N -Fusion Approach in Construction of Contracted Carbaporphyrinoids: Formation of N -Fused Telluraporphyrin

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N-Fusion Approach in Construction of Contracted Carbaporphyrinoids: Formation of *N*-Fused Telluraporphyrin

Ewa Pacholska-Dudziak, Filip Ulatowski, Zbigniew Ciunik, and Lechosław Latos-Grażyński*[a]

Dedicated to Professor Marilyn M. Olmstead

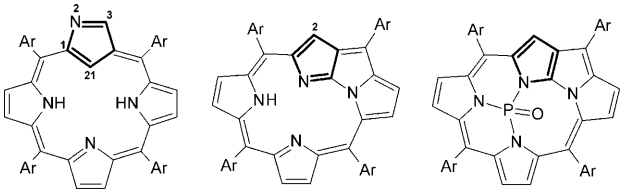
Abstract: Insertion of PCl_3 into 5,10,15,20-tetraaryl-21-telluraporphyrin leads to a phosphorus complex of *N*-fused dihydrotelluraporphyrin with an inverted tellurophene ring. Its CNN coordination core places the macrocycle in the family of contracted carbaporphyrinoids. A cycle of direct transformations affords an elegant triangle of three mutually convertible *N*-fused porphyrinoids, with distinct spectroscopic features: antiaromatic, nonaromatic and aromatic. The nonaromatic species has a dome shaped skeleton which forms in the solid state a ball and socket structure with C_{60}.

Keywords: fullerenes · macrocycles · porphyrinoids · template synthesis · supramolecular chemistry

Introduction

Porphyrins reveal considerable structural flexibility that results in severely nonplanar core conformations. The formation of *N*-fused porphyrin (**2**)[1] occupies a very special place in the search for the limits of porphyrin skeleton distortions. *N*-Confused porphyrin **1** transforms into an 18-π-electron aromatic porphyrinoid with a fused tripentacyclic ring in the macrocyclic core: *N*-fused porphyrin **2**.[2,3]

Significantly, inversion of the *N*-confused pyrrole ring in the *N*-confused porphyrin skeleton is a prerequisite for an intramolecular fusion step that clearly demonstrates the peculiar plasticity of the [18]porphyrin(1.1.1.1)-like frame. The intermediary inverted macrocyclic conformation was trapped in the bis[iridium(I)] complex of *N*-confused porphyrin[4] or obtained by cleavage of the bridging C–N bond in the C2–C2′ dimer of **2**.[5] A template factor has been recognized as the fusion driving force; that is, insertion of rhenium(I),[6] boron(III),[7] or phosphorus(V)[8] into *N*-confused porphyrins initiated the *N*-confused pyrrole inversion followed by C–N bond formation (e.g., [$\mathbf{2}_{reduced}$]-PO).



1 **2** [$\mathbf{2}_{reduced}$]-PO

Herein we explore a possibility to create a heteroanalogue of *N*-fused porphyrin derived from 21-telluraporphyrin by applying a coordination template approach. 5,10,15,20-Tetraaryl-21-telluraporphyrin **3** with a large core heteroatom is nearly planar[9;10] and reveals characteristic spectroscopic features of an aromatic 21-heteroporphyrin. Bearing in mind the nonorthodox structure of 5,10,15,20-tetraaryl-21,23-ditelluraporphyrin,[11] one can presume that the conformation of **3**, which has an inverted tellurophene ring, might be energetically accessible if stabilized by coordination or as a transient species of *N*-fusion process.

Results and Discussion

21-Telluraporphyrin **3** reacts with PCl_3 in triethylamine to give phosphorus(V) dihydro-*N*-fused 21-telluraporphyrin, **4**-

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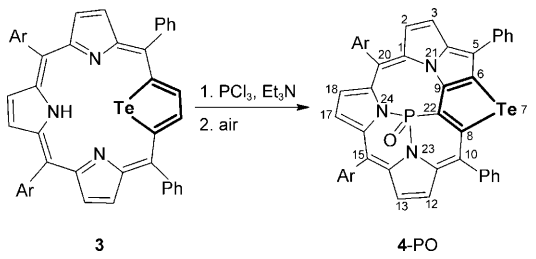
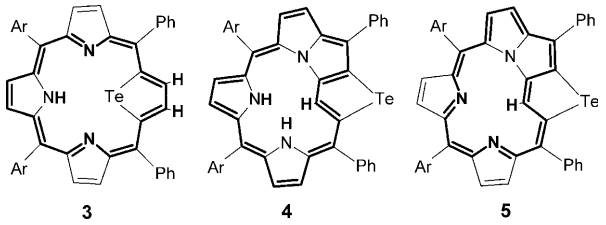
PO (55%), after chromatographic workup. The rearranged macrocycle acts as a triaanionic tridentate ligand (Scheme 1). Therefore, the insertion of phosphorus into **3** prompted inversion of the tellurophene ring and formation



Scheme 1. Insertion of phosphorus into telluraporphyrin (Ar = *p*-methoxyphenyl).

of antiaromatic **4**-PO, in which the contracted CNN core of the *N*-fused porphyrin provides a favorable match for the small radius of phosphorus(V). Although the appropriate mechanism remains unknown at present, the coordination of phosphorus is obviously a precondition of a sequence of transformations that lead to **4**-PO. Despite several attempts, we could not remove phosphorus(V) from **4**-PO. Significantly, the dihydro-*N*-confused telluraporphyrin ligand **4**, albeit built into the **4**-PO structure, can be recognized as an antiaromatic constitutional isomer of aromatic 21-telluraporphyrin **3** (Scheme 2). Novel porphyrinoid **4** is also related to hypothetical aromatic *N*-fused 21-telluraporphyrin **5** because



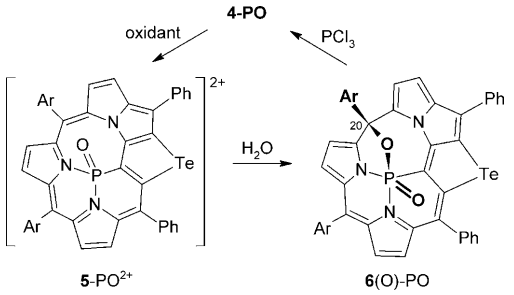
Scheme 2. Telluraporphyrin **3** (aromatic), dihydro-*N*-fused 21-telluraporphyrin **4** (antiaromatic), and *N*-fused 21-telluraporphyrin **5** (aromatic).

Abstract in Polish: *W wyniku insercji trójchlorku fosforu do 5,10,15,20-tetraarylo-21-telluraporfiryny otrzymano fosforowy kompleks skondensowanej dihydrotelluraporfiryny z odwróconym pierścieniem tellurofenowym. Trójkoordynacyjny rdzeń CNN tak powstałego makrocykla klasyfikuje go do rodziny zmniejszonych karbaporfirynoidów. Zsyntezowano trzy pokrewne kompleksy tego typu (antyaromatyczny, niearomatyczny i aromatyczny), mogące wzajemnie przekształcać się w siebie. Różnią się one zasadniczo właściwościami spektroskopowymi. Związek niearomatyczny charakteryzuje się bardzo pofałdowanym szkieletem i kokrystalizuje z fulerenem C_{60} dopasowując się wklęsłą stroną do jego wypukłej powierzchni.*

both contain identical macrocyclic frames. In the same line of consideration, macrocycles **4** and **5** are (formally) mutually convertible by a hydrogenation/dehydrogenation step. In terms of oxidation state, *N*-fused 21-telluraporphyrin **5** is two-electron oxidized with respect to 21-telluraporphyrin **3**.

Cyclic voltammetry (Figure S5 in the Supporting Information) demonstrates that **4**-PO undergoes two consecutive, reversible one-electron oxidations with half-wave potentials of -0.127 and $+0.239$ V and two consecutive, reversible one-electron reductions with half-wave potentials of -1.568 and -1.708 V (vs. ferrocene/ferrocenium (Fc/Fc^+), tetra-*n*-butylammonium perchlorate, CH_2Cl_2). Two-electron oxidation of **4**-PO affords a reactive dicationic species, **5**-PO^{2+}.

Treatment of **4**-PO with *m*-chloroperoxybenzoic acid (MCPBA) produces nonaromatic *N*-fused telluraphlorin **6**(O)-PO (i.e., heteroderivative of *N*-fused phlorin[8]). The macrocyclic skeleton of **6**(O)-PO (Scheme 3) contains an sp^3



Scheme 3. Oxidation of **4**-PO (oxidant = MCPBA, DDQ or $AgBF_4$).

meso carbon atom as confirmed by ^{13}C NMR spectroscopy. The ^{13}C chemical shift of C20 ($\delta = 73.8$ ppm) is consistent with tetrahedral hybridization of a carbon atom substituted with one oxygen. Oxidation of **4**-PO with DDQ (2,3-dichloro-5,6-dicyanobenzoquinone) or with $AgBF_4$ followed by addition of water gave **6**(O)-PO as well. Formation of a transient **5**-PO^{2+} dication that is prone to nucleophilic attack is readily included into the mechanism of **6**(O)-PO formation. The oxidation may be reversed by treating **6**(O)-PO with PCl_3 in boiling pyridine.

Titration of **6**(O)-PO with acids (HX: trifluoroacetic acid (TFA), HBF_4, (1*R*)-(−)-10-camphorosulfonic acid), monitored by ^1H NMR spectroscopy, initially results in a protonation to give a nonaromatic **6**(O)-POH^+ ion (Figure 1, traces a)–d); Scheme 4) that remains in fast exchange with **6**(O)-PO, as indicated by smooth changes in the chemical shifts observed in this titration range. Subsequent addition of excess acid gave an aromatic [**5**-$P(OH)_2X]^+$ ion that adopts a macrocyclic structure of **5** with an 18-π-electron delocalization pathway (Scheme 4; Figure 1, trace f).

In fact, all phosphine oxide complexes of *N*-fused telluraporphyrin derivatives (**4**-PO, [**5**-$P(OH)_2X]^+$, and **6**(O)-PO) are chiral and their syntheses lead to racemic mixtures. Thus, once a chiral acid ((1*R*)-10-camphorosulphonic acid) is used in reaction with **6**(O)-PO instead of achiral TFA or

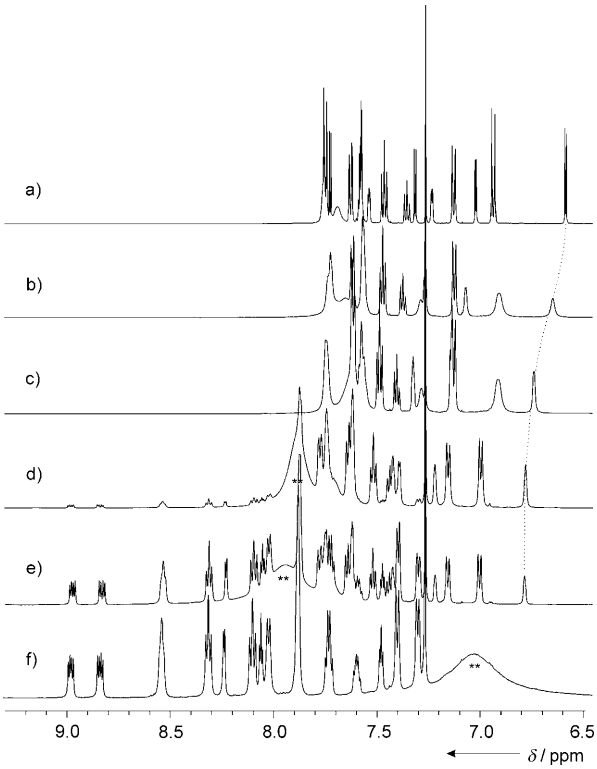
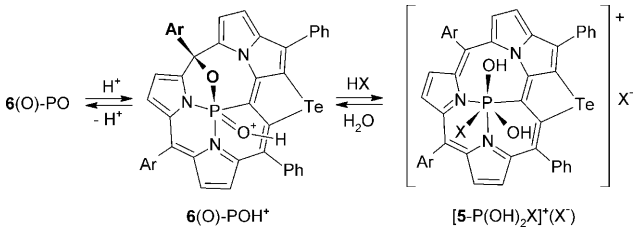


Figure 1. Titration of **6**(O)-PO with (1R)-(−)-10-camphorsulfonic acid monitored by ^{1}H NMR spectroscopy ($CDCl_3$, 298 K, 600 MHz). Molar ratio of **6**(O)-PO to added (1*R*)-(−)-10-camphorsulfonic acid: a) 1:0, b) 1:0.3, c) 1:1, d) 1:6.5, and e) 1:6.5 after 1 day, f) 1:6.5 after 3 weeks. The signal marked with ** indicates SO_3H.



Scheme 4. Reactions of **6**(O)-PO with acid (X = TFA^-, (1*R*)-(−)-10-camphorosulfonate anion).

HBF_4, the β-pyrrolic signals are doubled in the ^{1}H NMR spectrum (Figure 2c, inset). This observation reflects the coordination of the chiral anion and formation of two diastereoisomers.

The ^{1}H NMR spectra of **4**-PO, $[\mathbf{5}\text{-P(OH)}_2\text{X}]^+$, and **6**(O)-PO present essential features consistent with suggested molecular and electronic structures (Figure 2). The perimeter hydrogen atoms of **4**-PO reveal a relatively widely spread set of upfield β-H resonances. The observed spectral range ($\delta = 3.8$–4.7 ppm) indicates the paratropic effect and proves the essential influence of the macrocyclic 20-electron π-delocalization pathway.[12] In contrast with the clearly antiaromatic character of **4**-PO, **6**(O)-PO presents nonaromatic macrocyclic behavior as manifested on the ^{1}H NMR spectrum (β-H: $\delta = 6.6$–7.7 ppm)[13–16] caused by the presence of tetrahedral carbon atom (C20) that disrupts the delocalization pathway. Finally, clear aromatic features have been detected for $[\mathbf{5}\text{-P(OH)}_2\text{X}]^+$ ($\delta = 7.5$–9.0 ppm). The marked changes in electronic structures detected for **4**-PO, **6**(O)-PO, and $[\mathbf{5}\text{-P(OH)}_2\text{X}]^+$ corroborate well with the distinct differences in ^{31}P chemical shifts: $\delta = 10.09$, -71.38, and 1.08 ppm respectively. The $\delta = -16.9$ and -32.3 ppm chemical shifts have been determined for related phosphorus(V) complexes of *N*-fused porphyrin and *N*-fused phlorin, respectively,[8] whereas the $\delta = -160$ to -230 ppm range is characteristic for phosphorus complexes of regular porphyrins.[17] An enormously large ^1J(C,P) coupling constant (214 Hz) has been detected for P-C22 bond in **6**(O)-PO whereas the corresponding, ^1J(C,P) value for **4**-PO is 161 Hz.

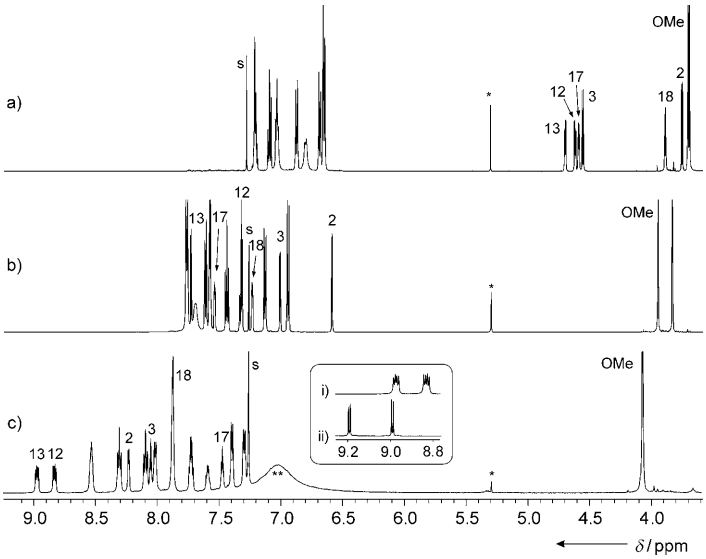


Figure 2. ^{1}H NMR spectra ($CDCl_3$, 298 K) of a) **4**-PO, b) **6**(O)-PO, c) $[\mathbf{5}\text{-P(OH)}_2\text{X}]^+$ (X = (1*R*)-(−)-10-camphorosulfonic acid anion). The numbering is given for pyrrolic protons. The signal marked with * indicates CH_2Cl_2 and ** indicates SO_3H. The inset shows a doubled number of AB-pattern signals for one pyrrole for X = (1*R*)-10-camphorosulfonate (i) as compared with an achiral pyrrole X = TFA^- (ii).

Compounds **4**-PO and **6**(O)-PO were structurally characterized (Figures 3 and 4).[18] X-ray quality crystals were obtained by slow diffusion of **4**-PO in benzene into hexane to give **4**-PO·C_6H_6. For compound **6**(O)-PO, addition of fullerene C_{60} in benzene to the porphyrinoid solution was essential for monocrystal growth. Compound **6**(O)-PO cocrystallizes with fullerene to give 2(**6**(O)-PO)·C_{60}·3 C_6H_6 similar to examples of fullerene–regular metalloporphyrin assemblies.[19–22]

The coordination environment of phosphorus(V) in **4**-PO resembles a distorted trigonal pyramid with one carbon and two nitrogen atoms occupying equatorial positions with the oxygen atom lying at the unique apex. The P–N bond lengths of **4**-PO resemble those determined for phosphorus(V) *N*-fused porphyrin.[8] The porphyrin skeleton contains two pyrrole rings and the fused, practically planar tripentacyclic ring. The localization of double bonds within the *N*-

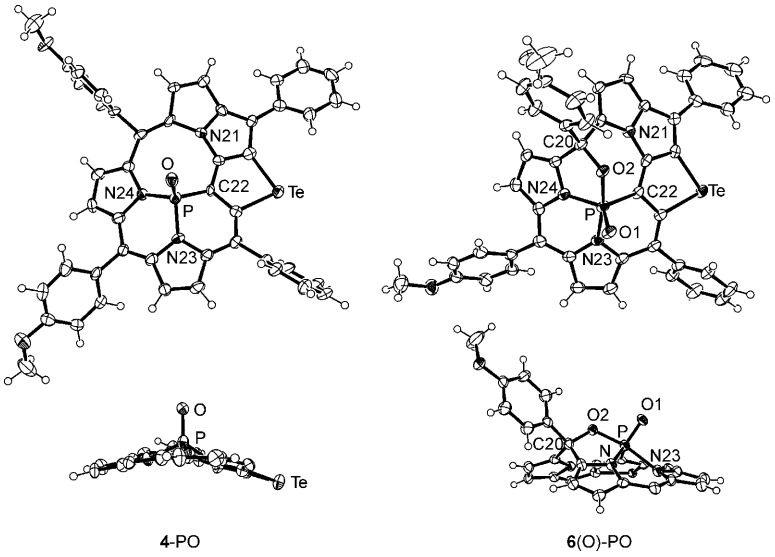


Figure 3. Molecular structures of **4**-PO (left) and **6**(O)-PO (right). Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] for **4**-PO: P–C22 1.754(6), P–N23 1.689(5), P–N24 1.681(5); and for **6**(O)-PO: P–C22 1.816(5), P–N23 1.989(4), P–N24 1.743(4), C22–O2 1.430(6), P–O2 1.709(3).

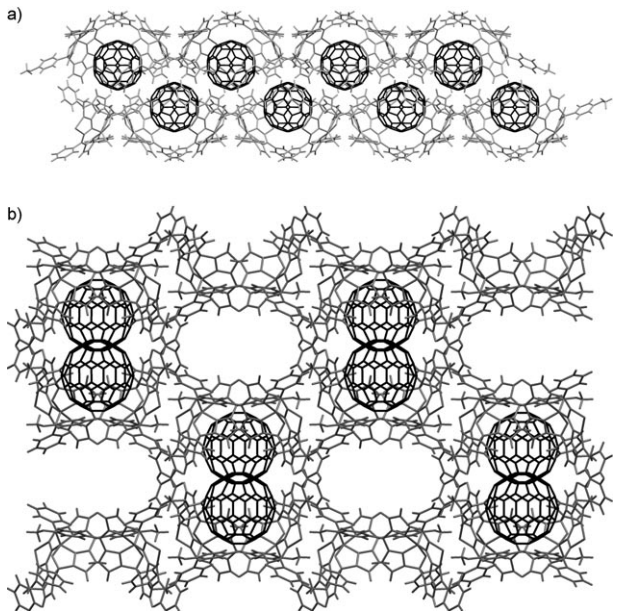


Figure 4. Packing in 2·(**6**(O)-PO)·C_{60}·3C_6H_6. a) The view down the crystallographic *a* axis shows a ribbon of (**6**(O)-PO) and C_{60} molecules in 2·(**6**(O)-PO)·C_{60}·3C_6H_6. b) The view down the *c* axis (disordered solvent (benzene) molecules that fill the clearly visible channels have been omitted for clarity). A color version of this figure is available in the Supporting Information (Figure S6).

fused framework indicates the structure depicted at Scheme 2 is the major resonance contributor.

The **6**(O)-PO molecule is strongly distorted from planarity, however, the condensed tripentacyclic ring preserves the approximately planar shape although the deviation is a bit bigger than in the structure of **4**-PO (mean deviation 0.08 Å compared with 0.065 Å for **4**-PO). The coordination polyhedron of phosphorus resembles a trigonal bipyramid. The macrocylic ligand coordinates in the facial mode because the two pyrrolic nitrogen (N23, N24) and one carbon (C22) donors lie at the vertices of the single trigonal face. The equatorial plane is formed by C22, N24, and O1 atoms. The apical position are occupied by O2 and N23 donors and the O2-P-N23 angle is somewhat bent (167°) and the P–N23 bond elongated as a consequence of strain imposed by O2 bound to the skeleton of restricted plasticity. In fact, the aryl ring bound to the sp^3 C20 carbon, the phosphorus, and two coordinated oxygen atoms are located on the same crowded side of the CN_2 macrocyclic plane. The other side is bowl-shaped and forms a ball-and-socket structure with C_{60}, making contact with the shortest $H_{porph}\cdots C_{fuller}$ distance being 2.73 Å. The fullerene is ordered and each C_{60} cage is surrounded by two identical enantiomers of **6**(O)-PO that sit on opposite sides of the fullerene. The racemic pairs of **6**(O)-PO are aligned in close face-to-face proximity.

Conclusions

In conclusion, an insertion of phosphorus into 21-telluraporphyrin triggers a profound rearrangement of the macrocyclic structure and gives a series of compounds that contain new types of contracted carbaporphyrinoids imprinted into an *N*-fused porphyrin frame. These molecules introduce unique structural patterns as distinguished by the location of two nitrogen atoms and one carbon atom at corners of CNN coordination triangle. Importantly, their formation extends the *N*-fusion concept, which until recently was applicable to *N*-confused[2;3] and expanded (hetero)porphyrins,[23–30] on 21-heteroporphyrins. In addition, a new structural element has been introduced that can be applied for supramolecular assemblies that place molecular surfaces around the curved exteriors of fullerenes.

Experimental Section

NMR spectroscopy: NMR spectra were recorded by using high-field spectrometers (^{1}H frequency 500.13 or 600.15 MHz), equipped with a broadband inverse gradient probehead. Spectra were referenced to the residual solvent signals ([D]chloroform, $\delta_{1H}=7.26$, $\delta_{13C}=77.16$ ppm) or H_3PO_4 as an external ^{31}P reference. Two-dimensional NMR spectra were

recorded with 2048 to 4096 data points in the t_2 domain and up to 1024 points in the t_1 domain, with a 1 s recovery delay.

Electrochemistry: Cyclic voltammograms were measured in nitrogen-deaerated dichloromethane solutions at RT (nBu$_4$NClO$_4$ as the supporting electrolyte, Ag/AgCl as the reference electrode, and glassy carbon as the working electrode, scan rate 50 mV s^{-1}, ferrocene as the internal reference).

Synthesis of 4-PO: 5,20-Bis(4-methoxyphenyl)-10,15-diphenyl-21-telluraporphyrin [10] (**3**; 100 mg, 1.27×10^{-4} mol) was dissolved in freshly distilled triethylamine (20 mL). Nitrogen was bubbled through the solution for 20 min and the solution was brought to a boil. Freshly distilled PCl_3 (0.35 mL, 2.5×10^{-3} mol) was added dropwise and the mixture was heated at reflux under nitrogen for 1 h (or more if TLC monitoring still showed the presence of substrate). The solvent was evaporated and the solid residue was dissolved in dichloromethane, filtered through basic Al_2O_3, and separated by column chromatography on SiO_2. The first fraction (eluent: CH_2Cl_2) was substrate **3**, the second orange fraction (eluent: 2% MeOH in CH_2Cl_2) was recrystallized from CH_2Cl_2 and hexanes to give the desired product **4-PO** as a black solid (55% yield). ^{1}H NMR (500 MHz, C_6D_6, 305 K): $\delta=3.14$ (s, 3H; OMe(20)), 3.16 (s, 3H; OMe(15)), 3.82 (d, ^3J(H,H) = 6.0 Hz, 1H; H-2), 4.11 (dd, ^4J(H,P) ≈ 4 Hz, ^3J(H,H) ≈ 4 Hz, 1H; H-18), 4.29 (m, 2H; H-3, H-12), 4.43 (dd, ^4J(H,P) ≈ 3 Hz, ^3J(H,H) ≈ 6 Hz, 1H; H-13), 4.75 (dd, ^4J(H,P) ≈ 4 Hz, ^3J(H,H) ≈ 4 Hz, 1H; H-17), 6.44 (d, ^3J(H,H) = 8.8 Hz, 2H; *m*-Ar-20), 6.48 (d, ^3J(H,H) = 8.6 Hz, 2H; *m*-Ar-15), 6.59 (br s, 2H; *o*-Ar-15), 6.68 (d, ^3J(H,H) = 7.1 Hz, 2H; *o*-Ph), 6.76 (d, ^3J(H,H) = 6.5 Hz, 2H; *o*-Ph), 6.81 (d, ^3J(H,H) = 8.6 Hz, 2H; *o*-Ar-20), 6.86 (m, 4H; *p*-Ph, *m*-Ph), 6.94 ppm (t, ^3J(H,H) = 7.3 Hz, 2H; *m*-Ph); ^{13}C NMR (150.9 MHz, $CDCl_3$, 298 K): $\delta=159.6$ (*p*-Anis), 158.6 (*p*-Anis), 154.3 (C1/C4), 150.4 (d, ^3J(C,P) = 2.0 Hz, C15), 147.3 (d, J(C,P) = 11.6 Hz), 145.8 (d, ^2J(C,P) = 2.3 Hz, C16/C19), 143.4 (C11/C14), 141.5 (C11/C14), 141.1 (d, ^2J(C,P) = 5.0 Hz, C16/C19), 140.1 (C1/C4), 137.5 (d, ^3J(C,P) = 1.5 Hz, C10), 135.3 (C2), 133.3 (C_{ipso}-Anis), 132.7 (C_{ipso}-5), 131.5 (*o*-Anis), 129.6 (*o*-Anis), 128.9 (Ph), 128.76 (d, ^3J(C,P) = 10.2 Hz, C18), 128.75 (Ph), 128.61 (Ph), 127.1 (d, ^3J(C,P) = 5.6 Hz, C12), 126.6 (Ph), 126.3 (d, ^3J(C,P) = 3.9 Hz, C13), 125.0 (C_{ipso}-Anis), 124.0 (*o*-Ph-5), 123.4 (C_{ipso}), 122.5 (d, ^3J(C,P) = 1.6 Hz, C20), 121.7 (d, ^3J(C,P) = 17.0 Hz, C3), 120.9 (d, J(C,P) = 10.0 Hz), 116.8 (d, J(C,P) = 5.0 Hz, C17), 116.7 (d, ^1J(C,P) = 161.1 Hz, C22), 114.4 (C15), 114.0 (*m*-Anis), 113.5 (*m*-Anis), 55.28 (OCH_3), 55.25 ppm (OCH_3); ^{31}P NMR (202.4 MHz, $CDCl_3$, 298 K): $\delta=10.09$ ppm; UV/Vis (CH_2Cl_2): λ (log ε) = 346 (sh), 388 (4.54), 447 (sh), 463 nm (4.53); HRMS (ESI): *m/z* calcd for $C_{46}H_{30}N_3O_3P^{130}Te$: 833.10815; found: 833.1083 $[M]^+$.

6(O)-PO: Complex **4**-PO (30 mg, 3.6×10^{-5} mol) was dissolved in CH_2Cl_2 (20 mL) and $AgBF_4$ (37 mg, 9.4×10^{-5} mol) was added. After stirring for 5 min, a few drops of water were added and the solvents were evaporated on a rotary evaporator. The solid residue was dissolved in CH_2Cl_2 and passed through a short Al_2O_3 column. The first fraction (eluent: CH_2Cl_2) was the substrate, the second fraction (eluent: 5% MeOH in CH_2Cl_2) was recrystallized from CH_2Cl_2 and hexanes to give the desired product **6**(O)-PO as a dark brown solid (85% yield). ^{1}H NMR (600 MHz, $CDCl_3$, 300 K): $\delta=3.825$ (s, 3H; OCH_3(20)), 3.94 (s, 3H; OCH_3(15)), 6.58 (d, ^3J(H,H) = 3.6 Hz, 1H; H-2), 6.94 (d, ^3J(H,H) = 9.0 Hz, 2H; *m*-Ar(20)), 7.01 (d, ^3J(H,H) = 3.6 Hz, 1H; H-3), 7.13 (d, ^3J(H,H) = 8.9 Hz, 2H; *m*-Ar-15), 7.23 (dd, $J_1=2.6$ Hz; $J_2=3.7$ Hz, 1H; H-18), 7.32 (m, 2H; H-12, *p*-Ph-5), 7.44 (t, ^3J(H,H) = 7.8 Hz, 2H; *m*-Ph-5), 7.54 (dd, $J_1=2.6$ Hz; $J_2=3.7$ Hz, 1H; H-17), 7.55 (m, 3H; *m,p*-Ph-10), 7.61 (d, ^3J(H,H) = 7.7 Hz, 2H; *o*-Ph-5), 7.69 (br. d, 2H; *o*-Ar-15), 7.73 (d, ^3J(H,H) = 4.7 Hz, 1H; H-13), 7.76 ppm (m, 4H; *o*-Ar-20, *o*-Ph-10); ^{13}C NMR (150.9 MHz, $CDCl_3$, 298 K): $\delta=161.5$ (*p*-Ar-15), 159.8 (*p*-Ar-20), 158.9 (d, J(C,P) = 11.2 Hz), 154.6 (d, ^2J(C,P) = 1.5 Hz, C11/C14), 146.7 (d, J(C,P) = 6.3 Hz), 143.2 (d, ^2J(C,P) = 1.7 Hz, C11/C14), 142.2 (C10), 140.5 (C5), 138.4, 138.1, 137.9, 135.6 (d, ^3J(C,P) = 3.4 Hz, C-*ipso*-20), 135.0 (d, J(C,P) = 5.4 Hz), 133.8 (*o*-Ar-15), 133.4 (d, ^2J(C,P) = 1.7 Hz, C19), 133.09 (C-*ipso*-5), 132.06 (C13), 131.6 (d, ^3J(C,P) = 5.5 Hz, C17), 131.3 (d, ^2J(C,P) = 22.4 Hz, C16), 130.5 (*o*-Ph-10), 129.4, 129.3 (*m*-Ph-5), 129.2 (*p*-Ph-5), 129.1 (*m,p*-Ph-10), 127.9 (*o*-Ph-5), 127.8 (C-*ipso*-15), 127.5 (*o*-Ar-20), 126.6 (d, ^1J(C,P) = 213.7 Hz, C-22), 125.0 (C12), 114.3 (*m*-Ar-15), 113.9 (d, J(C,P) = 19.2 Hz), 113.6 (*m*-Ar-20), 112.7 (C2), 111.5 (C3), 108.6 (d, ^3J(C,P) = 12.4 Hz, C18), 74.0 (d, ^2J(C,P) = 5.7 Hz, C20), 55.7 (15-OCH_3), 55.4 ppm (20-OCH_3); ^{31}P NMR (202.4 MHz, $CDCl_3$, 298 K): $\delta=-71.38$ ppm; UV/Vis (CH_2Cl_2): λ (log ε) = 402 (4.68), 455 (4.20), 558 (4.08), 760 nm (3.92); HRMS (ESI): *m/z* calcd for $C_{46}H_{31}N_3O_4P^{130}Te$: 850.1109; found: 850.1064 $[M+H]^+$.

[5−P(OH)$_2$X]$^+$[X]$^-$ (X=(*1R*)-(−)-10-camphorsulfonate): An NMR sample of **6**(O)-PO (≈5 mg) in $CDCl_3$ was titrated with a saturated solution of (*1R*)-(−)-10-camphorsulfonic acid in $CDCl_3$ and formation of **6**(O)-POH$^+$ was observed. Solid (*1R*)-(−)-10-camphorsulfonic acid was then added to the sample to form a saturated solution and **6**(O)-POH$^+$ slowly transformed into [**5**−P(OH)$_2$X]$^+$ (two diastereoisomers). The compound was not isolated (evaporation of solvents led to **6**(O)-PO regeneration). ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): $\delta=4.07$ (s, 6H; OCH_3), 7.30 (d, $J=8.8$ Hz, 2H; *m*-Ar-15), 7.39 (d, $J=8.8$ Hz, 2H; *m*- Ar-20), 7.47 (2 overlapping d, $J\approx4.9$ Hz, 1H; H-17), 7.59 (m, 1H; *p*-Ph-10), 7.73 (m, 2H; *m*-Ph-10), 7.87 (m, 4H; H-18, *m,p*-Ph-5), 8.02 (d, $J\approx7.9$ Hz, 2H; *o*-Ar-15), 8.05 (2 overlapping d, $J\approx4.8$ Hz, 1H; H-3), 8.09 (2 overlapping d, $J\approx8.6$ Hz, 2H; *o*-Ph-10), 8.23 (d, $J=3.7$ Hz, 1H; H-2), 8.31 (2 overlapping d, $J\approx8.1$ Hz, 2H; *o*-Ar-20), 8.53 (br m, 2H; *o*-Ph-5), 8.84 (2×d, $J\approx5.3$ Hz, 1H; H-12), 8.98 ppm (2×d, $J\approx5.3$ Hz, 1H; H-13); coordinated (1R)-(−)-10-camphorsulfonate signals in exchange with the noncoordinated anions: $\delta=0.66$ (s, H-8), 0.80 (s, H-9), 1.22 (m, H-5), 1.39 (m, H-6), 1.81 (m, H-3, H-5), 1.96 (m, H-4, H-6), 2.27 (d, H-3), 2.47 (d, H-10a), 2.86 ppm (d, H-10b); ^{13}C NMR (150.9 MHz, $CDCl_3$, 298 K): $\delta=219.8$ (C-2$_{cam}$), 164.2 (*p*-Ar-20), 161.6 (*p*-Ar-15), 158.7 (br), 150.3 (br), 148.7 (br.), 148.4 (α-pyrr) , 148.3, 148.2, 147.73 and 147.68 (*ipso*-Ar), 145.6 (d, ^2J(C,P) = 26 Hz) and 145.5 (d, ^2J(C,P) = 26 Hz) (α-pyrr, 2 diastereoisomers), 143.9, 143.8 (C-13), 140.5, 140.4, 140.1 (*o*-Ar-20), 138.0 (*meso*-Ar), 137.90 and 137.87 (α-pyrr), 136.79 and 136.75 (*o*-Ar-15), 136.54 and 136.47 (*ipso*-Ar), 135.00 and 134.93 (*o*-Ph-5), 133.0 (ipso Ph), 132.4 (C-18), 131.23 and 131.19 and 131.09 and 131.05 (2 doublets, C-2, 2 diastereoisomers), 130.6 (*o*-Ph-10), 130.34 and 130.31 (*m*-Ph, 2 diastereoisomers), 129.93 (*p*-Ph-5), 129.89, 129.8 (C-17), 129.4 (Ar-5), 125.8 and 125.7 (C-3), 121.9 and 121.8 (C-12), 115.5 (*m*-Ar-20), 113.5 (*m*-Ar-15), 58.6 (C-1$_{cam}$), 56.1 (OCH_3), 55.9 (OCH_3), 48.7 (C-7$_{cam}$), 48.4 (C-10$_{cam}$), 43.0 (C-3$_{cam}$), 42.7 (C-4$_{cam}$), 26.8 (C-5$_{cam}$), 26.1 (C-6$_{cam}$), 19.9 (C-9$_{cam}$), 19.5 ppm (C-8$_{cam}$); ^{31}P NMR (202.4 MHz, $CDCl_3$, 298 K): $\delta=1.08$; HRMS (ESI): *m/z* calcd for $C_{46}H_{31}N_3O_4P^{130}Te$: 850.1109; found: 850.1127 $[M-X]^+$ (M=[**5**-P(OH)$_2$X]$^+$); *m/z* calcd for $[C_{46}H_{33}N_3O_5P^{130}Te]^+$: 868.1214; found: 868.1235 $[M-(X-O)]^+$.

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