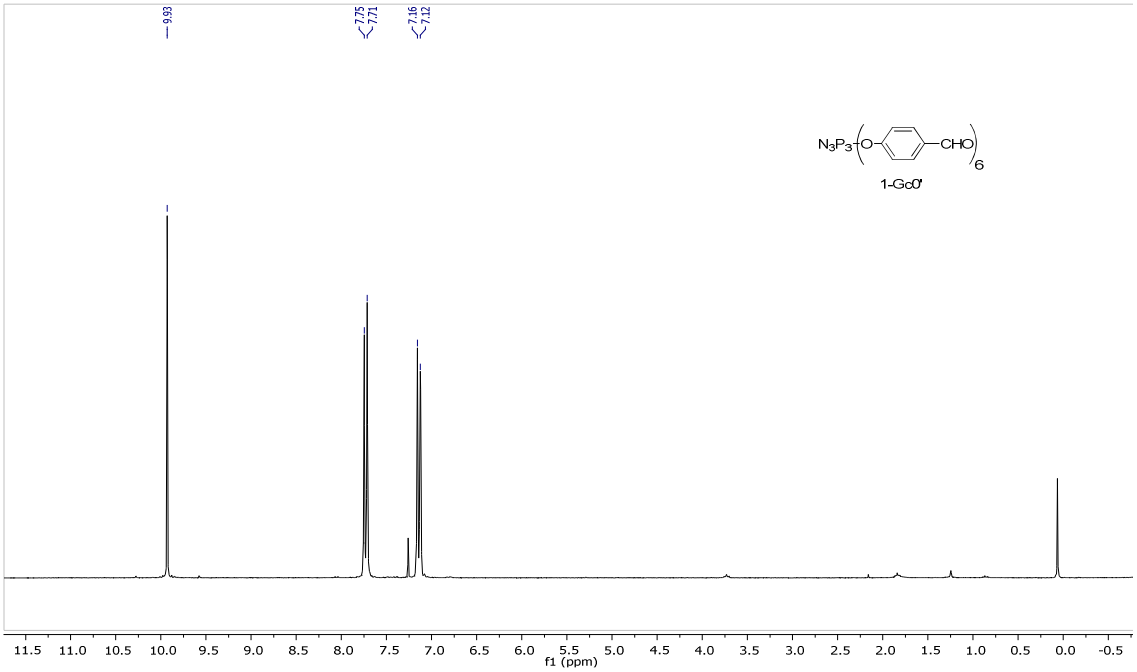
## 2. Collection of spectra

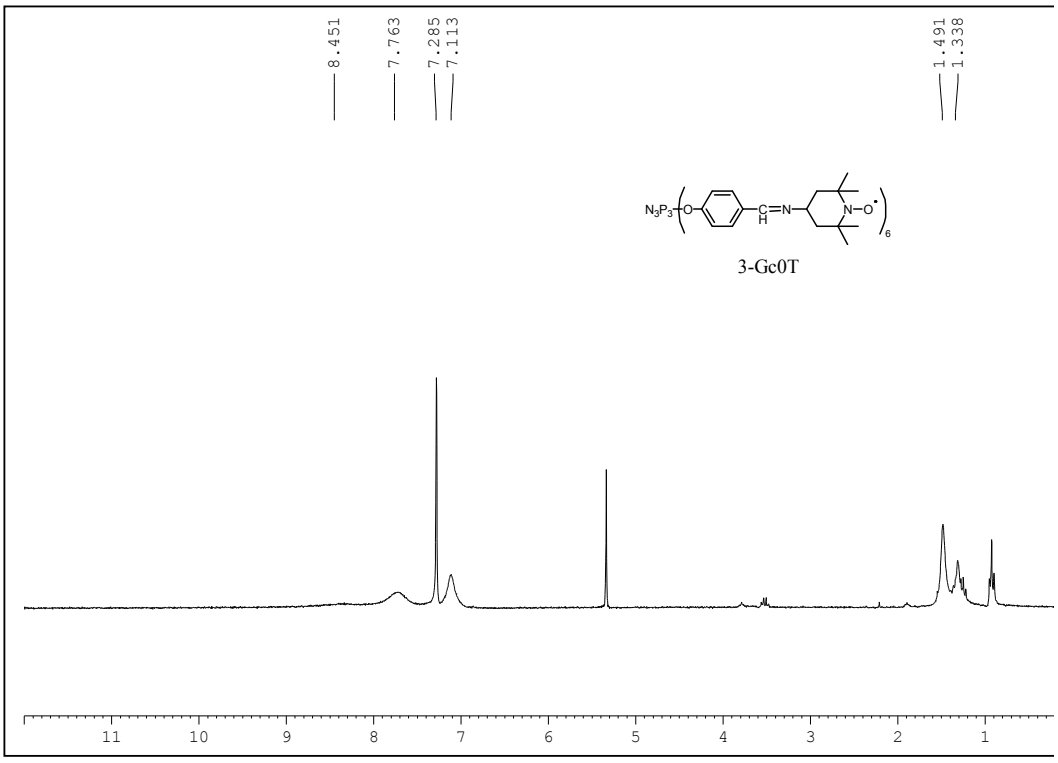
### FT-IR



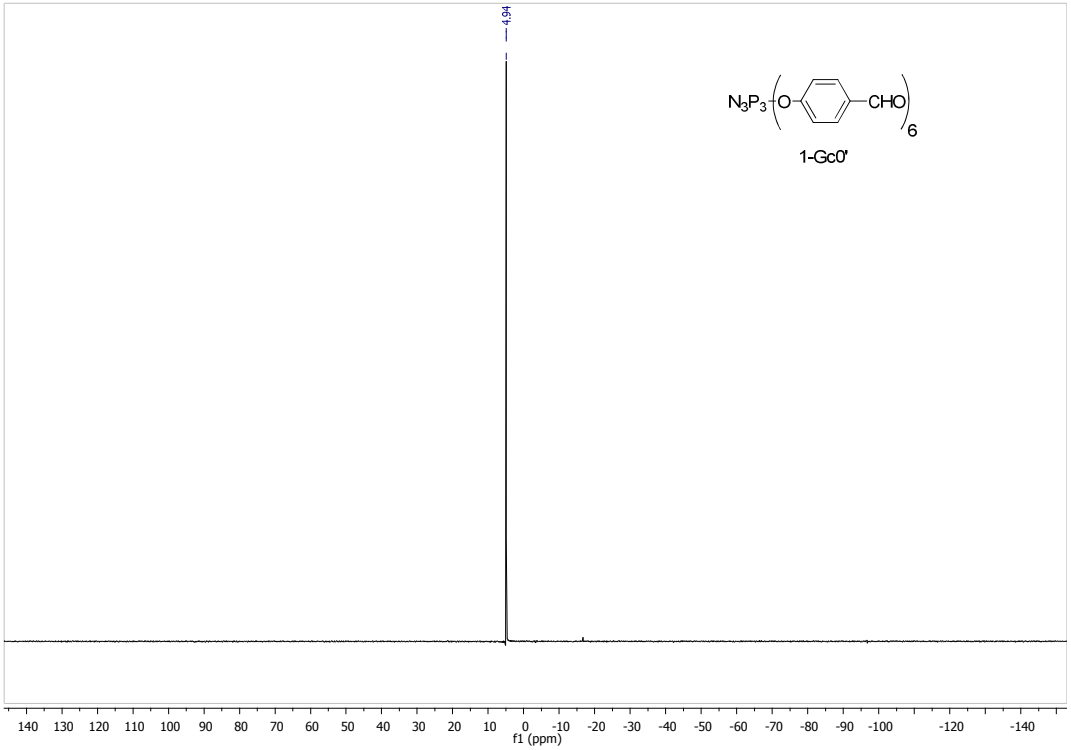
**$^{1}$H-NMR (250 MHz, $CDCl_3$) δ (ppm)**




The signals of the $^{1}$H NMR spectrum of **3-Gc$_0$T** are broad due to the presence of the paramagnetic radical units but it is possible to establish the appearance of the new imine proton (CH=N, 8.45 ppm) while the aldehyde proton at 9.93 ppm of **1-Gc$_0$'** clearly disappears. In addition, we can observe the phenyl ring protons of the dendrimeric branch at the same position: 7.76 and 7.11 ppm.

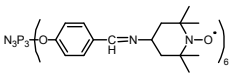
**$^{31}$P-NMR (101.3 MHz, $CDCl_3$) δ (ppm)**



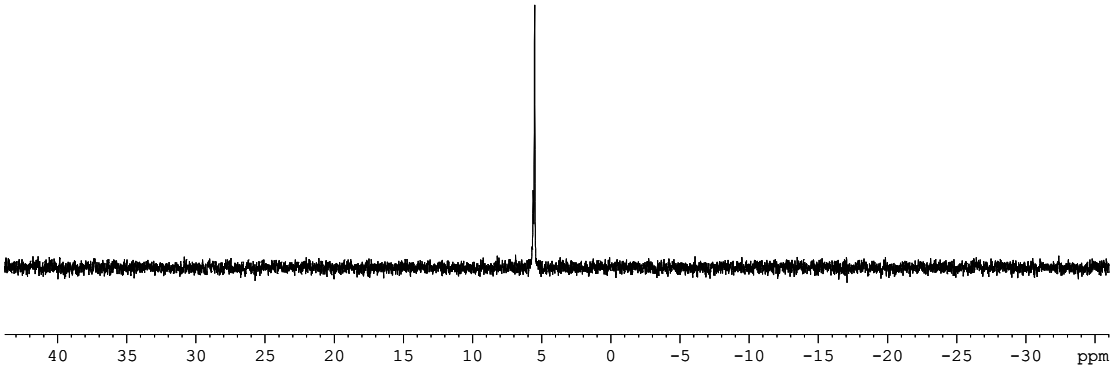




1-Gc0'

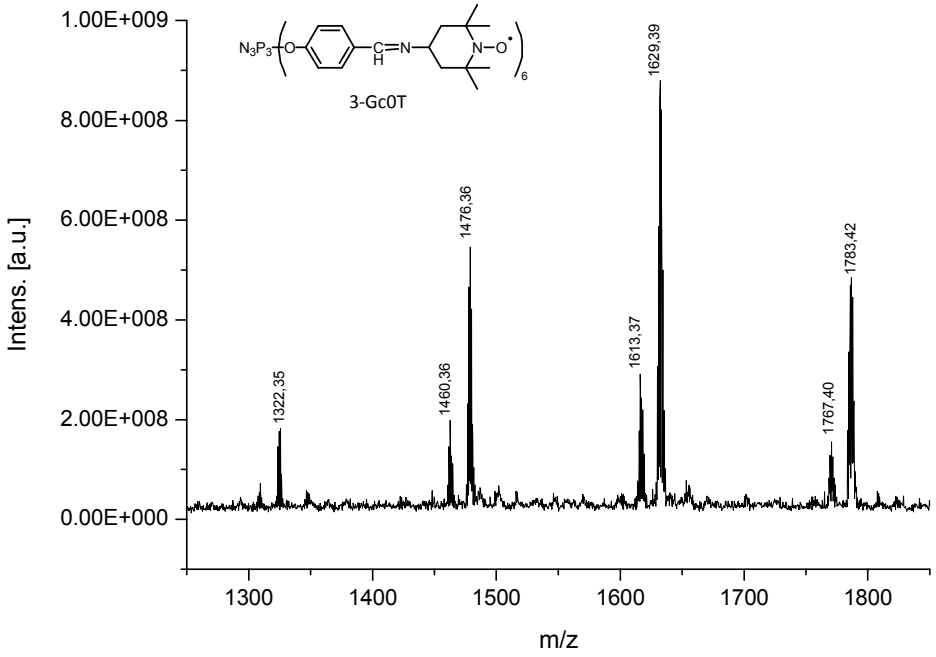


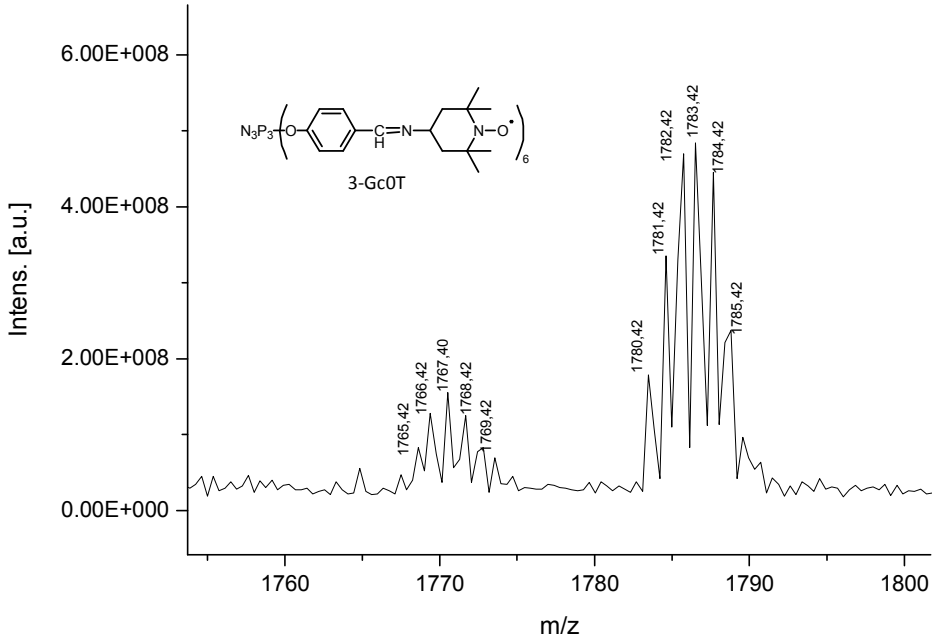

3-Gc0T



**MALDI-TOF MS (*m/z*)**

Matriz: 4-Hydroxy-3,5-dimethoxycinnamic acid (CIN)



### 3. X-ray diffraction analysis

The data collection conditions and the parameters of refinement process are listed in Table S1 while the most relevant structural parameters of **3-Gc$_0$T** are listed in Table S2. We can observe that there is a small asymmetry in the P-N-P and N-P-N bond angles of the phosphazene ring. The mean values of the N-P-N and P-N-P angles are 116.87 and 122.50 Å, respectively. This was also observed in the cyclic (*p*-halogenophenoxy)-phosphazene structures[2] and other related structures.[3-5] P-N bond lengths are 1.563(4)-1.585(4) retaining their phosphazenic character. On the other hand, there are elongations of *Ar*-O bond lengths of this compound compared with the normal value for *Ar*-O bonds.[6-8] Distances of P-O bonds also agree with normal P-O bonds[9-10] being these values similar to those observed in analogous structures deposited in the Cambridge Structural Database.

The molecular conformation of **3-Gc$_0$T** is defined by the twist of the branches around the P-O bonds which can be described by the torsion angles including the centroid X of the phospazene ring (Table S2). This molecular conformation is stabilised by C-H$\cdots\pi$ stacking interactions between the benzene rings of the closest branches as inferred from the analysis of atomic distances. Thus, the distance between atom $H_{102}$ ($C_{102}$) and the centroid of benzene ring 1 is around 2.74 Å, which is shorter than the distance between $H_{506}$ ($C_{506}$) and the centroid of ring 2 of 3.14 Å. The longer distance is probably caused by steric interactions, because on the opposite side of ring 2 an intermolecular C-H$\cdots\pi$ stacking of atom $H_{603}$ ($C_{603}$) occurs with a distance of 2.88 Å (see Figure S1). On the other side of the cyclotriphosphazene ring are only intramolecular interactions of 2.74 and 2.72 Å between $H_{406}$ and ring 5 and $H_{202}$ and ring 6, respectively. A worth noticing point of the molecular structure is that all TEMPO radical units have a distorted chair conformation with $C_s$ symmetry with the two $CH_2$-$C(Me)_2$-groups coplanar.

The global flat geometry of the molecule allows an optimised crystal packing of the molecules forming sheets perpendicular to the crystallographic *c*-axis. Figure S1 shows the build-up of sheets along the *a*-axis with alternate enantiomeric molecules connected by the C-H$\cdots\pi$ stacking interactions of $H_{603}$ ($C_{603}$) with benzene ring 2 and two weak hydrogen bonds between a $H_{methyl}$ of TEMPO 5 and the $O_3$ atom and between $H_{aryl}$ of benzene ring 5 and the $O_{12}$ of TEMPO 6, both with a distance of 2.52 Å. The

interactions within the sheet are completed by a hydrogen bond between two TEMPOs by a common translation along the *b*-axis with a distance of 2.44 Å between H atom at $C_{609}$ and $O_8$ (see Figure S2). Figure S2 shows two great cavities, A and B, existing between the branches of neighbouring molecules, which are filled with toluene solvent molecules and are covered by the neighbouring sheets. Note, that the thickness of the sheets is 12.9 Å, half the lattice constant of the *c*-axis, and that each cavity possess a volume of around 670 $Å^3$. Finally, the crystal packing is completed in the third dimension by connecting the sheets through one further hydrogen bond with a length of 2.53 Å between two TEMPOs.

All the geometric parameters are listed below in Tables S2, S3, S4 and S5.

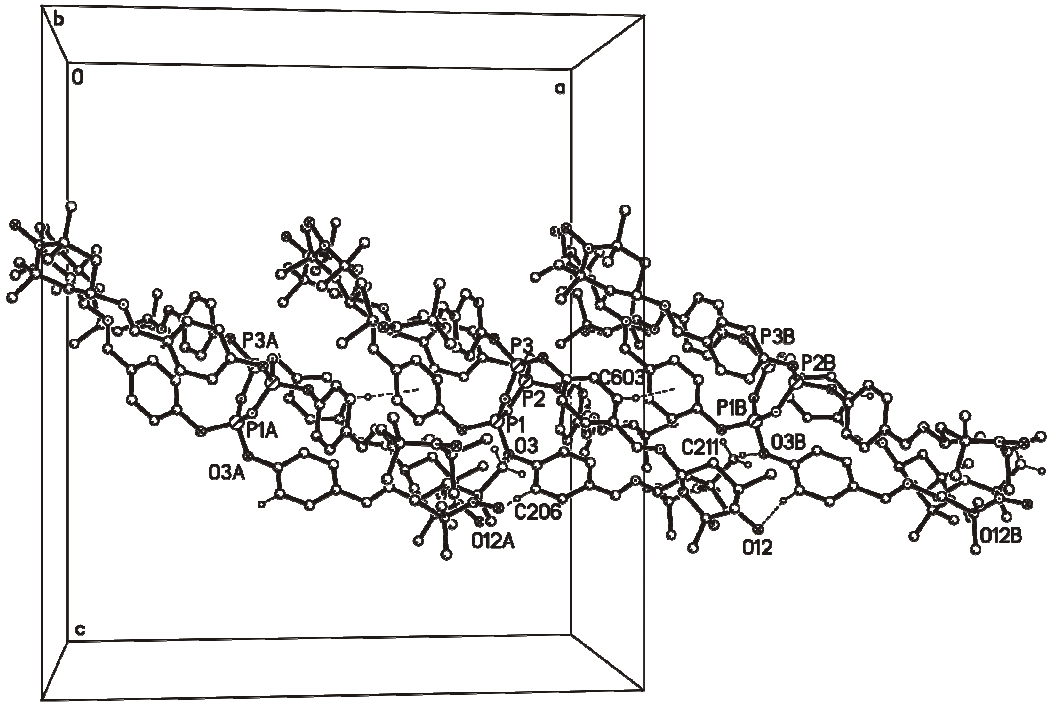



**Figure S1**. Packing scheme with hydrogen bonds along the *a*-axis. Symmetry codes: A: -0.5 + x, 0.5 – y, z; A: 0.5 + x, 0.5 – y, z.

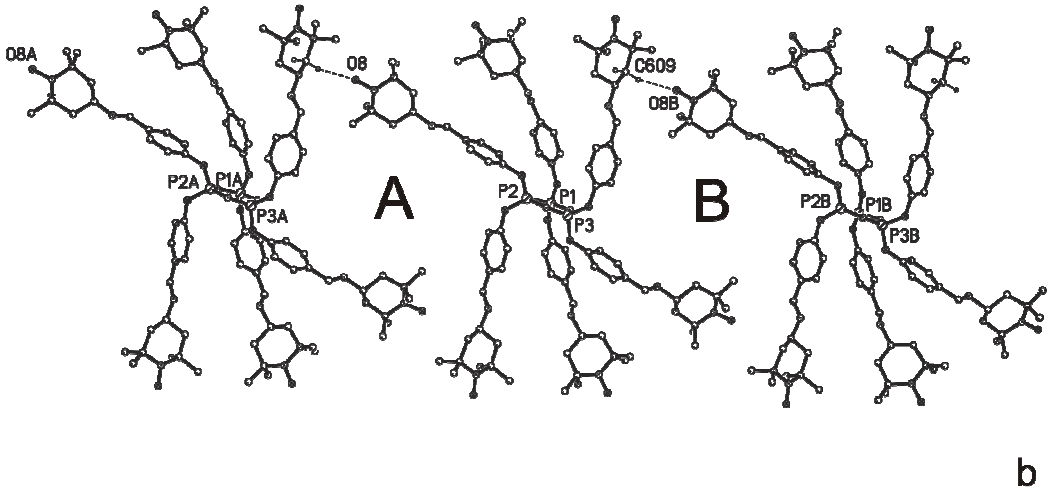



**Figure S2**. Packing scheme with hydrogen bonds along the *b*-axis. Symmetry codes: A: x, -1 + y, z; B: x, 1 + y, z.

**Table S1**. Data collection conditions and parameters of refinement process.

| | |
|---|---|
| Empirical formula | $C_{96}H_{132}N_{15}O_{12}P_3$ x 3 $C_7H_8$ |
| Formula weight | 2057.48 |
| Temperature | 233(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Orthorhombic |
| Space group | $Pna2_1$ (no. 33) |
| Unit cell dimensions | a = 22.7570(3) Å ; $\alpha$= 90° |
| | b = 19.7108(3) Å ; $\beta$= 90° |
| | c = 25.8479(4) Å ; $\gamma$ = 90° |
| Volume | 11594.3(3) $Å^3$ |
| z | 4 |
| Density (calculated) | 1.179 $Mg/m^3$ |
| Absorption coefficient | 0.116 $mm^{-1}$ |
| F(000) | 4416 |
| Crystal size | 0.35 x 0.31 x 0.19 $mm^3$ |
| Theta range for data collection | 1.37 to 22.00° |
| Index ranges | -23<=h<=23, -20<=k<=20, -26<=l<=27 |

| | |
|---|---|
| Reflections collected | 49072 |
| Independent reflections | 14004 [R(int) = 0.0568] |
| Reflections [I>2sigma(I)] | 11699 |
| Completeness to theta = 22.00° | 99.8 % |

**Table S2**. Selected bond lengths (in Å) angles and torsion angles (in degrees) with centroid X of the phospazene ring.

| | | | |
|---|---|---|---|
| P(1)-N(1) | 1.580(4) | N(1)-P(2)-N(2) | 117.0(2) |
| P(1)-N(3) | 1.585(4) | N(1)-P(1)-N(3) | 116.5(2) |
| P(2)-N(1) | 1.568(4) | N(2)-P(3)-N(3) | 117.1(2) |
| P(2)-N(2) | 1.584(4) | | |
| P(3)-N(2) | 1.563(4) | P(2)-N(1)-P(1) | 122.9(2) |
| P(3)-N(3) | 1.578(4) | P(3)-N(2)-P(2) | 122.5(3) |
| P(1)-O(1) | 1.585(3) | P(3)-N(3)-P(1) | 122.1(2) |
| P(1)-O(3) | 1.580(4) | | |
| P(2)-O(5) | 1.584(3) | O(1)-P(1)-O(3) | 96.19(19) |
| P(2)-O(7) | 1.581(3) | O(5)-P(2)-O(7) | 99.02(17) |
| P(3)-O(9) | 1.598(3) | O(9)-P(3)-O(11) | 98.32(16) |
| P(3)-O(11) | 1.593(3) | | |
| O(1)-C(101) | 1.426(6) | X-P(1)-O(1)-C(101) | -33.6 |
| O(3)-C(201) | 1.420(6) | X-P(2)-O(5)-C(301) | -9.8 |
| O(5)-C(301) | 1.412(6) | X-P(3)-O(9)-C(501) | 129.6 |
| O(7)-C(401) | 1.414(5) | X-P(1)-O(3)-C(201) | -31.4 |
| O(9)-C(501) | 1.391(5) | X-P(2)-O(7)-C(401) | 133.3 |
| O(11)-C(601) | 1.401(6) | X-P(3)-O(11)-C(601) | -14.9 |

**Table S3.** Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$). U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| P(1) | 8271(1) | 2283(1) | 6169(1) | 41(1) |
| P(2) | 8922(1) | 1490(1) | 5497(1) | 40(1) |
| P(3) | 8624(1) | 2799(1) | 5222(1) | 39(1) |
| O(1) | 7597(1) | 2208(2) | 6309(1) | 53(1) |
| O(2) | 4585(2) | 4244(3) | 2883(2) | 98(2) |
| O(3) | 8484(2) | 2469(2) | 6733(1) | 53(1) |
| O(4) | 13003(3) | -292(3) | 7499(3) | 132(2) |
| O(5) | 8729(1) | 809(2) | 5220(1) | 48(1) |
| O(6) | 4284(2) | -15(3) | 2980(2) | 93(1) |
| O(7) | 9585(1) | 1306(2) | 5614(1) | 45(1) |
| O(8) | 11909(3) | -3957(3) | 6394(2) | 128(2) |
| O(9) | 8151(1) | 2892(2) | 4771(1) | 44(1) |
| O(10) | 5708(2) | 8242(2) | 4611(2) | 96(2) |
| O(11) | 9033(1) | 3431(2) | 5089(1) | 46(1) |
| O(12) | 13067(2) | 4128(2) | 7944(2) | 73(1) |
| N(1) | 8546(2) | 1581(2) | 6000(2) | 43(1) |
| N(2) | 8940(2) | 2111(2) | 5108(2) | 46(1) |
| N(3) | 8363(2) | 2899(2) | 5783(2) | 42(1) |
| N(4) | 5841(2) | 3043(2) | 4466(2) | 64(1) |
| N(5) | 4880(2) | 3961(3) | 3254(2) | 69(1) |
| N(6) | 11108(3) | 1430(4) | 7222(3) | 106(2) |
| N(7) | 12568(3) | 104(3) | 7424(3) | 94(2) |
| N(8) | 6195(2) | 374(3) | 4230(2) | 75(1) |
| N(9) | 4710(2) | 50(3) | 3300(2) | 68(1) |
| N(10) | 10684(3) | -1570(2) | 6193(2) | 78(2) |
| N(11) | 11620(3) | -3389(3) | 6379(2) | 90(2) |

| | | | | |
|---|---|---|---|---|
| N(12) | 6820(3) | 5752(3) | 4589(2) | 77(2) |
| N(13) | 5970(2) | 7657(2) | 4600(2) | 67(1) |
| N(14) | 11204(2) | 3979(2) | 6601(2) | 62(1) |
| N(15) | 12644(2) | 4087(2) | 7625(2) | 52(1) |
| C(101) | 7146(2) | 2386(3) | 5950(2) | 46(1) |
| C(102) | 7127(2) | 2138(3) | 5464(2) | 53(1) |
| C(103) | 6693(2) | 2361(3) | 5130(2) | 57(1) |
| C(104) | 6287(2) | 2828(3) | 5290(2) | 51(1) |
| C(105) | 6287(2) | 3031(3) | 5795(3) | 68(2) |
| C(106) | 6719(2) | 2819(3) | 6136(2) | 62(2) |
| C(107) | 5830(2) | 3115(3) | 4938(3) | 66(2) |
| C(108) | 5379(2) | 3414(3) | 4179(2) | 67(2) |
| C(109) | 5649(3) | 4024(3) | 3911(3) | 81(2) |
| C(110) | 5228(3) | 4437(3) | 3593(3) | 88(2) |
| C(111) | 5567(5) | 4900(5) | 3230(5) | 158(5) |
| C(112) | 4788(5) | 4838(5) | 3930(4) | 146(4) |
| C(113) | 5135(3) | 2948(3) | 3756(3) | 70(2) |
| C(114) | 4675(3) | 3289(3) | 3420(2) | 65(2) |
| C(115) | 4570(4) | 2879(4) | 2926(3) | 109(3) |
| C(116) | 4085(3) | 3339(5) | 3709(3) | 109(3) |
| C(201) | 9049(2) | 2284(2) | 6920(2) | 45(1) |
| C(202) | 9545(2) | 2520(3) | 6684(2) | 64(2) |
| C(203) | 10096(3) | 2295(4) | 6877(3) | 78(2) |
| C(204) | 10131(2) | 1869(3) | 7280(2) | 61(2) |
| C(205) | 9619(2) | 1661(3) | 7520(2) | 62(2) |
| C(206) | 9070(2) | 1870(3) | 7340(2) | 58(1) |
| C(207) | 10691(3) | 1529(6) | 7472(3) | 112(3) |
| C(208) | 11607(3) | 1017(4) | 7434(3) | 89(2) |
| C(209) | 12181(4) | 1202(5) | 7157(5) | 136(4) |
| C(210) | 12713(4) | 816(4) | 7340(5) | 126(4) |
| C(211) | 13182(5) | 812(6) | 6882(6) | 166(5) |
| C(212) | 13000(5) | 1156(5) | 7785(5) | 144(4) |

| | | | | |
|---|---|---|---|---|
| C(213) | 11508(4) | 327(5) | 7392(6) | 163(5) |
| C(214) | 12017(4) | -115(5) | 7656(4) | 122(3) |
| C(215) | 11908(4) | -836(4) | 7445(5) | 130(3) |
| C(216) | 12062(8) | -66(11) | 8253(4) | 244(10) |
| C(301) | 8135(2) | 686(2) | 5093(2) | 45(1) |
| C(302) | 7922(2) | 920(3) | 4630(2) | 60(2) |
| C(303) | 7347(2) | 764(3) | 4496(2) | 59(1) |
| C(304) | 6996(2) | 380(3) | 4817(2) | 51(1) |
| C(305) | 7219(2) | 166(3) | 5286(2) | 59(1) |
| C(306) | 7797(2) | 325(3) | 5425(2) | 53(1) |
| C(307) | 6405(2) | 182(3) | 4653(2) | 62(2) |
| C(308) | 5619(2) | 122(3) | 4061(2) | 70(2) |
| C(309) | 5727(3) | -227(5) | 3540(3) | 105(3) |
| C(310) | 5165(3) | -484(5) | 3276(3) | 96(3) |
| C(311) | 5297(5) | -636(8) | 2711(5) | 178(6) |
| C(312) | 4910(5) | -1130(5) | 3550(6) | 172(6) |
| C(313) | 5204(3) | 705(4) | 3978(3) | 88(2) |
| C(314) | 4616(3) | 512(3) | 3740(3) | 80(2) |
| C(315) | 4289(4) | 1125(4) | 3551(5) | 139(4) |
| C(316) | 4213(4) | 165(6) | 4131(4) | 122(3) |
| C(401) | 9772(2) | 691(2) | 5843(2) | 41(1) |
| C(402) | 10059(4) | 245(3) | 5536(2) | 90(2) |
| C(403) | 10284(4) | -332(4) | 5742(3) | 104(3) |
| C(404) | 10206(2) | -494(3) | 6256(2) | 53(1) |
| C(405) | 9927(3) | -28(3) | 6556(2) | 63(2) |
| C(406) | 9710(2) | 570(3) | 6350(2) | 57(1) |
| C(407) | 10455(3) | -1122(3) | 6481(2) | 63(2) |
| C(408) | 10934(3) | -2179(3) | 6434(2) | 79(2) |
| C(409) | 11591(3) | -2162(3) | 6340(3) | 89(2) |
| C(410) | 11926(4) | -2776(4) | 6553(3) | 100(3) |
| C(411) | 12543(5) | -2797(6) | 6318(5) | 150(4) |
| C(412) | 11963(6) | -2777(5) | 7152(4) | 155(5) |

| | | | | |
|---|---|---|---|---|
| C(413) | 10700(3) | -2795(3) | 6172(3) | 79(2) |
| C(414) | 10971(4) | -3478(3) | 6361(3) | 81(2) |
| C(415) | 10825(4) | -4019(4) | 5965(3) | 108(3) |
| C(416) | 10747(5) | -3669(4) | 6894(4) | 134(4) |
| C(501) | 7849(2) | 3491(2) | 4669(2) | 44(1) |
| C(502) | 7789(2) | 3668(3) | 4171(2) | 57(1) |
| C(503) | 7486(3) | 4263(3) | 4043(2) | 67(2) |
| C(504) | 7255(2) | 4674(3) | 4411(2) | 53(1) |
| C(505) | 7293(3) | 4465(3) | 4914(2) | 80(2) |
| C(506) | 7600(3) | 3872(3) | 5050(2) | 83(2) |
| C(507) | 6968(3) | 5319(3) | 4263(2) | 62(2) |
| C(508) | 6533(3) | 6379(3) | 4410(2) | 72(2) |
| C(509) | 6886(3) | 6987(3) | 4615(3) | 72(2) |
| C(510) | 6603(3) | 7673(3) | 4505(3) | 72(2) |
| C(511) | 6708(4) | 7884(4) | 3942(3) | 112(3) |
| C(512) | 6870(3) | 8210(4) | 4860(3) | 93(2) |
| C(513) | 5937(3) | 6417(3) | 4634(3) | 71(2) |
| C(514) | 5591(3) | 7054(3) | 4502(2) | 75(2) |
| C(515) | 5391(4) | 7033(4) | 3923(3) | 104(3) |
| C(516) | 5048(3) | 7103(4) | 4849(3) | 101(2) |
| C(601) | 9457(2) | 3649(2) | 5444(2) | 43(1) |
| C(602) | 10020(2) | 3391(3) | 5421(2) | 52(1) |
| C(603) | 10435(2) | 3605(3) | 5777(2) | 53(1) |
| C(604) | 10292(2) | 4072(2) | 6149(2) | 45(1) |
| C(605) | 9730(2) | 4351(2) | 6154(2) | 56(1) |
| C(606) | 9314(2) | 4139(3) | 5792(2) | 61(2) |
| C(607) | 10718(2) | 4257(3) | 6559(2) | 50(1) |
| C(608) | 11587(2) | 4173(3) | 7031(2) | 55(1) |
| C(609) | 12150(2) | 4450(3) | 6823(2) | 52(1) |
| C(610) | 12593(2) | 4651(3) | 7250(2) | 54(1) |
| C(611) | 13192(3) | 4764(3) | 7000(2) | 74(2) |
| C(612) | 12400(3) | 5298(3) | 7535(2) | 75(2) |

| | | | | |
|---|---|---|---|---|
| C(613) | 11724(2) | 3531(3) | 7332(2) | 57(1) |
| C(614) | 12145(2) | 3634(3) | 7778(2) | 56(1) |
| C(615) | 12420(3) | 2955(3) | 7923(3) | 86(2) |
| C(616) | 11842(3) | 3933(4) | 8256(2) | 75(2) |
| C(1) | 8399(8) | 7359(9) | 7952(7) | 211(6) |
| C(2) | 8495(6) | 8030(7) | 7762(6) | 167(4) |
| C(3) | 8799(8) | 8151(9) | 7297(7) | 216(7) |
| C(4) | 9051(10) | 7669(12) | 6996(9) | 268(9) |
| C(5) | 8963(11) | 7086(12) | 7277(9) | 271(9) |
| C(6) | 8688(8) | 6832(9) | 7697(8) | 211(6) |
| C(7) | 8095(10) | 7159(11) | 8414(9) | 266(9) |
| C(8) | 8635(5) | 8510(6) | 5101(5) | 154(4) |
| C(9) | 8549(5) | 7820(6) | 4980(5) | 144(4) |
| C(10) | 8516(6) | 7658(7) | 4446(5) | 169(4) |
| C(11) | 8537(8) | 8116(9) | 4043(7) | 223(7) |
| C(12) | 8633(7) | 8805(9) | 4206(7) | 214(6) |
| C(13) | 8673(6) | 8999(7) | 4710(6) | 169(4) |
| C(14) | 8784(10) | 8679(12) | 5630(8) | 284(10) |
| C(15) | 7942(8) | 5797(10) | 5862(8) | 225(7) |
| C(16) | 8181(8) | 5871(9) | 5370(7) | 205(6) |
| C(17) | 8687(11) | 6039(14) | 5113(10) | 315(12) |
| C(18) | 9155(9) | 6140(10) | 5457(8) | 239(7) |
| C(19) | 9007(8) | 6096(9) | 5996(8) | 219(7) |
| C(20) | 8455(8) | 5919(10) | 6231(8) | 230(7) |
| C(21) | 7401(14) | 5480(20) | 6086(17) | 450(20) |

**Table S4.** Bond lengths [Å] and angles [°] for geotem.

| | |
|---|---|
| P(1)-O(3) | 1.580(4) |
| P(1)-N(1) | 1.580(4) |
| P(1)-O(1) | 1.585(3) |
| P(1)-N(3) | 1.585(4) |
| P(2)-N(1) | 1.568(4) |
| P(2)-O(7) | 1.581(3) |
| P(2)-N(2) | 1.584(4) |
| P(2)-O(5) | 1.584(3) |
| P(3)-N(2) | 1.563(4) |
| P(3)-N(3) | 1.578(4) |
| P(3)-O(11) | 1.593(3) |
| P(3)-O(9) | 1.598(3) |
| O(1)-C(101) | 1.426(6) |
| O(2)-N(5) | 1.295(6) |
| O(3)-C(201) | 1.420(6) |
| O(4)-N(7) | 1.275(7) |
| O(5)-C(301) | 1.412(6) |
| O(6)-N(9) | 1.281(6) |
| O(7)-C(401) | 1.414(5) |
| O(8)-N(11) | 1.298(7) |
| O(9)-C(501) | 1.391(5) |
| O(10)-N(13) | 1.299(6) |
| O(11)-C(601) | 1.401(6) |
| O(12)-N(15) | 1.271(5) |
| N(4)-C(107) | 1.228(8) |
| N(4)-C(108) | 1.481(7) |
| N(5)-C(114) | 1.469(8) |
| N(5)-C(110) | 1.509(8) |
| N(6)-C(207) | 1.163(9) |
| N(6)-C(208) | 1.502(9) |

| | |
|---|---|
| N(7)-C(210) | 1.456(11) |
| N(7)-C(214) | 1.457(11) |
| N(8)-C(307) | 1.251(7) |
| N(8)-C(308) | 1.468(7) |
| N(9)-C(314) | 1.472(8) |
| N(9)-C(310) | 1.478(8) |
| N(10)-C(407) | 1.266(7) |
| N(10)-C(408) | 1.467(7) |
| N(11)-C(410) | 1.466(10) |
| N(11)-C(414) | 1.487(10) |
| N(12)-C(507) | 1.247(7) |
| N(12)-C(508) | 1.473(7) |
| N(13)-C(510) | 1.462(8) |
| N(13)-C(514) | 1.490(8) |
| N(14)-C(607) | 1.239(6) |
| N(14)-C(608) | 1.462(7) |
| N(15)-C(610) | 1.480(7) |
| N(15)-C(614) | 1.497(7) |
| C(101)-C(102) | 1.349(8) |
| C(101)-C(106) | 1.380(7) |
| C(102)-C(103) | 1.385(8) |
| C(103)-C(104) | 1.368(7) |
| C(104)-C(105) | 1.364(8) |
| C(104)-C(107) | 1.493(8) |
| C(105)-C(106) | 1.384(8) |
| C(108)-C(109) | 1.517(9) |
| C(108)-C(113) | 1.531(9) |
| C(109)-C(110) | 1.502(9) |
| C(110)-C(111) | 1.518(12) |
| C(110)-C(112) | 1.545(12) |
| C(113)-C(114) | 1.517(9) |
| C(114)-C(115) | 1.532(10) |

| | |
|---|---|
| C(114)-C(116) | 1.539(10) |
| C(201)-C(206) | 1.358(7) |
| C(201)-C(202) | 1.365(7) |
| C(202)-C(203) | 1.419(9) |
| C(203)-C(204) | 1.340(9) |
| C(204)-C(205) | 1.384(8) |
| C(204)-C(207) | 1.523(10) |
| C(205)-C(206) | 1.394(8) |
| C(208)-C(213) | 1.383(11) |
| C(208)-C(209) | 1.533(13) |
| C(209)-C(210) | 1.506(12) |
| C(210)-C(212) | 1.485(13) |
| C(210)-C(211) | 1.594(16) |
| C(213)-C(214) | 1.601(14) |
| C(214)-C(215) | 1.543(13) |
| C(214)-C(216) | 1.549(16) |
| C(301)-C(306) | 1.356(7) |
| C(301)-C(302) | 1.371(7) |
| C(302)-C(303) | 1.387(8) |
| C(303)-C(304) | 1.380(7) |
| C(304)-C(305) | 1.379(8) |
| C(304)-C(307) | 1.464(7) |
| C(305)-C(306) | 1.399(7) |
| C(308)-C(313) | 1.502(9) |
| C(308)-C(309) | 1.533(10) |
| C(309)-C(310) | 1.535(10) |
| C(310)-C(311) | 1.521(13) |
| C(310)-C(312) | 1.569(15) |
| C(313)-C(314) | 1.521(9) |
| C(314)-C(315) | 1.500(11) |
| C(314)-C(316) | 1.527(12) |
| C(401)-C(406) | 1.341(7) |

| | |
|---|---|
| C(401)-C(402) | 1.353(8) |
| C(402)-C(403) | 1.355(8) |
| C(403)-C(404) | 1.379(8) |
| C(404)-C(405) | 1.359(7) |
| C(404)-C(407) | 1.479(7) |
| C(405)-C(406) | 1.383(8) |
| C(408)-C(413) | 1.489(10) |
| C(408)-C(409) | 1.516(11) |
| C(409)-C(410) | 1.531(9) |
| C(410)-C(411) | 1.531(14) |
| C(410)-C(412) | 1.550(12) |
| C(413)-C(414) | 1.559(9) |
| C(414)-C(415) | 1.516(11) |
| C(414)-C(416) | 1.516(10) |
| C(501)-C(502) | 1.340(7) |
| C(501)-C(506) | 1.364(8) |
| C(502)-C(503) | 1.401(8) |
| C(503)-C(504) | 1.353(8) |
| C(504)-C(505) | 1.367(8) |
| C(504)-C(507) | 1.479(7) |
| C(505)-C(506) | 1.407(8) |
| C(508)-C(513) | 1.477(9) |
| C(508)-C(509) | 1.537(9) |
| C(509)-C(510) | 1.523(8) |
| C(510)-C(512) | 1.528(10) |
| C(510)-C(511) | 1.533(10) |
| C(513)-C(514) | 1.522(9) |
| C(514)-C(516) | 1.530(10) |
| C(514)-C(515) | 1.564(10) |
| C(601)-C(606) | 1.357(8) |
| C(601)-C(602) | 1.378(7) |
| C(602)-C(603) | 1.383(7) |

| | |
|---|---|
| C(603)-C(604) | 1.370(7) |
| C(604)-C(605) | 1.391(7) |
| C(604)-C(607) | 1.485(7) |
| C(605)-C(606) | 1.398(8) |
| C(608)-C(609) | 1.494(8) |
| C(608)-C(613) | 1.517(8) |
| C(609)-C(610) | 1.546(7) |
| C(610)-C(611) | 1.524(8) |
| C(610)-C(612) | 1.537(8) |
| C(613)-C(614) | 1.513(8) |
| C(614)-C(615) | 1.522(8) |
| C(614)-C(616) | 1.535(9) |
| C(1)-C(6) | 1.396(15) |
| C(1)-C(2) | 1.427(14) |
| C(1)-C(7) | 1.434(16) |
| C(2)-C(3) | 1.408(15) |
| C(3)-C(4) | 1.356(16) |
| C(4)-C(5) | 1.375(17) |
| C(5)-C(6) | 1.348(16) |
| C(8)-C(13) | 1.399(13) |
| C(8)-C(9) | 1.408(12) |
| C(8)-C(14) | 1.447(16) |
| C(9)-C(10) | 1.420(13) |
| C(10)-C(11) | 1.380(15) |
| C(11)-C(12) | 1.437(15) |
| C(12)-C(13) | 1.363(14) |
| C(15)-C(16) | 1.392(15) |
| C(15)-C(21) | 1.496(19) |
| C(15)-C(20) | 1.526(15) |
| C(16)-C(17) | 1.369(17) |
| C(17)-C(18) | 1.401(17) |
| C(18)-C(19) | 1.436(16) |

| | |
|---|---|
| C(19)-C(20) | 1.438(15) |

| | |
|---|---|
| O(3)-P(1)-N(1) | 109.6(2) |
| O(3)-P(1)-O(1) | 96.19(19) |
| N(1)-P(1)-O(1) | 111.3(2) |
| O(3)-P(1)-N(3) | 111.3(2) |
| N(1)-P(1)-N(3) | 116.5(2) |
| O(1)-P(1)-N(3) | 110.08(19) |
| N(1)-P(2)-O(7) | 112.9(2) |
| N(1)-P(2)-N(2) | 117.0(2) |
| O(7)-P(2)-N(2) | 105.88(19) |
| N(1)-P(2)-O(5) | 108.63(19) |
| O(7)-P(2)-O(5) | 99.02(17) |
| N(2)-P(2)-O(5) | 112.0(2) |
| N(2)-P(3)-N(3) | 117.1(2) |
| N(2)-P(3)-O(11) | 111.65(19) |
| N(3)-P(3)-O(11) | 108.7(2) |
| N(2)-P(3)-O(9) | 105.8(2) |
| N(3)-P(3)-O(9) | 113.70(19) |
| O(11)-P(3)-O(9) | 98.32(16) |
| C(101)-O(1)-P(1) | 121.6(3) |
| C(201)-O(3)-P(1) | 122.1(3) |
| C(301)-O(5)-P(2) | 121.1(3) |
| C(401)-O(7)-P(2) | 124.4(3) |
| C(501)-O(9)-P(3) | 124.7(3) |
| C(601)-O(11)-P(3) | 120.1(3) |
| P(2)-N(1)-P(1) | 122.9(2) |
| P(3)-N(2)-P(2) | 122.5(3) |
| P(3)-N(3)-P(1) | 122.1(2) |
| C(107)-N(4)-C(108) | 115.3(5) |
| O(2)-N(5)-C(114) | 116.2(5) |
| O(2)-N(5)-C(110) | 115.7(5) |

| | |
|---|---|
| C(114)-N(5)-C(110) | 123.8(5) |
| C(207)-N(6)-C(208) | 120.3(8) |
| O(4)-N(7)-C(210) | 116.0(6) |
| O(4)-N(7)-C(214) | 115.0(6) |
| C(210)-N(7)-C(214) | 122.8(7) |
| C(307)-N(8)-C(308) | 119.9(5) |
| O(6)-N(9)-C(314) | 116.8(5) |
| O(6)-N(9)-C(310) | 115.6(5) |
| C(314)-N(9)-C(310) | 125.1(5) |
| C(407)-N(10)-C(408) | 118.8(5) |
| O(8)-N(11)-C(410) | 117.5(6) |
| O(8)-N(11)-C(414) | 113.7(6) |
| C(410)-N(11)-C(414) | 125.3(6) |
| C(507)-N(12)-C(508) | 118.7(5) |
| O(10)-N(13)-C(510) | 115.9(5) |
| O(10)-N(13)-C(514) | 116.5(5) |
| C(510)-N(13)-C(514) | 123.9(5) |
| C(607)-N(14)-C(608) | 118.8(4) |
| O(12)-N(15)-C(610) | 115.9(4) |
| O(12)-N(15)-C(614) | 116.2(4) |
| C(610)-N(15)-C(614) | 124.3(4) |
| C(102)-C(101)-C(106) | 121.7(5) |
| C(102)-C(101)-O(1) | 122.7(4) |
| C(106)-C(101)-O(1) | 115.6(5) |
| C(101)-C(102)-C(103) | 119.3(5) |
| C(104)-C(103)-C(102) | 120.4(5) |
| C(105)-C(104)-C(103) | 119.2(5) |
| C(105)-C(104)-C(107) | 118.2(5) |
| C(103)-C(104)-C(107) | 122.6(5) |
| C(104)-C(105)-C(106) | 121.4(5) |
| C(101)-C(106)-C(105) | 117.7(6) |
| N(4)-C(107)-C(104) | 123.3(5) |

| | |
|---|---|
| N(4)-C(108)-C(109) | 109.5(5) |
| N(4)-C(108)-C(113) | 108.6(5) |
| C(109)-C(108)-C(113) | 107.3(5) |
| C(110)-C(109)-C(108) | 114.9(5) |
| C(109)-C(110)-N(5) | 108.4(5) |
| C(109)-C(110)-C(111) | 109.9(7) |
| N(5)-C(110)-C(111) | 106.4(7) |
| C(109)-C(110)-C(112) | 112.4(7) |
| N(5)-C(110)-C(112) | 107.7(6) |
| C(111)-C(110)-C(112) | 111.8(8) |
| C(114)-C(113)-C(108) | 113.1(5) |
| N(5)-C(114)-C(113) | 110.4(5) |
| N(5)-C(114)-C(115) | 106.3(5) |
| C(113)-C(114)-C(115) | 110.7(6) |
| N(5)-C(114)-C(116) | 111.1(6) |
| C(113)-C(114)-C(116) | 110.7(5) |
| C(115)-C(114)-C(116) | 107.6(6) |
| C(206)-C(201)-C(202) | 122.1(5) |
| C(206)-C(201)-O(3) | 117.3(4) |
| C(202)-C(201)-O(3) | 120.6(4) |
| C(201)-C(202)-C(203) | 117.9(5) |
| C(204)-C(203)-C(202) | 121.4(5) |
| C(203)-C(204)-C(205) | 118.9(5) |
| C(203)-C(204)-C(207) | 125.4(6) |
| C(205)-C(204)-C(207) | 115.4(6) |
| C(204)-C(205)-C(206) | 121.1(5) |
| C(201)-C(206)-C(205) | 118.5(5) |
| N(6)-C(207)-C(204) | 125.1(8) |
| C(213)-C(208)-N(6) | 112.4(7) |
| C(213)-C(208)-C(209) | 109.6(8) |
| N(6)-C(208)-C(209) | 110.2(6) |
| C(210)-C(209)-C(208) | 114.7(9) |

| | |
|---|---|
| N(7)-C(210)-C(212) | 114.8(9) |
| N(7)-C(210)-C(209) | 110.6(7) |
| C(212)-C(210)-C(209) | 111.6(8) |
| N(7)-C(210)-C(211) | 104.9(7) |
| C(212)-C(210)-C(211) | 106.4(9) |
| C(209)-C(210)-C(211) | 107.9(10) |
| C(208)-C(213)-C(214) | 112.6(8) |
| N(7)-C(214)-C(215) | 105.3(7) |
| N(7)-C(214)-C(216) | 109.6(11) |
| C(215)-C(214)-C(216) | 114.9(11) |
| N(7)-C(214)-C(213) | 106.6(8) |
| C(215)-C(214)-C(213) | 103.6(9) |
| C(216)-C(214)-C(213) | 116.0(9) |
| C(306)-C(301)-C(302) | 122.0(5) |
| C(306)-C(301)-O(5) | 119.0(4) |
| C(302)-C(301)-O(5) | 119.0(4) |
| C(301)-C(302)-C(303) | 118.5(5) |
| C(304)-C(303)-C(302) | 121.1(5) |
| C(305)-C(304)-C(303) | 118.9(5) |
| C(305)-C(304)-C(307) | 120.8(5) |
| C(303)-C(304)-C(307) | 120.2(5) |
| C(304)-C(305)-C(306) | 120.2(5) |
| C(301)-C(306)-C(305) | 119.2(5) |
| N(8)-C(307)-C(304) | 121.6(5) |
| N(8)-C(308)-C(313) | 110.2(5) |
| N(8)-C(308)-C(309) | 105.6(5) |
| C(313)-C(308)-C(309) | 108.5(6) |
| C(308)-C(309)-C(310) | 113.9(6) |
| N(9)-C(310)-C(311) | 108.6(7) |
| N(9)-C(310)-C(309) | 109.3(6) |
| C(311)-C(310)-C(309) | 109.1(8) |
| N(9)-C(310)-C(312) | 107.5(7) |

| | |
|---|---|
| C(311)-C(310)-C(312) | 110.3(10) |
| C(309)-C(310)-C(312) | 112.0(7) |
| C(308)-C(313)-C(314) | 114.8(5) |
| N(9)-C(314)-C(315) | 108.7(7) |
| N(9)-C(314)-C(313) | 109.8(5) |
| C(315)-C(314)-C(313) | 111.5(6) |
| N(9)-C(314)-C(316) | 108.7(6) |
| C(315)-C(314)-C(316) | 106.2(7) |
| C(313)-C(314)-C(316) | 111.9(6) |
| C(406)-C(401)-C(402) | 120.5(5) |
| C(406)-C(401)-O(7) | 122.0(4) |
| C(402)-C(401)-O(7) | 117.3(4) |
| C(401)-C(402)-C(403) | 119.9(6) |
| C(402)-C(403)-C(404) | 121.6(6) |
| C(405)-C(404)-C(403) | 116.9(5) |
| C(405)-C(404)-C(407) | 121.3(5) |
| C(403)-C(404)-C(407) | 121.6(5) |
| C(404)-C(405)-C(406) | 121.6(5) |
| C(401)-C(406)-C(405) | 119.4(5) |
| N(10)-C(407)-C(404) | 120.6(5) |
| N(10)-C(408)-C(413) | 109.7(6) |
| N(10)-C(408)-C(409) | 107.4(6) |
| C(413)-C(408)-C(409) | 107.3(5) |
| C(408)-C(409)-C(410) | 114.6(7) |
| N(11)-C(410)-C(411) | 107.0(7) |
| N(11)-C(410)-C(409) | 107.8(6) |
| C(411)-C(410)-C(409) | 109.6(8) |
| N(11)-C(410)-C(412) | 109.3(8) |
| C(411)-C(410)-C(412) | 110.2(9) |
| C(409)-C(410)-C(412) | 112.8(6) |
| C(408)-C(413)-C(414) | 114.9(6) |
| N(11)-C(414)-C(415) | 108.8(6) |

| | |
|---|---|
| N(11)-C(414)-C(416) | 109.5(7) |
| C(415)-C(414)-C(416) | 111.4(6) |
| N(11)-C(414)-C(413) | 107.5(5) |
| C(415)-C(414)-C(413) | 108.0(6) |
| C(416)-C(414)-C(413) | 111.5(6) |
| C(502)-C(501)-C(506) | 120.5(5) |
| C(502)-C(501)-O(9) | 117.0(5) |
| C(506)-C(501)-O(9) | 122.4(5) |
| C(501)-C(502)-C(503) | 119.6(5) |
| C(504)-C(503)-C(502) | 121.8(5) |
| C(503)-C(504)-C(505) | 117.6(5) |
| C(503)-C(504)-C(507) | 120.3(5) |
| C(505)-C(504)-C(507) | 122.1(5) |
| C(504)-C(505)-C(506) | 121.3(6) |
| C(501)-C(506)-C(505) | 118.9(5) |
| N(12)-C(507)-C(504) | 122.2(5) |
| N(12)-C(508)-C(513) | 109.0(5) |
| N(12)-C(508)-C(509) | 108.4(5) |
| C(513)-C(508)-C(509) | 107.7(5) |
| C(510)-C(509)-C(508) | 114.0(5) |
| N(13)-C(510)-C(509) | 111.4(5) |
| N(13)-C(510)-C(512) | 107.8(5) |
| C(509)-C(510)-C(512) | 109.5(6) |
| N(13)-C(510)-C(511) | 108.7(6) |
| C(509)-C(510)-C(511) | 110.7(5) |
| C(512)-C(510)-C(511) | 108.6(6) |
| C(508)-C(513)-C(514) | 115.4(5) |
| N(13)-C(514)-C(513) | 108.7(5) |
| N(13)-C(514)-C(516) | 108.5(5) |
| C(513)-C(514)-C(516) | 109.8(6) |
| N(13)-C(514)-C(515) | 110.7(6) |
| C(513)-C(514)-C(515) | 110.0(6) |

| | |
|---|---|
| C(516)-C(514)-C(515) | 109.1(6) |
| C(606)-C(601)-C(602) | 121.0(5) |
| C(606)-C(601)-O(11) | 119.0(4) |
| C(602)-C(601)-O(11) | 119.9(4) |
| C(601)-C(602)-C(603) | 119.5(5) |
| C(604)-C(603)-C(602) | 120.6(4) |
| C(603)-C(604)-C(605) | 119.4(5) |
| C(603)-C(604)-C(607) | 120.9(4) |
| C(605)-C(604)-C(607) | 119.7(5) |
| C(604)-C(605)-C(606) | 119.8(5) |
| C(601)-C(606)-C(605) | 119.5(5) |
| N(14)-C(607)-C(604) | 122.4(5) |
| N(14)-C(608)-C(609) | 109.5(4) |
| N(14)-C(608)-C(613) | 107.1(4) |
| C(609)-C(608)-C(613) | 108.3(4) |
| C(608)-C(609)-C(610) | 113.3(4) |
| N(15)-C(610)-C(611) | 108.5(4) |
| N(15)-C(610)-C(612) | 109.3(4) |
| C(611)-C(610)-C(612) | 109.7(5) |
| N(15)-C(610)-C(609) | 109.1(4) |
| C(611)-C(610)-C(609) | 108.5(4) |
| C(612)-C(610)-C(609) | 111.7(4) |
| C(614)-C(613)-C(608) | 114.2(4) |
| N(15)-C(614)-C(613) | 111.0(4) |
| N(15)-C(614)-C(615) | 106.2(4) |
| C(613)-C(614)-C(615) | 109.3(5) |
| N(15)-C(614)-C(616) | 108.9(5) |
| C(613)-C(614)-C(616) | 112.3(4) |
| C(615)-C(614)-C(616) | 108.9(5) |
| C(6)-C(1)-C(2) | 117.0(17) |
| C(6)-C(1)-C(7) | 114.6(18) |
| C(2)-C(1)-C(7) | 127.9(19) |

| | |
|---|---|
| C(3)-C(2)-C(1) | 121.8(16) |
| C(4)-C(3)-C(2) | 125.4(19) |
| C(3)-C(4)-C(5) | 103(2) |
| C(6)-C(5)-C(4) | 143(2) |
| C(5)-C(6)-C(1) | 108.9(19) |
| C(13)-C(8)-C(9) | 121.0(12) |
| C(13)-C(8)-C(14) | 120.5(15) |
| C(9)-C(8)-C(14) | 117.6(15) |
| C(8)-C(9)-C(10) | 116.1(11) |
| C(11)-C(10)-C(9) | 125.8(14) |
| C(10)-C(11)-C(12) | 113.8(17) |
| C(13)-C(12)-C(11) | 123.7(17) |
| C(12)-C(13)-C(8) | 119.5(14) |
| C(16)-C(15)-C(21) | 136(3) |
| C(16)-C(15)-C(20) | 104.8(17) |
| C(21)-C(15)-C(20) | 117(2) |
| C(17)-C(16)-C(15) | 143(2) |
| C(16)-C(17)-C(18) | 111(2) |
| C(17)-C(18)-C(19) | 115(2) |
| C(18)-C(19)-C(20) | 128.9(19) |
| C(19)-C(20)-C(15) | 116.3(18) |

---

Symmetry transformations used to generate equivalent atoms

**Table S5.** Anisotropic displacement parameters ($Å^2 x\ 10^3$) for geotem. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| P(1) | 37(1) | 45(1) | 42(1) | 11(1) | 0(1) | 8(1) |
| P(2) | 34(1) | 35(1) | 50(1) | 7(1) | -1(1) | 4(1) |
| P(3) | 35(1) | 38(1) | 44(1) | 11(1) | -3(1) | 2(1) |
| O(1) | 36(2) | 70(2) | 53(2) | 21(2) | 8(2) | 14(2) |
| O(2) | 123(4) | 99(3) | 73(3) | 21(3) | -36(3) | 8(3) |
| O(3) | 56(2) | 60(2) | 44(2) | 3(2) | -5(2) | 17(2) |
| O(4) | 99(4) | 99(4) | 198(6) | 6(4) | -16(4) | 51(3) |
| O(5) | 39(2) | 41(2) | 63(2) | -4(2) | -2(2) | 3(1) |
| O(6) | 73(3) | 107(4) | 99(3) | 5(3) | -38(3) | -6(3) |
| O(7) | 31(2) | 39(2) | 64(2) | 11(2) | -6(2) | 5(1) |
| O(8) | 182(6) | 85(3) | 116(4) | 7(3) | -10(4) | 88(4) |
| O(9) | 42(2) | 40(2) | 50(2) | 10(2) | -8(2) | 5(2) |
| O(10) | 98(3) | 73(3) | 118(4) | -9(3) | 9(3) | 30(3) |
| O(11) | 46(2) | 43(2) | 50(2) | 17(2) | -8(2) | -3(2) |
| O(12) | 59(2) | 102(3) | 56(2) | -6(2) | -11(2) | 11(2) |
| N(1) | 42(2) | 38(2) | 48(2) | 9(2) | 0(2) | 6(2) |
| N(2) | 44(2) | 44(2) | 49(3) | 13(2) | 1(2) | 7(2) |
| N(3) | 42(2) | 38(2) | 44(2) | 12(2) | 0(2) | 5(2) |
| N(4) | 54(3) | 74(3) | 64(4) | 13(3) | -6(3) | 8(2) |
| N(5) | 75(3) | 67(3) | 66(3) | 12(3) | -18(3) | 5(3) |
| N(6) | 95(5) | 123(5) | 100(5) | 14(4) | -21(4) | 15(4) |
| N(7) | 80(4) | 67(4) | 137(5) | -2(4) | -5(4) | 22(3) |
| N(8) | 63(3) | 86(4) | 77(4) | 1(3) | -22(3) | -15(3) |
| N(9) | 54(3) | 73(3) | 75(3) | 2(3) | -25(3) | 1(3) |
| N(10) | 112(4) | 55(3) | 67(3) | 13(3) | 5(3) | 41(3) |
| N(11) | 118(5) | 64(4) | 89(4) | 11(3) | -4(4) | 40(4) |
| N(12) | 108(4) | 57(3) | 67(4) | 19(3) | -11(3) | 25(3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| N(13) | 77(3) | 54(3) | 69(3) | -1(2) | 4(3) | 16(3) |
| N(14) | 57(3) | 70(3) | 58(3) | -19(2) | -14(2) | 19(3) |
| N(15) | 48(3) | 65(3) | 44(3) | -4(2) | -15(2) | 10(2) |
| C(101) | 31(2) | 54(3) | 53(3) | 20(3) | 3(2) | 1(2) |
| C(102) | 42(3) | 54(3) | 64(4) | 2(3) | 3(3) | 10(2) |
| C(103) | 45(3) | 62(3) | 64(4) | 6(3) | 2(3) | 4(3) |
| C(104) | 39(3) | 64(3) | 51(4) | 13(3) | 1(2) | 5(3) |
| C(105) | 47(3) | 81(4) | 77(5) | 6(4) | 8(3) | 27(3) |
| C(106) | 49(3) | 76(4) | 60(4) | 5(3) | 4(3) | 24(3) |
| C(107) | 39(3) | 76(4) | 84(5) | 7(3) | 5(3) | 4(3) |
| C(108) | 50(3) | 82(4) | 69(4) | 10(3) | -11(3) | 16(3) |
| C(109) | 75(4) | 74(4) | 94(5) | 22(4) | -35(4) | -10(3) |
| C(110) | 88(5) | 68(4) | 108(6) | 4(4) | -45(4) | -4(4) |
| C(111) | 179(9) | 112(7) | 183(10) | 98(7) | -89(8) | -68(7) |
| C(112) | 184(10) | 121(7) | 134(8) | -47(6) | -82(7) | 89(7) |
| C(113) | 70(4) | 68(4) | 73(4) | 5(3) | -8(3) | -4(3) |
| C(114) | 59(3) | 76(4) | 60(4) | 5(3) | -12(3) | -11(3) |
| C(115) | 147(7) | 99(6) | 80(5) | 9(4) | -23(5) | -30(5) |
| C(116) | 59(4) | 176(9) | 91(6) | 31(5) | 3(4) | 2(5) |
| C(201) | 42(3) | 52(3) | 42(3) | 2(2) | -3(2) | 5(2) |
| C(202) | 61(4) | 75(4) | 57(4) | 26(3) | -13(3) | -15(3) |
| C(203) | 52(4) | 113(5) | 70(4) | 5(4) | -1(3) | -23(3) |
| C(204) | 48(3) | 89(4) | 45(3) | -1(3) | -7(3) | 3(3) |
| C(205) | 58(4) | 79(4) | 50(3) | 14(3) | -9(3) | 12(3) |
| C(206) | 54(3) | 67(4) | 53(3) | 12(3) | 3(3) | 10(3) |
| C(207) | 46(4) | 215(10) | 73(5) | -39(6) | 14(4) | -8(5) |
| C(208) | 77(5) | 117(6) | 72(4) | 28(4) | 0(4) | 52(4) |
| C(209) | 102(6) | 122(7) | 182(10) | 6(7) | -33(7) | 11(6) |
| C(210) | 85(5) | 77(5) | 215(11) | -16(6) | -34(7) | 15(4) |
| C(211) | 144(9) | 130(8) | 224(13) | 28(9) | 63(9) | -32(7) |
| C(212) | 170(10) | 96(6) | 166(9) | -21(6) | -97(8) | 14(6) |
| C(213) | 69(5) | 77(6) | 343(17) | -20(8) | -28(7) | 23(4) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(214) | 117(7) | 96(6) | 151(9) | 10(6) | 29(6) | 10(5) |
| C(215) | 125(7) | 73(5) | 190(10) | 13(6) | 10(7) | -8(5) |
| C(216) | 277(18) | 380(20) | 75(7) | 56(10) | 48(9) | 182(17) |
| C(301) | 45(3) | 38(3) | 51(3) | 0(2) | 0(3) | -1(2) |
| C(302) | 51(3) | 70(4) | 58(4) | 11(3) | 2(3) | -1(3) |
| C(303) | 58(3) | 68(4) | 50(3) | 15(3) | -7(3) | -1(3) |
| C(304) | 47(3) | 55(3) | 50(3) | 1(3) | -5(3) | -7(3) |
| C(305) | 54(3) | 67(3) | 58(4) | 9(3) | -7(3) | -17(3) |
| C(306) | 59(3) | 55(3) | 46(3) | 3(3) | -19(3) | -7(3) |
| C(307) | 58(3) | 63(3) | 65(4) | -1(3) | -14(3) | -15(3) |
| C(308) | 53(3) | 80(4) | 75(4) | -7(3) | -23(3) | -8(3) |
| C(309) | 67(4) | 142(7) | 105(6) | -38(5) | -38(4) | 27(4) |
| C(310) | 73(4) | 120(6) | 95(5) | -42(5) | -28(4) | 36(4) |
| C(311) | 124(8) | 275(15) | 136(9) | -108(10) | -47(7) | 55(9) |
| C(312) | 171(10) | 66(5) | 279(15) | -13(7) | -120(11) | 16(6) |
| C(313) | 61(4) | 88(5) | 115(6) | -33(4) | -19(4) | -12(4) |
| C(314) | 67(4) | 70(4) | 102(5) | -20(4) | -26(4) | 0(3) |
| C(315) | 88(6) | 81(6) | 248(12) | -19(7) | -31(7) | 15(5) |
| C(316) | 90(6) | 169(9) | 107(6) | -46(6) | 2(5) | -34(6) |
| C(401) | 35(2) | 35(3) | 53(3) | 1(2) | -2(2) | 11(2) |
| C(402) | 148(6) | 74(4) | 48(3) | 18(3) | 21(4) | 58(4) |
| C(403) | 185(8) | 73(4) | 54(4) | 5(3) | 15(5) | 76(5) |
| C(404) | 64(3) | 45(3) | 51(4) | -3(3) | 2(3) | 21(3) |
| C(405) | 82(4) | 56(3) | 53(3) | 5(3) | 2(3) | 26(3) |
| C(406) | 65(3) | 51(3) | 53(4) | -5(3) | 10(3) | 25(3) |
| C(407) | 96(4) | 43(3) | 52(3) | 10(3) | 5(3) | 24(3) |
| C(408) | 123(6) | 52(4) | 62(4) | 9(3) | 0(4) | 38(4) |
| C(409) | 103(5) | 57(4) | 108(6) | -1(3) | -22(5) | 29(4) |
| C(410) | 120(6) | 75(5) | 104(6) | -11(4) | -24(5) | 41(5) |
| C(411) | 108(7) | 161(9) | 183(11) | -18(8) | -16(7) | 44(7) |
| C(412) | 241(13) | 123(7) | 101(7) | -19(6) | -70(8) | 93(8) |
| C(413) | 101(5) | 59(4) | 77(4) | 7(3) | 10(4) | 25(4) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(414) | 127(6) | 46(4) | 69(4) | 11(3) | 11(4) | 12(4) |
| C(415) | 155(8) | 68(5) | 102(6) | 6(4) | 23(5) | 0(5) |
| C(416) | 220(11) | 83(5) | 99(6) | 39(5) | 63(7) | 33(6) |
| C(501) | 36(3) | 41(3) | 54(3) | 12(3) | -1(2) | 1(2) |
| C(502) | 64(3) | 63(3) | 45(4) | 1(3) | -14(3) | 16(3) |
| C(503) | 87(4) | 68(4) | 45(3) | 19(3) | -9(3) | 17(3) |
| C(504) | 55(3) | 47(3) | 57(4) | 16(3) | 0(3) | 4(3) |
| C(505) | 114(5) | 67(4) | 57(4) | 20(3) | 15(4) | 46(4) |
| C(506) | 117(5) | 80(4) | 53(4) | 25(3) | 9(4) | 44(4) |
| C(507) | 73(4) | 50(3) | 62(4) | 21(3) | -3(3) | 13(3) |
| C(508) | 89(4) | 61(4) | 64(4) | 5(3) | 3(3) | 25(4) |
| C(509) | 69(4) | 67(4) | 80(4) | 2(3) | 6(3) | 16(3) |
| C(510) | 74(4) | 60(4) | 81(4) | 6(3) | 27(3) | 11(3) |
| C(511) | 142(7) | 89(5) | 107(6) | 42(5) | 51(6) | 47(5) |
| C(512) | 81(4) | 71(4) | 127(6) | -9(4) | 6(4) | -1(4) |
| C(513) | 82(4) | 60(4) | 72(4) | 7(3) | -19(4) | -2(3) |
| C(514) | 79(4) | 82(4) | 63(4) | -5(3) | -12(3) | 6(4) |
| C(515) | 135(7) | 83(5) | 95(6) | -3(4) | -49(5) | 33(5) |
| C(516) | 60(4) | 125(6) | 117(7) | -9(5) | 3(4) | -3(4) |
| C(601) | 46(3) | 35(3) | 47(3) | 10(2) | -1(2) | -4(2) |
| C(602) | 45(3) | 63(3) | 48(3) | -1(3) | -4(2) | 8(3) |
| C(603) | 37(3) | 58(3) | 65(4) | 0(3) | 0(3) | 4(2) |
| C(604) | 44(3) | 33(2) | 58(3) | 2(3) | -2(3) | -2(2) |
| C(605) | 52(3) | 43(3) | 71(4) | -7(3) | -10(3) | 4(3) |
| C(606) | 44(3) | 52(3) | 86(4) | 4(3) | -7(3) | 8(3) |
| C(607) | 54(3) | 45(3) | 52(3) | -1(2) | 3(3) | -1(3) |
| C(608) | 58(3) | 56(3) | 49(3) | -13(3) | -10(3) | 12(3) |
| C(609) | 66(3) | 50(3) | 39(3) | -1(2) | -6(3) | 6(3) |
| C(610) | 59(3) | 49(3) | 54(3) | -4(3) | -4(3) | 2(3) |
| C(611) | 80(4) | 79(4) | 62(4) | -10(3) | 1(3) | -26(4) |
| C(612) | 107(5) | 55(3) | 63(4) | -17(3) | -14(4) | 9(3) |
| C(613) | 55(3) | 59(3) | 57(3) | -2(3) | 0(3) | 6(3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(614) | 47(3) | 65(4) | 57(3) | 5(3) | -4(3) | 12(3) |
| C(615) | 81(4) | 72(4) | 104(5) | 37(4) | -7(4) | 5(4) |
| C(616) | 63(4) | 111(5) | 51(4) | 2(3) | 0(3) | 11(4) |

**Table S6.** Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for geotem.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(102) | 7405 | 1816 | 5354 | 64 |
| H(103) | 6676 | 2191 | 4790 | 68 |
| H(105) | 5988 | 3320 | 5913 | 82 |
| H(106) | 6721 | 2966 | 6482 | 74 |
| H(107) | 5519 | 3362 | 5085 | 79 |
| H(108) | 5061 | 3559 | 4416 | 81 |
| H(10A) | 5824 | 4319 | 4174 | 97 |
| H(10B) | 5967 | 3866 | 3686 | 97 |
| H(11A) | 5294 | 5150 | 3015 | 237 |
| H(11B) | 5824 | 4630 | 3013 | 237 |
| H(11C) | 5801 | 5216 | 3431 | 237 |
| H(11D) | 4531 | 5103 | 3709 | 219 |
| H(11E) | 5002 | 5139 | 4160 | 219 |
| H(11F) | 4555 | 4523 | 4133 | 219 |
| H(11G) | 5460 | 2795 | 3536 | 84 |
| H(11H) | 4962 | 2546 | 3919 | 84 |
| H(11G) | 4278 | 3108 | 2714 | 163 |
| H(11H) | 4429 | 2430 | 3015 | 163 |
| H(11I) | 4935 | 2841 | 2734 | 163 |
| H(11J) | 3796 | 3551 | 3486 | 163 |
| H(11K) | 4135 | 3611 | 4019 | 163 |

| | | | | |
|---|---|---|---|---|
| H(11L) | 3953 | 2888 | 3803 | 163 |
| H(202) | 9523 | 2823 | 6404 | 77 |
| H(203) | 10443 | 2447 | 6718 | 94 |
| H(205) | 9640 | 1375 | 7810 | 75 |
| H(206) | 8723 | 1728 | 7505 | 69 |
| H(207) | 10701 | 1389 | 7819 | 134 |
| H(208) | 11652 | 1129 | 7806 | 107 |
| H(20A) | 12131 | 1120 | 6786 | 163 |
| H(20B) | 12254 | 1688 | 7204 | 163 |
| H(21A) | 13529 | 564 | 6990 | 249 |
| H(21B) | 13290 | 1275 | 6797 | 249 |
| H(21C) | 13012 | 595 | 6580 | 249 |
| H(21D) | 13322 | 878 | 7909 | 216 |
| H(21E) | 12716 | 1220 | 8060 | 216 |
| H(21F) | 13151 | 1594 | 7676 | 216 |
| H(21G) | 11480 | 205 | 7026 | 196 |
| H(21H) | 11132 | 216 | 7556 | 196 |
| H(21G) | 11871 | -818 | 7071 | 194 |
| H(21H) | 11550 | -1017 | 7593 | 194 |
| H(21I) | 12236 | -1126 | 7537 | 194 |
| H(21J) | 12134 | 402 | 8352 | 365 |
| H(21K) | 12384 | -348 | 8373 | 365 |
| H(21L) | 11698 | -220 | 8408 | 365 |
| H(302) | 8160 | 1180 | 4408 | 72 |
| H(303) | 7195 | 923 | 4180 | 70 |
| H(305) | 6982 | -87 | 5512 | 71 |
| H(306) | 7949 | 184 | 5746 | 64 |
| H(307) | 6177 | -95 | 4871 | 74 |
| H(308) | 5456 | -202 | 4316 | 83 |
| H(30A) | 5992 | -612 | 3594 | 126 |
| H(30B) | 5924 | 93 | 3308 | 126 |
| H(31A) | 4942 | -790 | 2540 | 267 |

| | | | | |
|---|---|---|---|---|
| H(31B) | 5595 | -986 | 2689 | 267 |
| H(31C) | 5438 | -227 | 2542 | 267 |
| H(31D) | 4827 | -1027 | 3909 | 258 |
| H(31E) | 5194 | -1496 | 3531 | 258 |
| H(31F) | 4550 | -1268 | 3378 | 258 |
| H(31G) | 5396 | 1038 | 3752 | 105 |
| H(31H) | 5132 | 925 | 4311 | 105 |
| H(31G) | 3924 | 984 | 3390 | 208 |
| H(31H) | 4528 | 1366 | 3301 | 208 |
| H(31I) | 4203 | 1421 | 3841 | 208 |
| H(31J) | 3851 | 32 | 3962 | 183 |
| H(31K) | 4126 | 477 | 4411 | 183 |
| H(31L) | 4407 | -234 | 4268 | 183 |
| H(402) | 10103 | 334 | 5181 | 108 |
| H(403) | 10499 | -628 | 5529 | 125 |
| H(405) | 9879 | -114 | 6911 | 76 |
| H(406) | 9521 | 887 | 6564 | 68 |
| H(407) | 10443 | -1188 | 6841 | 76 |
| H(408) | 10846 | -2190 | 6809 | 95 |
| H(40A) | 11752 | -1750 | 6498 | 107 |
| H(40B) | 11662 | -2133 | 5967 | 107 |
| H(41A) | 12746 | -3200 | 6438 | 226 |
| H(41B) | 12760 | -2397 | 6425 | 226 |
| H(41C) | 12514 | -2807 | 5944 | 226 |
| H(41D) | 11569 | -2770 | 7296 | 232 |
| H(41E) | 12177 | -2379 | 7268 | 232 |
| H(41F) | 12166 | -3183 | 7267 | 232 |
| H(41G) | 10771 | -2753 | 5799 | 95 |
| H(41H) | 10274 | -2812 | 6224 | 95 |
| H(41G) | 10973 | -3883 | 5629 | 163 |
| H(41H) | 10402 | -4077 | 5946 | 163 |
| H(41I) | 11006 | -4445 | 6066 | 163 |

| | | | | |
|---|---|---|---|---|
| H(41J) | 10842 | -3311 | 7137 | 201 |
| H(41K) | 10931 | -4089 | 7004 | 201 |
| H(41L) | 10324 | -3730 | 6881 | 201 |
| H(502) | 7950 | 3394 | 3909 | 69 |
| H(503) | 7441 | 4381 | 3693 | 80 |
| H(505) | 7111 | 4724 | 5174 | 96 |
| H(506) | 7632 | 3741 | 5399 | 100 |
| H(507) | 6895 | 5405 | 3911 | 74 |
| H(508) | 6515 | 6389 | 4027 | 86 |
| H(50A) | 6933 | 6937 | 4990 | 87 |
| H(50B) | 7278 | 6980 | 4460 | 87 |
| H(51A) | 6550 | 7540 | 3712 | 169 |
| H(51B) | 7127 | 7931 | 3881 | 169 |
| H(51C) | 6515 | 8314 | 3876 | 169 |
| H(51D) | 6686 | 8645 | 4793 | 139 |
| H(51E) | 7289 | 8244 | 4794 | 139 |
| H(51F) | 6806 | 8083 | 5218 | 139 |
| H(51G) | 5971 | 6385 | 5011 | 86 |
| H(51H) | 5713 | 6022 | 4516 | 86 |
| H(51G) | 5188 | 7451 | 3838 | 157 |
| H(51H) | 5129 | 6651 | 3871 | 157 |
| H(51I) | 5733 | 6984 | 3702 | 157 |
| H(51J) | 4826 | 7506 | 4760 | 151 |
| H(51K) | 5170 | 7128 | 5208 | 151 |
| H(51L) | 4804 | 6705 | 4799 | 151 |
| H(602) | 10121 | 3073 | 5165 | 63 |
| H(603) | 10818 | 3428 | 5763 | 64 |
| H(605) | 9632 | 4681 | 6402 | 67 |
| H(606) | 8937 | 4333 | 5788 | 73 |
| H(607) | 10616 | 4599 | 6797 | 60 |
| H(608) | 11391 | 4510 | 7256 | 65 |
| H(60A) | 12064 | 4850 | 6611 | 62 |

| | | | | |
|---|---|---|---|---|
| H(60B) | 12332 | 4109 | 6598 | 62 |
| H(61A) | 13318 | 4350 | 6830 | 111 |
| H(61B) | 13475 | 4889 | 7263 | 111 |
| H(61C) | 13163 | 5126 | 6746 | 111 |
| H(61D) | 12016 | 5227 | 7688 | 113 |
| H(61E) | 12382 | 5672 | 7292 | 113 |
| H(61F) | 12682 | 5402 | 7805 | 113 |
| H(61G) | 11356 | 3344 | 7467 | 68 |
| H(61H) | 11892 | 3196 | 7094 | 68 |
| H(61G) | 12699 | 3022 | 8201 | 129 |
| H(61H) | 12620 | 2767 | 7624 | 129 |
| H(61I) | 12114 | 2645 | 8035 | 129 |
| H(61J) | 12130 | 4000 | 8528 | 112 |
| H(61K) | 11540 | 3623 | 8376 | 112 |
| H(61L) | 11664 | 4365 | 8167 | 112 |

**4. Variable-temperature EPR study.**

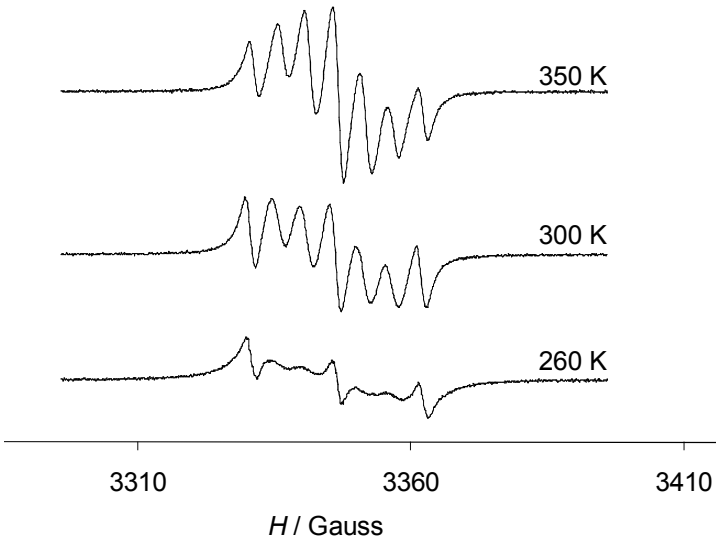



**Figure S3.** EPR spectra of a $10^{-4}$ M solution of **3-Gc$_0$T** recorded at different temperatures in dichloromethane:toluene (1:1).

The alternating linewidth effect is clearly visible in the 260 K spectrum but at 350 K there is a strong reduction of this effect because we are in the fast exchange region.

**5. EPR spectra in different solvents.**

The shape of EPR spectra of **3-Gc$_0$T** depends slightly on the nature of the solvent, as shown in Figure S3. This is originated because the line widths are smaller in polar solvents than in apolar solvents.

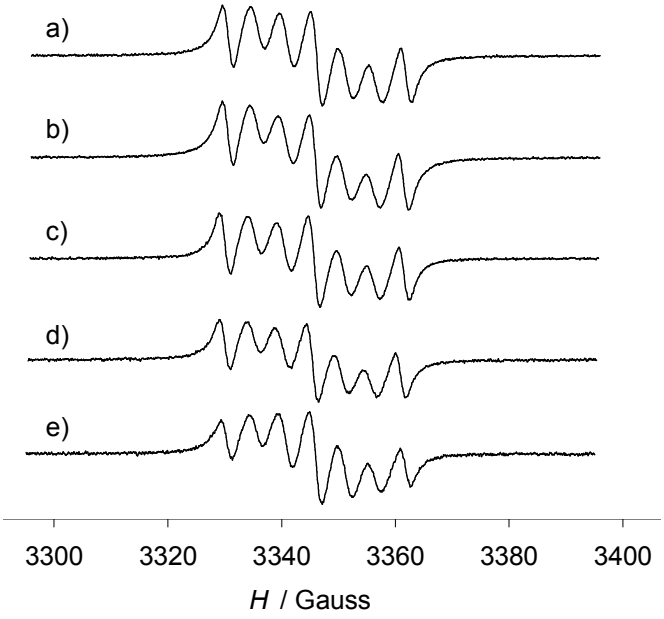



**Figure S4.** EPR spectra of a $10^{-4}$ M solution of **3-Gc$_0$T** recorded at room temperature in a) dichloromethane:toluene (1:1), b) toluene, c) dichloromethane, d) tetrahydrofuran and e) acetonitrile.

**6. Simulations of N-containing triradical system.**

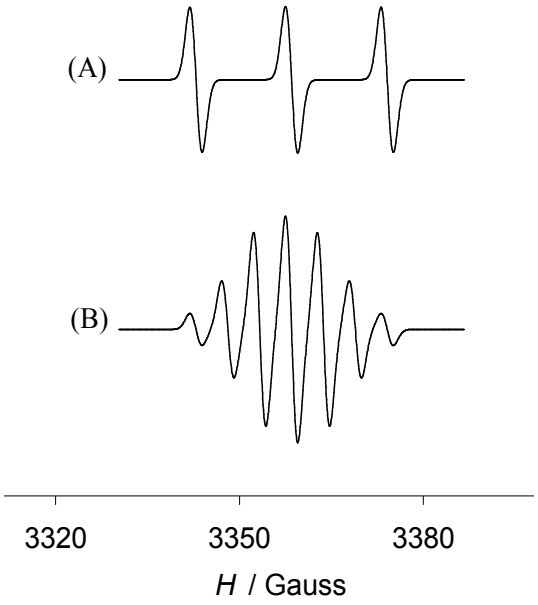



**Figure S5**. Simulation of two limit cases for a N-containing triradical system. A) When the radical fulfil the condition $|J| << |a_N|$, the spectrum exhibits three lines separated by the hyperfine coupling $a_N$ with relative intensities 1:1:1. B) When the radical fulfil the condition $|J| >> |a_N|$, it shows a seven line hyperfine pattern with a separation of 1/3 $a_N$ and relative intensities of 1:3:6:7:6:3:1.

**7. References.**

1.- Badetti, E.; Caminade, A.M.; Majoral, J.P.; Moreno-Mañas, M.; Sebastián, R.M. *Langmuir* **2008**, *24*, 2090.

2.- H. R. Allcock, D. C. Ngo, M. Parvez, K. B. Visscher, *Inorg. Chem.* **1994**, *33*, 2090.

3.- J. Sopkova-de Oliveira Santos, D. Bauchart, C. Besset, I. Dez, *Acta Crystallogr., Sect. C* **2004**, *60*, 751.

4.- N. Lejeune, I. Dez, P. A. Jaffrès, J. F. Lohier, P. J. Madec, J. Sopkova-de Oliveira Santos, *Eur. J. Inorg. Chem.* **2008**, 138.

5.- Ç. Albayrak, B. Kos,ar, M. Odabas,oglu, O. Büyükgüngör, *Crystallogr. Rep.* **2010**, *55* (7), 1203.

6.- A. Özek, Ç. Albayrak, M. Odaba o lu, O. Büyükgüngör, *Acta Crystallogr. C* **2007**, *63*, ol77.

7.- N. Karadayi, Ç. Albayrak, M. Odabas,oglu, O. Büyükgüngör, *Acta Crystallogr. E* **2006**, *62*, ol699.

8.- N. Karadayi, Ç. Albayrak, M. Odabas,oglu, O. Büyükgüngör, *Acta Crystallogr. E* **2006**, *62*, ol727.

9.- M. Odabas,oglu, O. Büyükgüngör, Ç. Albayrak, *Acta Crystallogr. E* **2005**, *61*, o2525.

10.- M. Odabas,oglu, O. Büyükgüngör, Ç. Albayrak, *Acta Crystallogr. E* **2005**, *61*, e4.