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A Straightforward Access to Chiral Phosphangulene Derivatives

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ABSTRACT: Polycyclic aromatic hydrocarbons including heteroatoms have found a wide range of applications for instance in supramolecular chemistry or material science. Phosphangulene derivatives are P-containing polycyclic aromatic hydrocarbons presenting a concave aromatic surface suitable for building supramolecular receptors. However, the applications of this convenient building block have been strongly hampered by a difficult and multistep preparation requiring several protection-deprotection sequences along with the use of harmful reagents. Here, we report a straightforward, protecting-group-free, three steps **and hundred milligram**-scale synthesis of a chiral phosphangulene oxide derivative via a triple phospho-Fries rearrangement. This compound was easily resolved by chiral HPLC and further functionalized, giving rise to versatile chiral phosphangulene derivatives. Following this strategy, chiral phosphangulene oxides with low symmetry were synthesized. Molecular crystal structures revealed the variety of molecular organization in the solid. This opens the way to a wider use of this compound as a building block for cages or materials.

INTRODUCTION

Polycyclic aromatic hydrocarbons are key building blocks in material sciences, organic electronic or supramolecular chemistry.¹ Incorporation of heteroatoms can modulate the electronic properties of polycyclic aromatic compounds, leading to new functional materials, self-assembled structures or covalent cages with improved and controlled properties.^{2,3} Among the P-containing polycyclic aromatic hydrocarbons, phosphangulene derivatives appear as an appealing class of compounds.⁴ Indeed, most of the building blocks used to prepare covalent or self-assembled cages are concave aromatic surfaces. The bowl-shaped geometry of phosphangulene appears to be particularly relevant to build supramolecular receptors (Figure 1a).⁵ Moreover, the cone angle and the concavity of the molecule can be tuned by oxidizing the phosphine into its chalcogenide derivatives, allowing a possible and easy modularity of the shape of the cavity.⁶ In addition, both phosphangulenes and phosphangulene oxides present remarkable complexation properties towards fullerenes. Furthermore, chiral derivatives have been resolved and the enantiomers exhibited interesting chiroptical properties.⁷ However, the applications of phosphangulene derivatives are still limited, few articles dealing with their properties, mainly in solid state, have been published since their discovery in 1997 by Krebs et al.,^{4,7, 8,9} and only one article used them to build a cage receptor.⁵ The lack of an easy and simple method to functionalize phosphangulene derivatives could account for the narrow scope of applications of these fascinating molecules. Thus, an innovative synthetic approach leading to a facile and straightforward preparation of a phosphangulene derivative and its subsequent easy and selective functionalization is of high interest. Here, we propose a convenient four-step synthesis of functionalized chiral phosphangulene derivatives. Phosphangulene oxide **1** can be obtained on the hundred milli-

gram scale, and resolved by chiral HPLC (Figure 1d). Then, its easy and highly

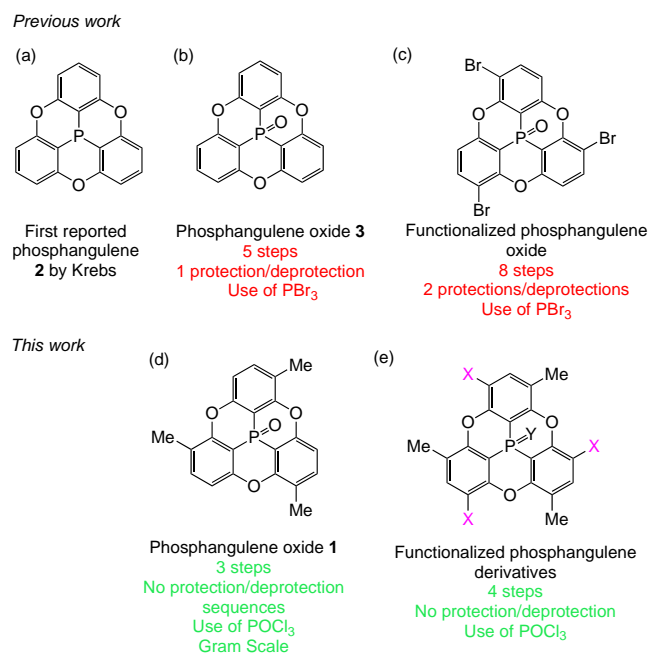


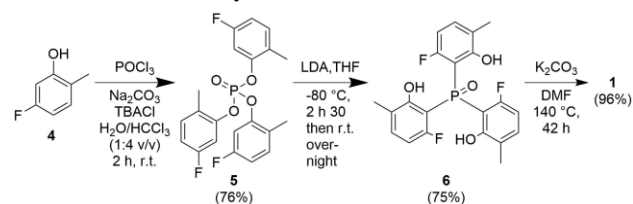
Figure 1. Comparison between the work previously described and this work.

selective post-functionalization provides new chiral molecules. In contrast with the previous approach described to synthesize functionalized phosphangulene derivatives, which involved two different protection/deprotection sequences, our synthesis excludes both protecting groups and toxic PBr₃. It therefore approaches the criterion of the 'ideal synthesis' and extends the

scope of these concave bowl-shaped molecules (Figure 1). Moreover, phosphangulene derivatives with C_1 symmetry can be obtained, answering to the current need for methods for preparation of receptors with low symmetry.¹⁰

RESULTS AND DISCUSSION

Synthesis of phosphangulene oxide 1. Phosphangulene oxide **1** was chosen as a key target as we anticipated that the methyl group should permit to control the regioselectivity of the subsequent electrophilic aromatic substitution, allowing its selective and direct post-functionalization (Figure 1). Indeed, functionalization of phosphangulene derivatives reveals tedious as direct electrophilic aromatic substitution on phosphangulene oxide **3** was found to be poorly regioselective, providing a complex mixture of products.^{7c} As a consequence, the functional groups have to be introduced during the synthesis and require protecting groups leading to a longer, more complicated and not modulable synthetic pathway. Our approach provides a single phosphangulene **1** that can be easily post-functionalized, giving various derivatives and avoiding the use of any protecting groups during the synthesis. We anticipate that three simultaneous phospho-Fries rearrangements on phosphate **5** should provide the key aryl phosphine precursor **6** in a single step without any protecting group and that phosphate **5** should be easily accessible (Scheme 1). Phosphate **5** was synthesized by a phase transfer procedure, and was obtained in 76 % yield.¹¹ Then, three phospho-Fries rearrangements gave the expected aryl phosphine **6** in 75 % yield. The subsequent cyclizations were performed using K_2CO_3 as a base.¹² Although the use of *t*-BuOK was previously described for the formation of phosphangulene derivatives, a better yield was obtained in our case using these conditions (10% vs 96% with *t*-BuOK and K_2CO_3 respectively). Thus, the synthesis of phosphangulene oxide **1** was achieved in only three steps following a protecting-group-free strategy involving an aryl-phosphate to aryl phosphine rearrangement that avoids the use of PBr_3 . Hundred milligram scale of **1** can be easily obtained.



Scheme 1. Three-step, protecting group-free synthesis of phosphangulene oxide 1.

Characterization of phosphangulene oxide 1. Phosphangulene oxide **1** was fully characterized by 1H NMR and displays the expected C_3 symmetry (Figure S3). Importantly, crystals suitable for X-ray diffraction were obtained by slow evaporation of a chloroform solution of *rac*-**1**. The X-ray analysis confirms unambiguously the structure of phosphangulene oxide **1** (Figure 2 (a)). In contrast with phosphangulene, which crystallizes in parallel π -stacks due to their conical shape and electron-rich aromatic surface, structures of phosphangulene oxides and other chalcogenide derivatives, which often exist as multiple polymorphs, provide crystals that cannot form packed conical stacks.⁴ With phosphangulene oxide **1**, the stacking reveals an original arrangement where two phosphangulene oxides **1** face their concave surfaces providing homochiral *PP* and *MM* pseudo-

cages with C_3 symmetry, aligned with the *c*-axis, and including a chloroform molecule. Molecular packing in the highly symmetrical structure of the crystal (trigonal $R\bar{3}c$) is mainly maintained through multiple π - π interactions (centroid-centroid distances 3.593 Å) between columns of pseudo-cages and forming layers of *PP* and *MM* pseudo-cages perpendicular to the *c*-axis. Chloroform solvent molecules play a key role in crystal packing and are arrayed along the *c*-axis and form layers orthogonal to the *c*-axis. (Figures 2 and S45). A cavity volume of 232 Å³ was calculated for the pseudo-cage (Figure 2 (b)). This demonstrates that concave surface of phosphangulenes **1** can be combined and used to complex guest molecules, suggesting that phosphangulene **1** is a relevant building block of cage-like covalent receptors.

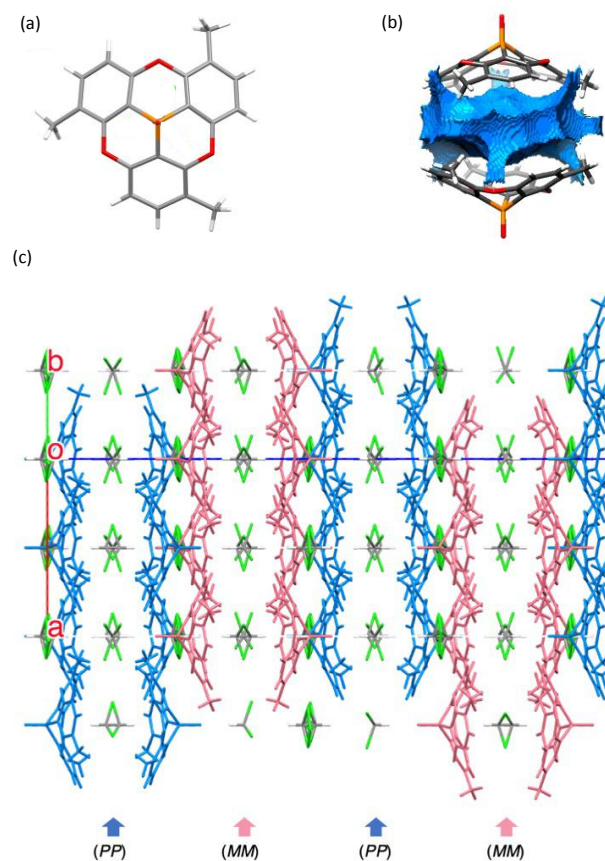


Figure 2. (a) Top view of the X-ray structure of phosphangulene oxide **1**; (b) Structure of two phosphangulene oxides **1** with concave surfaces facing each other and representation of the volume of the cavity (in blue, 232 Å³); (c) View of the layers of *PP* (blue) and *MM* (pink) pseudo-cages perpendicular to the *c*-axis.

Resolution of phosphangulene oxide 1. Given the remarkable chiroptical properties of enantiopure phosphangulene derivatives and the interest arose by the development of bowl-type π -conjugated enantiopure molecules,^{7c} we performed the resolution of racemic **1** by preparative chiral HPLC. This allows for isolating both enantiomers of **1** with high *ee* >99.5% (Figure 3 (a)). Moreover, the two enantiomers can be isolated on a hundred milligram scale. The assignment of the absolute configuration was achieved by comparison of their electronic circular dichroism spectra (Figure 3 (b)). The two enantiomers display mirror images ECD spectra and the ECD spectrum of *M*-**1** (second eluted) was calculated using

the TD-DFT method. The experimental and theoretical spectra are highly similar, allowing to propose the following assignment: the first eluted enantiomer (levogyre) has a *P* configuration, whereas the second one (dextrogyre) presents a *M* one.

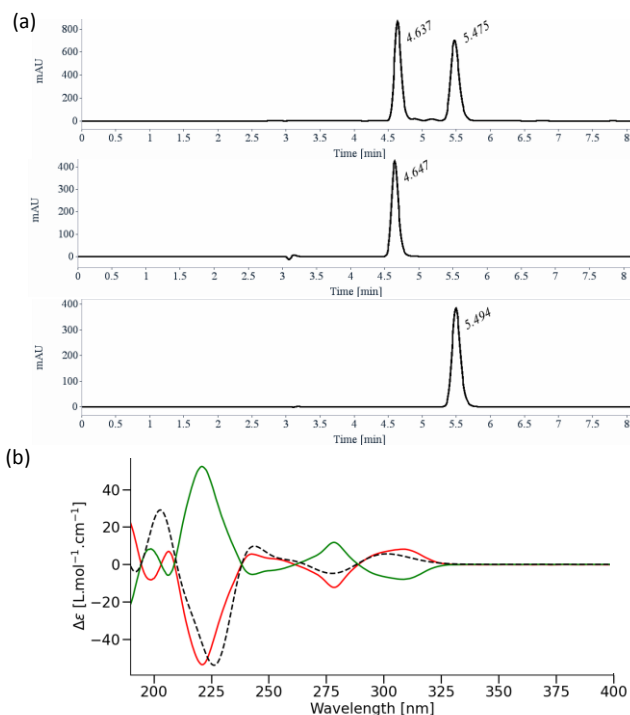
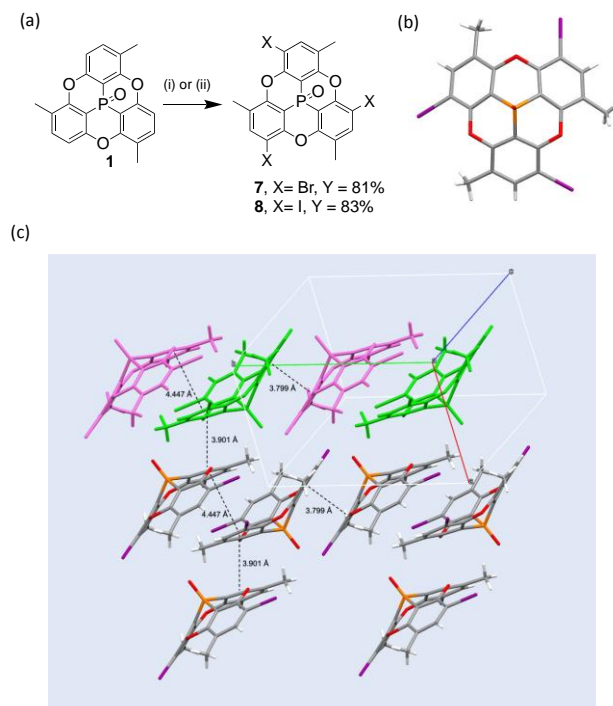


Figure 3. (a) Chiral HPLC chromatogram of *rac*-**1** (top), the first eluted enantiomer after preparative HPLC (middle), the second eluted enantiomer after preparative HPLC (bottom) (Chiralpak IG; Heptane/ethanol /dichloromethane (30/30/40)); (b) Experimental ECD spectra of the first eluted (*P*-**1**) enantiomer (green solid line (0.36 mmol.L⁻¹ in CH₃CN)), and of the second eluted (*M*-**1**) enantiomer (red solid line (0.36 mmol.L⁻¹ in CH₃CN)). The black dashed line represents the simulated ECD spectrum of the *M*-**1** enantiomer, red-shifted by 0.55 eV and simulated at the CAM-B3LYP-D3/def2-SVP level of theory.

Reduction of phosphangulene oxide **1.** With this easily accessible phosphangulene oxide **1** in hand, we then investigated whether it could be possible to modify its structure to access a library of such building blocks. Firstly, we examined some possible reactions at the phosphorus center of **1**. Phosphangulene oxide **1** reacted with one equivalent of the Lawesson's reagent, at 110 °C for 24 h, providing the phosphangulene sulfide in quantitative yield, which was then further reduced into its phosphangulene counterpart by adding an excess of HMPT and heating at reflux in toluene for 24 h (68% yield, Scheme S1).^{13,14} Nevertheless, it can be noticed that a minor amount of oxide **1** is still present, as can be observed in the ¹H NMR spectrum (Figure S5). Thus, **1** can be converted both in another chalcogenide derivative or in its phosphine parent in high and modest yields respectively, as previously described for other phosphangulene oxides.

Selective halogenation of phosphangulene oxide **1.** We next envisaged a functionalization of the aromatic rings of **1** using a direct aromatic electrophilic substitution. Whereas the bromination of phosphangulene oxide **3** is poorly regioselective, giving a mixture of compounds,^{7c} the methyl groups in ortho position of the oxygen atoms of **1** leave only one position suitable for aromatic electrophilic substitution, according the Holleman rules. Bromination and iodation of

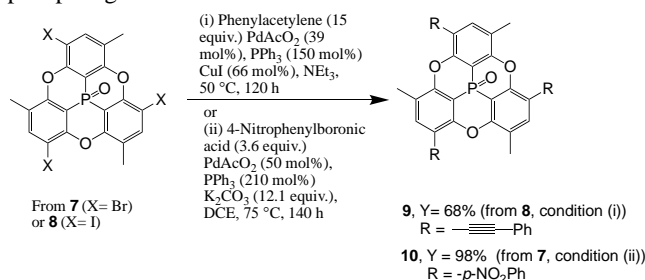
phosphangulene oxide **1** were successfully achieved using respectively (i) Br₂ in the presence of Fe in DCM and (ii) I₂ in the presence of AgNO₃ in MeOH (see Scheme 2). The yields are similar, brominated phosphangulene oxide **7** is obtained with 81% yield and its iodinated parent **8** with 83% yield. The ¹H NMR spectra of these functionalized phosphangulene oxides are consistent with C₃ symmetrical structures, supporting a high regioselectivity (Figures S6 and S7). The ³¹P NMR spectra displays close chemical shift (-45.28 and -46.15 ppm for **7** and **8** respectively, Figures S17 and S18)). It can be noted that we were not able to detect or isolate any product corresponding to C₁ symmetrical brominated or iodinated compounds that could arise from various regioselectivity during the halogenation reactions. X-ray structure of **8** (Scheme 2 (b)) is fully consistent with NMR analysis and confirms the structure of this functionalized phosphangulene oxide and the regioselectivity of this reaction. The packing observed for the iodo-phosphangulene oxide **8** is similar to that found in other structures of phosphangulene oxides with the formation of offset clamshell pairs. The paired molecules consist in centrosymmetric *MP* dimers facing each other via their concave surface (centroid-centroid distance 4.447 Å). In the crystal, adjacent pairs are connected by π -stacking (centroid-centroid distances 3.799 and 3.901 Å) (Figure S46).



Scheme 2. (a) Regioselective halogenation of phosphangulene oxide **1**; (i) for bromation: Br₂ (16 equiv.), Fe (2.3 equiv.), DCM, 15 °C, 24 h; (ii) for iodation: I₂ (35 equiv.), AgNO₃ (31 equiv.), MeOH, sealed 90 °C, 90 h. (b) X-ray structure of **8**. (c) Principal π - π interactions marked by broken lines; first raw: offset clamshell pairs formed with *P* (green) and *M* (pink) iodo-phosphangulenes **8**.

Access to π -extended concave phosphangulene oxide. Our strategy allows a simple and highly selective post-functionalization of phosphangulene oxide **1**. We then investigated if these halogenated phosphangulene oxides can give an access to π -extended concave molecules. Indeed, π -extended phosphangulenes, were found to display remarkable recogni-

tion properties of fullerenes.^{5,7c} Sonogashira coupling with **1** was performed using phenylacetylene as substrate, providing **9** in 68% yield (Scheme 3). Suzuki coupling is another very convenient method to provide π -extended and functionalized system. Once applied to phosphangulene oxide **1**, in the presence of 4-nitrophenylboronic acid, it gives the expected compound **10** in 98% yield. This underlines the ability of our approach to give a convenient access to π -extended phosphangulene derivatives.

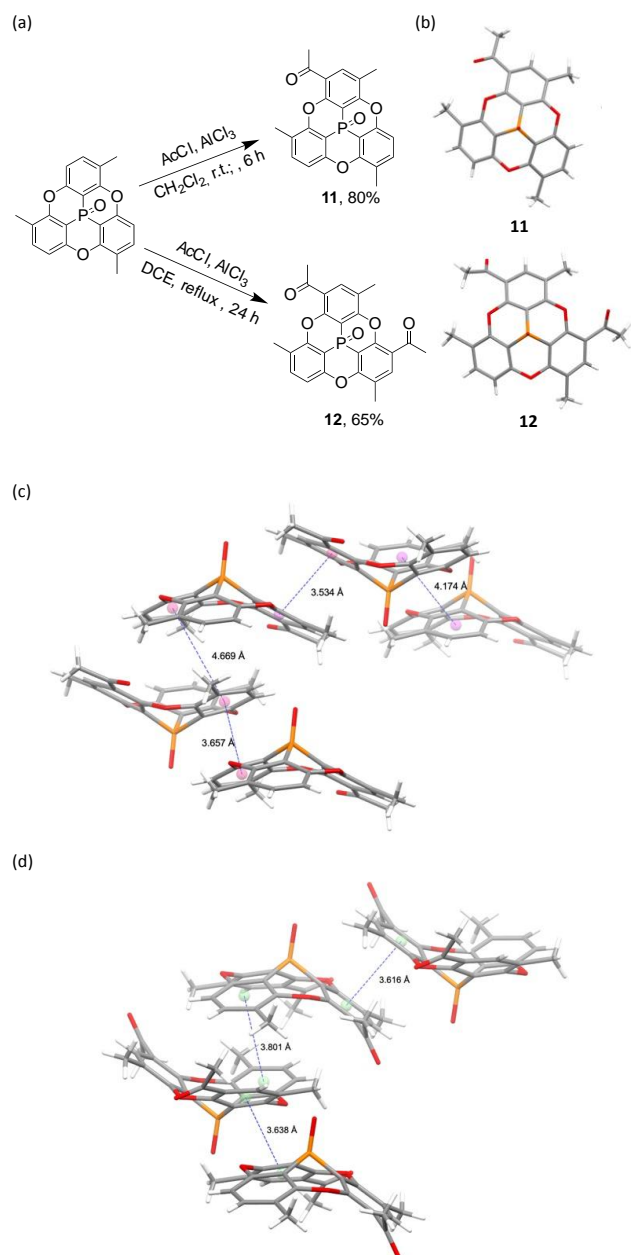


Scheme 3. Examples of Sonogashira and Suzuki coupling with halogenated phosphangulenes **7** or **8**.

Access to C₁ symmetrical phosphangulene oxides. The two approaches described above afford two-steps access to π -extended phosphangulene derivatives from the key compound **1**. We then wondered if we could directly form C-C bonds in a single step from **1** by a Friedel–Crafts reaction. Stirring phosphangulene **1** in CH₂Cl₂ for 6 h at room temperature in the presence of three equivalents of acyl chloride, solely provides the mono-acetylated product **11** (80% yield, Scheme 4). This could be explained by the de-activation by the ketone function of the two other aromatic rings. Heating at reflux during 24 h in DCE gives the di-acetylated compound **12** in 65% yield. Further heating, or the use of microwave conditions do not allow us to obtain the C₃ symmetrical acetylated phosphangulene. The structure of these two phosphangulene oxides were first proposed based on the ¹H NMR and mass spectrometry analysis and then further confirmed by their X-ray structures (scheme 4 (b)). As previously observed with the iodo-derivative **8**, the packing in crystals of mono-acetylated **11** and di-acetylated **12** phosphangulene oxides reveals offset clamshell pairs. Interestingly, in all three structures, adjacent pairs are maintained by π - π interactions with distances between convex faces of 3.5 to 3.9 Å. Main differences concern the weakest aromatic interactions in the clamshell dimers whose centroid-centroid distances are 4.447 and 4.669 Å in **8** an **11**, and 3.801 Å in **12**, respectively. Thus, in the solid, the stacking of the clamshell pairs via their convex faces is probably one of the main stabilizing interactions favoring crystallization (Figure S47).

CONCLUSIONS

In conclusion, we have described a straightforward and protecting group-free access to phosphangulene oxide derivatives. An original phospho-Fries rearrangement has been developed, providing the key chiral phosphangulene oxide **1** on the hundred milligram scale in only three steps. **1** can be resolved by HPLC, providing the two enantiomers with high *ee*. This scaffold can then be easily modulated by highly regioselective one-step functionalization reactions, giving an access to various functionalized phosphangulene compounds, including C₁ symmetrical derivatives. Furthermore, this method opens the way for a larger use of phosphangulenes, in particular as chiral building blocks for supramolecular assemblies.



Scheme 4. (a) Regioselective Friedel–Crafts acylation of phosphangulene oxide **1**. (b) X-ray structures of mono-acetylated phosphangulene oxide **11** and di-acetylated phosphangulene oxide **12**. (c) Partial view of the crystal packing in mono-acetylated phosphangulene oxide **11**, and (d) di-acetylated phosphangulene oxide **12**.

ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.joc.3c2674>.

Synthesis procedures; ¹H, ¹³C and ³¹P NMR; mass spectra and X-ray; and DFT data.

Accession Codes

CCDC 2304897–2304900 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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