

Structural Modifications of Dithienophospholes for Applications as Functional Materials

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Abstract

Recent breakthroughs in synthetic chemistry have revolutionized main-group molecules, elevating them from mere laboratory curiosities to powerful materials with broad applications. A primary focus has been on electron-accepting or -deficient materials, driven by their historical limitations in availability and stability, which have hindered practical applications. The incorporation of heavier main-group elements, including Si, Ge, P, As, Sb, Bi, S, Se, and Te, has proven advantageous for electron-accepting materials due to their polarizable molecular orbitals (MOs) readily accessible to electrons and nucleophiles. This foundation has spurred research in materials chemistry across various applications, encompassing optoelectronic devices (OLEDs, OPVs), energy storage (batteries, capacitors), fluorescent sensors (biological, physiological), catalysis, and synthesis. Among main-group-element-based materials, organophosphorus compounds hold a privileged status, with their frontier orbitals easily modifiable through chemical, structural, or electronic means at the phosphorus center itself, without necessitating kinetic stabilization. The five-membered phosphorus-based heterocycle, phosphole, is particularly captivating in this context. Extensive studies have unveiled the intricate $\sigma^*-\pi^*$ interaction within phospholes, endowing them with intriguing electron-accepting properties, while preserving morphological and physiological stability for practical utilization. Furthermore, phosphorus introduces easily accessible, low-lying antibonding orbitals, leading to Lewis acidic phosphorus species, a departure from the conventional perception of phosphorus as an electron-rich element. These species exhibit unconventional chemical reactivity through hypervalency. This thesis advances conjugated materials by employing the unique structures and electronics of organophosphorus compounds. It discusses how these materials can be harnessed to design functional materials with exceptional electronic, chemical, and structural properties, contributing to the realm of functional materials.

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Dedication

To Sindhuamma and Sathiamma, my guiding lights.

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List of Symbols, Abbreviations and Nomenclatures

Symbols	Definitions
MOs	molecular orbitals
OLEDs	organic light-emitting diodes
OPVs	organic photovoltaics
LUMO	Lowest Unoccupied Molecular Orbital
HOMO	Highest Occupied Molecular Orbital
LA _s	Lewis acids
Cp ₂ Zr	zirconyl cyclopentadiene
SC-XRD	single-crystal X-ray diffraction
SEM	scanning electron microscopy
NMR	nuclear magnetic resonance
FIA	fluoride ion affinity
HSAB	hard-soft acid-base
LB	Lewis base
FLAs	fluorescent Lewis acid
EN	electronegativity
FMO	frontier molecular orbital
BCF	tris(pentafluorophenyl)borane
3c-4e bond	3-center-4-electron bond
4SQ	square pyramidal
VSEPR	valence shell electron pair repulsion
3BP	trigonal bipyramidal

<i>o</i>	ortho
DCM/CH ₂ Cl ₂	dichloromethane
SPS	solvent purification system
THF	tetrahydrofuran
RT	room temperature
h	hours
<i>J</i>	coupling constant
Hz	Hertz
UV/UV-Vis	ultraviolet/ultraviolet-visible
ppm	parts per million
M	molar
λ	wavelength
abs, ex, em	absorption, excitation, emission
ACQ	aggregation caused quenching
δ	chemical shift
kcal/mol	kilocalorie per mole
TfO ⁻	triflate anion (CF ₃ SO ₃ ⁻)
CHCl ₃	chloroform
<i>t</i>	tertiary
nm	nanometer
c	concentration
ESP	electrostatic potential
kJ/mol	kilojoule per mole

ZPE	zero-point energy
DFT	density functional theory
TD	time dependent
HIA	hydride abstraction affinity
TIPS	triisopropylsilyl
Et ₂ O	diethyl ether
Dipp	2,6-diisopropylphenyl
OFETs	organic field-effect transistor
CT	charge transfer
TMS	trimethylsilyl
eV	electron-volt
ε	extinction coefficients
f	high oscillator strength
QY	quantum yield
PMMA	polymethyl methacrylate
DME	dimethoxyethane
μ M	microwave conditions
μ	micro

List of Publications

1. **Asok, N.**; Zondag, B. A.; Pradhan, E.; Odagwe, O.; LeBlanc, J.; Walsh, J. C.; Bodwell, G. J.; Zeng, T.; Baumgartner, T. Exploring the Lewis Acidity and Reactivity of Neutral Hypervalent Dithienophospholes. *Chem. Eur. J.* **2023**, e202300173.
2. **Asok, N.**; Gaffen, J. R.; Baumgartner, T. Unique Phosphorus-based Avenues for the Tuning of Functional Materials. *Acc. Chem. Res.* **2023**, 56, 5, 536-547.
3. **Asok, N.**; Gaffen, J. R.; Pradhan, E.; Zeng, T.; Baumgartner, T. Structure-Reactivity Studies on Hypervalent Square-Pyramidal Dithieno[3,2-*b*:2,3'-*d*]phospholes. *Dalton Trans.* **2021**, 50, 2243–2252.
4. Wang, Z.; **Asok, N.**; Gaffen, J.; Gottlieb, Y.; Bi, W.; Gendy, C.; Dobrovetsky, R.; Baumgartner, T. An Unexpected “Step-Conjugated” Biphosphole via Unique P–P Bond Formation. *Chem* **2018**, 4, 2628–643.
5. Hussein, A.; **Asok, N.**; Béland, V. A.; Gaffen, J. R.; LeBlanc, J.; Baumgartner, T. P-Arylation of Dithieno[3,2-*b*:2',3'-*d*]phospholes using Aryl Iodonium Salts: A New Approach Toward Conjugated Phospholium Species. *ChemPlusChem* **2023**, e202300133.

CHAPTER ONE: INTRODUCTION

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1.1 Organic π -Conjugated Materials

Organic π -conjugated materials can be effectively designed through structural, chemical, and electronic modifications that tailor their properties toward functional material applications. Thanks to decades of research, practical devices such as OLEDs, organic batteries, OPVs, and optical sensors derived from these materials are now finding their way into the commercial market. With the successes of *p*-type organic systems, the development of *n*-type conjugated materials is now gaining equivalent traction. Heteroatom-incorporated conjugated materials are an attractive avenue toward electron-acceptor species as they offer unique opportunities for the tuning of optoelectronic, electrochemical, and structural properties. Moreover, heteroatom incorporation can also afford Lewis-acidic compounds with utility as reagents and catalysts for chemical transformations in organic synthesis.¹

For example, boron-based materials are well known for their electron-accepting (or Lewis-acidic) character that arises from the empty low-lying *p* orbital at boron but the heavier *p*-block element-containing compounds exhibit similar characteristics that evolve through less obvious interactions. Nonetheless, the mixing of the heteroatom orbitals with the π -MOs of the organic fragment is

necessary in both the scenarios. Heavier p-block elements inherit atomic orbitals with a reduced tendency for hybridization, but a higher degree of polarizability. This, and the overall lower orbital energies, potentially make antibonding orbitals of the heavier main-group elements available for an interaction with a π -scaffold or a σ -donor. The case of phosphorus is an excellent representative example in this context.¹

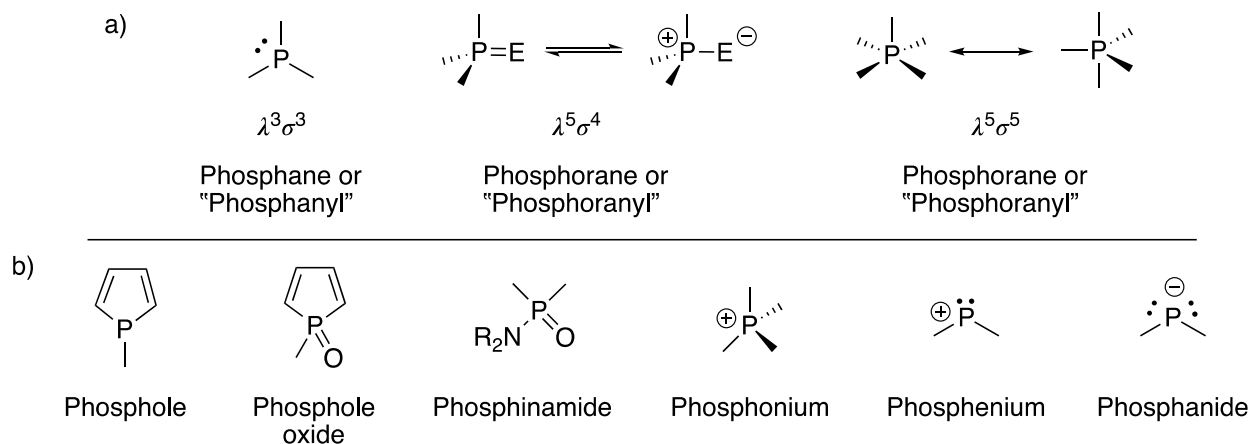


Figure 1-1. a) General *P*-nomenclature and b) specific building blocks used in this dissertation.

1.1.1 Organophosphorus Compounds

Pentavalent (λ^5) phosphorus species that exceed the valence-shell octet are a structural motif with obvious electron-accepting character, since phosphoranyl groups have an increased relative electronegativity (compared to trivalent (λ^3) phosphanyl groups) that inductively withdraws electron density from the conjugated main scaffold as a function of the formal positive charge on the phosphorus atom (Figure 1-1). While the accepting behavior of a λ^5 -phosphorus center is attributed to its hypervalency, trivalent (λ^3) phosphorus species can still acquire similar characteristics despite the inherent electron-donating nature of the lone pair at phosphorus. Trivalent $\lambda^3\sigma^3$ -phosphorus generally adopts a pyramidal geometry due to its high inversion barrier arising from the strong s-character of the phosphorus lone pair, which is in stark contrast to its

congener nitrogen. This is true for the five-membered phosphorus ring systems as well. Phosphole, the relative of pyrrole is considered only slightly aromatic by virtue of the pyramidal P-atom while the latter are inherently planar and have a more pronounced aromatic character.^{1,2}

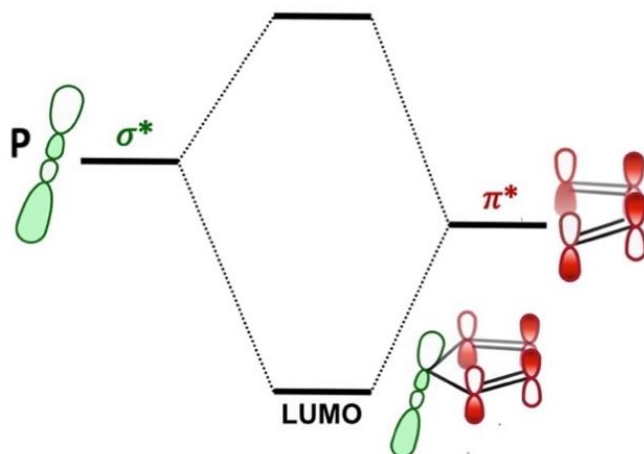


Figure 1-2. σ^* - π^* orbital mixing leading to favorable orientation of the σ^* orbital for negative hyperconjugation with the π -system of the main scaffold.

The pyramidal phosphorus atom is also the key contributing factor that gives rise to the electron-acceptor properties in conjugated phosphole materials. They are generated via a σ^* - π^* interaction between the σ^* orbital of the exocyclic P–R bond and the π^* system of the butadiene fragment of the five-membered system leading to an energetically stabilized MO (Figure 1-2). In most cases, this extended orbital represents the Lowest Unoccupied Molecular Orbital (LUMO) of the organophosphorus-based conjugated materials. This interaction provides a key component for the tuning of the acceptor properties by variation of the exocyclic substituent. The latter has direct implications for the energy of the σ^* orbital, as a function of the polarity of the exocyclic bond. Moreover, in the $\lambda^3\sigma^3$ state, the lone pair at phosphorus is available for further chemical functionalization, such as oxidation, alkylation, or coordination to LAs ($E = O, S, Me^+, [M]$). This

allows installing a second exocyclic P-substituent that, with its inherent P–E σ^* orbital, can engage in a second $\sigma^*-\pi^*$ interaction thus further lowering the energy level of the LUMO (Figure 1-3).^{2,3}

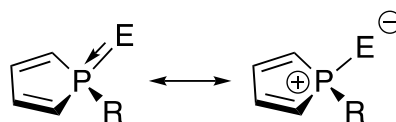


Figure 1-3. Electron-withdrawing E groups can impart a highly electrophilic P center in phosphole.³

1.1.2 Functional Application of Phospholes

The scope of phosphole-based materials in functional applications is broad and diverse. Incorporation of the phosphole unit into a fused framework with flanking thiophenes, i.e., in dithieno[3,2-*b*;2',3'-*d*]phospholes (**1-1**, Figure 1-4) leads to highly luminescent species with pronounced acceptor character. The functionalization of phosphorus with organic substituents R in **1-1** allows tailoring the properties for a variety of applications, including highly fluorescent sensory probes,^{4,5} stimuli-responsive chromism,⁶ self-assembly,^{6,7} and polyelectrolytes,⁸ whereas amino-functionalized dithienophospholes^{7,9} are precursors for materials with beneficial electron acceptor or self-assembly properties (*vide infra*).²

The related bridged bithiophene systems of the heavier group 15 heteroles also exhibit similar $\sigma^*-\pi^*$ interaction but only show poor orbital overlap between the small carbon atoms and the increasingly larger and diffuse heteroatomic orbitals. Nevertheless, the dithieno[3,2-*b*;2',3'-*d*]heteroles **1-2**, **1-3**, and **1-4** shown in Figure 1-4 are thermodynamically stable and exhibit phosphorescence that has not been seen for the P-containing relatives to date. The heavier pnictogens also resist oxidation due to the stronger s-character of their lone pair, while the phosphorus congener is more readily oxidized, affording a new functionalization avenue for tuning the electronic properties of these systems.¹ Additionally, larger phosphorus-containing ring

systems, such as phosphepines(**1-5**),^{10,11} have similarly pronounced optical properties as their five-membered congeners, but are synthetically less accessible than dithienophospholes.

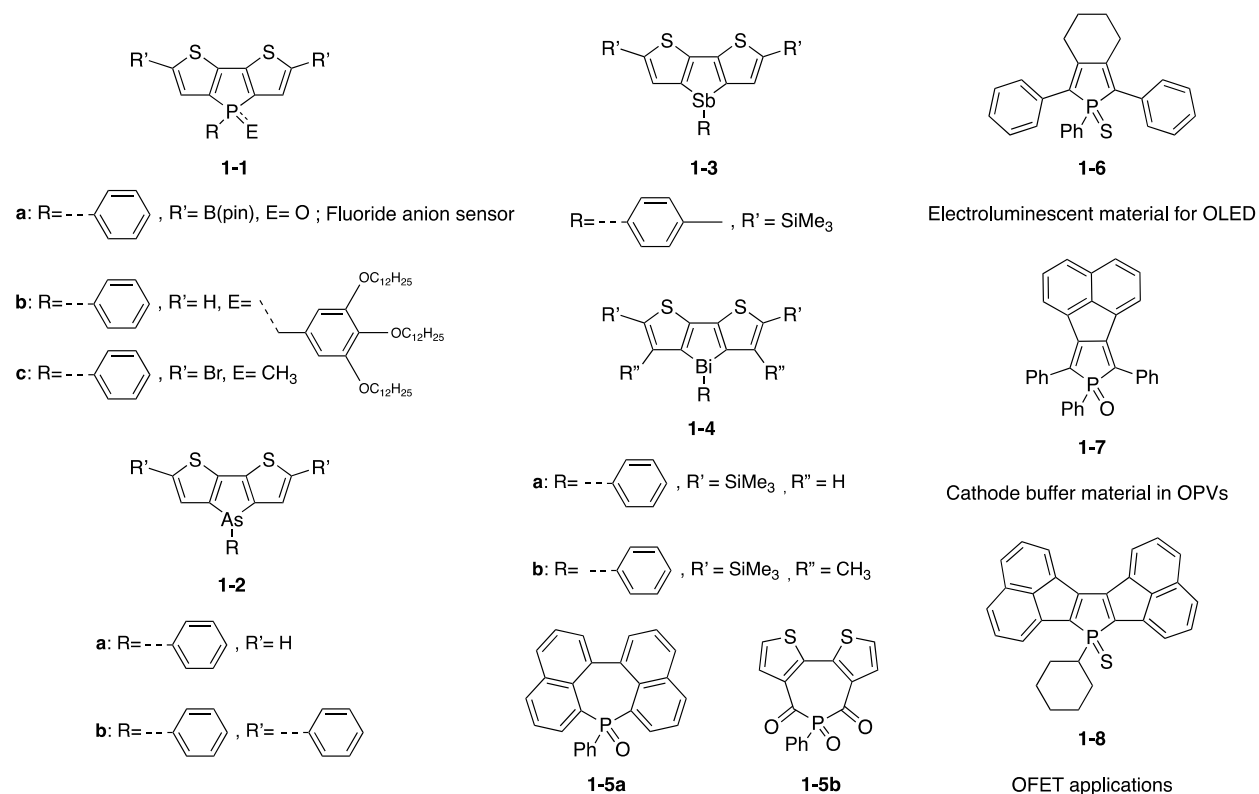


Figure 1-4. Representative examples of dithieno[3,2-*b*;2',3'-*d*]heteroles, phosphepines.^{1,10,11} and organic electronic applications of phosphole-based materials.¹²

The above examples address σ^* - π^* interactions through chemical modification of **1-1** at R and E and to a minor extent, R' toward specific application environments. An alternative and worthwhile strategy in designing P-functional materials relies on structural modification of the P center in **1-1**. Such modification affects the σ^* - π^* interactions more directly but there is much room for further development that goes beyond a simple exchange of substituents (R or E) to explore dithienophospholes as value-added materials. The following sections briefly overview various 'next level' structural modifications.

1.2 Enhancing $\sigma^*-\pi^*$ Interactions Through Various Next-level Structural Modifications

1.2.1 P–P Bond Formation Towards Biphospholes

The electron-affinity of phosphole-based materials can be enhanced by dimerizing them via the P center to generate 1,1'-biphospholes (**1-6**). The P–P bridging in **1-6** is theoretically expected to double the LUMO stabilization, thereby providing a more easily accessible orbital (Figure 1-5). The highly polarizable P–P bond is expected to allow $\sigma-\pi$ conjugation while effectively controlling the dihedral angle between the two phosphole units to exhibit a decreased Highest Occupied Molecular Orbital (HOMO)-LUMO gap, consequently affording a unique avenue to enhance $\sigma^*-\pi^*$ interaction. The extension of a biphosphole with thiophene units, as in dithienophosphole, has shown to be advantageous for further LUMO stabilization by offering additional modification sites on S that impact the photophysical and electrochemical properties of this material.^{13,14}

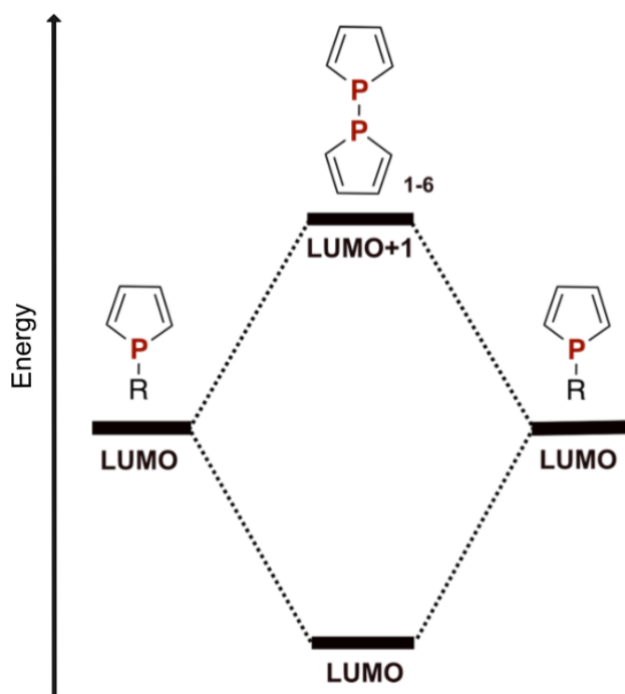
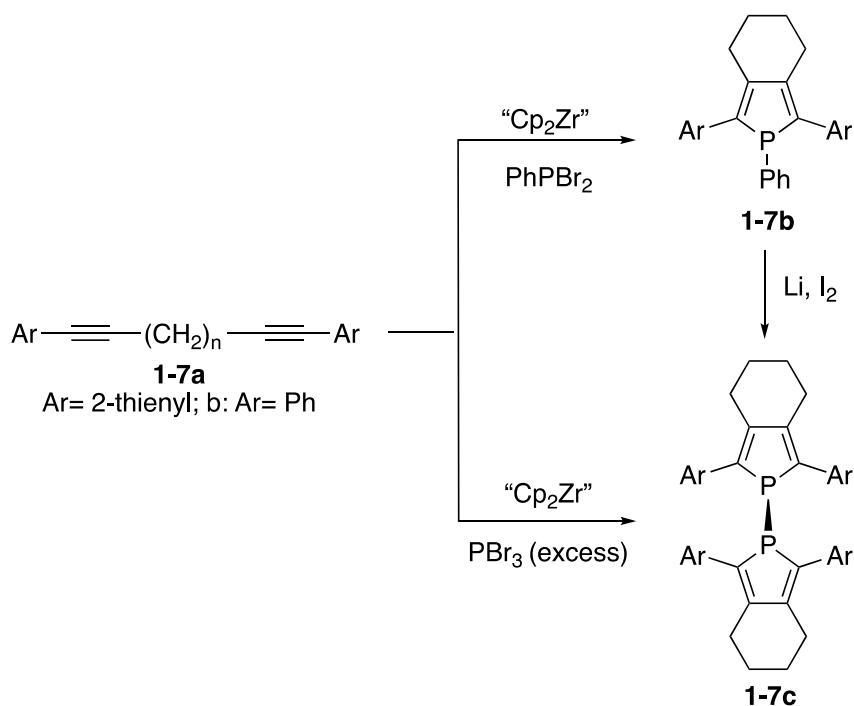


Figure 1-5. LUMO stabilization on P–P dimerization of R-functionalized phosphole to biphosphole.

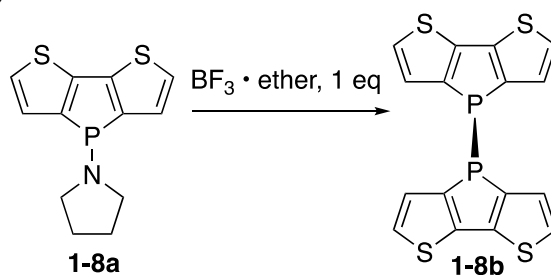
Symmetric and asymmetric biphospholes are generally accessed by (i) reductive cleavage of the exocyclic P–R bond (R = phenyl), (ii) oxidative coupling of metal phosphanides, or (iii) intramolecular oxidative coupling of ethynyl derivatives using zirconyl cyclopentadiene (Cp₂Zr).¹⁵ The latter was successfully used by the Réau group in their groundbreaking work on the synthesis of biphospholes of type **1-7c** from stable *P*-phenyl phospholes **1-7b** or the corresponding *P*-brominated species (Scheme 1-1).¹³ However, our own efforts have shown that this route cannot be extended to the dithienophosphole system, due to its distinct reactivity from that of non-ring fused phosphole systems.



Scheme 1-1. Synthesis of Réau's biphosphole, **1-7c**.¹³

Serendipitously, in the context of another project investigated by former group member Dr. Zisu Wang at the University of Calgary, purification attempts of amino-dithienophosphole **1-8a** provided high-quality crystals for single-crystal X-ray diffraction (SC-XRD) after column chromatography with alumina under nitrogen (*vide infra*). The molecular structure confirmed that

the isolated species was, in fact, the elusive bi(dithienophosphole) **1-8b**. This observation was rather puzzling as there was no obvious reaction sequence that would lead to P–N σ -bond cleavage followed by P–P bond formation. Considering that the surface of alumina is covered with Lewis-acidic sites, **1-8a** was treated with BF_3 at room temperature to observe the formation of an asymmetric intermediate, which upon refluxing led to biphosphole **1-8b** (Scheme 1-2, see Chapter 3 for detailed mechanism).⁹



Scheme 1-2. Synthesis of biphosphole, **1-8b**.⁹

The two phosphole subunits in **1-8b** are connected through an out-of-plane P–P σ bond leading to a phenomenon referred to as “step conjugation” (Figure 1-6a). The step-like shape of **1-8b** imparts electronic communication through π - σ - π conjugation between the individual dithienophosphole subunits through the P–P σ bond (via two mutual σ^* - π^* interactions). As the angle between the P–P σ bond and the conjugated planes is contracted to 75° , the phosphorus centers retain their pyramidal geometry. While Réau’s biphosphole system **1-7c** (Ar = 2-thienyl) adopts a twisted geometry in the solid state (Figure 1-6c),¹³ biphosphole **1-8b** exhibits a tight head-to-head conformation of the phosphole subunits (Figure 1-6b) suggesting potentially high charge carrier mobilities in a device setting. However, devices using **1-8b** as active material have not been reported to date.⁹

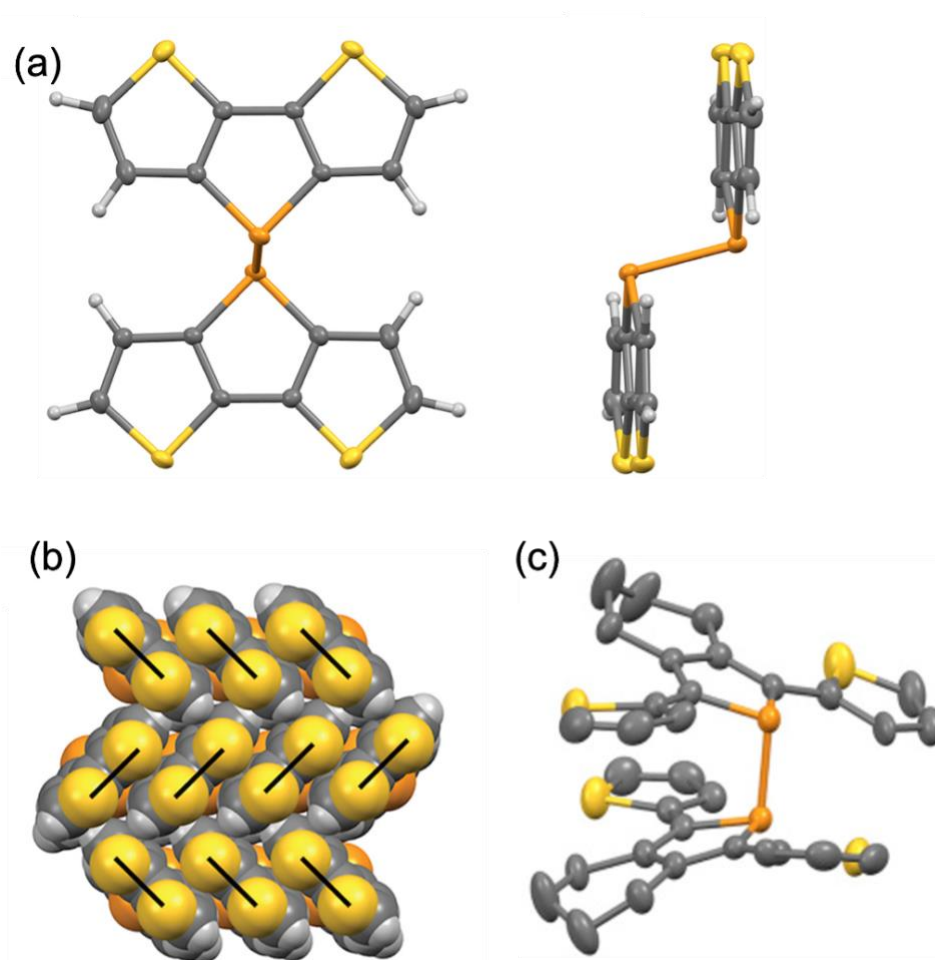
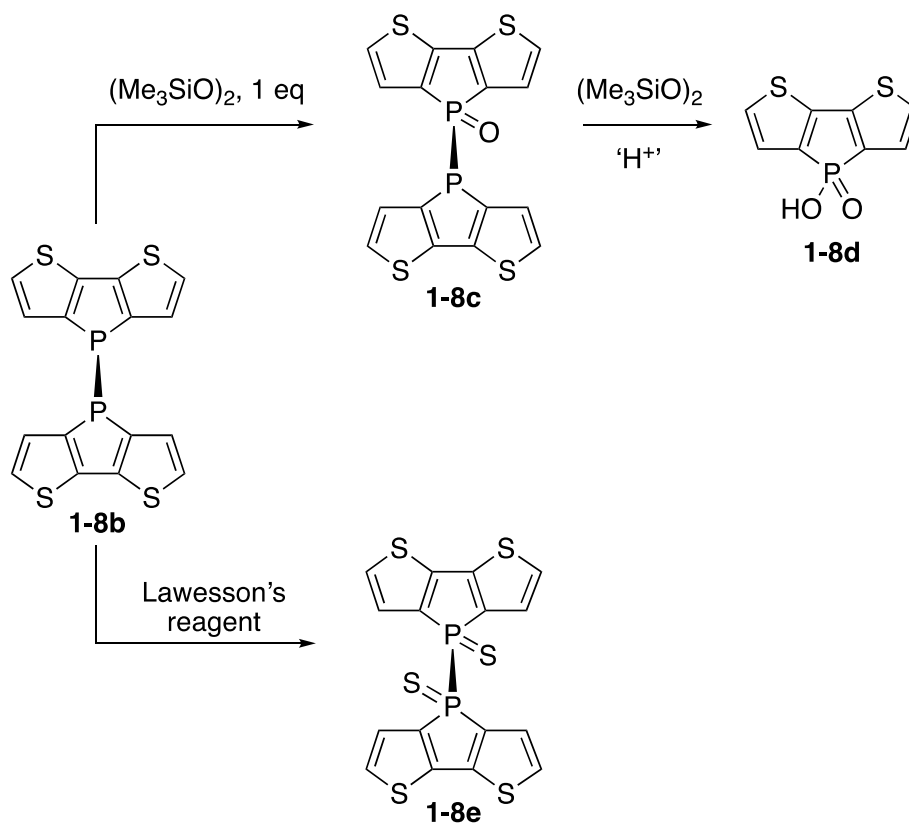


Figure 1-6. Solid-state structure of **1-8b** showing a) head-to-head conformation and step-like structure, b) herringbone arrangement with layer structure (intermolecular π - π distance, 3.5 Å), c) solid-state structure of **1-7c** (Ar = 2-thienyl)¹³. Reproduced with permission from ref. 9. Copyright 2018 Elsevier.

To study the effect of modification of the P center on the σ^* - π^* interaction and the resulting electronic and optical properties, post-functionalization of the biphosholes was also investigated. Compound **1-8c** was synthesized by treating **1-8b** with one equivalent of $(\text{Me}_3\text{SiO})_2$ but further oxidation was found to cleave the P-P bond, resulting in the formation of **1-8d**. On the other hand, disulfide species **1-8e** was accessible without cleavage of the P-P σ bond on reacting **1-8b** with Lawesson's reagent (Scheme 1-3).⁹



Scheme 1-3. *P*-Functionalization of biphosphole, **1-8b**.⁹

The absorption onsets of all bi(dithienophosphole)s are shifted bathochromically, compared to **1-9** (Figure 1-7), indicating effective extension of conjugation through the P–P bond within the entire scaffold. Interestingly, the similarities in the absorption spectra of **1-8b** and **1-8e** suggest that optical features are dominated by the entire step-conjugated scaffold rather than the oxidation state(s) of the phosphorus atoms, which is in stark contrast to ‘monomeric’ dithienophosphole **1-9**.¹⁶ In mono-oxidized **1-8c**, the scaffold experiences desymmetrization, leading to two distinct absorption peaks for the independent λ^5 - and λ^3 -P subunits respectively, instead of the broad absorption profile for the symmetric congeners **1-8b** and **1-8e**. However, all three species maintain the same absorption onset, supporting the electronic dominance of the step-conjugated scaffold

overall. This is an illustrative example for how electronically modified biphospholes with distinct optoelectronic characteristics can be accessed on different levels by simple manipulation of the $\sigma^*-\pi^*$ interaction.⁹

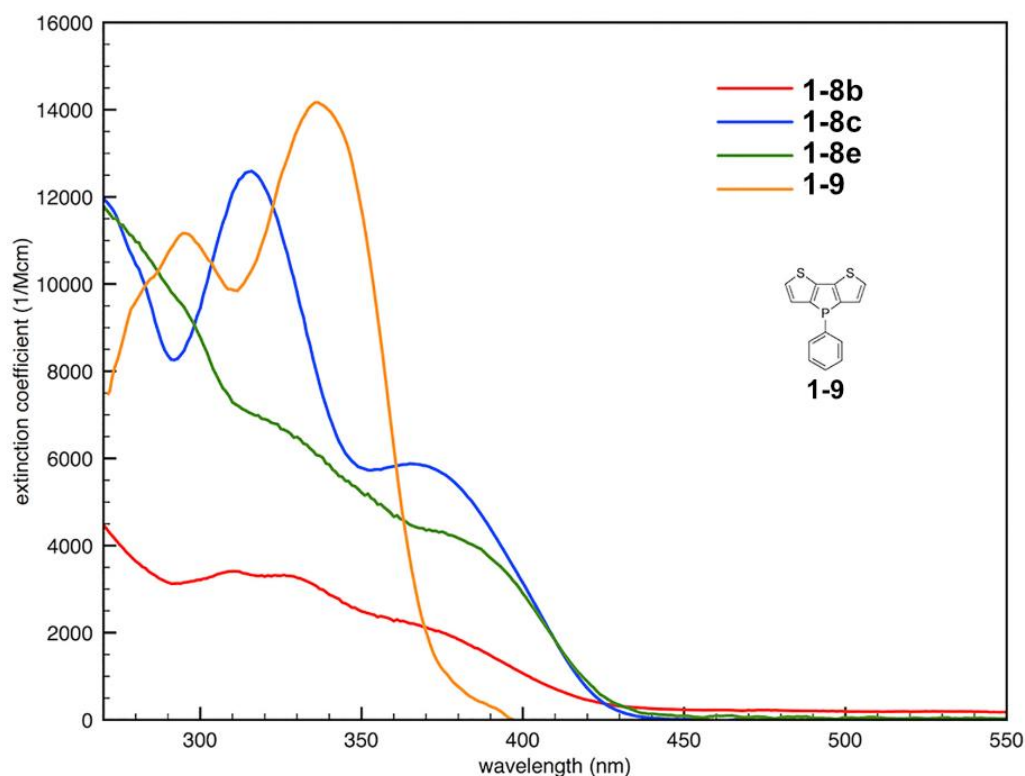
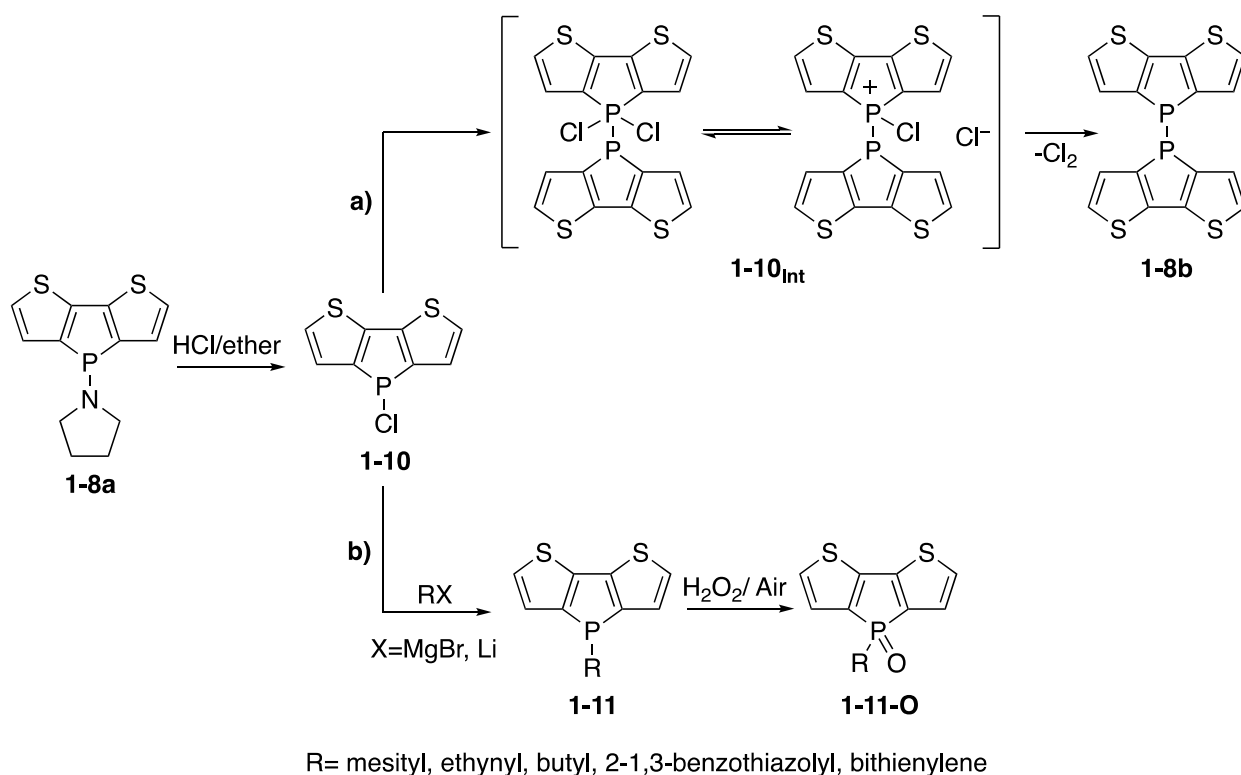


Figure 1-7. Absorption spectra of biphospholes **1-8b-e** compared to **1-9**. Adapted with permission from ref. 9. Copyright 2018 Elsevier.

In addition to the pyrrolidine-functionalized dithienophosphole **1-8a**, the trivalent *P*-chloro-dithienophosphole **1-10** also serves as a precursor for biphosphole **1-8b** (Scheme 1-4). This compound reacts *in situ* at room temperature to generate an asymmetric intermediate (**1-10_{Int}**) that reductively eliminates molecular chlorine to form **1-8b**. However, considering the highly reactive and transient nature of **1-10**, this method is not very practical for the synthesis of **1-8b**. Nonetheless, its reactivity can be leveraged for the synthesis of various *P*-substituted dithienophosphole and corresponding oxides that are inaccessible otherwise. For example, compound **1-10** can be treated with organometallic reagents, such as Grignard and organolithium

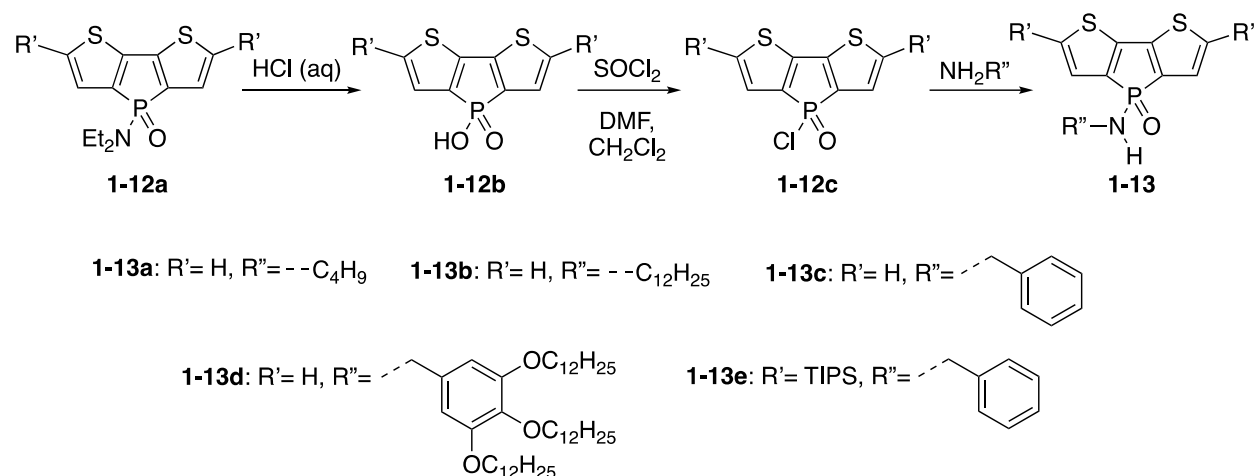
species to afford dithienophospholes with a variety of P-R groups (**1-11**, **1-11-O**) (Scheme 1-4).^{17,18,19}



Scheme 1-4. a) Alternate route towards the synthesis of biposphole **1-8b**, b) synthesis of various P-functionalized dithienophospholes from P-chloro-dithienophosphole.¹⁷

1.2.2 P-N Bond Formation Towards Self-Assembled Materials

Amino-dithienophospholes (**1-12a**) are also robust precursors for the generation of a series of phosphinamides (**1-13a-e**) with unique hydrogen-bond self-organization properties (Scheme 1-5).⁷ Notably, the central PO-NH fragments in **1-13** give rise to a much richer set of secondary bonding and structures when compared to the CO-NH-based carbamide congeners.^{20,21} While the latter are strictly limited to two bonding motifs, *syn*/head-to-head (i.e., 0°) and *anti*/head-to-tail (i.e., 180°), the P-based system essentially provides a highly adjustable dial that easily adapts to any given secondary/tertiary structure dictated by other intermolecular interaction types.²² To this end, the



Scheme 1-5. Synthesis of self-organizing phosphinamides.⁷

combination of intermolecular π - π interactions and H-bonding in **1-13a** causes the molecules to π -stack in unusual H-aggregate type²³ 1D columnar arrangement (Figure 1-8a), with head-to-tail linked PO–NH units at an angle of 131° between the PO and the NH groups. By contrast, the π -conjugated backbones in **1-13c** align in a *syn*-type, parallel fashion favoring a zigzag pathway for H-bonding with PO–NH at an intermediate angle of 47° between the PO and the NH groups. The bulky TIPS groups in **1-13e** suppress π -stacking and the compound only adopts H-bonding in a “head-to-head” dimer with a PO–NH angle of 17° (Figure 1-8c). The mesogenic versions, **1-13b**

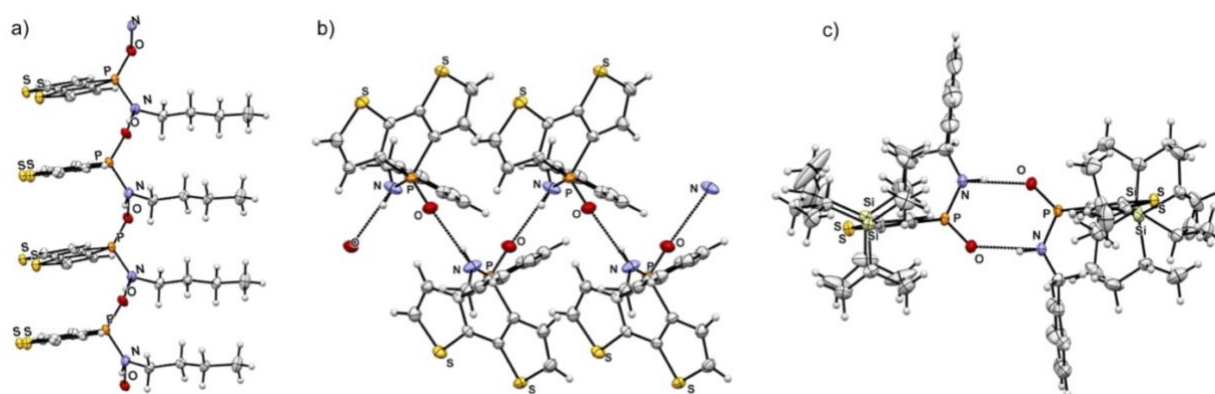


Figure 1-8. Solid-state structures of a) **1-13a** showing parallel alignment and columnar H-bonding, b) **1-13c** showing zigzag packing, and c) **1-13e** showing H-bonded dimers. Adapted with permission from ref. 7. Copyright 2016 John Wiley and Sons.

and **1-13d** exhibit soft-crystalline and liquid-crystalline features respectively at elevated temperatures, where **1-13d** is also able to form an organogel with n-heptane (Figure 1-9). While these phosphinamides enforce the functional application of the dithienophospholes, it is an illustrative account on how manipulation through flexible nitrogen substituents at the P-center can influence the aggregation properties in highly organized self-assembled materials.⁷

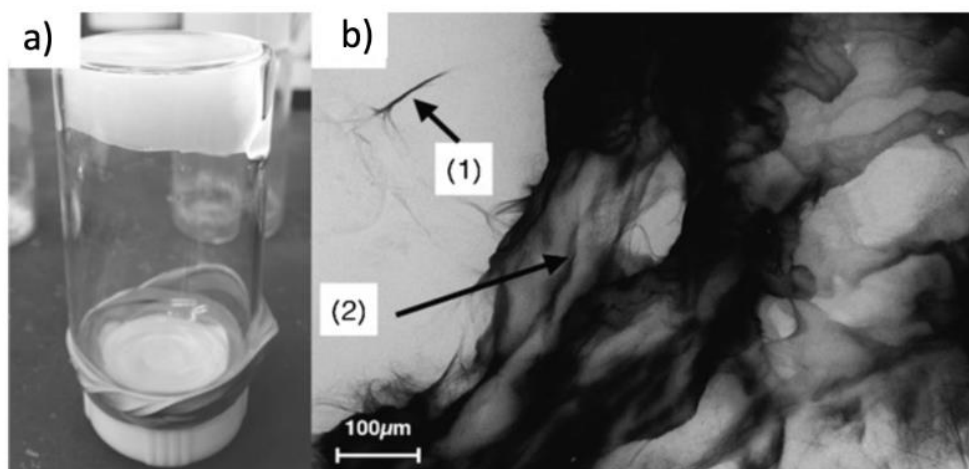


Figure 1-9. a) Organogel of **1-13d**, b) xerogel of **1-13d** visualized via SEM showing fiber bundles (1) and a sheet-like microstructure (2). Reproduced with permission from ref. 7. Copyright 2016 John Wiley and Sons.

1.2.3 Polarization of the P=O Bond

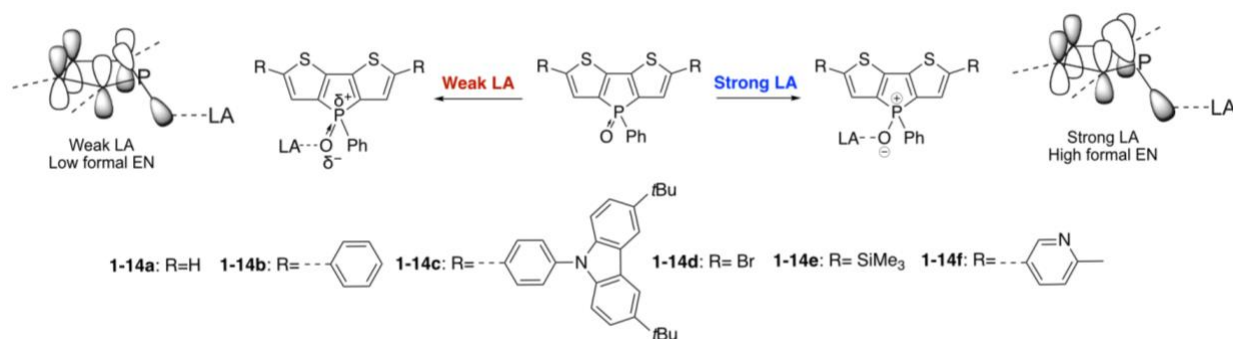
While the hydrogen-bonding ability of the P=O bond is beneficial for generating self-assembled materials as discussed above, its Lewis-basic donor character has proven quite advantageous for the determination of Lewis acidity. LAs in general have been established as catalysts, anion sensors, and are increasingly used in materials science as well.^{1,24,25,26} For these reasons, several methodologies currently exist that measure Lewis acidity through a variety of select parameters. Of the more prolific ones, the Gutmann-Beckett (GB) method correlates LA strength to the charge separation of the P=O bond as measured by ³¹P NMR spectroscopy.²⁷ Other methods similarly

correlate to spectroscopic or computational parameters, such as the Childs method,²⁸ fluoride ion affinity (FIA),²⁹ or the global electrophilicity index (GEI)³⁰. But a comprehensive study on Lewis acidity has not yet been accomplished due to the difficulty for correlative parameters to accurately account for the complexity of Lewis acidity. One reason for this is the hard-soft acid-base theory (HSAB) theory³¹ and the propensity for these methods to rely on a single Lewis base (LB), potentially influencing the measured parameter.

In this context, the Baumgartner group, in collaboration with the Caputo group, showed that dithienophosphole oxides provide access to a simple and effective method for the determination of Lewis acidity via fluorescent Lewis acid-base adducts (FLAs). Generally, fluorescent probes allow detection of very low concentrations of LA while exhibiting a high degree of analyte specificity and they often provide easily detectable and visible color changes. Considering the highly sensitive nature of LAs, the FLA method allows for safe and air-free testing condition for a wide range of LAs across the periodic table.^{5,32,33}

It is well established that P=O bonds are polar and better described with the canonical structure P^+-O^- (Figure 1-3), which inherently creates the possibility for the oxide species to interact with electrophiles; this scenario also applies to the highly fluorescent dithienophosphole oxides.³ Correspondingly, upon adduct formation, the polarization of the P=O bond is enhanced by the coordinated LA, which in turn strengthens the $\sigma^*-\pi^*$ interaction and lowers the energy of the LUMO. The polarization effect that is used to correlate Lewis acidity with the GB method also applies to the Lewis-adduct formation with a dithienophosphole oxide, but a photophysical alteration will also be established through FLA formation. Here, a stronger LA will considerably increase the polarity of the P=O bond, which leads to a much stronger contribution of the phosphorus atom to the σ^* orbital that then enhances the interaction with the π^* fragment and

lowers the LUMO correspondingly. The extent of emission redshift directly correlates to the strength of LA, where the most prominent difference is observed for strong LAs and not so much for weak ones (Scheme 1-6).^{5,32,33}



Scheme 1-6. Impact of weak and strong LAs on the polarization of the P=O bond via change in $\sigma^*-\pi^*$ interaction.⁵

For example, parent dithienophosphole oxide **1-14a**¹⁶ shows a visibly distinct, immediate shift in emission color from sky blue (λ_{em} 446 nm) to aquamarine (λ_{em} 509 nm) on adduct formation with the strong LA $B(C_6F_5)_3$. Here, the fluorescence of the adduct correlates LA strength to the frontier molecular orbitals (FMOs), i.e., via the $\sigma^*-\pi^*$ interaction, instead of the core shell electrons, allowing for much higher sensitivity of the parameter to small changes in Lewis acidity. Notably, the FLA method relies on combined data sets from three to four dithienophosphole probes with different emission colors and the method thus minimizes potential bias from the LB itself. It is also important to note that the FLA method measures the chromaticity of the corresponding adducts, rather than relying on simple emission (maxima). The chromaticity values of the three FLAs from a single LA, e.g., $B(C_6F_5)_3$ or 'BCF', and that of free phosphole oxide probes can be fit well with a parabolic function. Similarly, a well-defined parabolic function can also be used to compare the emission of all the free probes. These parabolas intersect at the point that corresponds to the chromaticity of an ideal adduct (cf.: HSAB) of a theoretical dithienophosphole oxide that can

generate FLA with a given LA in 1:1 mole ratio at saturation (Figure 1-10). The Commission Internationale de l'éclairage (CIE) coordinates³⁴ at this point correlate precisely with the strength of the LAs and the FLA method successfully determines the Lewis acidity of different compound classes, such as neutral boranes, heavy group 13 elements, cationic, and metallic species, including rare-earth metal triflates ($\text{RE}(\text{OTf})_3$).^{5,32,33} The latter is quite intriguing considering they usually display similar physicochemical properties with minimal detectable changes.

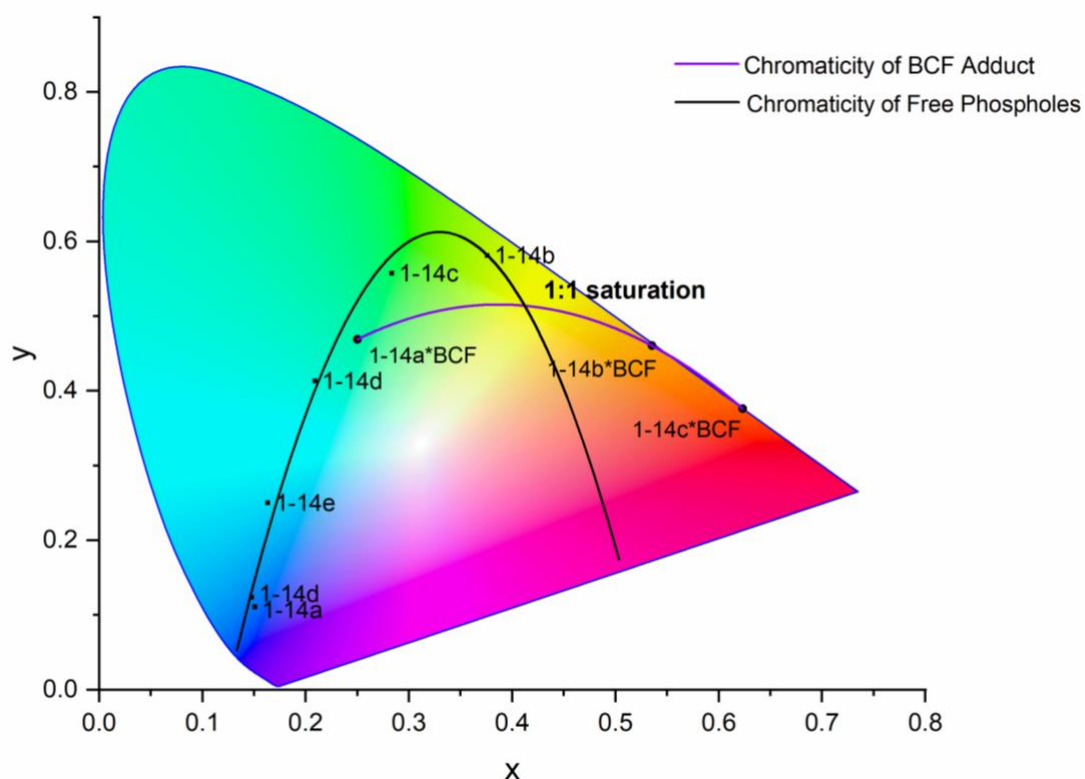
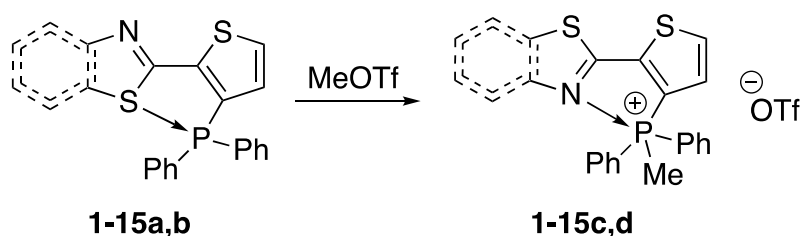


Figure 1-10. Critical point used to determine LA strength from the CIE space of free probes and their corresponding BCF adducts. Reproduced with permission from ref. 5. Copyright 2019 Elsevier.

The complexity of measuring and comparing LAs in solution is not strictly overcome by the choice of parameter being measured, but by the design of the experiment itself. The use of a reliable metric, such as the polarization of the $\text{P}=\text{O}$ bond by coordination to a LA, with the added sensitivity of the influence on the FMOs via the $\sigma^*-\pi^*$ interaction, allows for a much more sensitive measure.

However, an additional metric by which the complexity of LAs in solution can be addressed is still necessary, as evidenced by the difference in emission maxima across the individual probes. As chromaticity is a linear combination of all emissions from solution, all available emissive adducts, regardless of the nature of the acid-base adduct or the specifics of the LA in solution can be summarized in one measure. As such, the use of dithienophosphole oxides for measuring LA strength allows for both a highly sensitive measure and one that more appropriately represents the solution-state or *effective nature* of the LA.^{5,32,33}

1.2.4 Lewis Acidity Through $\lambda^5\sigma^5$ Hypervalency



Scheme 1-7. *P*-Methylation of 2-(2'-thiazolyl)-3-thienylphosphanes changes coordination mode.³⁶

A more traditional route to manipulating the σ^* and π^* contributions to the HOMO and LUMO (or more generally, the FMOs) of phosphorus-based molecular species is via $\lambda^5\sigma^5$ hypervalency. A sufficiently strong acceptor σ^* orbital on phosphorus, especially arising from an electronegative substituent, can allow for a highly Lewis-acidic phosphorus center.³⁵

The phosphanyl group in 2-(2'-thiazolyl)-3-thienylphosphanes **1-15a,b** can serve as soft LA in its trivalent state, but upon functionalization of the phosphorus center is converted into a relatively hard Lewis-acidic species, as defined by the HSAB theory (Scheme 1-7).³¹ The phosphorus centers in **1-15a,b** are capable of engaging in weak intramolecular LA/LB interactions through S→P coordination with a P–Ph σ^* orbital acting as the acceptor for the sulfur lone pair. This interaction

provides a covalent, albeit weak, 3c-4e bond type involving the now hypervalent phosphorus center (Figure 1-11a,b).³⁷ Upon methylation of phosphorus (**1-15c,d**), the coordination switches to N→P as evident from their solid-state structures (Figure 1-11c,d). The N→P interaction is better described as σ -hole bond type³⁸ involving the hypervalent P center through a strong electrostatic contribution that lies more closely at the ionic end of the spectrum for hypervalent bonding.³⁶

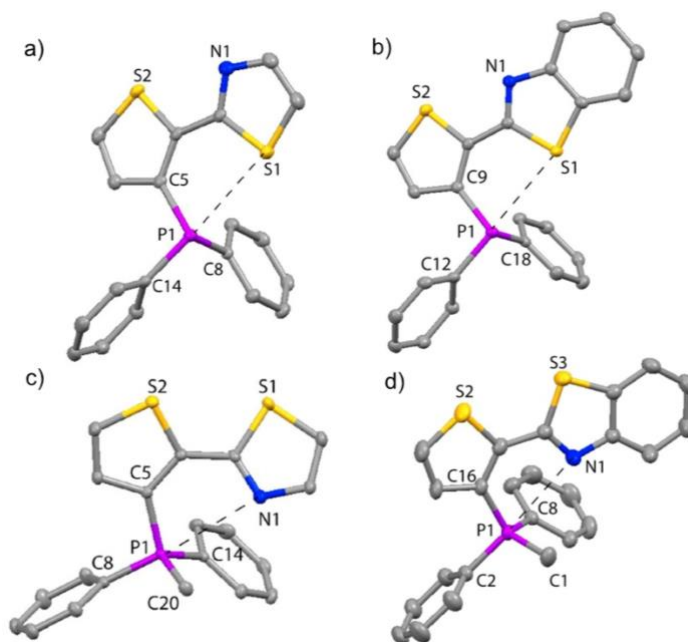


Figure 1-11. Solid-state structure of a) **1-15a**, b) **1-15b**, c) **1-15c**, and d) **1-15d**. Counter anion in **1-15c,d** omitted for clarity. Reproduced with permission from ref. 36. Copyright 2018 American Chemical Society.

The heavier analogues of phosphorus also exhibit intriguing Lewis-acidic character through hypervalency. For example, neutral $\lambda^5\sigma^5$ As (**1-16**) and Sb (**1-17**) species (Figure 1-12) adopt distorted square pyramidal (4SQ) geometries that project out a σ^* orbital to serve as an electron-acceptor site. The Lewis acidity arising from Sb/As–C_{Ph} σ^* orbital in these species is enhanced by stabilization of the π -system and/or electron-withdrawing substituents.^{1,39,40} While hypervalency is a prominent route towards Lewis acidity, a recent study shows that geometrical constraints of trivalent pnictogen centers can also serve as effective design strategy towards neutral LAs.

Recently, trivalent bismuthanes **1-18** with a constrained planar geometry around Bi, were found to be borderline hard/soft acids. The Bi center engages lone pairs conventionally through vacant p orbitals, rather than a low-lying antibonding orbital, thus behaving analogous to electrophilic triaryl boranes. The tethered ligand imposes rigidity to the Bi center to retain planarity upon ligand binding allowing the addition of a second ligand (L) to form nearly linear L–Bi–L arrangement.^{41,42}

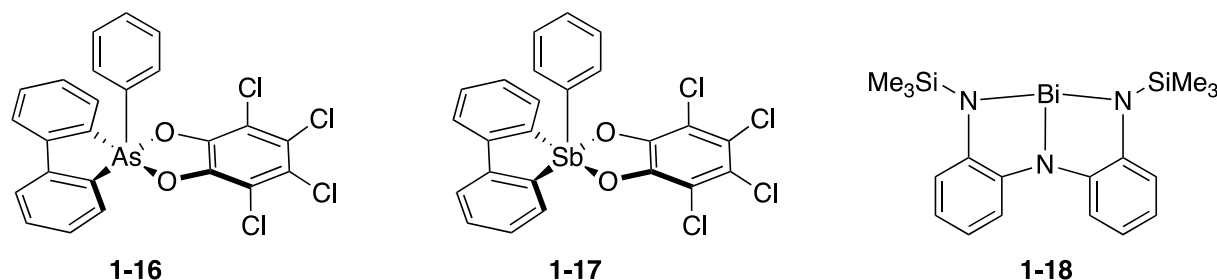


Figure 1-12. Select main-group element-centered LAs.^{39,40,41}

1.3 Scope of this Thesis

The central focus of this thesis is the structural modification of the phosphorus atom in dithienophospholes and related systems using advanced strategies to tailor their properties for functional material applications. The following chapters are structured to explore diverse methodologies for achieving spatial alterations in dithienophospholes, while also briefly delving into the characteristics and potential applications of these modified constructs. The chapters, although largely independent, have been organized to provide a comprehensive understanding of the possibilities and implications arising from the structural adaptation of the dithienophosphole scaffold. While extensive research has delved into the functional properties of these materials, additional investigation is imperative to fully explore their practical utility, particularly in the context of device implementation.

Chapter Two delves into the concept of hyper-coordination, leading to the development of neutral Lewis-acidic phosphorus-containing compounds. Within this context, geometrically constrained pentacoordinate dithienophospholes have been synthesized. These novel structures exhibit intriguing chemical reactivity when exposed to specific reagents. The initial section of this chapter recounts the serendipitous discovery of unexpected structures and reactivity patterns. A subsequent generation of these hypervalent LAs was synthesized to address the limitations observed in the first generation. This phase of research involved the exploration of diverse strategies to enhance the Lewis-acidic strength of these compounds, ultimately leading to the discovery of new reaction pathways facilitated by these LAs.

Chapter Three extends the initial research conducted on "Step-Conjugated Biphospholes" published in 2018. While my contribution to this original publication focused on experimental validation and electrochemical characterizations, Chapter Three now extensively investigates bi(dithienophosphole) materials. It examines in detail various electronically modified systems, scrutinizing their optoelectronic and electrochemical properties. Notably, this chapter introduces a novel synthetic route that circumvents the need for additional reagents, thereby significantly advancing the field considering the relative under-exploration of the chemistry and properties of this system.

Shifting the focus to Chapter Four, the exploration continues by investigating the potential of bi(dithienophosphole)s as stable precursors for synthesizing an easily transferable and emissive reagent 'dithieno-phospholide'. The contents of this chapter present preliminary and exploratory findings that briefly discuss optimized conditions for synthesizing the reactive phospholide species through reductive cleavage of P–P bond in bi(dithienophosphole)s. Furthermore, the chapter investigates the reactivity of this transfer reagent with various other halogenated compounds,

supplemented by the evaluation of the stability of newly synthesized phosphorus derivatives primarily using spectroscopic techniques. Extensive laboratory experiments are ongoing to comprehensively assess the potential of this research.

The thesis concludes with a forward-looking section that outlines potential avenues stemming from the various topics covered. Despite the presence of numerous tangential projects during the course of this thesis (several of which are concisely presented in the corresponding Chapters or the Supporting Information), other promising opportunities necessitate further experimental exploration. These immediate research directions are elaborated upon in the outlook section, reflecting the ongoing dedication to advancing the frontiers of knowledge in this domain.

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CHAPTER TWO: PENTACOORDINATE HYPERVALENT DITHIENOPHOSPHOLES: A JOURNEY THROUGH REACTIVITY AND STRUCTURAL VARIATIONS

2.1 Structure-Reactivity Studies on Hypervalent Square-Pyramidal Dithieno[3,2-*b*:2',3'-*d*]-phospholes

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2.1.1 Introduction

As discussed briefly in Chapter One, dithieno[3,2-*b*:2',3'-*d*]phosphole (**2-I**) is extensively researched due to its value as a *n*-type scaffold. Its electron-accepting capability comes from

σ^* - π^* hyperconjugation, where the σ^* orbital of the P-R bond interacts with the π^* orbital of the butadiene unit, leading to a stable LUMO level (Figure 2-1a). Altering the LUMO energy via P center (R) or framework (R') modification, coupled with strong fluorescence, has spurred thorough exploration of dithienophospholes for potential use in organic electronics.^{1,2} While most of the previous work focused on amendment of the electronics by exocyclic substitution reactions, including the functionalization of the phosphorus lone pair,³ the alteration of the geometry of the P center as a methodology to influence the energies of the FMOs is relatively less explored.^{4,5} An interesting structural platform for this purpose are hypervalent phosphorus compounds with coordination numbers of five or six.^{2,6}

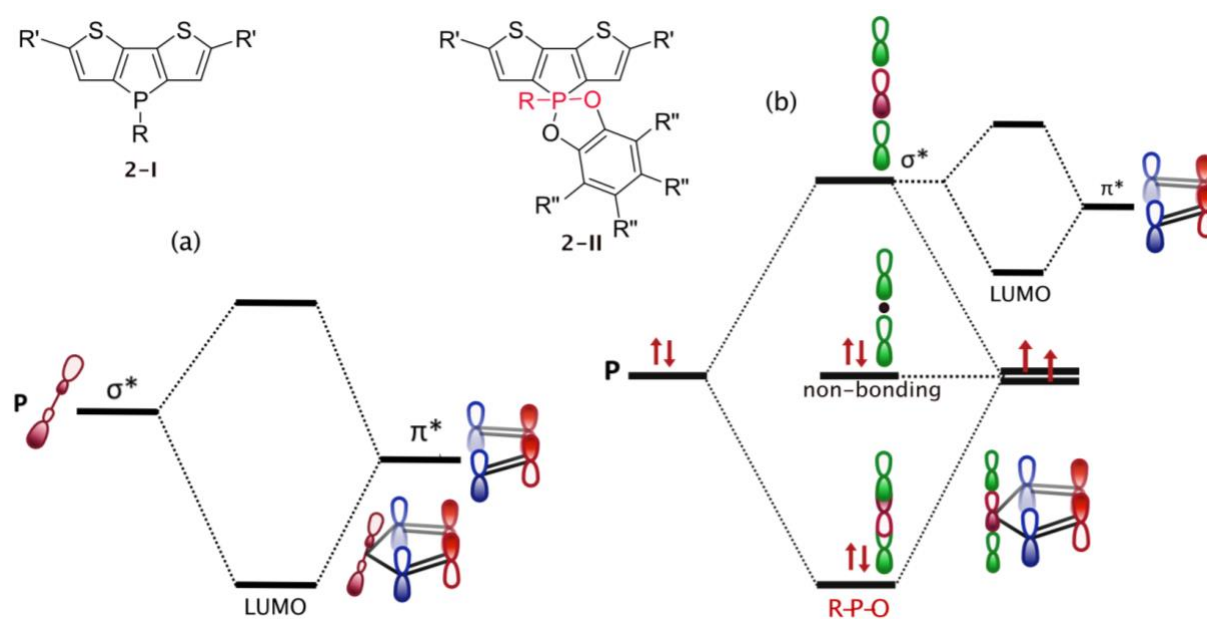


Figure 2-1. (a) σ^* - π^* Hyperconjugation in dithienophosphole, b) 3c-4e bond in the proposed hypervalent molecules.

Since trivalent phosphorus species are known to undergo [4+1] cycloaddition with *o*-quinones to form pentacoordinate molecules,⁷ we were interested in exploring if this approach could be extended to dithienophospholes as well. The Valence Shell Electron Pair Repulsion (VSEPR) model-predicted trigonal bipyramidal (3BP) geometry of the proposed molecule **2-II** with

pentavalent phosphorus exists by virtue of a 3c-4e bond (shown in red), with its three MOs of which the bonding and non-bonding MOs are filled.⁸ This non-classical bond would impart the electron-accepting properties by providing a vacant σ^* orbital that can interact with the π^* orbital of butadiene moiety. Importantly, the σ^* orbital is oriented perfectly orthogonally to the butadiene moiety and should thus lead to better overlap with the π -system (Figure 2-1b). We expected the hypervalency to be effectively leveraged in generating neutral and stable pentavalent phosphorus compounds with enhanced electron-accepting abilities compared to that of their parent trivalent analogue.

To our surprise, however, many unexpected observations, chiefly the generation of square pyramidal (4SQ) structures, arose during the course of this study, and we were afforded with an intriguing opportunity to shift our focus with these new species. Pentacoordinate phosphorus in a 4SQ geometry is uncommon, but not unprecedented.⁹⁻¹⁵ However, literature largely only provides a nebulous description of what dictates the geometry of such species. Structural assignments are generally based on a competing mixture of steric forces and undefined electronic arguments, using the withdrawing nature of the phosphorus substituents. While the reported 4SQ systems do result in Lewis-acidic neutral phosphorus species,¹⁶⁻¹⁸ the studies do not strictly afford an understanding of the electronic requirements for a 4SQ P(V) center. For better insight into that question, one can look into the heavier congeners of stibanes. Antimony pentahalides are well known LAs, but several typical pentacoordinate Sb(V) species also have nebulous geometric configurations.¹⁹⁻²⁶ Even the simple SbPh_5 exhibits a distorted 4SQ geometry.^{19,20} Counterintuitively, the perhalogenated species $\text{Sb}(\text{C}_6\text{X}_5)_5$ exhibit a fairly regular 3BP geometry, as typically a more withdrawing substituent is presumed to enforce a 4SQ geometry in phosphorus species.²¹ The SbPh_5 geometry is proposed to exist in the solid state due to the isoergic nature of the 3BP and

4SQ geometries, yet this similarity in energy is, not quite understood.^{19,20} Finally, a related series of heterobicycles reported by Holmes et al. strictly exhibits 4SQ geometry, highly reminiscent of the new series of structures reported herein.^{22,23}

With this contribution, we investigate what ultimately dictates the geometric orientation of these species, and what impact does it have on the inherent Lewis acidity of the phosphorus center. To this end, we report the synthesis, structures, properties, and reactivity of the new hypervalent dithienophospholes that provide an exciting opportunity for understanding these types of system more deeply.

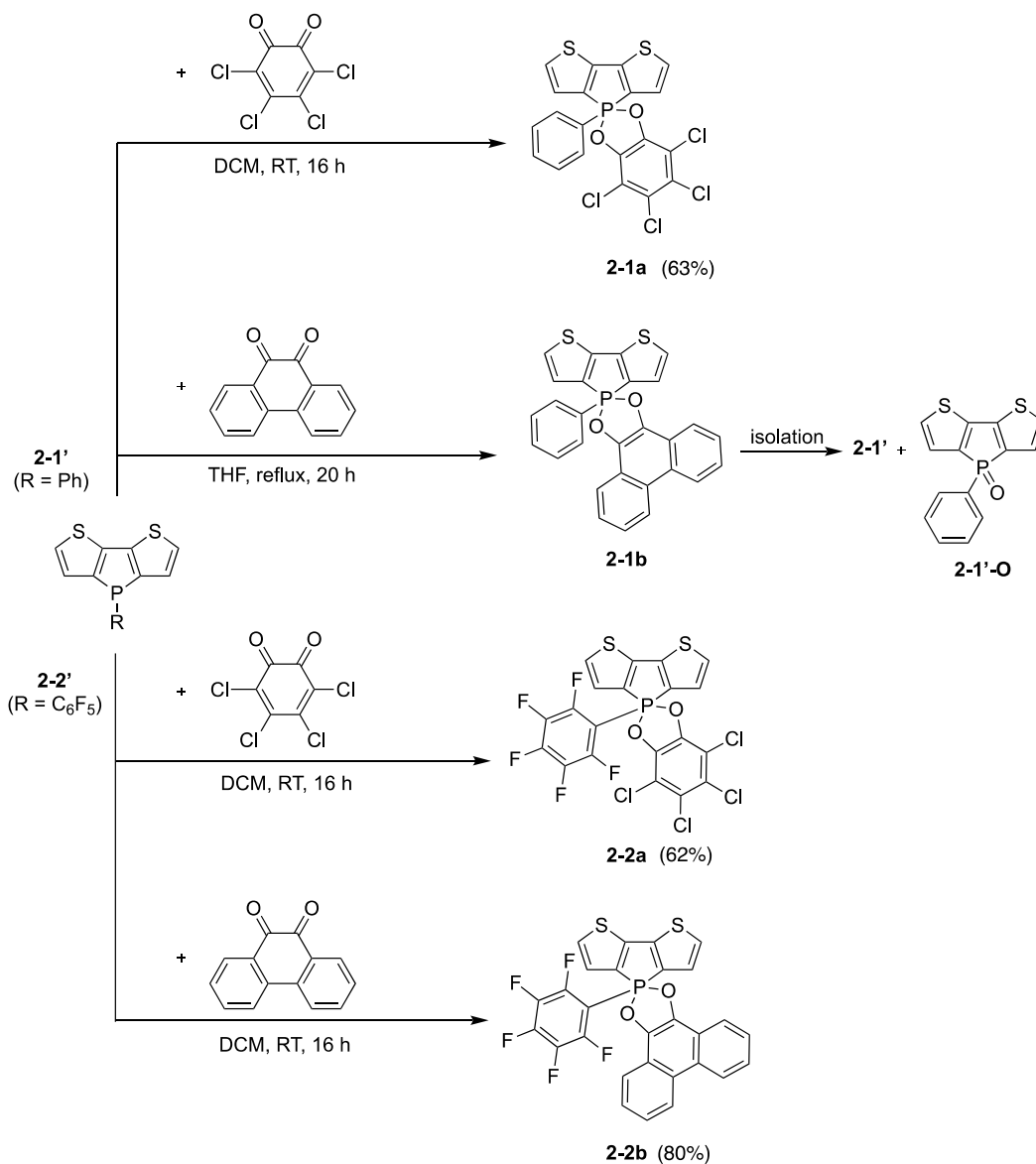
2.1.2 Results and Discussion

2.1.2.1 Synthetic Procedures

For our study, we focused on species that would potentially be able to a) stabilize the hypervalent state and/or b) enhance the electron-acceptor properties of the target species. To this end, we identified *o*-chloranil and phenanthrene quinone as suitable quinones, while the phenyl- and perfluorophenyl-substituted **2-1'**³ and **2-2'**²⁷ were our dithienophospholes of choice.

An equimolar solution of compound **2-1'** and *o*-chloranil in degassed, dry dichloromethane (DCM, MBraun SPS) afforded compound **2-1a**, which was isolated after column chromatography (Silica, DCM) in 63% yield. The same reaction conditions worked well with the perfluorophenyl phosphole **2-2'** with *o*-chloranil and phenanthrene, resulting in the isolation of compounds **2-2a** in 62% yield and **2-2b** in 80% yield, respectively. A similar equimolar reaction of compound **2-1'** and phenanthrene quinone was initially conducted in refluxing tetrahydrofuran (THF) as the solubility of the quinone was better in this solvent. Even though the reaction exhibited a new phosphorus species after 20 hours, later revealed to be compound **2-2b**, upon isolation only the

starting material **2-1'** and corresponding oxide **2-1'-O** were detected. We thus revisited synthesis of **2-2b** with meticulously dried DCM (degassed DCM, dried by passing through activated neutral alumina, followed by three cycles of freeze-pump-thaw). Using these conditions, compound **2-2b** was successfully synthesized in a glovebox and isolated by crystallization from toluene in 61% yield. (Scheme 2-1) The successful generation of the 5-coordinate species was supported by the shift in fluorescence emission and a significant highfield shift of the ^{31}P NMR resonances, consistent with a 5-coordinate phosphorus(V) center.^{28,29} (See SI 2.1.1)



Scheme 2-1. Synthesis of quinone-functionalized hypervalent dithienophospholes.

2.1.2.2 Solid-State Characterization

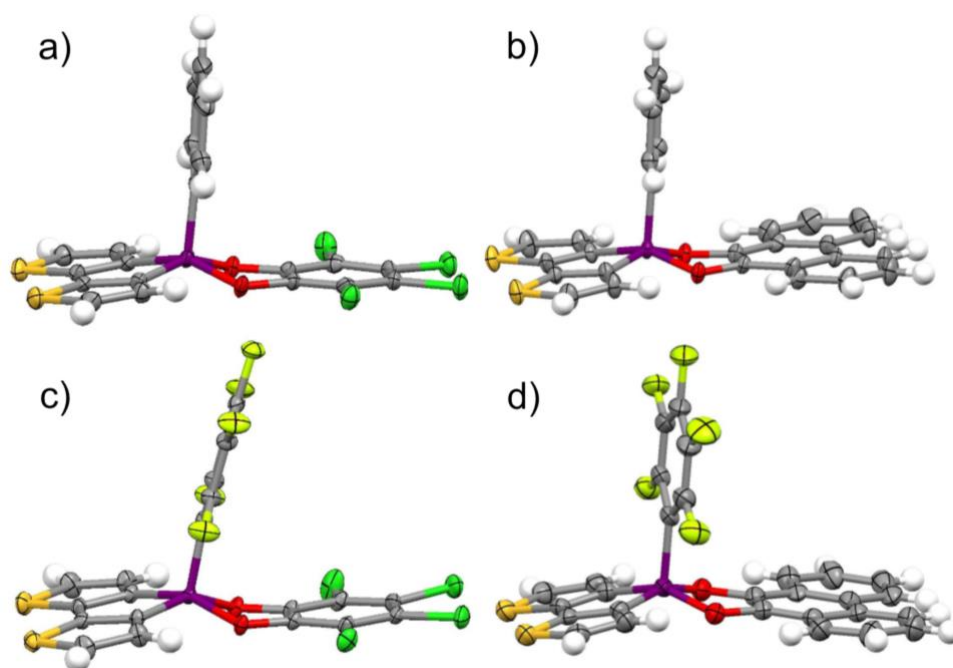


Figure 2-2. Molecular structures of compounds a) **2-1a**, b) **2-1b**, c) **2-2a**, and d) **2-2b**. Ellipsoids are set at 50% probability. Colour depiction; purple for P, grey for C, yellow for S, red for O, white for H, dark green for Cl, and light green for F.

Single crystals suitable for XRD were readily grown from compounds **2-1a**, **2-2a**, and **2-2b** and with some difficulty of compound **2-1b**. Rather unexpectedly, all the structures exhibited a distorted 4SQ geometry (Figure 2-2) as opposed to the more typical, and VSEPR supported 3BP geometry containing a 3c-4e bond.

The central phosphorus atom is moved out of the plane of the π -conjugated scaffolds by approximately 0.4 Å, with the aryl groups (phenyl for **2-1a** and **2-1b**, perfluorophenyl for **2-2a** and **2-2b**) arranged nearly orthogonally to the plane containing the quinone unit and dithienophosphole moiety (angles are 103.7(7)°, 103.6(5)°, 105.6(2)° and 103.2(4)° **2-1a**, **2-1b**, **2-2a**, and **2-2b**, respectively) to form the apex of the square pyramid. While the average P–C bond lengths in these structures (1.8 Å) are very close to usually observed P–C bond lengths of 1.84 Å,³⁰ the P–O bonds

are elongated to 1.7 Å from normally observed P–O bond lengths of 1.63 Å,³¹ but consistent with a catecholate chelating to a P(V) center.^{11,15,32}

Precedent for these structures, albeit uncommon, is found in the literature,¹⁴ but previous studies do not afford a clear explanation of what constrains such systems to this 4SQ geometry. While the related 3BP structures predominantly orient the substituents about the phosphorus center to afford the most favorable 3c-4e bonds, a similar argument is not obviously applicable to the 4SQ equivalent species.⁹ While it has been suggested that a strong electron-withdrawing ligand will instill 4SQ geometry,^{12,14} that is not often the case; oxalates and tetrachlorocatecholates readily afford 3BP structures, as found in chirality resolution agents.³³⁻³⁵ The 4SQ geometry can also be enforced via geometric constraints;^{12,14,36} Holmes et al. leveraged the strain of a 4-membered ring to offset the presumably higher-energy 4SQ geometry.¹¹ Gilhula and Radosevich employ tetradentate or scorpionate ligands to enforce a 4SQ geometry in order to make use of the reactivity of the 4SQ phosphorus center in chemical transformations.³⁷ Our species, however, consist instead of a catecholate and phosphole. The bite angle of the 1,2-diol system is geometrically restrictive. The resultant 5-membered ring with the phosphorus center exhibits a nearly 90° O–P–O bond angle. However, while catecholates form strong chelates with P(V) centers, they are often labile, detaching and reattaching to afford the preferred geometric isomers;^{38,39} and even allow for the generation of reactive sites at either the unbound P or O atoms. These available sites are short lived, however, and are typically observed only if captured, such as by a silyl group or cation for O[−] or a base such as F[−] for P⁺, to prevent the re-association of the oxygen with the phosphorus center.^{38,39} With respect to the phosphole unit, while breaking a P–C bond within the phosphole is not entire impossible, it is a less labile substituent than the catecholate. In addition, the geometry of the C–P–C unit of the phosphole ring is not dictated by, for example like above the strain of a

4-membered ring system, but the electronic interactions between the phosphorus center, the diene system and the exocyclic substituents. Our system would therefore, intuitively, generate the most favorable isomer in solution due to the lability of the catecholate and the geometry at the phosphole being dictated by the association of said catecholate, when compared to these structures of precedent.^{38,39} Still, the small bite angle of the catecholate prohibits the formation of the most favourable 3c-4e bond, an O–P–O bond, in which the optimized 3BP structure is formed by the axial oxygen donating a lone pair into the opposing σ^*_{PC} orbital, requiring instead a weaker 3c-4e C–P–O bond between one catecholate oxygen and one *ipso*-carbon to retain a 3BP structure. To better understand the complex interplay between these factors, we turned our focus to computational chemistry. A detailed analysis of the 3BP vs. 4SQ structural preference is given in section 2.1.9(i) of the SI using compound **2-1a** as a representative species.

The natural bond orbital (NBO) population analysis⁴⁰ shows expected electron transfer from phosphorus to both oxygen atoms, with natural atomic charges of +1.90 and –0.75 for P and O atoms, respectively. Both oxygen atoms, somewhat unexpectedly, are available to donate a lone pair to their opposite σ^*_{PC} orbitals to generate two 3c-4e bonds. In the 3BP structure, one strong formal 3c-4e bond exists between the axial O and the axial C(*ipso*), while in the 4SQ structure, two symmetrically equivalent 3c-4e bonds persist in the square base. Our calculation shows that the conversion from the 3BP to the 4SQ structure involves the process of weakening the 3c-4e bond of the 3BP isomer, relaxing the 120° bond angles between the equatorial substituents, and developing a second 3c-4e bond. This energy compensation results in comparable stabilities of the 3BP and 4SQ structures, and thus their dynamic solution-state nature.^{2,36,41} Since the 4SQ structure is in-between two 3BP structures (each having one or the other O atom at the axial position), the sampling results in an averaged 4SQ structure, which is observed in our structural

characterizations. In the solid-state, 4SQ structures are exclusively observed because their parallel arrangements of the extended conjugated scaffolds between adjacent molecules also enhances their π - π stacking interactions (*vide infra*). As such the ability to generate stable 4SQ species relies on generating two 3c-4e bonds of intermediate strength that afford the system similar stability as the strong 3c-4e bond of the 3BP isomer. This process may be performed either electronically, geometrically, or both as long as the resultant 3c-4e bonds of the 4SQ isomer are sufficiently strong so as to afford an isoergic isomer to the thermodynamically favorable 3BP structure. This explanation can be seen in the computational analysis of structures **2-1a,b**, and **2-2a,b** whose energy differences between the two isomers are -0.4, 0.1, 1.7, and 1.1 kcal/mol, respectively (negative means 4SQ being more stable). With the small energy differences, the molecules in fact likely dynamically rock between the 3BP and 4SQ structures (akin to Berry pseudorotation),^{2,36,41} affording some insight into the aforementioned dynamic solutions state nature of these compounds. This dynamical rocking reflects the lability of the bidentate interaction between P and the catecholate O atoms, despite their rigid O-P-O angle. Such an in-depth analysis of the preference towards 4SQ structure of a P(V) structure has not been previously explored. Note that, as expected, compounds **2-2a** and **2-2b** exhibit slightly more favorable 3BP geometric isomers. But this is not due to the more electronegative C₆F₅ ring, which always occupy an equatorial position in the 3BP structures.

2.1.2.3 Reactivity Studies of the Hypervalent Compounds

We surmised that the unexpected 4SQ geometry could also impart intriguing reactivity to these hypervalent compounds, similar to related species in the literature,^{16-18,42,43} as suggested by the electron-density mapping (Quantum Theory of Atoms in molecules; QTAIM)⁴⁴ representatively

on compound **2-1a**.⁴⁵ An area of low electron density on the P center, often referred to as sigma hole,⁴⁶ is a potential coordination site for nucleophiles such as OH⁻ or F⁻, which would make these hypervalent compounds neutral LAs (Figure 2-3a).^{16-18,42,43} Recent examples of such rare neutral LAs, include the bis(perchlorocatecholato)silane (**2-IIIA**) with a Lewis-acidic Si (IV) center, reported by Greb et al.^{42,43} This compound has been classified as Lewis super acid by virtue of its high FIA (507 KJ/mol) and acquires similar 4SQ geometry on abstraction of a fluoride anion (**2-IIIB**) (Figure 2-3b).⁴²

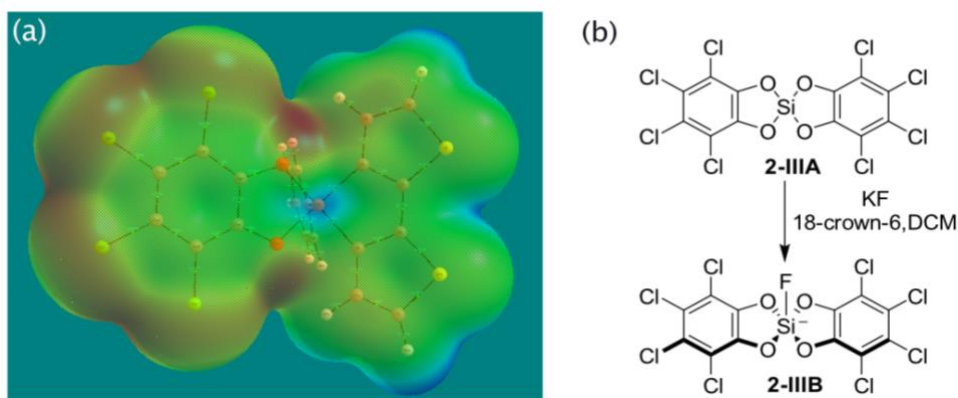
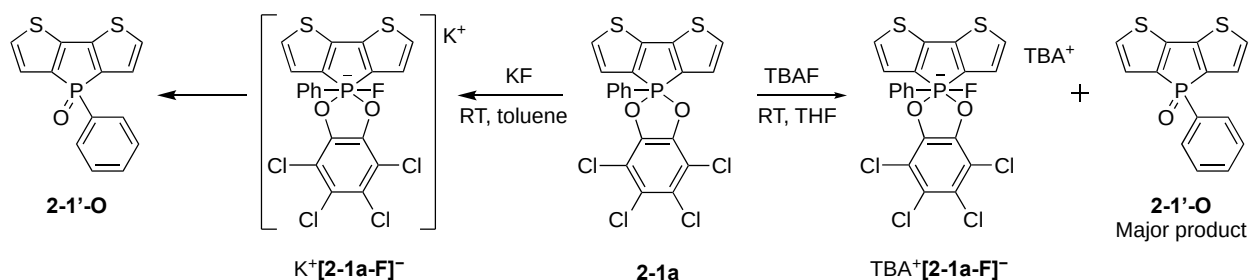


Figure 2-3. a) ESP mapping showing the sigma hole in **2-1a**, b) silicon-based neutral LA.⁴²

Consequently, we were interested in the FIAs^{47,48} of the new pentacoordinate dithienophospholes of this series to determine the Lewis acidity of the hypervalent P center. The calculated FIAs for compounds **2-1b**, **2-1a**, **2-2b**, and **2-2a** (gas phase) are 306, 334, 348, and 381 kJ/mol in increasing order (compared to the isodesmic reaction $\text{Me}_3\text{SiF} \rightarrow \text{Me}_3\text{Si}^+ + \text{F}^-$), respectively, that are correlated with the electron-withdrawing effects of both the *o*-chloranil and perfluorophenyl groups; the latter at the axial position has an expectedly stronger impact on enhancing the FIA. However, while the phosphorus center in these compounds is Lewis-acidic, clearly none of the new hypervalent species are Lewis super acids. It is noteworthy, however, that the FIA values for **2-1a,b** and **2-2a,b** are significantly higher than that of the isoelectronic (**2-IIIB**; 71 kJ/mol).⁴² This

highlights the effect of their neutral character in contrast to the anionic nature of (**2-IIIB**) with its already present fluoride substituent.

Fluoride abstraction: With the computational data suggesting moderate Lewis acidity, we followed up with fluoride abstraction experiments. Compound **2-1a** was initially reacted with one equivalent of potassium fluoride (KF) in dry toluene, but the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture after one hour confirmed the formation of compound **2-1'-O** instead of $\text{K}^+[\text{2-1a-F}]^-$. Similarly, the reaction of **2-1a** with one equivalent of tetrabutylammonium fluoride (TBAF) showed weak doublets (d) with $^1J(\text{P-F})$ coupling for $\text{TBA}^+[\text{2-1a-F}]^-$ ($^1J_{\text{P-F}} \sim 780 \text{ Hz}$)²⁹ after one hour of reaction time, but with **2-1'-O** as the major product. The results were overall inconclusive regarding the Lewis acidity of this series of compounds, but suggested a different reaction was clearly occurring, at least for compound **2-1a** (Scheme 2-2; SI 2.1.3).



Scheme 2-2. Transformation of **2-1a** to **2-1'-O** via fluoride abstraction reaction.

Solvatochromism study of compound 2-1a: Due to the polar nature of its scaffold (as well as the presence of the sigma hole), we surmised that compound **2-1a** would exhibit solvatochromism. Solutions of **2-1a** ($c = 10^{-4} \text{ M}$) in DCM and toluene showed an absorption maximum $\lambda_{\text{max}} = 388 \text{ nm}$ that is blue-shifted to 358 nm in coordinating solvents such as acetone, THF, and acetonitrile (Figure 2-4). The change in λ_{max} was accompanied by a change in solution color from yellow in toluene (and DCM) to colorless in coordinating solvents, indirectly supporting the Lewis acidity of **2-1a** (see SI, section 2.1.7(i)).

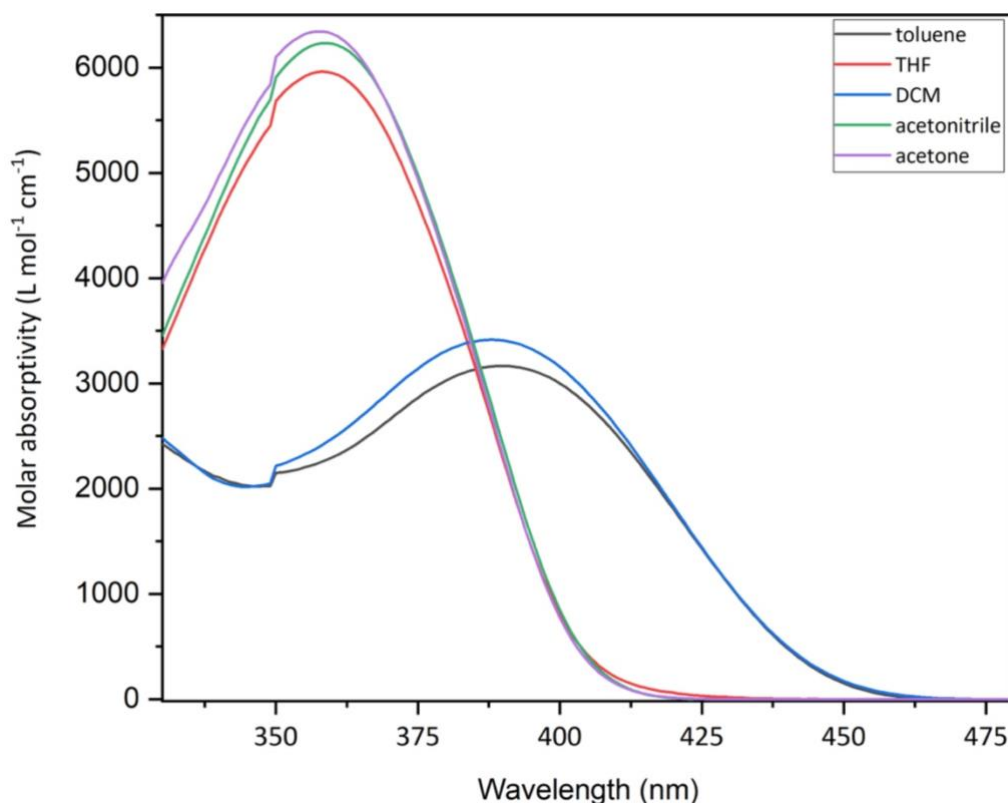


Figure 2-4. UV-Vis spectra of **2-1a** in coordinating (THF, acetonitrile, and acetone) and non-coordinating (toluene and DCM) solvents.

Reactivity with water: The fluoride abstraction studies suggested that presence of trace amounts of water trigger the transformation of **2-1a** to **2-1'-O** by a nucleophilic addition,^{38,39} rather than a simple retro-[4+1] cycloaddition to the starting phosphole **2-1'**. Notably, a solution of **2-1a** in THF that was rigorously dried over neutral alumina and freeze-pump-thawed, does indeed not show any formation of **2-1'-O** by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (SI, section 2.1.4). To further verify the adventitious water hypothesis, compound **2-1a** was exposed to a controlled quantity of water in solution. Upon addition of 50% degassed water, to a similarly dried THF solution of **2-1a**, its blue-green fluorescence quickly changed to the bright blue emission characteristic of dithienophosphole oxide **2-1'-O** (Figure 2-5a). The formation of **2-1'-O** was further confirmed by a downfield shift of the $^{31}\text{P}\{^1\text{H}\}$ NMR signal from -39.4 ppm for **2-1a** (THF) to 13.9 ppm for **2-1'-O** (THF/H₂O)

(see SI 2.1.4). While compound **2-1'-O** was clearly identified by NMR spectroscopy, the nature of the C₆Cl₄O₂-fragment, however, was unclear due to the ambiguity of the ¹³C{¹H} NMR spectroscopic data.

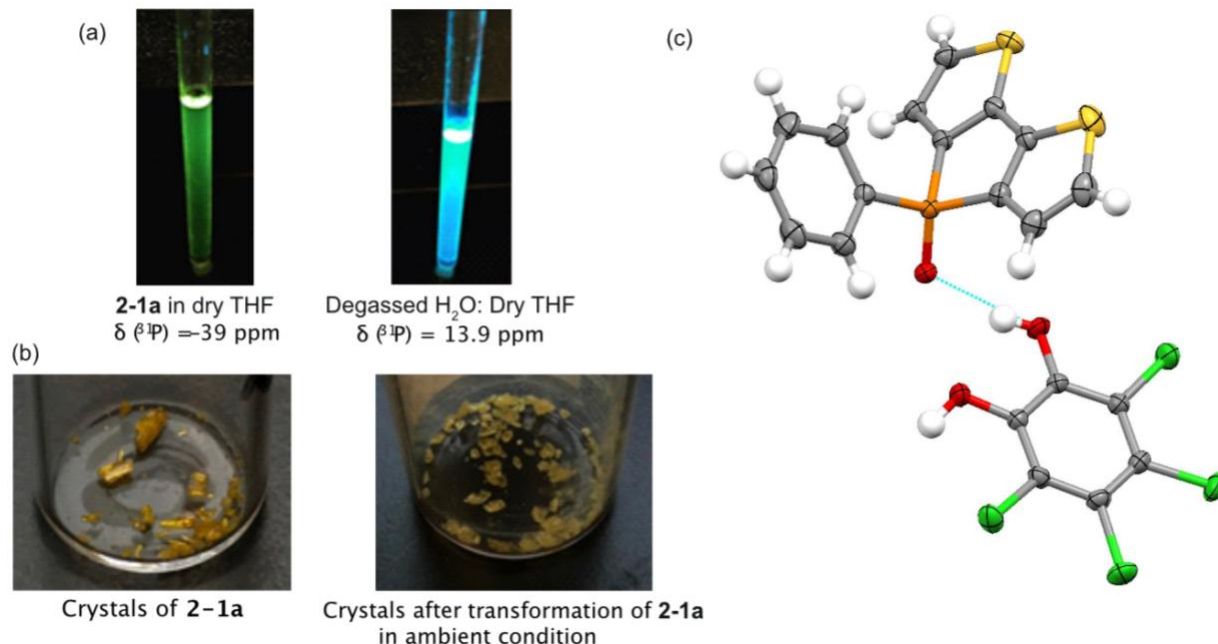


Figure 2-5. a) Solution-phase transformation, b) crystal-to-crystal transformation, and c) products **2-1'-O** and **2-3** of the crystal-to-crystal transformation (**2-1a**•H₂O). Colour depiction; orange for P, grey for C, yellow for S, red for O, dark green for Cl, and white for H.

Intriguingly, the rod-shaped golden yellow crystals of **2-1a**, when left on the bench and exposed to atmospheric moisture in a loosely closed vial, transformed into pale yellow hexagonal crystals after two weeks, yet maintained suitable single-crystal characteristics for XRD analysis (Figure 2-5b). X-ray crystallography on the transformed crystals confirmed the formation of phosphole oxide **2-1'-O** with 3,4,5,6-tetrachloro-1,2-benzenediol **2-3** as the other by-product. On the contrary to reactions happening exclusively on the surface, i.e., the direct interface with the atmospheric moisture, the crystals are completely transformed to **2-1'-O** and **2-3** showing that the decomposition of the outer layer opens the core of the unreacted crystal to a cascade of reactions. Notably, the crystallinity is preserved even as entropy increases. While the hydrolysis of P(V)

catecholates is not unknown,^{49-48, 50-52} the intriguing crystal-to-crystal transformation suggests that the corresponding mechanism for **2-1a** may not necessarily require the breaking of a P–O catecholate bond (*vide supra*) as the initial step.

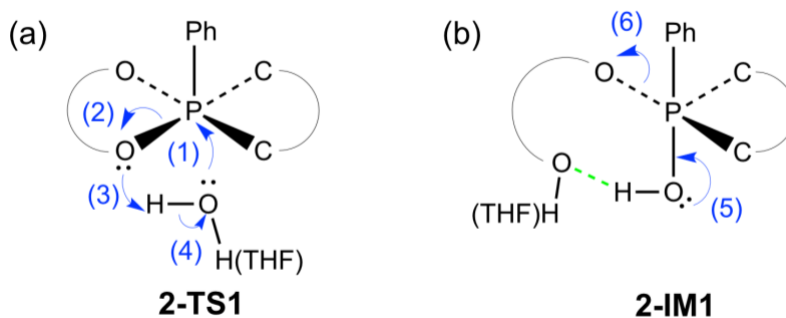


Figure 2-6. Concerted electron-pair migrations for the reaction with water.

To gain more insights into the detailed mechanism of the reaction with water in general, we again turned our focus to computational chemistry. We first focused on the reaction in solution. The calculations employ a THF solvent model with one explicit THF molecule coordinated to H₂O via a hydrogen bond. The whole reaction is calculated to be exoergic by 20.0 kcal/mol, and there is essentially only one 20.3 kcal/mol barrier (**2-TS1**), which is feasible to overcome at room temperature. This rate-determining step involves concerted migrations of four electron pairs (Figure 2-6a): (1) the addition of a H₂O lone pair to the acidic P center, forming the new O–P bond; (2) the heterolytic breakage of one original quinone O–P bond and the transfer of the bond electrons to the O atom; (3) this O atom donating its lone pair to a proton of the H₂O molecule to form an OH bond; and (4) heterolytic breakage of one OH bond in H₂O. (see SI Section 2.1.9 (ii)) In our experiments, alteration of the electronegativities of the axial group (C₆H₅ vs. C₆F₅) and the side group (chloranil vs. phenanthrene quinone) did not indicate a clear trend of reaction rates. Logic dictates that an electronegative axial group favors electron pair migration (1) but disfavors (2). An electronegative side group favors (2) but disfavors (3). The stochastic rates of the transformation of **2-1a**, **2-2a**, and **2-2b** are reflections of these contradictory features. Once the

H₂O-addition intermediate (**2-IM1**, Figure 2-6b) is formed, the subsequent steps (in essence, second O–P breakage and proton transfer) are all thermodynamically and kinetically favorable (see Fig. S2.1-28 in SI). In the whole process, the phosphorus atom acts as a LA in electron pair migrations (1) and (5) and the aryloxy oxygen atom acts as a LB in (3). The calculations show that an essentially similar mechanism is also applicable to the solid-state transformation of the crystals of **2-1a** in the presence of water (see Section S2.1.9(ii) in SI). This proposed mechanism is uniquely supported by our observed reactivity, as the typical alternate reaction, requiring the breakage of a P–O bond first, instead of the acidity of the phosphorus center, relies on the basicity or electron-withdrawing nature of the substituent of which the O–P bond is broken, dictating a more intuitive ordering of the rates of transformation.^{14,16-18,38,39,42,43}

2.1.2.4 Supramolecular Stabilization of the Hypervalent Compounds

Despite the Lewis acidity of the phosphorus center and the resulting increased reactivity to trace amounts of water, these kinetically labile compounds can nonetheless be crystallized from a concentrated solution on the bench. We assumed that their stability in the crystalline state would likely arise from intermolecular stabilization effects, given the fairly planar scaffold that allows for π - π interactions. The crystal packing of **2-1a** shows molecules arranged in a parallel conformation where the exposed P center of one molecule is protected by the plane of a second molecule (3.5 Å; Figure 2-7a). Similar π - π interactions were also observed in single crystals of compounds **2-1b** and **2-1c**, while **2-1d** forms π -stacked tetramers, likely due to the presence of both highly electron-withdrawing and -donating groups that complement each other intermolecularly (see SI Section 2.1.7(ii)).

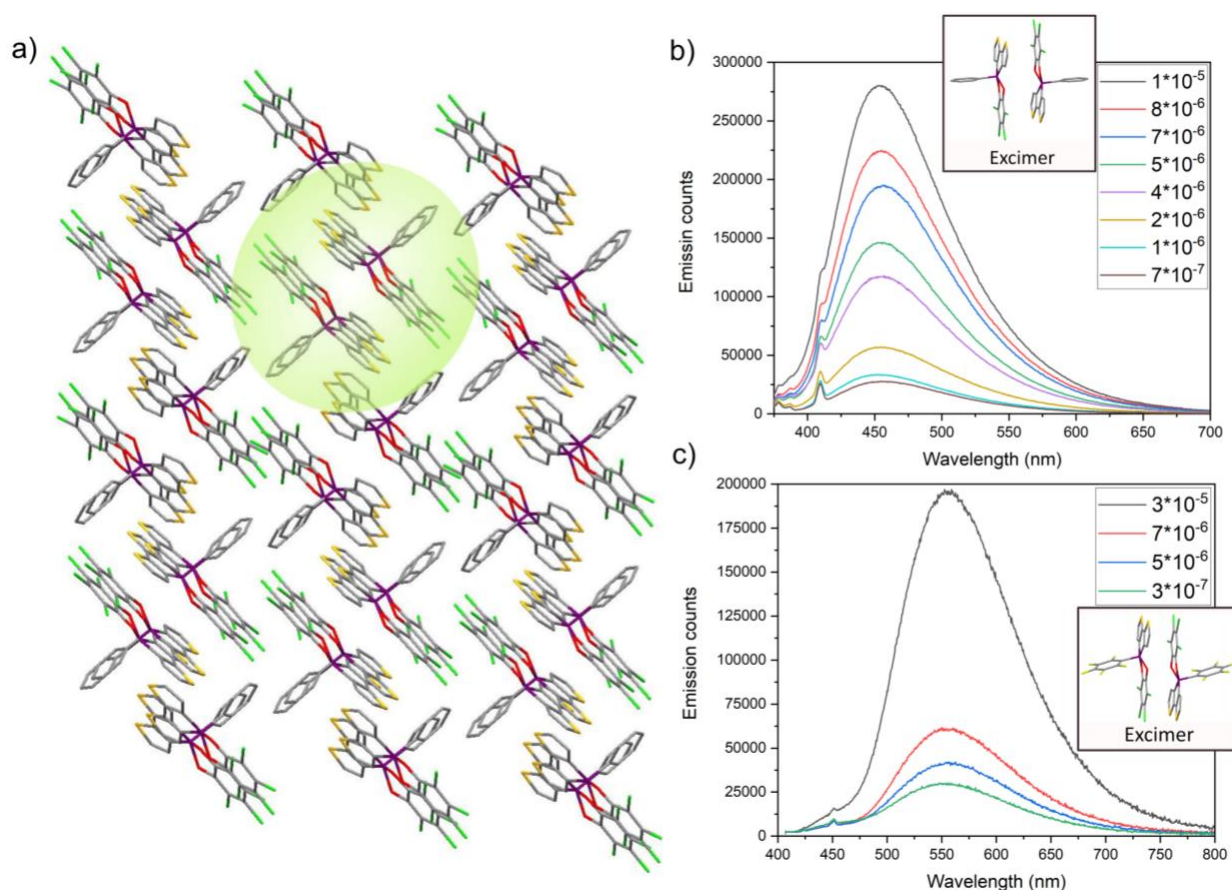


Figure 2-7. a) Crystal packing in **2-1a** showing supramolecular π -stacking dimers, b) fluorescence emission spectra showing monomer and excimer of **2-1a** (excitation at 365 nm); c) fluorescence emission spectra showing only excimers in **2-2a** (excitation at 397 nm).

The supramolecular dimerization provides kinetic stability (at least for the medium term and the absence of nucleophiles), while the close intermolecular distance may afford electronic transitions across the dimers. To investigate both this, as well as the fate of these dimers in the solution state, the luminescence of these emissive compounds was studied as a function of concentration in dry toluene.

Notably, the interactions were found to be considerably strong, as excimer-type emissions⁵³ were observed even at concentrations as low as 10^{-13} M. The excimer of compound **2-1a** emits at 459 nm, while lowering the concentration to 10^{-7} M revealed a peak with vibronic structure centered around 409.5 nm that can be assigned to the monomeric species (Figure 2-7b; we were able to

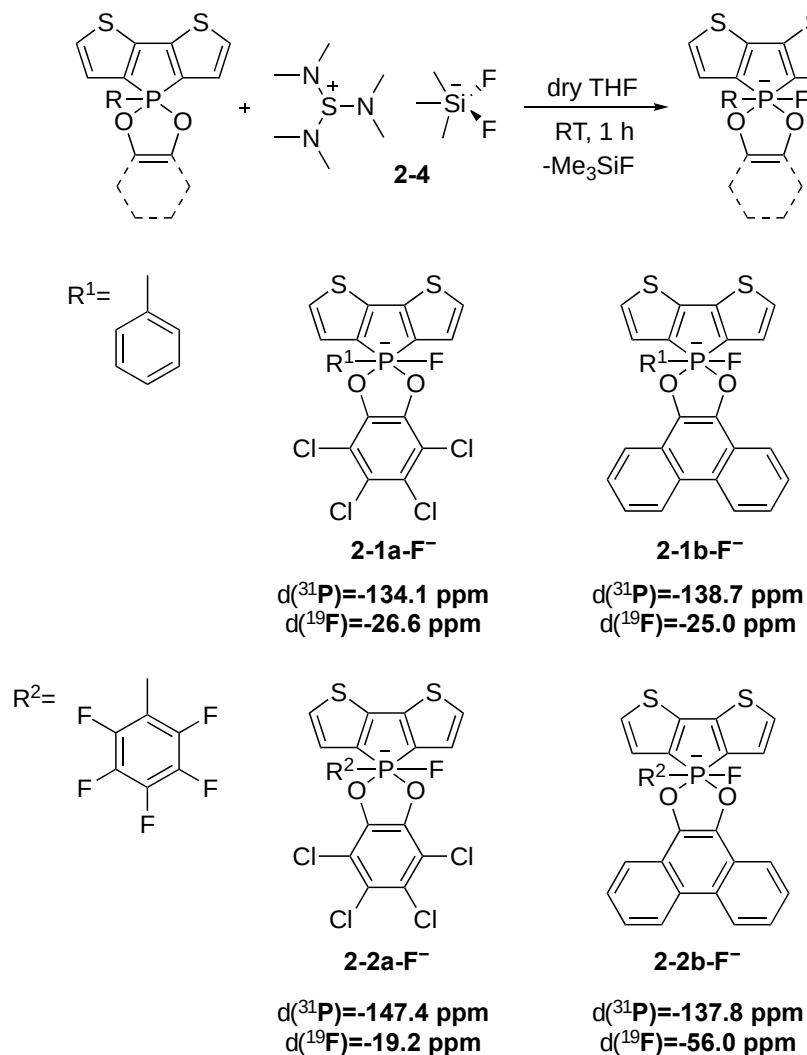
exclude Raman scattering for these peaks by varying the excitation wavelength, λ_{ex}). Similarly, the monomer for compound **2-1b** is detected at 396.5 nm (see SI Section 2.1.7(ii)).

Compound **2-2a** does not show clear monomer peaks even at a concentration of 10^{-6} M, which indicates extremely strong supramolecular interaction due to the increased Lewis acidity of the P(V) center hosting two highly electron-withdrawing substituents (Figure 2-7c; here, the peak at 450 nm corresponds to Raman scattering). As already suggested by its solid-state structure, compound **2-2b** also behaves differently in solution. The emission spectrum resolves into multiple peaks on dilution, as several different π - π interactions may persist, while exhibiting aggregation caused quenching (ACQ; SI, section 2.1.7(ii)).⁵⁴

2.1.2.5 Revisiting the Fluoride Abstraction Reaction

As the initial fluoride abstraction reactions using typical fluoride salts ultimately led to the formation of **2-1'-O** in all cases (Scheme 2-2), we concluded that this was due to the presence of adventitious water (*vide supra*). To eliminate this scenario, tris(dimethylamino) sulfur (trimethylsilyl) difluoride (**2-4**) was employed as a dry fluoride source.⁴² Reactions of one equivalent of **2-4** with the hypervalent compounds **2-1a,b** and **2-2a,b** in meticulously dried solvent under argon, after one hour each gave rise to highfield-shifted $^{31}\text{P}\{^1\text{H}\}$ NMR doublets with strong P-F coupling (as corroborated by $^{19}\text{F}\{^1\text{H}\}$ NMR spectroscopy). The shifts are consistent with octahedral P(V) species, and align well with related systems in the literature (Scheme 2-3).^{55,56} Coupling constants ($^1J_{\text{P-F}}$) of 776 Hz (**2-1a-F⁻**), 752 Hz (**2-1b-F⁻**), 795 Hz (**2-2a-F⁻**), and 764 Hz (**2-2b-F⁻**), respectively, confirm the abilities of the pentavalent molecules to expand their

coordination sphere to generate hexacoordinate species that are indeed reasonably stable under inert conditions.^{29,55-59}



Scheme 2-3. Fluoride abstraction using **2-4** as dry source.

Notwithstanding, also within one hour of reaction time, we observed the additional formation of a noticeable amount of dithienophosphole oxide **2-1'-O** (or its C₆F₅-substituted relative **2-O**) by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, along with the fluoride adducts (SI, section 2.1.6). Despite the anaerobic conditions under which the reactions were conducted, the presence of dithienophosphole oxide suggests that further reactions beyond that of the fluoride abstraction must occur. This also indicated a fleeting nature for the corresponding fluoride adducts. Importantly however, given that

there is no available external oxygen source for the formation of **2-1'-O** (or its C₆F₅-substituted relative), the reaction pathway for this transformation must be clearly distinct from the one observed in the presence of water. Reaction of **2-4** with **2-1b** shows the formation of **2-1b-F⁻** and **2-1'-O** after one hour in the ³¹P{¹H} NMR spectrum in a roughly 11:7 ratio (see SI, section 2.1.6). The reaction mixture was then refluxed for 17 days to fully convert **2-1b-F⁻** into **2-1'-O**. After completion, the ¹³C{¹H} NMR spectrum of the reaction mixture was recorded to establish the fate of the former phenanthrene quinone unit (see SI, section 2.1.6). In addition to the eight peaks for **2-1'-O**, seven other peaks suggested the presence of a symmetric, 9,10-dioxo-phenanthrene fragment (Scheme 2-4 and SI section 2.1.6). The anaerobic reaction conditions imply that the P=O unit of **2-1'-O** must have been formed by breaking a C–O bond of **2-1b-F⁻**. There is precedence for a similar oxygen-transfer reaction in the literature, but the authors were unable to determine the fate of the corresponding diolate substituent.³⁸

Scheme 2-4. Transformation of **2-1b-F⁻** by deoxyaryloxylation reactions.

Given the highly symmetric nature of the phenanthrene-based moiety that was confirmed via $^{13}\text{C}\{^1\text{H}\}$ and ^1H NMR spectroscopy after its separation (see SI, section 2.1.6), formation of diphenanthro[9,10-*b*:9',10'-*e*][1,4]dioxin (**2-5**) is the only plausible outcome for this reaction. The observed reaction could then be classified as an double deoxyaryloxylation, where one of the quinone oxygen atoms is transferred to phosphorus while the remaining forms an ether bond

between the aryl groups. This intriguing observation indicates the potential utility of the new species as mediator in other organic transformations.⁶⁰⁻⁶⁷

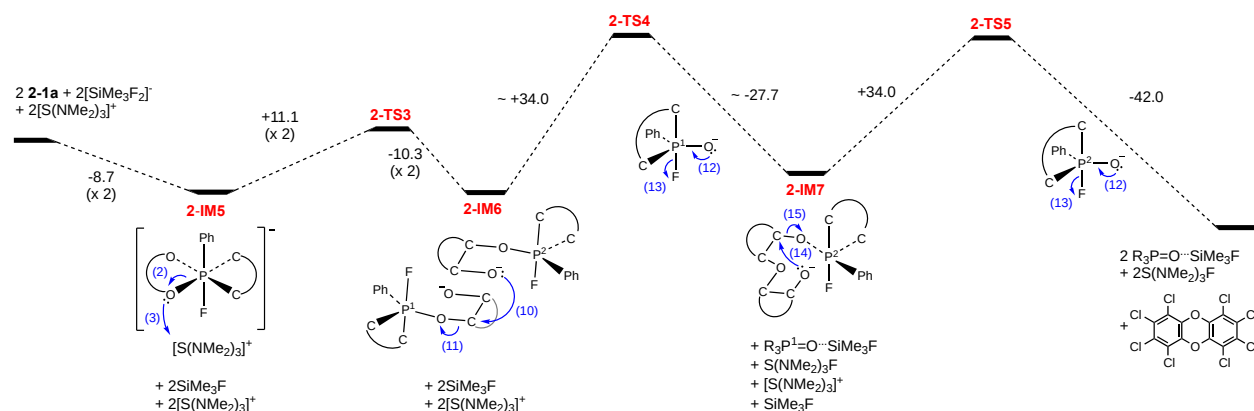


Figure 2-8. Energy landscape for the deoxyaryloxylation reaction of **2-1a**. In this figure two curves are used to schematically represent the *o*-chloranil and dithieno groups for better clarity. When necessary, the two carbon atoms connected to oxygen in the *o*-chloranil group are explicitly shown, while the other atoms of the group are omitted for clarity. Electron pair movements are shown in blue. Key structures are shown in Figure S2.1-31 (SI). Energy differences between structures connected by dashed lines are given in kcal/mol. The energies for the first two dashed lines are for each **2-1a** unit, while the others are for the whole system with two **2-1a** units. The "x 2" denotes that the given energies are for each **2-1a** unit and should be multiplied by two for the total system with two **2-1a** units. **2-IM** and **2-TS** are numbered consecutively for all mechanism studies. **2-IM1-4** and **2-TS1-2** are shown in Section 2.1.9 of SI for **2-1a** + H₂O reaction mechanism. Similarly, details on pair migrations (1)-(9) are provided in section 2.1.9 of the SI. The energies were obtained CAM-B3LYP/MA-DEF2-SVP calculations and with zero-point energy corrections.

To lend more credence to this proposed reaction, we again turned to computational chemistry using compound **2-1a** as representative species for determination of a suitable reaction mechanism. The mechanism of the deoxyaryloxylation is shown in Figure 2-8. The first step is the abstraction of F[−] from **2-4** by **2-1a**. This step is barrierless and exoergic by 8.7 kcal/mol. The abstraction results in a hexacoordinate compound **2-IM5** that aligns with the experimental observations (*vide supra*). Subsequently, **2-IM5** undergoes heterolytic O–P bond breakage to return to the pentacoordinate **2-IM6**, whose dangling O[−] is stabilized by the $[\text{S}(\text{NMe}_2)_3]^+$ counteranion. The barrier for this step (**2-TS3**) is calculated to be 7.2 kcal/mol. Compared to the addition of H₂O to **2-1a** (**2-TS1** in Figure S2.1.29, SI), only the migration arrows (2) and (3) are applicable here, and the barrier is lower by

two thirds (vs. 20.3 kcal/mol of **2-TS1**). This is because: (1) the hexacoordinate phosphorus center with formal -1 charge in **2-IM5** has a stronger tendency to break the O–P bond and release the charge to the more electronegative oxygen center; (2) the $[\text{S}(\text{NMe}_2)_3]^+$ counteranion is readily available to stabilize the anionic oxide. Both aspects are prototypical for the reactivity of octahedral P(V) catecholates.^{66,67} Without the rigid $\sim 90^\circ$ O–P–O bite angle, the pentacoordinate **2-IM6** adopts a 3BP structure, consistent with the discussion above, and described in more detail in the SI (section 2.1.9). An *ipso*-C atom of the dithieno-unit and the most electronegative fluoride occupy the axial positions. In the third step, electron pair migrations (10) and (11) occur in concerted fashion between a dimer of **2-IM6**; the remaining P–O–C unit is broken across the O–C bond in order to form a new O–C bond across the two *o*-chloranil groups. Since it is computationally costly to search for the transition state (**2-TS4**) for this large reaction complex, we estimate the barrier to be about 34.0 kcal/mol without running the search (*vide infra*). The barrier-less pair migrations (12) and (13) convert the pentacoordinate anion of P^1 (the two P atoms are labelled as P^1 and P^2 in Figure 2-8 for better clarity) to **2-1'-O**, whose oxygen atom weakly coordinates to the Si atom of an SiMe_3F molecule (shown as $\text{R}_3\text{P}=\text{O}\cdots\text{SiMe}_3\text{F}$, with a 1.9 kcal/mol binding energy), and release an F^- to the solution (shown as $\text{S}(\text{NMe}_2)_3\text{F}$). The product **2-IM7** of this step has a similar electronic structure as **2-IM6**, with a dangling O^- stabilized by $[\text{S}(\text{NMe}_2)_3]^+$. The difference between **2-IM6** and **2-IM7** is that the C_6Cl_4 unit has been replaced by the $\text{C}_6\text{Cl}_4\text{-O-C}_6\text{Cl}_4$ dimer. **2-IM7** then undergoes the concerted pair migrations (14) and (15) to form perchlorodibenzodioxin (the *o*-chloranil congener to **2-5**). The remaining pentacoordinate anion of P^2 undergoes barrier-less migrations (12) and (13) to form another molecule of **2-1'-O** (also coordinated to SiMe_3F) and returns an F^- to the solution. The transition state for this step (**2-TS5**) was found to be 34.0 kcal/mol above **2-IM6**. Since the pair migrations (14) and (15) resemble (10)

and (11), the barrier of **2-TS4** is expected to be similar to that of **2-TS5**. We thus estimated the energy of **2-TS4** to be about 34.0 kcal/mol (*vide supra*). However, one should note that this conjecture is for the activation energy. Considering that **2-TS4** is in a bimolecular interaction, while **2-TS5** is in a intramolecular interaction, the reduction of entropy would give a higher Gibbs free energy barrier for **2-TS4** than **2-TS5**. But this does not change the overall picture of the reaction, which is held as a mixture of **2-IM5** and **2-IM6** for a long time.

The proposed mechanism suggests F^- to act as a catalyst and is exoergic by 17.5 kcal/mol. However, the two >30 kcal/mol barriers severely slow down the process. Also, the reaction may be trapped at the first step of forming **2-IM5**, which is isoergic with the final product. In fact, the addition of **2-4** to **2-1a** results in a long-lasting mixture of the fluorinated **2-IM5** and the final products **2-1'-O** and perchloro dibenzodioxin for more than a month. Similarly, persistent mixtures are observed for **2-2a** and **2-2b** and for all the three species, the final products (-17.5, -20.9, -27.5 kcal/mol for **2-1a**, **2-2a**, and **2-2b**, respectively) are slightly lower or even substantially higher in energy than **2-IM5** (-17.4, -29.9, -24.5 kcal/mol for **2-1a**, **2-2a**, and **2-2b**, respectively), leading to the prolonged observation of **2-IM5** in solution. Compound **2-1b** is the only species that undergoes a complete deoxyaryloxylation since the fluorination is much less exoergic than the deoxyaryloxylation (-11.2 vs. -28.1 kcal/mol). This lowest exoergicity in fluorination among **2-1a,b-2-2a,b** is consistent with the least electronegative side and axial groups of **2-1b**. Still, the two approx. 30 kcal/mol barriers of **2-TS4** and **2-TS5** are in line with the experimentally observed deoxyaryloxylation using **2-1b** that took 17 days to complete.

The mechanism also relies on the dynamic nature of the geometric structure present in these species. The fluoride abstraction requires the available coordination site of the 4SQ phosphorus center. The subsequent P-O bond breaking is, again, not uncommon among octahedral P(V)

catecholates as a means to optimize the three 3c-4e bonds present in the structure. The less favorable F–P–C bond drives the ring opening and the subsequent reactivity along with the thermodynamic stability of a tetrahedral P(V) oxide. The generation of **2-1'-O** during the reaction with more typical fluoride ion sources is also readily explained via this mechanism. Instead of a simple competition between F[−] and water reacting at the Lewis-acidic phosphorus center, the decomposition occurs from **2-IM5**. Upon ring opening, the water reacts with the now accessible phosphorus center instead of either rebinding the catechol or generating the dimer **2-IM6**. This would explain the presence of both **2-IM5** and **2-1'-O** in solution from these reactions, as well as the slow rate of hydrolysis.

2.1.3 Conclusions

A facile method toward hyper-coordinate dithieno[3,2-*b*:2',3'-*d*]-phospholes via the [4+1] cycloaddition of *o*-quinones to trivalent species is reported. Our approach alleviates the requirements for additional kinetic stabilization, as often observed in previously reported systems. The structure of the obtained pentacoordinate derivatives deviates from the VSEPR theory-dictated 3BP geometry to form 4SQ molecules, that in turn create a well-exposed Lewis-acidic phosphorus center, evident in the presence of a sigma hole. This structural preference arises from the shallow potential energy surface connecting the two types of structure, which respectively balance two intermediate 3c-4e bonds on the one side, and both a strong and a weak 3c-4e on the other side. While we do not and cannot strictly rule out steric constraints about the phosphorus center, through this series of compounds, we were able to establish a thermodynamic model of the restrictions on forming a λ⁵-P(V) center with 4SQ geometry. Additionally, based on the limited Lewis acidity of these compounds, we can propose the constraints of this model on Lewis acidity: (i) the stability

of dimers formed even in solution; (ii) the dynamic geometry of these structures due to the extremely low energy difference between 3BP and 4SQ geometries; and (iii) the alternative reactivity of these species upon reacting with the LB. The latter potentially affords this series of compounds an alternate use in the synthesis of other organic molecules. We can ascribe its Lewis acidity to these properties arising from the competing electronic effects of the system, in which the favorability of one strong 3c-4e bond is in direct competition of the generation of two 3c-4e bonds. By understanding the difference between the phosphorus bonding in, for example catechol versus dithienophosphole, this model may allow for the specific generation of λ^5 -P(V) species strictly with either 4SQ or 3BP geometries. This would in turn enable targeted reactivities by adjusting the favorability of one 3c-4e bond to be much stronger or weaker than, serendipitously, this series of compounds in which both geometries are nearly isoergic. The Lewis-acidic character of the 4SQ phosphorus center imparts high electrophilicity to water. The ensuing rapid transformation of the pentacoordinate compounds to dithienophosphole oxide, and an intriguing crystal-to-crystal transformation can be ascribed to the unique reactivity of these compounds as well as the significance of the geometric state toward their reactivity. Despite their high electrophilicity, the peculiar geometry of these compounds allows for kinetic intermolecular stabilization by supramolecular interactions in the solid state under ambient conditions. Hexacoordinate P-species are accessible by fluoride abstraction, which reveals the potential of these derivatives to facilitate interesting organic transformations such as the deoxyaryloxylation reaction that involves a generally challenging C–O bond activation. The synthesized class of hypervalent phosphorus compounds presents an innovative structural platform while hosting desirable chemical properties that showcase once more the intriguing opportunities arising from conjugated main-group species. Consequently, these species may have the potential to be exploited

as neutral and stable hypervalent main-group catalysts (or mediators) in organic chemistry. Now with a model to design these uniquely reactive compounds in hand, the next section of this thesis expands on the scope of applications of these reactive species.

2.2 Exploring the Lewis Acidity and Reactivity of Neutral Pentacoordinate Dithienophospholes

This section has been formally published in the following reference: Asok N.; Zondag, B. A.; Pradhan, E.; Odagwe, M.; LeBlanc, J.; Walsh, J. C.; Bodwell, G. J.; Zeng, T.; Baumgartner, T. *Chem. Eur. J.* **2023**, 29, e2023001 (<https://doi.org/10.1002/chem.202300173>). The inclusion of the content in this work is made possible through explicit permission granted by John Wiley and Sons. The supporting information for this Chapter is available online: https://chemistry-europe.onlinelibrary.wiley.com/action/downloadSupplement?doi=10.1002%2Fchem.202300173&file=chem202300173-sup-0001-misc_information.pdf. Notably, assistance in the form of undergraduate research for the synthesis of derivatives reported was provided by Benjamin A. Zondag and Mary Odagwe. Acknowledgment is extended to Dr. Ekadeshi Pradhan and Dr. Tao Zeng for their dedicated execution of computational calculations. Joshua C. Walsh and Dr. Graham J. Bodwell generously supplied the *o*-quinones; pyrene-4,5-dione; and 2,7-di-*t*-butyl-4,5-pyrenedione essential for synthesizing the hypervalent derivative. Their individual contributions are recognized and appreciated.

2.2.1 Introduction

LAs have become important reagents in organic chemistry by affording unique and selective reactivity at relatively mild conditions. They are thus increasingly used in the synthesis of pharmaceuticals, polymers, agrochemicals, and high-performance materials.⁶⁸⁻⁷⁰ Since the establishment of halogenated triaryl boranes such as $\text{B}(\text{C}_6\text{F}_5)_3$ as Lewis-acidic components in Frustrated Lewis Pair (FLP) chemistry, the field of main-group based LAs has been witnessing rapid development, thus simultaneously addressing previous concerns regarding cost, toxicity, and carbon footprint of commonly employed transition metal-based LAs.^{66,71,72} The Lewis acidity of these group 13 LAs (but also that of cationic group 14 species) is derived from vacant p orbitals on the central atom, making them highly intolerant to an aqueous (or sometimes even protic) environment as they tend to decompose by irreversibly binding to water, thus demanding the exploration of more stable and neutral main-group LAs.⁷³

A recent, practical strategy for synthesizing efficient and stable LAs is to enforce geometrical constraints onto a main-group center, thereby generating a low-lying orbital for accepting electrons.^{42,74-78} This approach has proven advantageous for exploring the Lewis acidity of group 15 species, despite generally being considered LBs due to the availability of an energetically accessible lone pair.⁷⁹ The Stephan group reported various electrophilic phosphonium cations (EPCs; **2-IV**, as a representative example) that host a σ^* orbital opposite to an electron-withdrawing substituent on the sterically shielded P center to act as an acceptor orbital. This species was found to catalyze various organic transformations, such as hydrodefluorination, hydroarylation, hydrosilylation, and $\text{C}(sp^3)\text{--C}(sp^3)$ cross-coupling.⁸⁰⁻⁸⁶ The energetic accessibility of the σ^* orbital can be further improved, when a cationic P-center is embedded in a 1,3,2-dioxaphosphacyclic structure **2-V**, as shown by Terada and Kouchi.⁸⁷ These cyclic phosphonium

cations utilize hypervalent bonding as a strategic interaction for the generation of an active pentavalent species that efficiently catalyzes Diels-Alder type reactions.

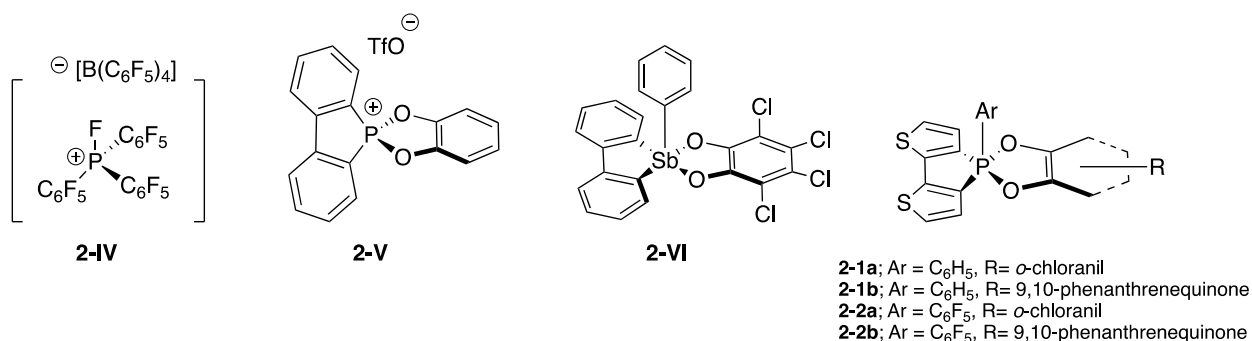


Figure 2-9: Examples of main-group LAs.^{80,87,88,91}

While these species illustrate the influence of electron-withdrawing substituents and molecular charge on Lewis acidity, the phosphonium cations are largely transient and immediately decompose in protic environments, emphasizing the importance of neutral LAs that are stable under ambient conditions. In this context, Gabbaï et al.⁸⁸⁻⁹⁰ successfully reported triarylsbonyl catecholates **2-VI** that adopt a 4SQ geometry to project out a σ^* orbital for adduct formation with various LBs. Inspired by the above results, we recently reported neutral 4SQ P(V)-based dithieno[3,2-*b*:2',3'-*d*]phosphole systems **2-1a,b** and **2-2a,b** that show Lewis acidity derived from a σ -hole originating from a P-aryl σ^* orbital (see Chapter 2.1).⁹¹ This low-lying orbital is further stabilized through the σ^* - π^* interaction with the dithienophosphole scaffold and the electron-withdrawing catecholate. The unusual 4SQ geometry provides a sterically accessible Lewis-acidic phosphorus center that can efficiently react with nucleophiles to form hexacoordinate species. However, this geometry also allows strong supramolecular dimerization in these species that is significant in solution, even at very low concentrations. This interaction kinetically stabilizes the active P center in both solution and the solid-state via mutual steric protection, thereby limiting the

scope of nucleophiles that could be utilized towards activating these hypervalent species. Consequently, easily polarizable, small nucleophiles have been the substrate scope of these LAs to date.⁹¹ Nonetheless, the reactivity of these neutral hypervalent species arising from their constrained structure is highly intriguing. Considering the increasing demand for stable LAs, in this Chapter section, we investigate the possibility to tune the Lewis acidity and reactivity of the hypervalent P center in this system by altering the catecholate substituents as well as modifying the main dithieno-framework. As part of this study, we provide comprehensive insights into how the supramolecular interactions and geometry can be controlled through bulky substituents.

2.2.2 Results and Discussions

2.2.2.1 Synthesis of Hypervalent LAs

In our initial study, we focussed on combinations of aryl-functionalized dithienophospholes (aryl = C₆H₅, C₆F₅) with electron-withdrawing (e.g., *o*-chloranil) and -donating (e.g., phenanthrene) quinones (Chapter 2.1).⁹¹ In this contribution, we now present a systematic study of a new generation of stable and neutral P-based hypervalent LAs. Our first design strategy involves chemical modification of the hypervalent system by electronic alterations, either at the catecholate moiety, or by modifying the dithieno-scaffold (Figure 2-10). We expected that such alterations would provide a direct correlation of the various electronic functionalities with the LA strength of the P center, and an opportunity to further functionalize this system through a methodically selected quinone. The second strategy relies on structurally perturbing the 4SQ geometry through steric hinderance from bulky groups to reduce the π -stacking interactions between monomers of the supramolecularly stabilized dimers.⁹¹ We expected this to improve the steric accessibility of

the P center by nucleophiles, thus reducing reaction time and extending the scope of nucleophiles that could potentially react with the hypervalent LAs.

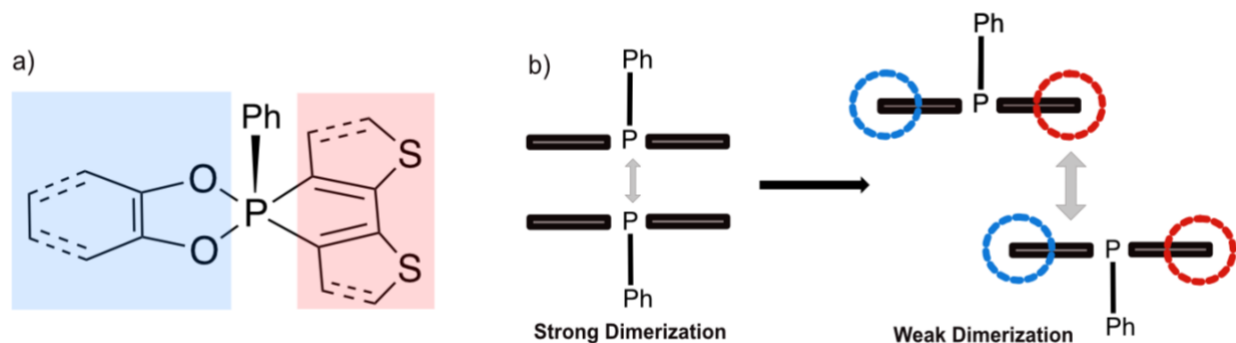
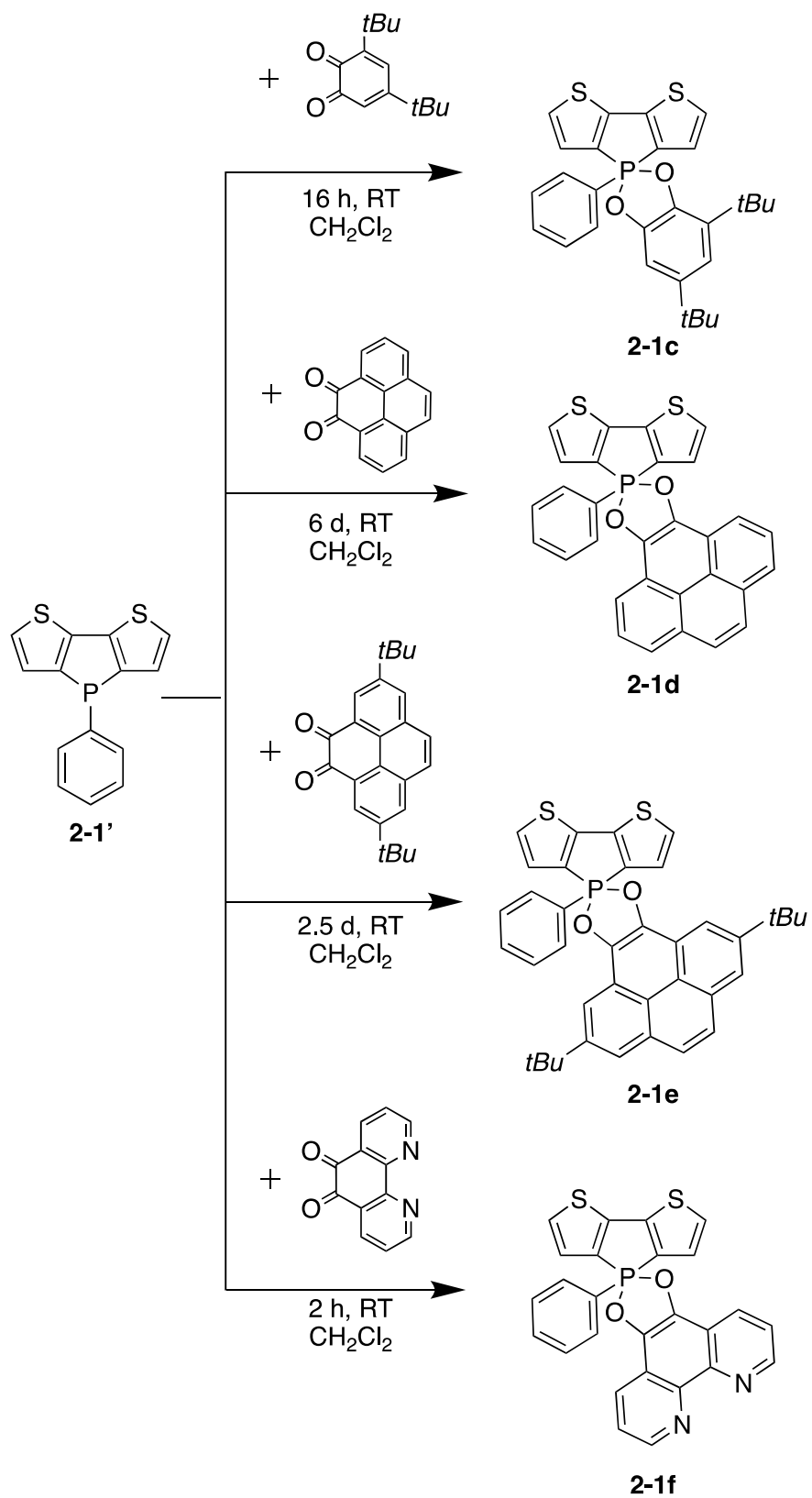


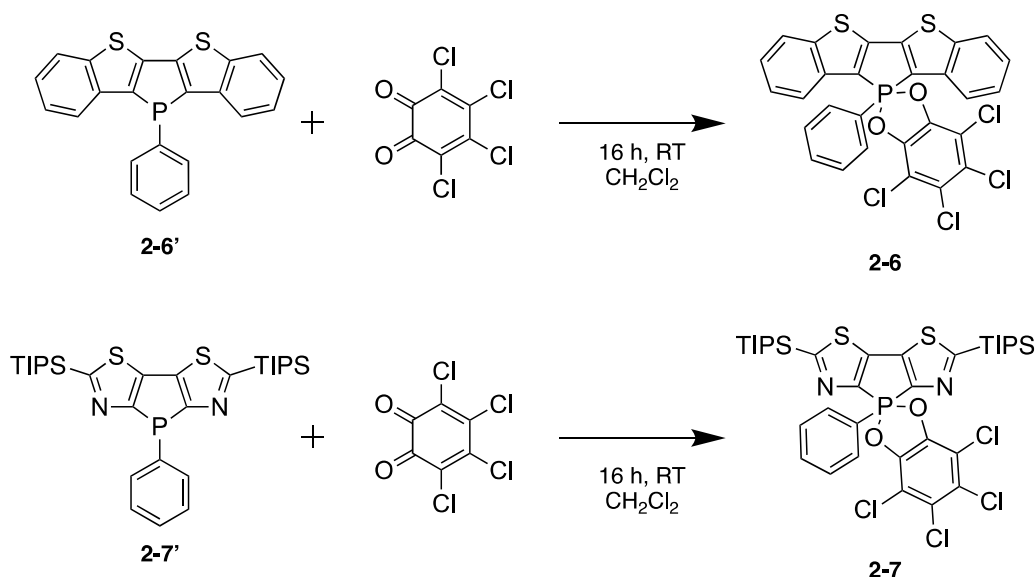
Figure 2-10. Two-pronged strategy that involves changing a) electronics and b) sterics at the catecholate moiety (blue) and the dithieno-scaffold (red).

The new family of compounds was synthesized via our previously established [4+1] cycloaddition protocol⁹¹ using one equivalent of trivalent dithienophosphole **2-1**⁹³ and various quinones such as 3,5-di-*tert*-butyl-*o*-benzoquinone, pyrene-4,5-dione,⁹² 2,7-di-*t*-butyl-4,5-pyrenedione,⁹² and 1,10-phenanthroline-5,6-dione, respectively (Scheme 2-5). Compound **2-1c** was synthesized by stirring a mixture of **2-1'** and the corresponding quinone at room temperature under argon overnight in dry DCM; it was isolated at 73% yield by eluting through alumina micropipette columns with dry solvents (50:50 DCM/hexane). While a similar protocol was used for the synthesis of **2-1d** and **2-1e**, the time towards complete formation of these derivatives is longer compared to that for **2-1c** and **2-1f**. We attribute this to the bulky and electron-rich nature of the reacting quinones. Derivatives **2-1d** and **2-1f** were isolated after drying the reaction mixture under high vacuum and then washing the residue with dry pentane to yield 69% and 42% of pure product, respectively; **2-1e** was purified by an alumina column with dry DCM in 19% yield. The presence of the bulky *t*-butyl groups in compounds **2-1c** and **2-1e** was expected to help induce a structural alteration from 4SQ geometry, since the tendency for π -stacking should be reduced in these species.⁹³ (see SI section 2.2.1 for details)



Scheme 2-5: Synthesis of quinone-modified hypervalent dithienophospholes.

In addition, we also synthesized two hypervalent species with differently modified dithieno-scaffolds to investigate the significance of such modification on the Lewis acidity of the P center (Scheme 2-6). While compound **2-6** hosts an electron-donating benzo-fused dithieno-scaffold, the thiazole functionalization in **2-7** imparts more electron-accepting characteristics onto the phosphorus center compared to **2-1a**. Compounds **2-6** and **2-7** were synthesized from the corresponding trivalent phospholes **2-6'**⁹⁴ and **2-7'**,⁹⁵ respectively, using similar synthetic conditions as above. Compound **2-6** was isolated in 32% yield after drying the reaction mixture under vacuum and washing with dry pentane. A similar isolation protocol was used for **2-7** on complete conversion of starting material to the product as monitored by ³¹P NMR spectroscopy, but the product was found to decompose during purification, emphasizing its reactive nature toward trace amounts of water; compound **2-7** was thus synthesized and characterized *in situ*.⁹³ (see SI section 2.2.1 for details)



Scheme 2-6. Synthesis of dithieno-modified hypervalent dithienophospholes.

2.2.2.2 Solid State Characterization

Solid-state structures of **2-1c**, **2-1e** and **2-6** were confirmed by SC-XRD studies; suitable crystals were obtained from a saturated CHCl₃ solution in the case of **2-1c**, or directly by slow evaporation of reaction mixture of **2-1e**. While we expected the bulky *t*-butyl substitution to disfavor the supramolecular dimerization, compound **2-1c** nonetheless exhibits the kinetically stabilized distorted 4SQ structure (Figure 2-11a) as observed in case of the earlier reported relatives **2-1a,b** and **2-2a,b**.⁹¹ The aryl group in **2-1c** is arranged nearly orthogonally to the plane containing the quinone (100.5°) and dithienophosphole moieties (103.0°), with P–C and P–O distances of 1.8 Å and 1.7 Å (as observed in case of the chloranil species **2-1a**)⁹¹ but the central phosphorus atom is slightly contracted towards the π -conjugated plane at 0.4 Å. The planarization of the P-containing π -system in **2-1c** consequently still favors supramolecular dimerization in the solid state. Nonetheless, the geometrical distortion through steric functionalization is still considered an effective strategy in separating the dimers, as **2-1c** interacts through a slipped- π -stack dimer geometry (3.5 Å) in the solid state (Figure 2-11b), rather than the head-to-head π -stacking seen for **2-1a**.^{91,96} Notably, the unsymmetrically substituted quinone gives rise to two enantiomers of **2-1c** that crystallize as racemic mixture.⁹⁷ The arrangement of the dimers of **2-1c** not only increases the accessibility to the P center but also allows dissociation to the corresponding monomers in solution with dilution (*vide infra*), which is suppressed for **2-1a**, due to the strong donor-acceptor interaction of the dimers that persists even at low concentration. The latter was a significant limiting factor for the practical utility of the earlier reported species **2-1a,b** and **2-2a,b**.⁹¹ The rotational flexibility associated with fluctional *t*-butyl group favors the dynamic exchange between the 4SQ and 3BP geometries that were calculated to be energetical comparable in the gas phase before.^{50,91,93,98}

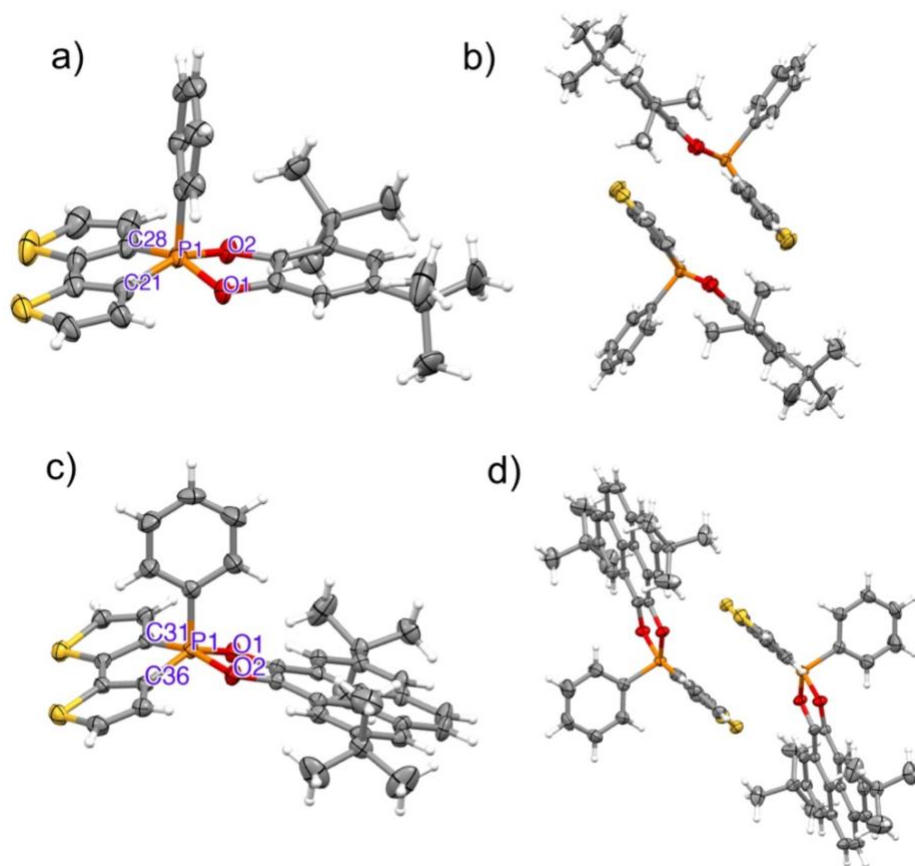


Figure 2-11. a) Molecular structure, and b) supramolecular dimerization of **2-1c** in the solid state; c) molecular structure, and d) supramolecular dimerization of **2-1e** in the solid state. Ellipsoids are set to 50% probability.

Notably, SC-XRD data of the di-*t*-butylpyrene-based species **2-1e** are quite intriguing as a distinctly different geometry is observed for this species. The data imply that a bulky quinone, such as pyrenedione with two symmetrically arranged *t*-butyl groups, distorts the 4SQ geometry even further toward a 3BP-based structure (Figure 2-11c). The bond lengths in **2-1e** are comparable to those of **2-1c**; however, the bond angles show larger deviation. The phenyl group is arranged at an angle of 107.6(1)° from the P1–C36 bond, simultaneously contracting the angle to 99.1(1)° from the other P1–C31 bond. This twists the structure towards the VSEPR-supported 3BP geometry, while projecting out the phosphorus atom from the conjugated plane by about 0.4 Å. The transition of the geometry from 4SQ in **2-1c** (or **2-1a**) to 3BP in **2-1e** is further justified by comparing the

change in bond angles associated with the dithieno-carbon and catecholate-oxygen atoms at the square base to form the trigonal planar base on modification. The C28–P1–O1 and C21–P1–O2 angles in **2-1c** are both 156.2(2)° (**2-1a**: 155°) but in the case of **2-1e**, the C31–P1–O2 angle expands to 163.46(1)° and C36–P1–O1 angle contracts to 144.5(1)°, suggesting a noticeable deviation from 4SQ towards 3BP. The C31–P1–O2 bond is approaching linearity towards the 3c-4e bond in an ideal 3BP geometry. Since the substituents at the trigonal base of an ideal 3BP geometry are aligned at 120°, we expect that the contraction of the C36–P1–O2 angle in **2-1e** to bring the geometry towards the ideal 3BP.⁹⁹ Even though the geometries of **2-1c** and **2-1e** support the preferred formation of two moderately strong C–P–O bonds over a strong O–P–C 3c-4e bond, the implementation of the bulky substituents is an effective way to enforce 3BP geometry.⁹¹

On the other hand, the solid-state packing of **2-1e** shows slipped π -stacking⁹⁶ interactions only between the neighboring dithieno-scaffolds at 3.4 Å, which appears to be the consequence of the steric hindrance from the *t*-butyl groups. While the molecules maintain strong supramolecular aggregation through the formation of dimers via the dithieno-moieties in the solid, the P atom is no longer fully kinetically shielded by the neighboring molecule (Figure 2-11d). Additionally, the plane of the phenyl substituent in **2-1e** is aligned with the direction of the π -conjugated plane defined by the dithieno- and quinone scaffold, thus hindering any additional supramolecular stabilization in the bulk phase (Figure 2-12b). This suggests that the dimers of **2-1e** should be separated effortlessly in solution. This feature is unique to **2-1e**, since the other group-15 4SQ derivatives (including **2-1a,b** and **2-2a,b** series)^{88-91,100} usually possess aryl-groups that are arranged perpendicularly to the conjugated square base, and thereby engaging in π -stacking with neighboring molecules. This orientation is largely maintained in **2-1c**, except that the bulky *t*-butyl groups of the quinone moiety interrupt any π -stacking interaction between neighboring phenyl

rings (Figure 2-12a), potentially leading to easier separation of the dimer in solution relative to **2-1a,b** and **2-2a,b**. On the other hand, **2-6** shows a distinct chain-like π -stacking interaction where the electron-rich dithieno-scaffold of the overall T-shaped base allows donor-acceptor interaction with the *o*-chloranil species of the neighboring molecules that is further stabilized by solvent molecules (DCM; Figure 2-12c and SI 2.2.3).⁹¹

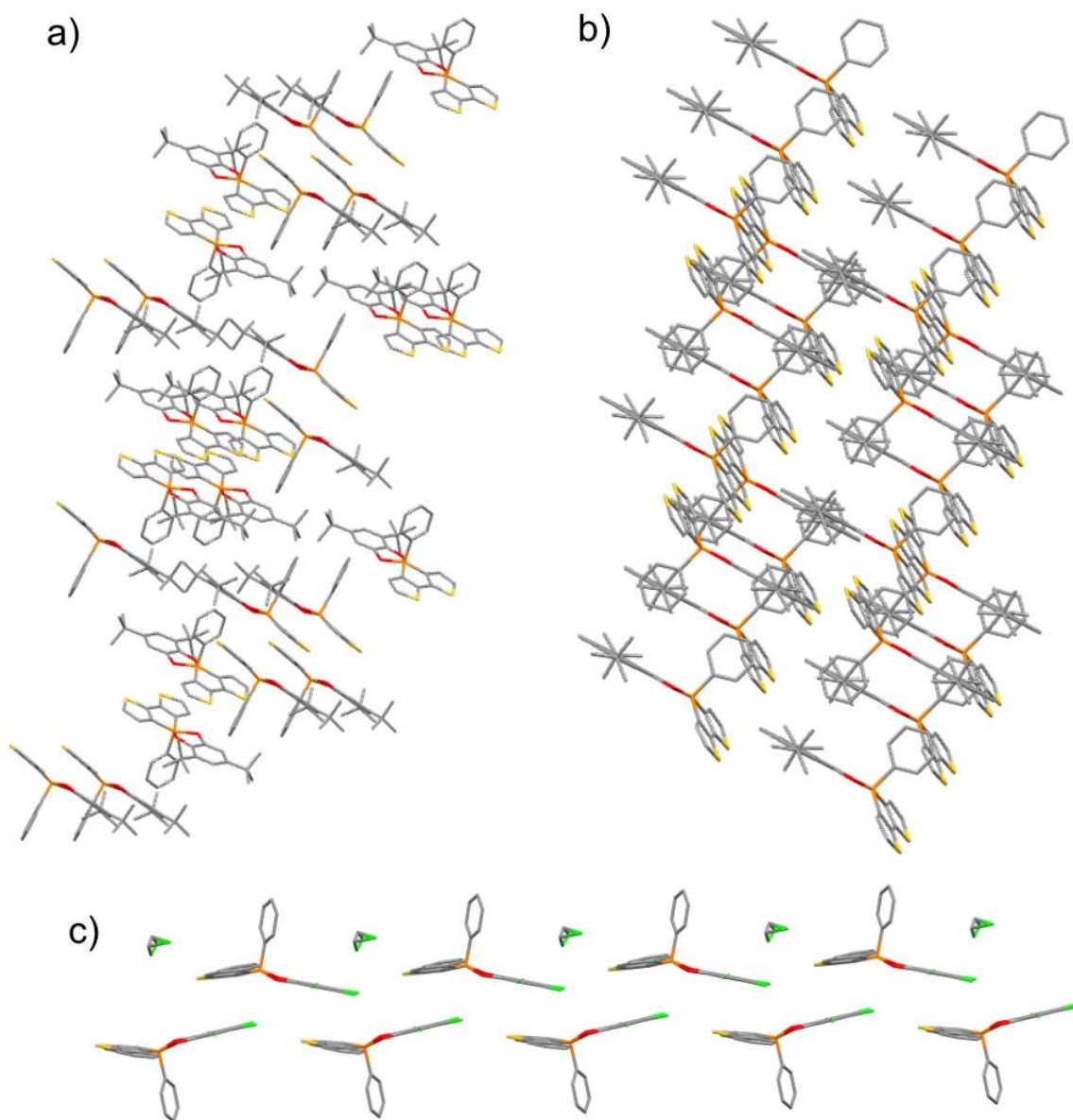


Figure 2-12. a) Crystal packing of **2-1c**, showing perpendicular alignment of phenyl group with the square base; b) crystal packing of **2-1e**, showing parallel alignment of phenyl group with the square base; c) crystal packing of **2-6**, showing donor-acceptor type chain-like arrangement.

2.2.2.3 Concentration-Dependent Fluorescence Study

The fluorescent nature of dithienophospholes has been effectively used for the detection of the monomers of the hypervalent LAs.³ Even though the solution-phase exchange between the geometrical isomers can influence the fluorescence emission through non-radiative decay, the close intermolecular distance affords electronic transitions across the dimer and is observed as characteristically broad emission that corresponds to excimers.^{53,91,101} Upon dilution, the broad emission profiles resolve to sharper vibronic peaks supporting the formation of the corresponding monomer. By contrast, the observed supramolecular interaction in the previously reported, first-generation hypervalent compounds (Chapter 2.1) was considered strong, as excimer-type emissions were observed even at concentrations as low as 10^{-13} M.⁹¹

This observation is further validated as the new species also follow a similar trend, however, with some notable exceptions. Interestingly, at higher concentrations ($c = 5 \times 10^{-4}$ M), compound **2-1c** exhibits an emission peak at 457 nm upon excitation at 340 nm (Figure 2-13a). While the broad emission can again be attributed to excimer formation, we also observe a blue shift of the emission maximum to 417 nm upon dilution to 5×10^{-6} M, corresponding to monomeric **2-1c**. Since the solution of **2-1c** nearly exclusively consists of monomers at lower concentration, we surmise that the bulky substituents suppress dimer formation in solution. While the monomeric entities of **2-1c** show a hypsochromically shifted emission maximum from the excimer (when compared to the other species), the monomers are significantly more emissive than the earlier reported relatives, even at a very low concentration of 5×10^{-8} M.⁹¹

We expected a similar observation for **2-1e** due to the presence of steric bulk, but it surprisingly follows the same trend as the previous generation derivatives, where the excimer emission at 451 nm resolves to multiple vibronic peaks (310, 347, 380 nm; additional peaks correspond to Raman

scattering at low concentration) upon dilution (Figure 2-13b). This suggests a weakly emissive monomer compared to **2-1c**. Since the resolution of the peaks was observed only at considerably higher concentration (6×10^{-6} M), it suggests a relatively weaker π -stacking interaction in **2-1e** that likely arises from a 3BP geometry, as would be expected from the presence of the bulky substituents and absence of any additional supramolecular interaction. This is further justified by the fact that **2-1d** (without any bulky functionalization) shows stronger aggregation at this concentration and produces a considerably lower concentration of monomer with respect to the excimer (see SI section 2.2.4(iii)).^{91,101}

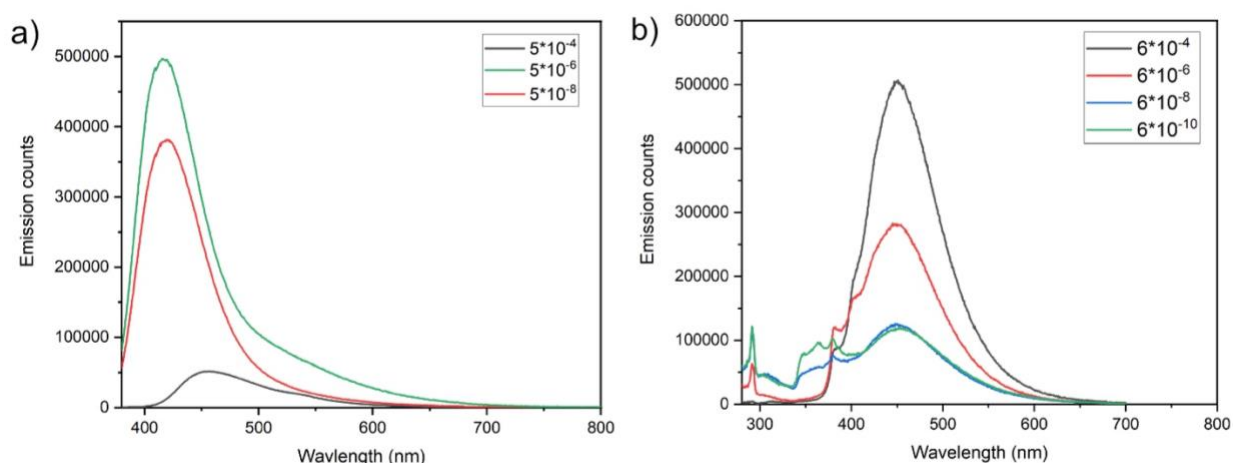


Figure 2-13. Fluorescence emission spectra showing monomer and excimer for a) **2-1c** on excitation at 340 nm and b) **2-1e** on excitation at 269 nm.

The modified dithieno-scaffold of **2-6** extends the conjugation significantly, not only resulting in emission at longer wavelength but also promoting strong supramolecular interactions (see SI 2.2.4).^{91,94} Compound **2-6** shows comparable behavior to the original species **2-1a,b** and **2-2a,b**, where the excimers are still prominent at low concentrations. This is obvious when comparing emission spectra of **2-6** at $c = 10^{-9}$ M, where the solution of **2-6** is almost at a 50:50 ratio of excimer (555 nm) to monomer (360, 380, 405, and 443 nm). Unfortunately, photophysical experiments could not be conducted for **2-7** on account of its transient nature. The excimer-monomer equilibria

were further scrutinized by similar concentration-dependent studies in the presence of a weakly coordinating solvent that could potentially interact with the σ -hole and suppress dimer formation. However, we found that dilution of DCM solutions of compounds **2-1e** and **2-6** with THF, respectively, had no detectable impact on the amount of monomer present.

2.2.2.4 Reactivity of Neutral Pentacoordinate LAs

In addition to the structural and supramolecular behavior, what makes these hypervalent species an interesting system to study, is their selective reactivity to nucleophiles. During our studies on the interaction of selected nucleophiles with the original series of compounds (Chapter 2.1), we determined that the nucleophiles interact with the Lewis-acidic phosphorus center through a σ -hole type interaction, facilitated by the orthogonally arranged low-lying σ^* P-aryl orbital.^{80,88-91,102} This allows the P center to interact with small and hard LBs such as F^- and OH^- , resulting in transient hexacoordinated species that further propagate towards the formation of dithienophosphole oxide and corresponding catecholate-based by-products.⁹¹ These reactive pathways are mediated by the Lewis-acidic phosphorus center and may have the potential to be leveraged into a suitable synthetic route towards otherwise arduous organic transformations. To confirm similar (or deviating) behavior for the new series of compounds, we investigated their reactivity toward two distinct reagents in this present study.

(i) *Fluoride abstraction:* The σ -hole in the new species is visible as an area of positive electrostatic potential⁴⁶ depicted as the blue/green regions at P atom on the electrostatic potential (ESP) map, obtained from the computationally optimized structures at the B3LYP/6-31G+(d) level of theory. The more intense this region, the higher the Lewis acidity of these species. As observed from ESP

mapping, **2-7** features the most intense σ -hole, followed by **2-6**, **2-1f**, **2-1e**, **2-1d**, and **2-1c** (Figure 2-14).

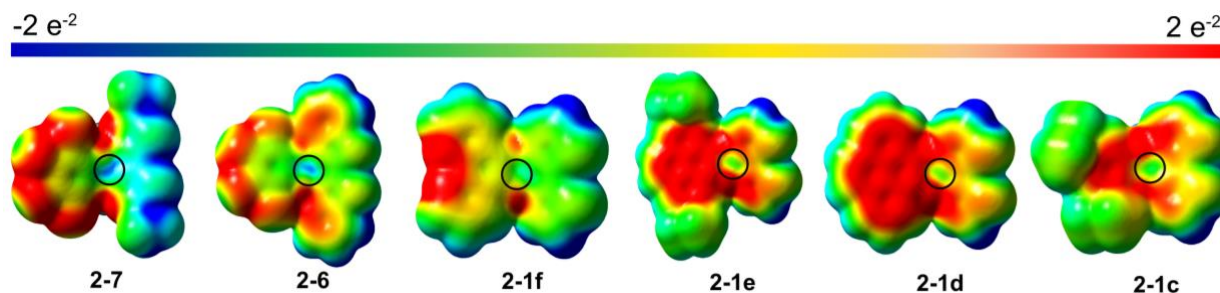
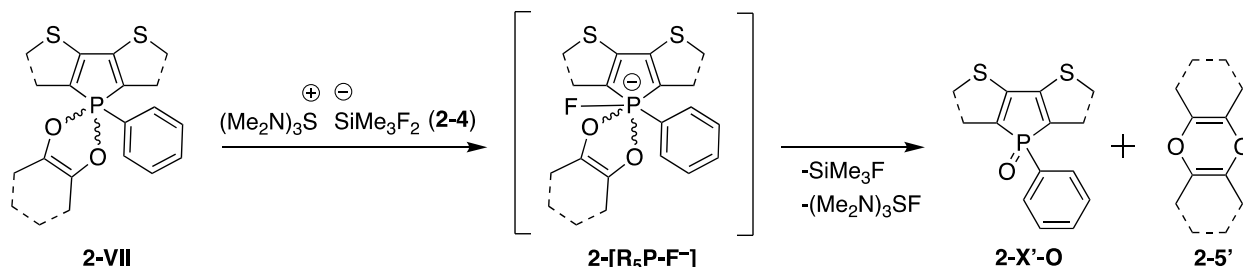


Figure 2-14. ESP mapping of the pentacoordinate derivatives; blue to red indicated electron deficient to electron rich. The Lewis-acidic P center (σ -hole) is marked within the circle.

The calculated FIA (compared to the isodesmic reaction $\text{Me}_3\text{SiF} \rightarrow \text{Me}_3\text{Si}^+ + \text{F}^-$; PWB95/DEF2-QZVPP level of theory) for these molecules correlates with the above observation as well.⁴⁷ Compound **2-6** (331 kJ mol⁻¹) has the highest FIA out of this series, followed by **2-7** (326 kJ mol⁻¹), **2-1f** (299 kJ mol⁻¹), **2-1e** (290 kJ mol⁻¹), **2-1d** (285 kJ mol⁻¹), and **2-1c** (272 kJ mol⁻¹). Overall, these values qualify the new pentacoordinate P-species as moderate LAs.^{42,47} The previously reported pentacoordinate dithienophospholes (Chapter 2.1) have FIA values of 306-381 kJ mol⁻¹, where the lowest value corresponds to the most electron-rich system, **2-1b** (Ph, phenanthrene quinone) and the highest value is attributed to the most electron-poor species, **2-2a** (C₆F₅, *o*-chloranil). Not surprisingly, the electron-donating quinones in **2-1c-f** impart electron density onto the phosphorus center through donation into P-C_(dithieno) σ^* -orbital, thus reducing the electrophilicity of the P center in these compounds.⁹¹ The extended conjugated main scaffold in **2-6** withdraws electron density from the P center, resulting in higher FIA value.

The calculated FIA values were further justified by fluoride abstraction reactions. The pentacoordinate dithienophosphole species were reacted under the strict exclusion of air and moisture with tris(dimethylamino) sulfur (trimethylsilyl) difluoride (**2-4**) to generate

corresponding hexacoordinated fluoride adducts **2-[R₅P-F⁻]** *in situ*. Due to their transient nature, the fluoride adducts were only identified by ³¹P and ¹⁹F NMR spectroscopy via their distinctive doublets with coupling constants ¹J_{P-F} of ~700 Hz.⁹¹ All newly synthesized derivatives show ¹J_{P-F} coupling constants varying from 745 Hz for **2-1e**, 746 Hz for **2-1c**, 757 Hz for **2-1f**, 766 Hz for **2-1d** to 773 Hz for **2-6**. While the computationally calculated FIA values and ¹J_{P-F} coupling constants correlate very well for nearly all new species, a compelling result was observed for **2-1e**. Even though the FIA of **2-1e** is intermediate among all measured species, its ¹J_{P-F} coupling constant is the lowest in this series. The discrepancy between the computational and experimental data could be explained by the occurrence of a 3BP structure in **2-1e** that possibly favors Berry-pseudo rotation in solution,^{103,104} facilitated by the absence of strong supramolecular stabilization.



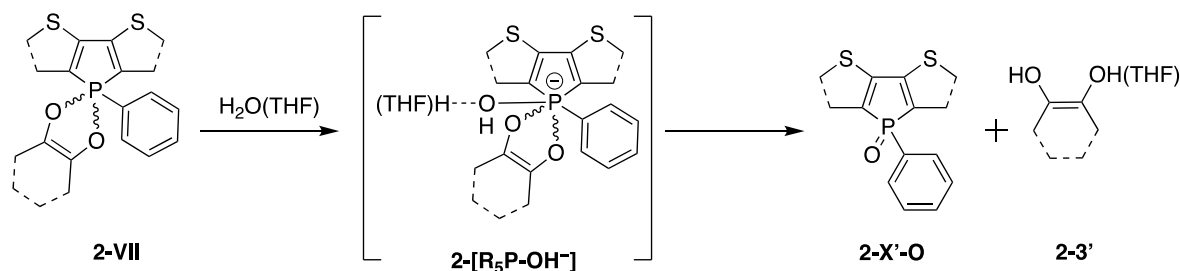
Scheme 2-7. Double deoxyaryloxylation proceeding through **2-[R₅P-F⁻]** towards formation of corresponding phosphole oxide **2-X'-O** and dioxin **2-5'**.^[9] Note, **2-VII** and **2-X'** is used representatively for the differently modified dithienophospholes reported here.

For compound **2-7**, the corresponding species **2-[R₅P-F⁻]** was not detected *in situ*; we instead observed the immediate formation of the oxide of **2-6'** (cf.: **2-X'-O** in Scheme 2-7). This observation was in contrast to the earlier reported double deoxyaryloxylation reaction of the corresponding **2-[R₅P-F⁻]** species to generate phosphole oxide **2-X'-O** and the corresponding dioxin **2-5'** (Scheme 2-7).⁹¹ In this context, the most reactive congener toward generation of the transient **2-[R₅P-F⁻]** species is **2-7** that undergoes deoxyaryloxylation within one hour (as monitored by ³¹P NMR spectroscopy), followed by **2-1e** (**2-R₅P-F⁻**-adduct: **2-1'-O**; 15:6), **2-1f**

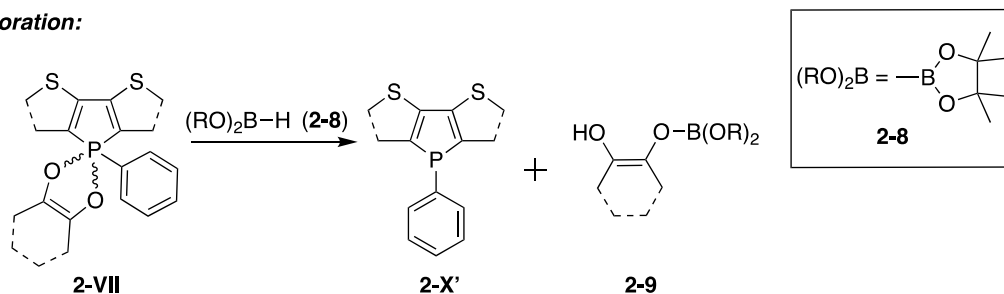
(**2-R₅P-F⁻**-adduct: **2-1'-O**; 15:5), **2-6** (**2-R₅P-F⁻**-adduct: **2-6'-O**; 11:15), **2-1d** (**2-R₅P-F⁻**-adduct: **2-1'-O**; 15:1.25) and **2-1c** (**2-R₅P-F⁻**-adduct: **2-1'-O**; 15:0). While formation of **2-[R₅P-F⁻]** species is thermodynamically favored in all cases, the kinetic parameters that control the rate-determining step for the formation of **2-X'-O** and **2-5'** are effectively altered by the modification employed. For example, the reaction proceeds to completion toward **2-1'-O** within two days for **2-1e** and **2-1f**, which is the fastest among the entire family, suggesting that the modifications applied here (such as distorted 3BP geometry and heteroatom containing quinones, respectively) are effective in moderating the Lewis acidity and reducing the kinetic energy barrier associated with the formation of **2-1'-O**. While **2-6** shows significant formation of **2-6'-O** within one hour, the reaction slowly proceeds to completion only within five days. The strong supramolecular interaction in **2-6** plays a crucial role here by reducing the accessibility to the Lewis acidic P center, hence kinetically disfavoring the formation of **2-6'-O**. Compounds **2-1c** and **2-1d** have the slowest rate of conversion to **2-1'-O** and **2-5'**, which could be attributed to their relatively low FIA value (*vide supra*).

(ii) *Hydride abstraction*: In addition to fluoride affinity, the Lewis acidic P center in these pentacoordinate compounds was observed to be susceptible to degeneration in a protic environment. Our previous study confirmed that in aqueous solution, water/hydroxide coordinates to the P center **2-[R₅P-OH⁻]** to heterolytically cleave the O-P bonds to generate **2-X'-O** and catechol **2-3'** (Scheme 2-8).⁹¹ Since the water acts as a proton source in that case and cannot directly interact with electropositive P center, we were interested in reversing the polarity towards hydride to study the resulting reaction pathway and the products. In this context, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2-8**) was used as a dry hydride source.

a) Earlier reported hydrolysis:



b) Observed hydroboration:



Scheme 2-8. a) Hydrolysis of the hypervalent dithienophospholes reported previously;⁹¹ b) observed hydroboration products on reaction of hydride with pentacoordinate dithienophospholes. Note, **2-VII** and **2-X'** is used representatively for the differently modified dithienophospholes reported here.

We expected the hydride to react with **2-VII** in a similar manner as shown in Scheme 2-8a. However, upon addition of **2-8** to a solution of **2-1d** in CDCl_3 , we observed the formation of **2-1'** by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy rather than **2-1'-O** (the observation is same for all the derivatives reported in this Chapter). While we initially suspected a retro-[4+1] cycloaddition toward the starting trivalent phosphole and *o*-quinone, the NMR spectroscopic data did not confirm the formation of *o*-quinone (see SI 2.2.6). This suggested that the reactivity of pentacoordinate dithienophospholes with hydride follows a different mechanism to the earlier established transformation of this system leading to phosphole oxide. Here, a possible reaction mechanism could formally involve a 1,4-hydroboration,^{105,106} leading to the formation of **2-9** that was identified in the reaction mixture by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy (Scheme 2-8b).

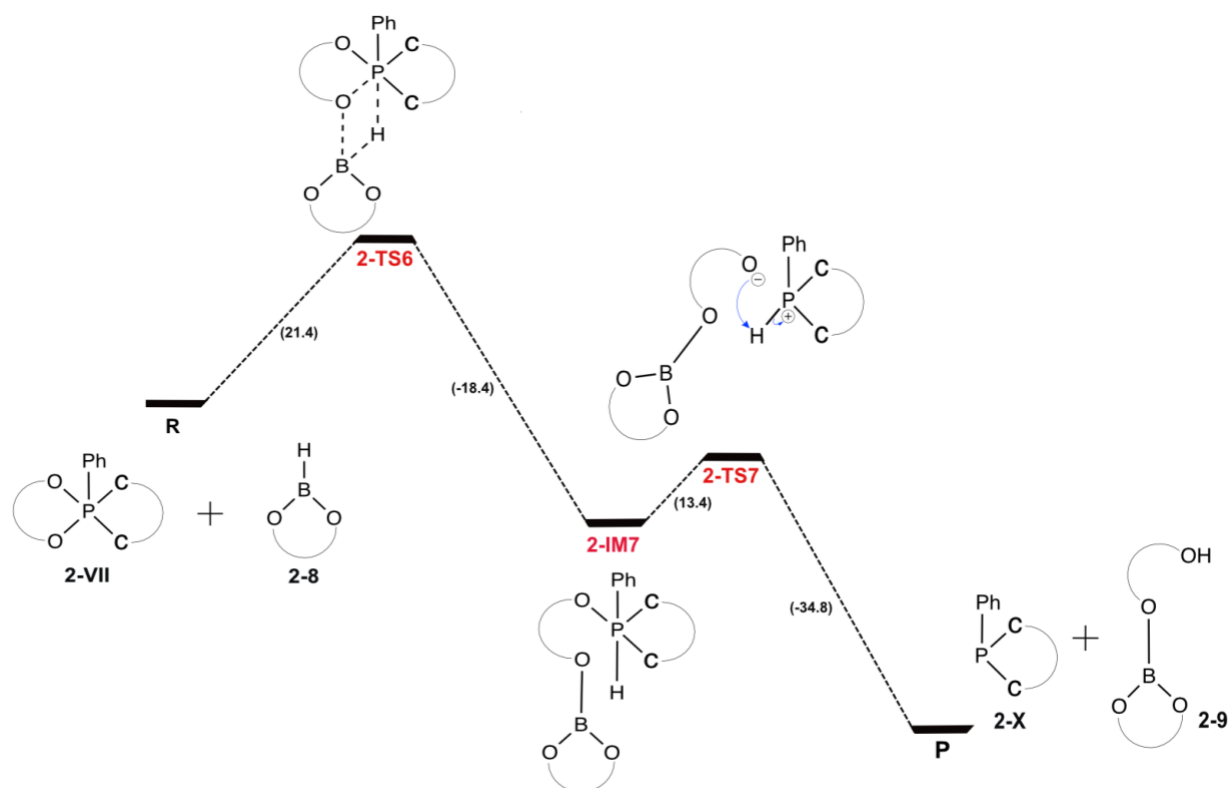


Figure 2-15. Energy landscape for the hydroboration reaction of **2-VII** species. In this figure, three curves are used to schematically represent the catecholate, dithieno and $(\text{RO})_2\text{B}$ groups, respectively, and other atoms of the group are omitted for clarity. Electron migrations are shown by blue arrows. Energy differences between structures connected by dashed lines are given in kcal/mol. **2-IM** and **2-TS** are numbered consecutively for all reaction/mechanism discussed. ZPE corrected energies of the stationary points were calculated using CAM-B3LYP/MA-DEF2-SVP/CPCM(THF) level of theory.

To support the observed reaction, we studied the mechanism for the hydride abstraction and formation of **2-VII** and **2-8** using density functional theory (DFT) calculations (Figure 2.15). The transition state, **2-TS6** that leads to the abstraction of the hydride by the Lewis acid ‘ PR_5 ’ has an energy barrier of 21.4 kcal/mol, suggesting that the steric bulk of the hydride source kinetically limits access to the reactive P center, leading to longer reaction times in certain derivatives, such as **2-6** with stronger π -interaction in solution. Breaking of the B-H bond leads to intermediate **2-IM7** where the hydride coordinates to the P center generating a transient hexacoordinated species. **2-IM7** is thermodynamically stabilized by 18.4 kcal/mol compared to the reactants. However, the

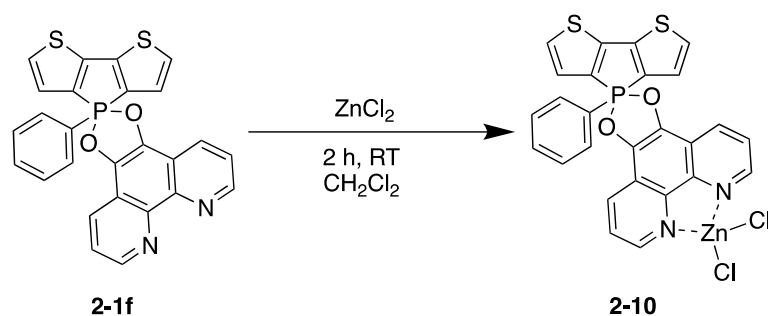
P–O bond is highly polar and can easily undergo P^+-O^- heterolytic cleavage. Subsequently, the H–P σ -bond electrons form the phosphorus lone pair, while the leftover proton is simultaneously attacked by the dangling oxide of the catecholate. This process involves a second transition state, **2-TS7** with a low kinetic barrier, which allows effortless conversion of **2-IM7** to the final product **P** and explains why **2-IM7** was never identified spectroscopically in the reaction mixture, in contrast to the **2-[R₅P-F]** adducts. The electron migrations in **2-TS7** distinguish the hydride abstraction reaction from the earlier established transformation of **2-VII** leading to **2-X'-O**. The electron migration in **2-TS7** is intriguing as it reduces the Lewis-acidic P-center and converts the hydrogen entity from a hydride to a proton. This highly exoergic redox step (–34.8 kcal/mol) results in the products of **2-X'** and **2-9**.

It should be noted that while quinones can generally be reduced in the presence of a hydride source, the observed hydroboration reaction here is specific to pentavalent compounds. In the absence of LA, such reductions usually proceed either through radical mechanism or other symmetric addition reactions.¹⁰⁷⁻¹¹² Moreover, hydroboration using pentacoordinate dithienophospholes is a rare instance, where the phosphorus center facilitates reversibility of polarity (umpolung) of a hydride anion to a proton. Kawashima and coworkers first reported such a behavior of pentacoordinate phosphoranes in the early 2000s.^{113,114} The redox step involves conversion of a hydride to a proton along with reduction of P(V) to P(III) and is only possible in the presence of a LA, such as the pentavalent dithienophospholes. In addition, the formation of the trivalent phosphole as the end-product has the potential for a catalytic cycle, by allowing the regeneration of pentacoordinate dithienophosphole in principle upon further addition of *o*-quinone. This scenario is impossible for the earlier reported deoxyaryloxylation or hydrolysis reactions of pentacoordinate compounds as the end-product is an oxidized dithienophosphole **2-X'-O**.

We then computationally studied the hydride abstraction by calculating their hydride abstraction affinity, HIA^{47,115,116} akin to the FIA (PWB95/DEF2-QZVPP level of theory). The HIA values decrease in the order; **2-6** (379 kJ mol⁻¹) > **2-7** (372 kJ mol⁻¹) > **2-1f** (341 kJ mol⁻¹) > **2-1e** (332 kJ mol⁻¹) > **2-1d** (330 kJ mol⁻¹) > **2-1c** (312 kJ mol⁻¹) and follow similar trend as the calculated FIA values but with overall higher HIA values. We also calculated the HIA for derivatives **2-1a** (362 mol⁻¹) and **2-1b** (329 kJ mol⁻¹) for comparison. Surprisingly, we observed that **2-6** with the highest HIA value reacts considerably slower to hydroboration (10 days for completion), which we ascribe to the strong supramolecular interaction reducing the accessibility of the P-center, that is overlooked in the gas-phase theoretical calculations. On the other hand, compound **2-7** reacts immediately to form the corresponding trivalent species **2-7'**, followed by **2-1e** and then **2-1c**. While this observation does not follow the expected trend, hydroboration is thermodynamically favored when the rotational fluxionality of bulky substituents such as TIPS or *t*-butyl group kinetically favors hydride abstraction. This suggests that the modification applied to the quinone/dithieno moieties indeed improves the reactivity of these species by reducing their π -stacking interactions. Compounds **2-1d** and **2-1f** immediately form **2-1'** and completely react with **2-8** within five and four days, respectively. To correlate the results with our initial study, we representatively used **2-1b** in the hydroboration as well and the reaction completed within two days. The faster reaction rate towards the formation of **2-1'** in the case of **2-1b**, when compared to the (approximately) electronically equivalent **2-1d**, can be justified by the strong supramolecular stabilization arising from the planarity of the pyrene moiety in **2-1d**. This observation further supports that the first-generation derivatives **2-1a,b** and **2-2a,b** are capable of similar hydroboration reactions as the new series.

2.2.2.5 Metal Coordination of Compound 2-1f

An advantage of implementing a heteroatom-containing catecholate is the ability to further modify the scaffold to potentially enhance its Lewis acidity. In this context, the phenanthroline moiety of **2-1f** offers an interesting opportunity to functionalize the hypervalent derivative via complexation to a metal center that may impact the overall electronics of the system.¹¹⁷⁻¹¹⁹ Upon exposure of compound **2-1f** to one equivalent of ZnCl₂ (in Et₂O) in dry DCM, a yellow precipitate of **2-10** was formed within two hours in 29% yield (Scheme 2-9).



Scheme 2-9. Synthesis of the metal coordinated species **2-10**.

Coordination of Zn(II) to the nitrogen centers of **2-1f** is an effective modification strategy of the Lewis acidity of the P-center. The FIA value of **2-10** is calculated to be 352 kJ mol⁻¹, constituting a significant improvement from its parent, **2-1f** (299 kJ mol⁻¹). This is consistent with the most intense σ -hole on the phosphorus compared to the rest of the series (Figure 2.16). The metal-coordination also has an obvious effect on the electrophilicity of the P center considering any chemical modifications to π -scaffold of the hypervalent compounds. Compound **2-10** also follows a similar reaction pathway upon exposure to fluoride, generating the hexacoordinated adduct (¹J_{P-F} coupling constants ~830 Hz) that ultimately transforms to the dithienophosphole oxide **2-1'-O**. The reaction mixture of **2-10** and **2-4** shows formation of significant amount of **2-1'-O** within 10 min, as monitored by ³¹P NMR spectroscopy, revealing the highest reaction rate towards

deoxyaryloxylation in the entire series. Computationally, the high FIA value suggests a thermodynamically stabilized hexacoordinated adduct that slows down the transformation toward **2-1'-O**.^{80,91} However, the rapid formation of **2-1'-O** suggests that the process is kinetically favored, likely from a cumulative effect of the electron-withdrawing Zn(II) center and its tetrahedral coordination geometry that reduce the overall degree of π -stacking. Similarly, the hydroboration of **2-10** also proceeds significantly faster to generate **2-1'** completely within in one day, which also coincides with the highest calculated HIA value (398 kJ mol⁻¹).

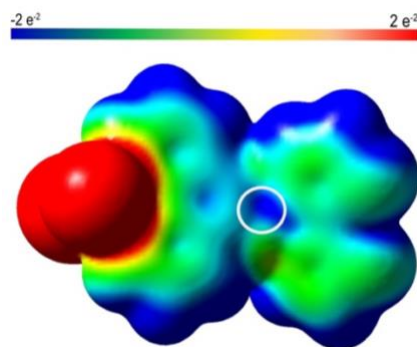


Figure 2-16. ESP mapping of **2-10** showing the most intense σ -hole on the phosphorus; blue to red indicated electron-deficient to electron rich. The Lewis-acidic P center is marked within the circle.

2.2.3 Conclusion

We synthesized a new series of pentacoordinate dithieno[3,2-*b*:2',3'-*d*]phospholes via [4+1] cycloaddition to generate stable and neutral LAs. Comprehensive exploration of the electronic and geometric alterations revealed that the Lewis acidity of the main-group center could effectively be modified. The electronic variations include electron-rich quinones that host bulky substituents, as well as fundamental modification of the dithieno-scaffold. The sterically bulky substituents were methodologically placed to minimize the strong supramolecular interactions that suppress the accessibility of the Lewis-acidic phosphorus center. While such modifications alleviate the π -

interactions, they surprisingly also led to the deviation of the overall geometry from the previously established 4SQ to a 3BP geometry, which we were unable to achieve in our earlier endeavors. With this new series of compounds, we have now successfully established an effective strategy for deliberate perturbations to achieve a specific geometry at the hypervalent main-group center. This was further justified from concentration-dependent fluorescence studies, where the derivatives with bulky substituents showed the formation of monomers at relatively higher concentrations, indicating weak supramolecular interactions. By contrast, most of the derivatives without bulky substituents persist as dimers in solution. The ability of these pentavalent compounds to serve as LAs was investigated computationally via their FIAs and experimentally via fluoride abstraction, where the new dithieno-scaffold modifications show most significant improvement in the FIA values. The hexacoordinated fluoride adducts initiate organic transformations like the earlier reported derivatives, but with a higher rate of conversion due to the reduced tendency for dimerization. To further expand the reactive scope for the hypervalent LAs with small nucleophiles, hydride abstraction, along with their HIA values was explored. The reaction follows a mechanism that involves a redox step where the hydride reverses polarity to generate a proton by simultaneously reducing the P(V) center into a P(III) species. The intriguing umpolung reactivity mediated by phosphorus leads to the formation of the original trivalent dithienophosphole precursor, which potentially enables a catalytic cycle for this system for the first time. Further insights into the refinement strategies of Lewis acidity of these species were gained by metal-coordination of the quinone-moiety to significantly improve the Lewis acidity of the P center. Studies to further optimize the system for enhanced reactivity toward suitable nucleophiles and closing the catalytic cycle are currently ongoing in our laboratories.

2.3 Experimental Section

General. All reagents were purchased from Sigma Aldrich and Oakwood Chemical. Compounds **2-1'**, **2-2'**, **2-6'** and **2-7'** were prepared according to literature procedures. All solvents were purchased from Sigma Aldrich and Fisher chemical. SPS grade solvents (MBraun) from Sigma Aldrich were used for synthesis and characterisations. These solvents were further dried by passing them through neutral alumina, followed by three freeze-pump-thaw cycles. ^1H , $^{31}\text{P}\{^1\text{H}\}$, $^{19}\text{F}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$ spectra were acquired on Bruker NEO 700, 600, 400 and 300 NMR spectrometers on a 5mm ATM probe using TOPSPIN software version 4.0.8. Chemical shifts are reported in parts per million (ppm). Multiplicities are reported as: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), multiplet (m), quartet (q), and broad (br). Elemental analysis was performed by using Vario EL Cube Elemental Analyzer. All runs were performed with approximately 5 mg of sample. Results were obtained in duplicates. The solid-state structures of the compound were determined using Bruker DQ Quest eco. The structures were solved and refined using OLEX2 software. Deposition Number(s) 2044241 (for **2-1a**), 2044242 (for **2-1b**), 2044243 (for **2-2a**), 2044244 (for **2-2b**), 2044245 (for **2-1a** • H_2O), 2235915 (for **2-1c**), 2235916 (for **2-1e**), and 2235917 (for **2-6**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service. All absorption measurements were recorded on an Agilent Technologies Cary 5000 UV-Vis spectrometer at room temperature. All samples for UV-Vis experiments were run in solvents from Sigma Aldrich using 10 mm quartz cuvettes. All emission measurements were recorded using an Edinburgh FS5 spectrofluorometer. QY measurements were collected using integrating sphere; model SC-30 at room temperature. All solutions were prepared using solvents from Sigma Aldrich and measurements were acquired using 10 mm quartz cuvettes.

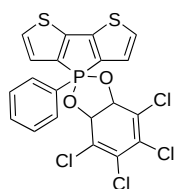
All electrochemical studies were obtained using Metrohm Autolab potentiostat, with 0.1 M n-Bu₄NPF₆ (Sigma Aldrich, electrochemical grade) that was used after recrystallization from THF as electrolyte. The working, reference and counter electrodes used were glassy carbon, silver/silver chloride (Ag/Ag⁺) and platinum wire, respectively. The electrochemical measurements were carried out at room temperature in dry, degassed THF by bubbling argon through the solution for at least 5 min, and an argon flow was kept over the solution during measurements. The electrochemical cell was recorded using the software NOVA.

Additional Experimental data are available online.

For Chapter 2.1, see: <https://doi.org/10.1039/D1DT00062D>

For Chapter 2.2, see: <https://doi.org/10.1002/chem.202300173>

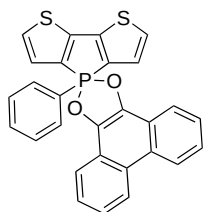
Preparation of **2-1a**



Phenyl-dithienophosphole **2-1'**³ (1.68 g, 6.2 mmol) was dissolved in dry, degassed DCM (25 ml) and added to one equivalent of *o*-chloranil (1.5g) dissolved in DCM (25 ml). The green-yellow, fluorescent solution mixture was stirred overnight at room temperature under argon. The mixture was concentrated to one-third of the original volume and the yellow solution purified by column chromatography (silica, DCM) was dried with roto-evaporation to obtain a bright yellow powder at a yield of 63% (2.0 g, 3.9 mmol). ¹H NMR (600 MHz, CD₂Cl₂, ppm): δ 7.81 (dd, 2H, ³J_P=14.40 Hz, ³J_H=7.20 Hz), 7.48 (dd, 2H, ³J_H=6.00 Hz), 7.45 (dd, 1H, ³J_H=7.20 Hz, ⁵J_P=0.60 Hz), 7.35 (m, 2H), 7.30 (dd, 2H, ³J_P=4.80 Hz, ³J_H=4.20 Hz). ³¹P{¹H} NMR (162 MHz, CD₂Cl₂, ppm): δ -39.1. ¹³C{¹H} NMR

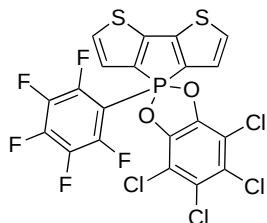
(100 MHz, CD₂Cl₂, ppm): δ 144.9 (d, $^2J_P=123.8$ Hz), 144.4 (d, $^1J_P=36.2$ Hz), 141.8 (s), 132.9 (d, $^1J_P=135.9$ Hz), 132.2 (d, $^4J_P=25.7$ Hz), 131.9 (d, $^2J_P=12.1$ Hz), 130.7 (d, $^2J_P=9.1$ Hz), 129.1 (d, $^3J_P=13.6$ Hz), 127.0 (d, $^3J_P=15.1$ Hz), 124.0 (s), 115.1 (d, $^2J_P=13.6$ Hz). E.A. (%) calc'd for C₂₀H₉S₂PO₂Cl₄ (518.20): C 46.36, H 1.74, S 12.37, found: C 46.47, H 1.67, S 12.54.

Preparation of **2-1b**



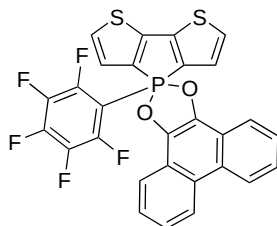
1:1 equiv. of **2-1**³ (0.25 g, 0.9 mmol) and 9,10 phenanthrene quinone (0.20 g) was reacted in the glovebox under dry conditions using DCM (alumina dried and freeze-pump-thaw cycled) (50 ml). The solution was stirred for 24 hours at room temperature and the product was isolated by recrystallization from the reaction mixture at 61% yield (0.50 g, 1 mmol). ¹H NMR (600 MHz, CDCl₃, ppm): δ 8.62 (d, 2H, $^3J_H=8.34$ Hz), 8.10 (d, 2H, $^3J_H=7.80$ Hz), 7.85 (dd, 2H, $^3J_H=7.38$ Hz, $^2J_P=0.74$ Hz), 7.61 (m, 4H), 7.50 (t, 2H, $^3J_H=8.84$ Hz), 7.25 (m, 2H), 7.25 (m, 2H), 7.21 (m, 2H), 7.16 (m, 1H). ³¹P{¹H} NMR (121.5 MHz, CDCl₃, ppm): δ -44.1. ¹³C{¹H} NMR (151 MHz, CDCl₃, ppm): δ 146.5 (d, $^2J_P=122.3$ Hz), 143.1 (d, $^1J_P=34.7$ Hz), 135.5 (s), 134.1 (d, $^1J_P=135.9$ Hz), 131.4 (d, $^2J_P=12.1$ Hz), 130.9 (d, $^4J_P=3.0$ Hz), 130.7 (d, $^5J_P=9.1$ Hz), 128.2 (d, $^3J_P=13.6$ Hz), 126.5 (d, $^3J_P=4.5$ Hz), 126.5 (s), 125.6 (d, $^2J_P=13.6$ Hz), 124.2 (s), 123.1 (s), 122.8 (d, $^2J_P=10.6$ Hz), 120.7 (s). E.A. (%) calc'd for C₂₈H₁₇O₂PS₂ (480.54): C 69.99, H 3.57, S 13.34, found: C 68.97, H 3.65, S 11.57. Aromatic hydrocarbons consistently exhibit lower carbon content, a characteristic inherent to pentacoordinate systems as well.

Preparation of **2-2a**



Trivalent phosphole **2-2'**²⁷ (1.56 g, 4.3 mmol) was stirred overnight (16 hours) with *o*-chloranil (1 equiv., 1.06 g) in 30 ml dry, degassed DCM at room temperature to obtain a yellow, fluorescent solution of compound **2-2a**. The solution was filtered at 0° C to remove unreacted quinone and dried by roto-evaporation to obtain a bright yellow powder with a yield of 62% (1.61g, 2.6 mmol). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.36 (dd, 2H, ³J_H=1.60 Hz, ⁴J_P=5.20 Hz), 7.23 (dd, 2H, ³J_H=4.04 Hz, ³J_P=4.80 Hz). ³¹P{¹H} NMR (162 MHz, CDCl₃, ppm): δ -50.3. ¹⁹F{¹H} NMR (376.5 MHz, CDCl₃, ppm): δ -132.2 (*o*-F, m), -148.5 (*m*-F, m), -158.9 (*p*-F, m). ¹³C{¹H} NMR (100.6 MHz, CDCl₃, ppm): δ 146.4 (d(m), ²J_P=262.6 Hz), 144.5 (d, ²J_P=191.0 Hz), 143.7 (d, ¹J_P=286.7 Hz), 143 (d(m), ⁴J_P=332.0 Hz), 141.0 (s), 137.8 (d(m), ²J_P=260.6 Hz), 130.3 (d(t), ²J_P=11.1 Hz, ⁵J_F=3.0 Hz), 128.6 (d, ²J_P=81.5 Hz), 126.7 (d, ³J_P=17.1 Hz), 124.6 (s), 115.0 (d, ²J_P=14.1 Hz). E.A. (%) calc'd for C₂₀H₄S₂PO₂Cl₄F₅ (608.14): C 39.50, H 0.66, S 10.54, found: C 39.84, H 0.73, S 10.12.

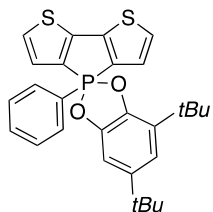
Preparation of **2-2b**



A similar synthetic protocol as for **2-1a**, was used in synthesis of compound **2-2b**, with 4 mmol of **2-2'** (1.46 g) and 9,10-phenanthrene quinone (1.0 equiv., 0.84 g) in 70 ml dry, degassed DCM. The orange-yellow powder of **2-2b** was obtained after evaporation of the solvent at a yield of 80% (1.83 g, 3.2 mmol). ¹H NMR (300 MHz, CDCl₃, ppm): δ 8.66 (d, 2H, ³J_H=8.10 Hz), 8.06 (dd, 2H, ⁵J_P=8.10 Hz, ³J_H=1.29 Hz), 7.63 (d(t), 2H, ³J_H=6.00 Hz, ⁶J_P=3.00 Hz), 7.56 (m, 4H), 7.24 (dd, 2H, ³J_H=1.11 Hz, ³J_P=4.89 Hz). ³¹P{¹H} NMR (121.5 MHz, CDCl₃, ppm): δ -53.7. ¹⁹F{¹H} NMR (282 MHz,

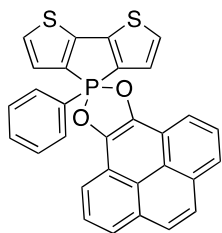
CDCl₃, ppm): δ -132.3 (*o*-F, m), -150.3 (*m*-F, m), -160 (*p*-F, m). ¹³C{¹H} NMR (75 MHz, CDCl₃, ppm): δ 207.0 (s), 145.3 (d, ²J_P=132.0 Hz), 144.5 (d, ¹J_P=38.3 Hz), 136.1 (s), 135.3 (s), 130.7 (d(t), ¹J_F=3.8 Hz, ⁴J_P=10.6 Hz), 130.0 (d, ¹J_P=71.3 Hz), 126.9 (s), 126.8 (d, ³J_P=15.8 Hz), 125.8 (d, ²J_P=15.8 Hz), 124.7 (s), 123.1 (s), 122.4 (d, ²J_P=11.3 Hz), 120.7 (s). E.A. (%) calc'd for C₂₈H₁₂S₂PO₂F₅ (570.50): C 58.95, H 2.12, S 11.24, found: C 59.37, H 1.80, S 11.12.

Preparation of **2-1c**



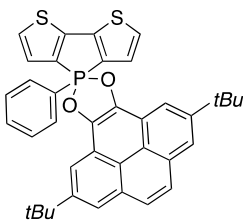
One equivalent of 3,5-di-*tert*-butyl-1,2-benzoquinone (0.5g, 2.30 mmol) dissolved in dry CH₂Cl₂ (10 ml) was added to a solution of phenyldithienophosphole (**2-1**³; 0.62 g, 2.30 mmol). The solution turned dark brown immediately on mixing and was stirred for 16 hours in the glove box. The mixture was dried, and the product was isolated by passing through a micro-pipette column of dry alumina by eluting with 50:50 mixture of dry hexane to dry CH₂Cl₂ in the glove box. The bright yellow solution was dried under high vacuum to yield **2-1c** (0.82 g, 73% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.86 (dd, 2H, ³J_P=14.08 Hz, ³J_H=7.00 Hz), 7.53 (d, 2H, ³J_H=4.64 Hz), 7.33 (3H, m), 7.24 (2H, s), 6.94 (1H, s), 6.85 (1H, s), 1.50 (9H, s), 1.33 (9H, s). ³¹P{¹H} NMR (162 MHz, CDCl₃ ppm): δ -47.5. ¹³C NMR (151 MHz, CDCl₃, ppm): δ 147.3 (d, ¹J_P=130 Hz), δ 146.5 (d, ¹J_P=124.4 Hz), 144.6 (s), 143.0 (s), 142.8 (d, ²J_P=35.3 Hz), 142.4 (d, ²J_P=35.5 Hz), 139.7 (s), 134.9 (d, ¹J_P=136.7 Hz), 132.4 (d, ³J_P=9.9 Hz), 131.5 (d, ²J_P=11.7 Hz), 130.7 (d, ²J_P=8.3 Hz), 130.5 (d, ⁴J_P=2.4 Hz), 130.2 (d, ²J_P=8.3 Hz), 128.1 (d, ³J_P=14.1 Hz), 125.3 (d, ³J_P=13.6 Hz), 125.2 (d, ³J_P=13.7 Hz), 114.5 (s), 105.8 (d, ³J_P=12.4 Hz), 34.7(s), 34.6(s), 31.7(s), δ 29.7(s). E.A. (%) calc'd for C₂₈H₂₉S₂PO₂ (492.63): C 68.27, H 5.93, S 13.02, found: C 68.34, H 6.45, S 11.25.

Preparation of **2-1d**



The synthesis of compound **2-1d** was conducted in the glovebox with 1:1 eq. of **2-1**³ (0.66 g, 2.40 mmol) and 1,2-pyrenedione⁹² (0.56 g, 2.40 mmol) dissolved in 25 ml of dry CH₂Cl₂. The mixture was stirred for six days, and the solvent was dried under high vacuum. The yellow solid was purified by washing with dry pentane several times to yield **2-1d** (0.84 g, 69% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.38 (d, 2H, ⁴J_H=6.72 Hz), 8.07 (m, 6H), 7.95 (dd, 2H, ³J_H=7.16 Hz, ²J_P=14.24 Hz), 7.74 (2H, ³J_H=4.76 Hz), 7.29 (m, 5H). ³¹P{¹H} NMR (162 MHz, CDCl₃, ppm): δ -43.9. ¹³C{¹H} NMR (100.6 MHz, CDCl₃, ppm): δ 146.6 (d, ¹J_P=123.1 Hz), 143.1 (d, ²J_P=35.28 Hz), 136.3 (s), 134.1 (d, ¹J_P=135.8 Hz), 131.5 (s), 131.4 (d, ²J_P=4.7 Hz), 130.9 (d, ⁴J_P=2.34 Hz), 130.7 (d, ²J_P=8.48 Hz), 128.2 (d, ³J_P=14.3 Hz), 127.5 (s), 125.8 (s), 125.6 (d, ³J_P=13.7 Hz), 123.2 (s), 121.9 (d, ²J_P=10.8 Hz), 120.6 (s), 117.7(s). E.A. (%) calc'd for C₃₀H₁₇S₂PO₂ (504.56): C 71.42, H 3.40, S 12.71, found: C 68.31, H 3.17, S 12.55. Aromatic hydrocarbons consistently exhibit lower carbon content, a characteristic inherent to pentacoordinate systems as well.

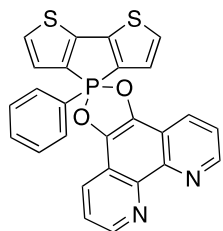
Preparation of **2-1e**



One equivalent of 1,10-phenanthroline 5,6-dione⁹² (0.55g, 2.02 mmol) dissolved in 12 ml dry CH₂Cl₂ was added to a stirring solution of **2-1**³ (0.69 g, 2.02 mmol) in 15 ml dry CH₂Cl₂ in the glove box. The reaction was stirred for 2.5 days until the ³¹P NMR showed completely conversion of starting material to the desired product. The reaction mixture was passed through a micro-pipette column of dry alumina and washed with dry CH₂Cl₂ to isolate a yellow solution. The solution was dried under high vacuum and the residue was washed with dry pentane to yield **2-1e** at 19% yield (0.24g). ¹H NMR (700

MHz, CDCl₃, ppm): δ 8.36 (s, 2H), 8.1 (s, 2H), 8.00 (s, 2H), 7.93 (dd, 2H, $^3J_H=7.70$ Hz, $^3J_P=14.28$ Hz), 7.71 (d, 2H, $^3J_H=4.62$ Hz) 7.33 (m, 3H), 7.27 (m, 2H), 1.64 (s, 18H). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl₃, ppm): δ -44.5. $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, CDCl₃, ppm): δ 148.6 (s), 146.9 (d, $^1J_P=122.5$ Hz), 143.1 (d, $^2J_P=34.8$ Hz), 136.5 (s), 134.5 (d, $^1J_P=136.2$ Hz), 131.2 (s), 131.2 (d, $^2J_P=38.1$ Hz), 130.8 (d, $^4J_P=2.2$ Hz), 130.8 (d, $^3J_P=8.7$ Hz), 128.3 (d, $^3J_P=14.6$ Hz), 127.6 (s), 125.6 (d, $^2J_P=13.5$ Hz), 121.5 (d, $^2J_P=10.4$ Hz), 120.5 (s), 118.9 (s), 114.5 (s), 35.3 (s), 32.0 (s). grease and impurity (less than 4%). E.A. (%) calc'd for C₃₈H₃₃S₂PO₂ (616.77): C 74.00, H 5.39, N 0.00, found: C 73.31, H 5.49, N 0.00.

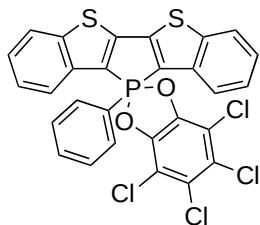
Preparation of **2-1f**



The synthesis of compound **2-1f** was conducted in the glovebox with 1:1 eq. of **2-1**³ (0.14 g, 0.52 mmol) and 1,10-phenanthroline-5,6-dione (0.11 g, 0.52 mmol) dissolved in 25 ml of dry CH₂Cl₂. The mixture was stirred for 2 hours,

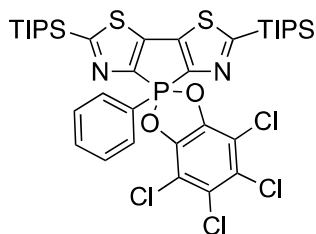
and the mixture was dried under high vacuum. The yellow solid was purified by washing with dry pentane several times to yield **2-1f** (0.10 g, 42% yield). ^1H NMR (700 MHz, CDCl₃, ppm): δ 9.06 (d, 2H, $^2J_H=2.80$ Hz), 8.46 (d, 2H, $^2J_H=7.77$ Hz), 7.85 (dd, 2H, $^3J_H=7.77$ Hz, $^3J_P=14.49$ Hz), 7.63 (dd, 2H, $^3J_H=4.2$ Hz, $^3J_P=9.38$ Hz), 7.61 (d, 2H, $^2J_H=20.65$ Hz), 7.34 (m, 1H), 7.30 (m, 2H). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl₃, ppm): δ -41.3. $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, CDCl₃, ppm): δ 147.9 (s), 145.7 (d, $^1J_P=123.1$ Hz), 143.5 (d, $^2J_P=34.7$ Hz), 142.2 (s), 134.8 (s), 133.5 (d, $^1J_P=135.9$ Hz), 131.2 (s), 131.2 (d, $^2J_P=12.4$ Hz), 130.4 (d, $^3J_P=8.9$ Hz), 128.4 (d, $^3J_P=14.2$ Hz), 128.4 (s), 126.0 (d, $^2J_P=14.0$ Hz), 122.7 (s), 119.7 (d, $^2J_P=10.1$ Hz). residual CH₂Cl₂, H₂O and grease. E.A. (%) calc'd for C₂₆H₁₅S₂PO₂N₂ (482.51): C 64.72, H 3.13, N 5.81, found: C 64.02, H 3.12, N 5.80.

Preparation of **2-6**



Compound **2-6'** was synthesized as mentioned in Ref. 94 and was isolated at 18% yield (0.18g). Compound **2-6'** (0.03g , $8.6 \times 10^{-5}\text{ mol}$) dissolved in dry CH_2Cl_2 and one equivalent of *o*-chloranil (0.02 g , $8.6 \times 10^{-5}\text{ mol}$) in dissolved in dry CH_2Cl_2 was added to the above solution with stirring. The mixture was stirred for 16 hours and the mixture, dried under high vacuum and residue was washed dry pentane and dried to yield 32% of **2-6** (0.016g). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , ppm): δ -30.2. ^1H NMR (400 MHz, CDCl_3 , ppm): δ 8.82 (d, 2H, $^3J_{\text{H}}=8.40\text{ Hz}$), 7.91 (dd, 2H, $^1J_{\text{H}}=7.63\text{ Hz}$, $^3J_{\text{P}}=14.98\text{ Hz}$), 7.87 (d, 2H, $^2J_{\text{H}}=7.98\text{ Hz}$), 7.58 (t, 2H, $^2J_{\text{H}}=7.42\text{ Hz}$), 7.39 (m, 3H), 7.29 (m, 2H). ^{13}C NMR (176 MHz, CDCl_3 , ppm): δ 145 (d, $^2J_{\text{P}}=39.5\text{ Hz}$), 143.1 (d, $^2J_{\text{P}}=15.3\text{ Hz}$), 141.5 (s), 138.6 (d, $^1J_{\text{P}}=122.2\text{ Hz}$), 138.5 (d, $^4J_{\text{P}}=10.1\text{ Hz}$), 132.2 (s), 132 (d, $^2J_{\text{P}}=13\text{ Hz}$), 131.3 (d, $^1J_{\text{P}}=132.2\text{ Hz}$), 128.9 (d, $^3J_{\text{P}}=15.0\text{ Hz}$), 126.4 (s), 126.1 (s), 124.8 (s), 124.3 (s), 123.5 (s), 121.9 (d, $^2J_{\text{P}}=14.3\text{ Hz}$). Residual acetone and grease from the NMR tube. E.A. (%) calc'd for $\text{C}_{28}\text{H}_{13}\text{Cl}_4\text{S}_2\text{PO}_2$ (618.30): C 54.39, H 2.12, N 0.00, found: C 53.87, H 2.28, N 0.00.

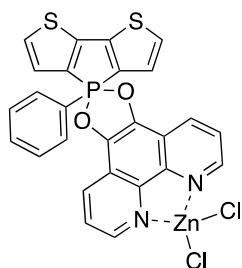
Preparation of **2-7**



Compound **2-7'** was synthesized as reported in Ref. 95 and was isolated at 89% yield (1.12g). Compound **2-7'** (0.37g , $6.35 \times 10^{-4}\text{ mol}$) was dissolved in dry CH_2Cl_2 and one equivalent of *o*-chloranil (0.16 g , $6.35 \times 10^{-4}\text{ mol}$) dissolved in dry CH_2Cl_2 was added to the above solution with stirring. The mixture was stirred for 16 hours. The ^{31}P NMR spectroscopy shows that the mixture completely transformed from starting material (**2-7'**, -31.6 ppm) to product (**2-7**, -54.3 ppm). Any purification attempts including column chromatography with alumina/DCM or washing with dry pentane

decomposes **2-7** to the oxide of **2-7'**. The reaction was repeated and **2-7** was isolated in the crude mixture and used in further reactions without purification. ^1H NMR (700 MHz, CDCl_3 , ppm): δ 8.34 (dd, 2H, $^3J_{\text{H}}=13.30$ Hz, $^3J_{\text{P}}=25.41$ Hz), 7.43 (m, 1H), 7.35 (m, 2H), 1.45 (q, 6H, $^3J_{\text{H}}=12.95$ Hz), 1.22 (d, 36H, $^3J_{\text{H}}=13.02$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , ppm): δ -54.3. $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, CDCl_3 , ppm): δ 171.9 (d, $^2J_{\text{P}}=30.7$ Hz), 160.9 (d, $^1J_{\text{P}}=249.9$ Hz), 141.5 (s), 138.8 (d, $^1J_{\text{P}}=75.3$ Hz), 134.5 (d, $^1J_{\text{P}}=11.95$ Hz), 132.1 (d, $^3J_{\text{P}}=3.4$ Hz), 130.3 (s), 128.1 (d, $^2J_{\text{P}}=25.5$ Hz), 123.8 (s), 115.0 (d, $^2J_{\text{P}}=24.3$ Hz), 18.5 (s), 11.7 (s). (Some starting material and corresponding oxide identified in the mixture).

Preparation of **2-10**



Compound **2-1f** (0.046 g, 9.5×10^{-5} moles) was dissolved in dry CH_2Cl_2 and 1.0 eq of ZnCl_2 in etherated (0.0195 g, 9.5×10^{-5} moles) dropwise to the solution with stirring. A yellow solid precipitate out of the solution with 2

hours of reaction time. The solid was isolated by filtration in the glove box and washed with dry pentane to wash away impurities. The bright yellow solid was dried to isolate **2-10** at 29% yield (0.017g). ^1H NMR (700 MHz, CDCl_3 , ppm): δ 9.17 (d, 2H, $^3J_{\text{H}}=1.26$ Hz, $^7J_{\text{P}}=4.69$ Hz), 8.75 (d, 2H, $^3J_{\text{H}}=1.26$ Hz, $^5J_{\text{P}}=8.33$ Hz), 7.96 (dd, 2H, $^3J_{\text{H}}=4.69$ Hz, $^3J_{\text{P}}=8.33$ Hz), 7.79 (dd, 2H, $^3J_{\text{H}}=7.42$ Hz, $^3J_{\text{P}}=14.84$ Hz), 7.56 (d, 2H, $^3J_{\text{H}}=4.83$ Hz), 7.39 (m, 1H), 7.34 (m, 2H), 7.31 (m, 2H). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , ppm): δ -36.1. $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, CDCl_3 , ppm): δ 207 (s), 144.4 (d, $^2J_{\text{P}}=34.0$ Hz), 143.9 (d, $^1J_{\text{P}}=55.2$ Hz), 136.0 (d, $^4J_{\text{P}}=9.3$ Hz), 132.7 (s), 131.84 (br, s), 130.9 (s), 130.8 (d, $^2J_{\text{P}}=12.3$ Hz), 130.1 (d, $^3J_{\text{P}}=9.5$ Hz), 128.8 (d, $^3J_{\text{P}}=15.1$ Hz), 126.7 (d, $^2J_{\text{P}}=14.3$ Hz), 125.3 (s), 120.4 (d, $^2J_{\text{P}}=11.4$ Hz). E.A. (%) calc'd for $\text{C}_{26}\text{H}_{15}\text{Cl}_2\text{N}_2\text{S}_2\text{PO}_2\text{Zn}$ (618.79): C 50.47, H

2.44, N 4.53, found: C 47.60, H 2.01, N 4.28. Aromatic hydrocarbons consistently exhibit lower carbon content, a characteristic inherent to pentacoordinate systems as well.

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CHAPTER THREE: SYNTHESIS, STRUCTURAL INSIGHT, AND OPTOELECTRONIC EXPLORATION OF STEP-CONJUGATED MATERIALS

Assistance in the form of undergraduate research for the theoretical calculations regarding structural optimization was conducted by Muzi Li. Acknowledgment is extended to Dr. Roman Dobrovetsky, Tel-Aviv University for the computational mechanistic calculations.

3.1 Introduction

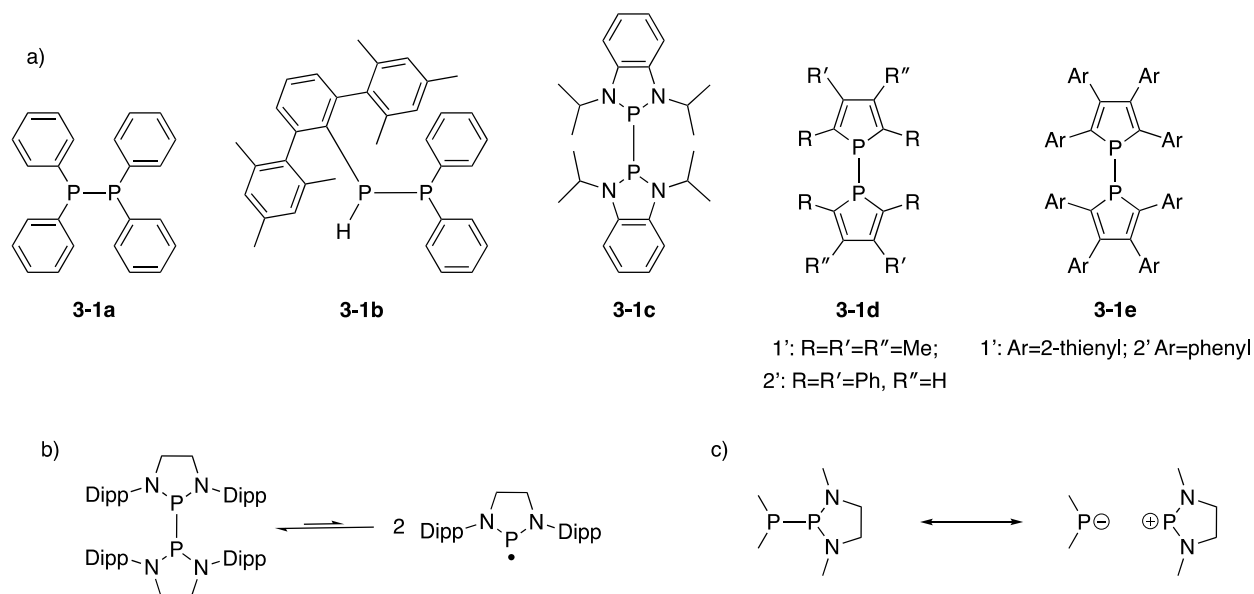


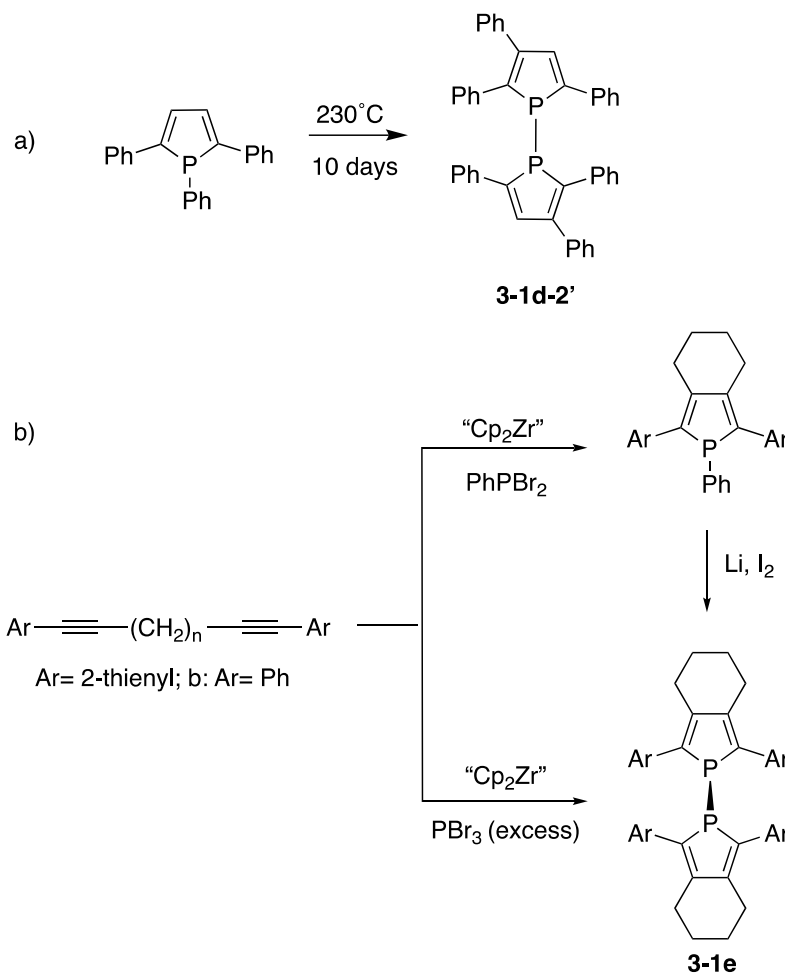
Figure 3-1. a) Some examples of diphosphanes^{4,8,10,14,15} b) homolytic⁶ and c) heterolytic cleavage¹³ of a P-P bond.

Diphosphanes are an interesting structural motif predominantly utilized for activating small molecules (Figure 3-1a). The species' electronic properties and reactivity depend heavily on the nature of the substituents attached to the phosphorus atoms of the P-P single bond. As a result,

symmetric or asymmetric substitution patterns on diphosphanes can prompt either homolytic or heterolytical cleavage of the P–P bond, respectively (Figure 3-1b,c) and these species are hence recognized as valuable synthons. Furthermore, when the P–P unit is embedded in a π -conjugated framework, this system offers a robust scaffold to establish through-bond electronic communication between chromophores.¹⁻¹³

An extensively π -conjugated system can potentially lead to strong absorbance and luminescence, high charge mobility, and reversible redox characteristics. These features are highly sought-after for functional materials for the design of high-performing OPVs, OLEDs, organic field-effect transistor (OFETs), and many more. 1,1'-Biphospholes have been investigated as an interesting scaffold in this context, as the P–P σ -bond shows high polarizability and a low σ - σ^* gap.¹⁵⁻¹⁹ Earlier research on biphospholes by Mathey *et al.* predominantly utilized the labile nature of the P–P bond in **3-1d** (and other similar species) for the synthesis of highly reactive phosphorus species to act as transfer reagent in organometallic chemistry.¹⁰ Subsequently, the Réau group extended the π -system on the biphospholes of type **3-1e** to study their material properties to find that the HOMO-LUMO gap can be effectively tuned towards various application by adjusting the torsion angle between the two chromophores connected through the σ -bond. This angle is controlled by both steric and electronic factors of the substituents on the respective (mono) phospholes. The best results were observed for conjugated systems containing phospholes and thiophenes (i.e., **3-1e**). The thiophene moieties impart appropriate kinetic stabilization but also provide an additional modification site on S (along with P) to impact the photophysical and electrochemical properties of these materials through oxidation of these elements.^{15,18,19} Another system that incorporates similar features, along with ambient stability, is bi(dithienophosphole) (**3-2**; Figure 3-2) but it is far less explored due to limited synthetic accessibility. However, this system

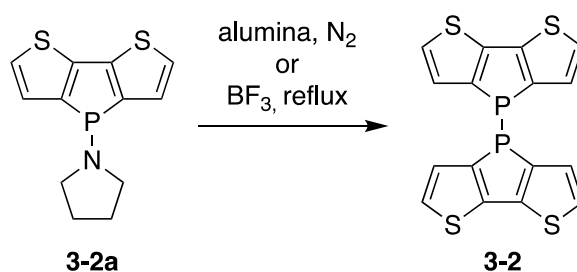
demands greater attention considering the remarkable electron-accepting and luminescent properties of the generic ‘monomeric’ dithienophosphole. It is also expected to host the beneficial features of the Mathey and Réau systems, such as labile P-P bond and advantageous optical and electrochemical properties, respectively.²⁰



Scheme 3-1. General synthesis of 1,1'-biphosphole by a) thermally induced reductive cleavage¹⁰ and b) intramolecular oxidative coupling.¹⁵

Biphospholes are generally accessed by reductive cleavage of the exocyclic P–R σ bond of trivalent phospholes, either thermally induced (in case of Mathey’s systems, **3-1d-2'**, Scheme 3-1a)¹⁰, or by intramolecular oxidative coupling of appropriate ethynyl derivatives using Cp_2Zr in Réau’s method (Scheme 3-1b).^{15,21} However, none of these methods or any other commonly used synthetic routes towards biphospholes^{11,17,22} can be extended to the bi(dithienophosphole) system,

due to its distinct reactivity, which provides a further reason to explore them. Recently, Dr. Zisu Wang in our group serendipitously observed the formation of bi(dithienophosphole) during an attempt to purify a *P*-amino-phosphole. The latter was used as a key precursor for hydrogen-bond-based self-organization materials (see Chapter 1).²³ The pyrrolidinyl-functionalized dithienophosphole (**3-2a**), when passed through a column of alumina under nitrogen, resulted in the formation single crystals from the eluent that were suitable for X-ray crystallography. The result was rather surprising as the isolated compound was the elusive bi(dithienophosphole) (**3-2**). Since such transformations had no literature precedence at the time, our initial rationale was that the cleavage of P–N σ bond was promoted by the Lewis acidic sites on the alumina chromatography column material. This assumption was then further confirmed by treating **3-2a** with BF₃ at room temperature (Scheme 3-2). The ³¹P{¹H} NMR spectrum of the reaction mixture showed a pair of doublets at 34 and -65 ppm (¹J_{P-P} = 287 Hz), that suggested the formation of an asymmetric intermediate that is stable at room temperature. On refluxing the solution overnight, the formation of symmetric **3-2** was observed by ³¹P NMR spectroscopy as a singlet at -37 ppm.²⁴



Scheme 3-2. LA mediated synthesis of bi(dithienophosphole), **3-2**.²⁴

The mechanism that leads to the intriguing bi(dithienophosphole) was then studied combining information from ¹H and ³¹P NMR spectroscopy and high-resolution mass spectrometry of the intermediate, isolated final by-products of the reaction, and DFT calculations. It was found that the first step of the mechanism is predominantly governed by the HSAB theory²⁵ and is initiated

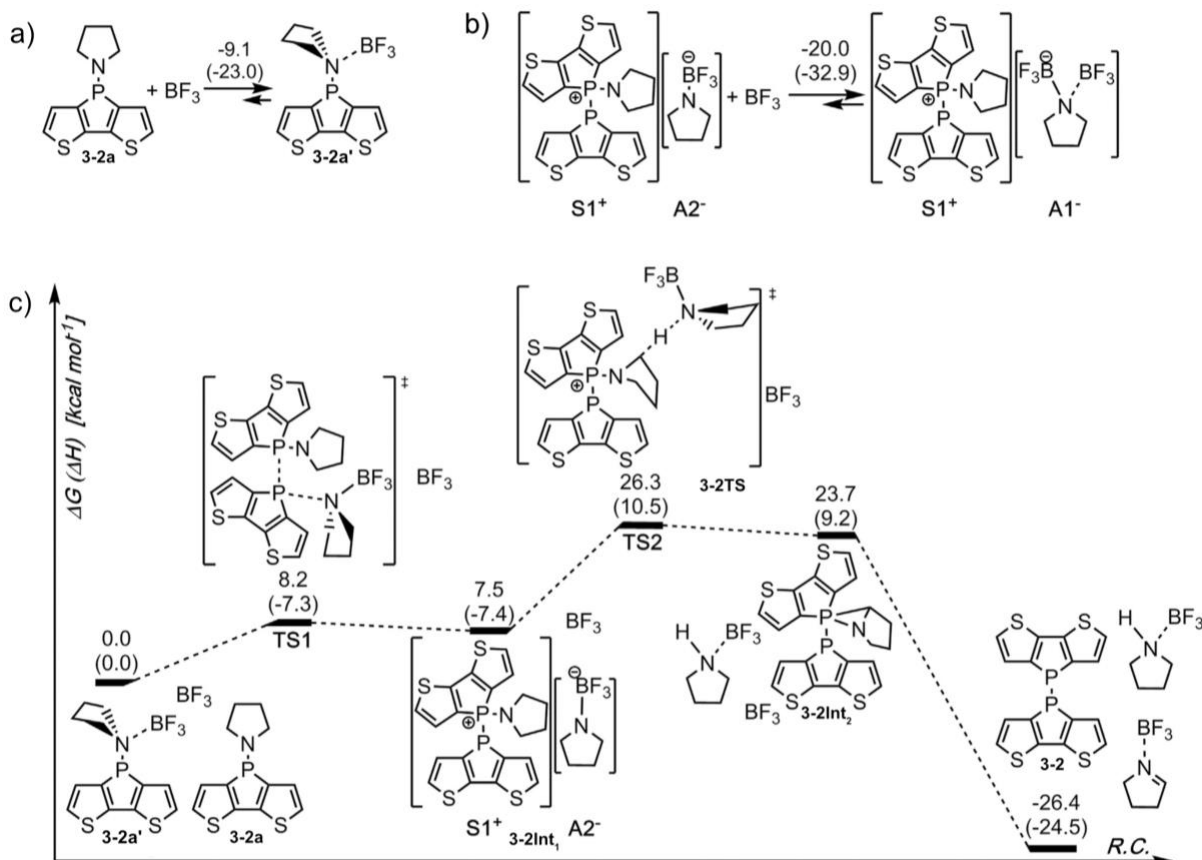


Figure 3-2. a) Calculated reaction of **3-2** with BF_3 b) calculated reaction of salt $[\text{S1}^+ + \text{A2}^-]$ with BF_3 , and c) reaction coordinates of the proposed mechanism; the energies are relative to the starting materials. Gibbs free energies and enthalpies (in parentheses) are given in kcal/mol. Reproduced with permission from ref. 24. Copyright 2018 Elsevier.

by the selective interaction of the hard LA BF_3 with the hard Lewis-basic nitrogen center of **3-2a** (Figure 3-2a). The formation of the adduct **3-2a'** is exergonic in nature and it immediately reacts with **3-2a** to form the key asymmetric phosphonium intermediate (**3-2Int₁**), which is stabilized by columbic interaction from the bis- BF_3 adduct **A1⁻**. The formation of the **A1⁻** is facilitated by the remaining unreacted BF_3 molecules since one equivalent of this reagent was used in Figure 3-2a. This adduct is unstable at high temperature and upon refluxing loses one of the BF_3 moieties to generate a Bronsted base **A2⁻** (Figure 3-2b). The formation of **A2⁻** is necessary for the reaction to progress as it deprotonates the α -carbon of the pyrrolidinyl substituent in **3-2Int₁** *in situ*; this is the

rate determining step of the reaction. The transition state **3-2TS**, then leads to another intermediate **3-2Int₂** and a by-product (pyrrolidine coordinated to BF₃) of which the latter was isolated as single crystals from the reaction mixture. The intermediate **3-2Int₂** eventually dissociates into **3-2** and an imine adduct (identified by NMR spectroscopy) resulting in an overall strongly exergonic and exothermic reaction (Figure 3-2c).²⁴

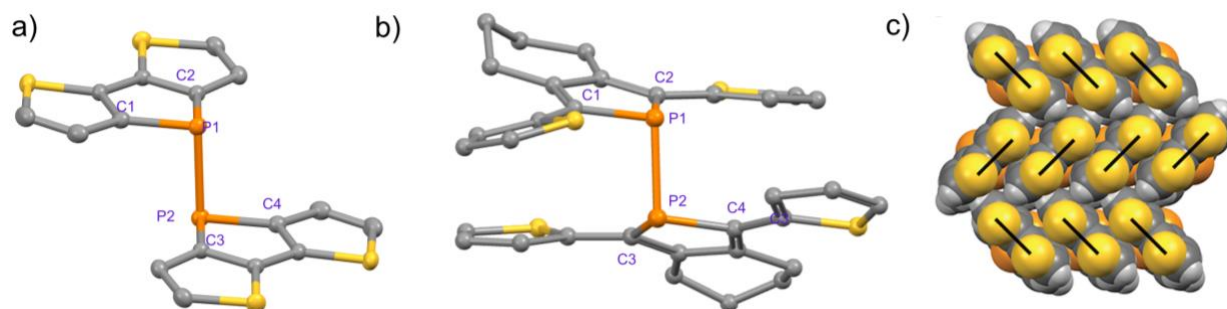
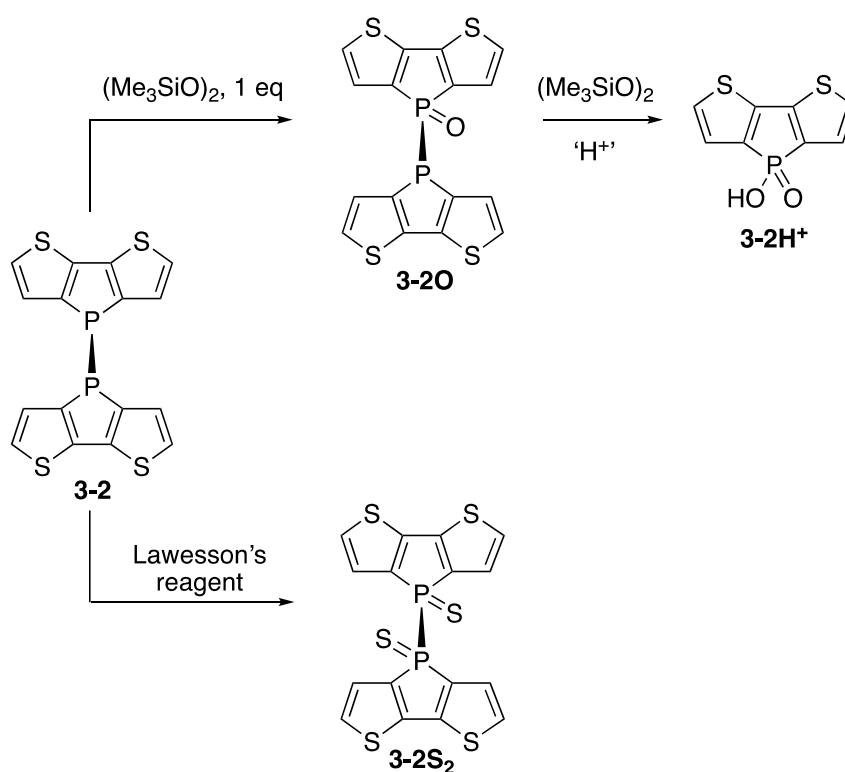


Figure 3-3. Solid-state structure of a) **3-2** showing step-like structure and b) **3-1e-1'** showing twisted “gauche-like” like structure; c) solid-state packing of **3-2** showing layered structure with herringbone arrangement. H atoms are omitted for clarity. Reproduced with permission from ref. 24. Copyright 2018 Elsevier.

The structure of **3-2** in the solid-state was studied using single-crystal X-ray crystallography. Compound **3-2** exhibits an intriguing step-like geometry facilitated by the pyramidal geometry of the trivalent P centers and an out-of-plane P–P σ bond (Figure 3-3a). The structure maintains π - σ - π conjugation by a phenomenon referred to as “step-conjugation”. While biphospholes generally adopt a twisted “gauche-like” or synclinal conformation, as observed in case of Réau’s biphosphole **3-1e** (Figure 3-3b), the antiperiplanar conformation as in **3-2** is rare but leads to beneficial head-to-head arrangement of the two phosphole subunits.^{11,12,14,15,26-30} As a result, this molecule stacks very closely in the solid-state through a slipped π -stack herringbone motif to allow for tight overlap between the chromophores (π -stacking distance of 3.5 Å; Figure 3-3c). This kind of packing promotes excellent intermolecular overlap of the MOs to potentially exhibit efficient

charge transfer (CT) in the bulk, suggesting the potential utility of this material in solid-state OFET devices.²⁴

To showcase the versatility of phosphorus-based conjugated materials, the chemical reactivity of the trivalent P centers in **3-2** was initially examined by oxidation to mono-oxide **3-2O** with one equivalent of bis(trimethylsilyl)peroxide ((Me₃SiO)₂); compound **3-2O**, on the other hand, decomposes to the phosphonic acid **3-2H⁺** on further exposure to excess oxidant (Scheme 3-3). However, on treatment with the milder Lawesson's reagent, the stable disulfide species **3-2S₂** was formed and isolated. The post-functionalization reactions confirmed that the reactivity of the lone pair on P is preserved on dimerization of the phosphole center and can be strategically exploited for synthesizing more stable symmetric and asymmetric bi(dithienophosphole)s.²⁴



Scheme 3-3. Post-functionalization of **3-2**.²⁴

All original bi(dithienophosphole)s show bathochromically shifted absorption maxima and onsets compared to the trivalent ‘monomer’ **3-3**²⁰, which is indicative of the effective extension of the conjugation of the π -system through the P–P σ bond. However, the photophysical characterization of these derivatives also suggests that their optical properties are governed predominantly by the symmetry of the molecule, rather than the oxidation state of the P center, in contrast to species based on **3-3**. For example, **3-2** and **3-2S₂** show similar, yet distinctive absorption profiles from that of **3-2O**. While both the symmetric **3-2** and **3-2S₂** have no dominant absorption maxima and rather broad absorption profiles, the asymmetric **3-2O** shows two distinct absorption peaks at 315 and 365 nm that correspond to localized transitions involving π - π^* transitions within the trivalent phosphole and the dithienophosphole oxide subunits, respectively. This was further verified by DFT analysis revealing nearly degenerate HOMO, HOMO–1, and LUMO energy levels for **3-2** and **3-2S₂** but spatially separated HOMO (localized on trivalent subunit) and LUMO (located on oxo-dithienophosphole moiety) for **3-2O** that support charge transfer characteristics (Figure 3-4).²⁴

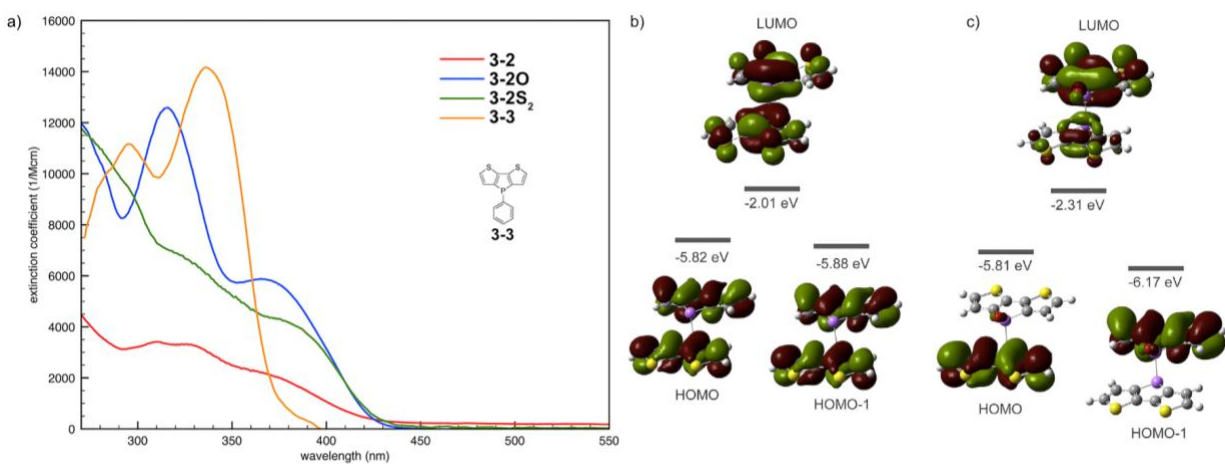


Figure 3-4. a) Absorption spectra of biphospholes compared to **3-3** b) calculated FMOs of **3-2** and **3-2O** by B3LYP/6-31G(d) level of theory. Adapted with permission from ref. 24. Copyright 2018 Elsevier.

While these features inherently support the bi(dithienophosphole) system as a potential functional material for various applications, **3-2** is unfortunately susceptible to decomposition at ambient conditions. It also exhibits a relatively low extinction coefficient, is essentially non-emissive (compared to the highly emissive **3-3**) and shows non-reversible redox processes that ultimately limit its practical utility. The major reason leading to these perceived deficits was deemed to be the rotational flexibility of the P–P σ bond that opens non-radiative decay pathway and/or instability leading to decomposition.^{27,31} The work in this Chapter now addresses the shortcomings of ring-fused π -conjugated 1,1'-biphospholes by modifying the π -scaffold in various ways. We expect that judicious modifications of the scaffold would impart stability onto the P–P bond and improve the photophysical and redox characteristics of this system as well.

3.2 Results and Discussion

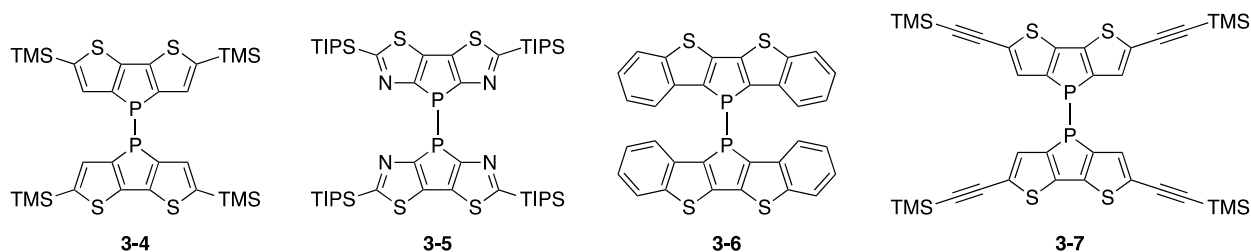


Figure 3-5. The targeted electronically modified bi(dithienophosphole)s.

While the initial work on bi(dithienophosphole) **3-2** gave us a wholistic understanding of the mechanistic, structural, and optical features of this system, there is considerable room for improvement with regard to effectively addressing the original shortcomings. A key target area for refinement is the stability and rotational flexibility of the P–P bond of bi(dithienophosphole)s. We therefore devised a strategy that focusses on the electronic modification of the π -scaffold with both electron-withdrawing and -donating motifs. In this work, we have thus targeted representative

functional groups to provide a small series of derivatives that are relatively easily accessed for the purpose of monitoring the effect on the strength of the P–P bond. A second strategy was to spatially restrict the rotation about the P–P bond by bulky substituents providing kinetic stabilization.⁷ Both these approaches were simultaneously explored to systematically study their impact on the structural, reactivity and photophysical properties of the resulting bi(phospholes).

The target species for this Chapter are shown in Figure 3-5. The somewhat bulky trimethylsilyl- (TMS) substituents in compound **3-4** provide some kinetic stabilization and display weak π -acceptor character³², while otherwise maintaining the electronic of the original congener **3-2**. As for compound **3-5**, the TIPS groups provide greater steric bulk than the TMS group of **3-4**, while the dithiazolo core, due to the presence of two imino nitrogen atoms, gives rise to a species with enhanced electron-acceptor character.³³ Compound **3-6** with heteropentacene units serve as an electron-rich representative³⁴, while the ethynyl-functionalized **3-7** was to provide a further modifiable electron-donating motif³⁵, with some kinetic stabilization provided by the remote terminal TMS groups.

3.2.1 Computational Analysis

The targeted bi(dithienophosphole)s were initially subjected to computational optimization using DFT at the B3LYP/6-31G(d) level of theory. With the exception of **3-7**, all derivatives adopt a twisted conformation similar to **3-1e** in the gas phase. The former, in fact, optimizes into a step-like structure akin to **3-2**. The functionalization of these molecules has a significant impact on the energies of their FMOs (predominantly LUMO and HOMO and HOMO-1 levels), implying the potential for distinct photophysical and/or electrochemical properties compared to the unfunctionalized parent system (Figure 3-6a).

The TMS functionalization in **3-4** has a notable effect on the HOMO and HOMO-1 energies, resulting in a reduced HOMO-LUMO gap of 3.56 eV (compared to 3.81 eV in **3-2**). While the LUMO levels were anticipated to shift due to the weak π -acceptor nature of the TMS group, it is inferred that the low electronegativity of the four silicon atoms (i.e., their +I effect) outweighs their weak π electron-withdrawing character. Conversely, the thiazole scaffold in **3-5** effectively stabilizes the LUMO level in line with its established electron-accepting behavior. This stabilization is coupled with a significant lowered HOMO level, resulting in the largest HOMO-LUMO gap of 3.73 eV for this series (Figure 3-6b).

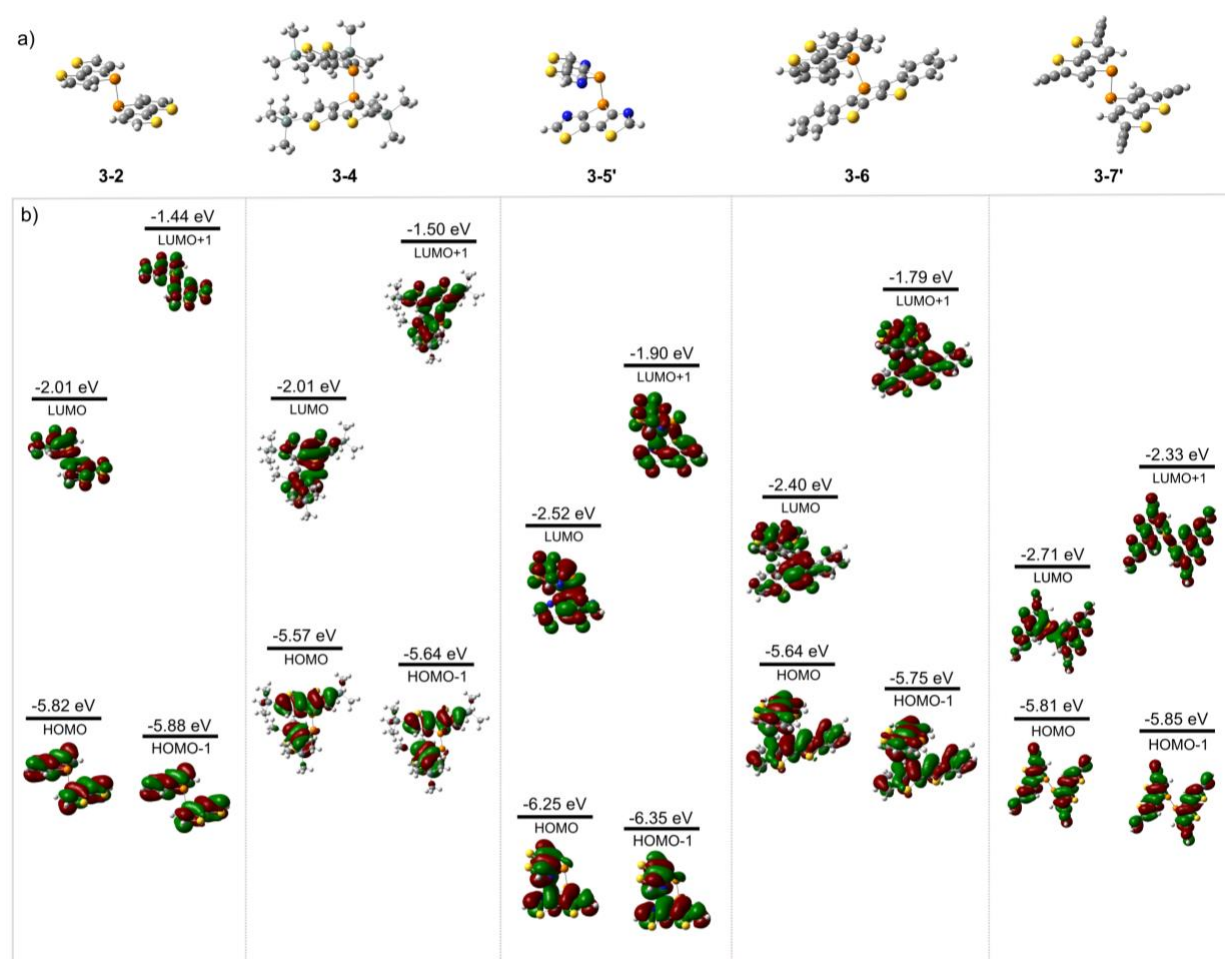
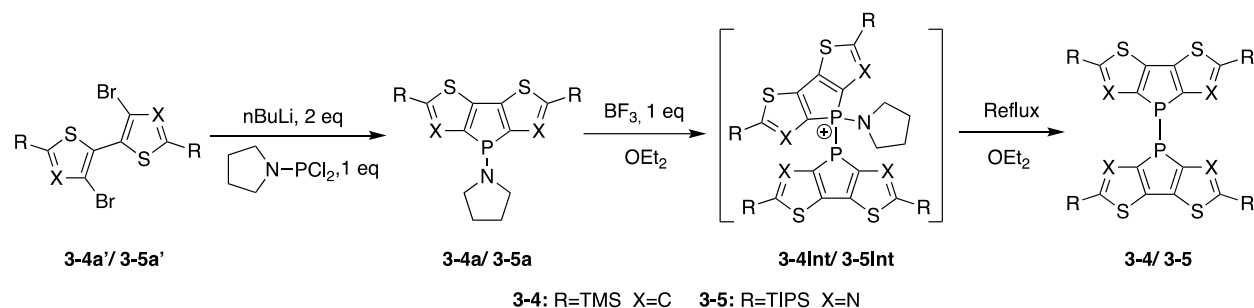


Figure 3-6. a) DFT (B3LYP/6-31G(d) level of theory) optimized structures of **3-4**, **3-5'**, **3-6** and **3-7'**. The bulky TIPS group in **3-5** (**3-5'**) and TMS group in **3-7** (**3-7'**) is omitted to reduce computation cost. b) Computationally calculated FMOs.

The extended π -system of **3-6** impacts both LUMO (stabilization) and HOMO (destabilization) levels, as expected, leading to a substantial reduction of the HOMO-LUMO gap to 3.23 eV. Although the symmetrically arranged acetylene derivatives were expected to influence HOMO levels due to the extended π -conjugation, a comparison with **3-2** reveals no significant alteration in HOMO levels. However, a pronounced stabilization of the LUMO level is observed, resulting in the smallest HOMO-LUMO gap within the series, measuring 3.01 eV (Figure 3-6b). Notably, the Time Dependent (TD) DFT analysis of these derivatives demonstrates closely spaced energy transitions spanning from HOMO-8 to LUMO+8 regardless of the functional groups employed, emphasising their step-conjugated nature (*vide infra*; see SI section S.3.2 for details).

3.2.2 Synthesis of Electronically Modified Bi(dithienophosphole)s

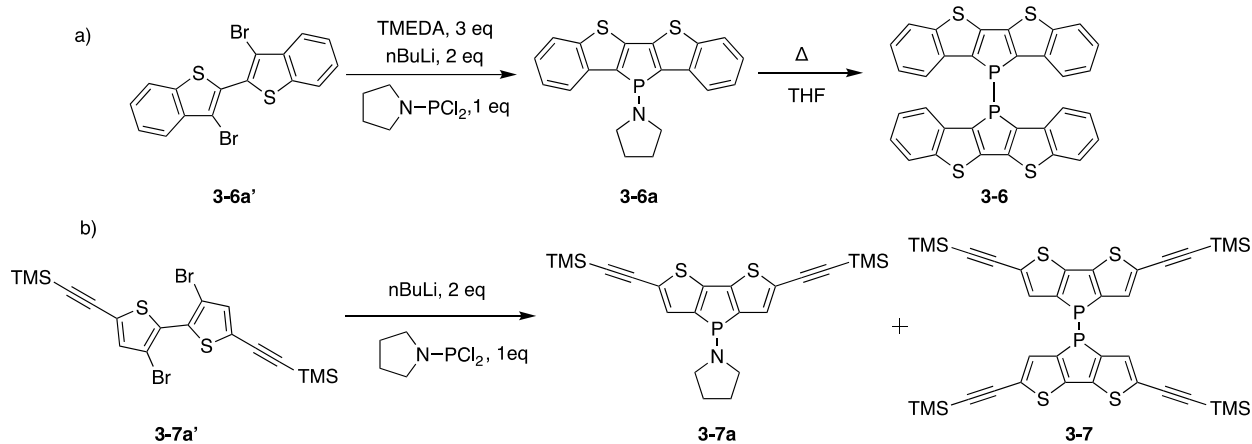


Scheme 3-4. LA triggered synthesis of bi(dithienophosphole)s with electron-withdrawing functionalization. $^{31}\text{P}\{^1\text{H}\}$ (162Mz, CDCl_3); δ (dd) 31.5 ppm, -69.3 ppm, $^1J_{\text{P-P}} \sim 290$ Hz for **3-4Int** and (dd) 32.6 ppm, -67.9 ppm, $^1J_{\text{P-P}} \sim 290$ Hz for **3-5Int**.

We initially aligned the synthesis of the new species with the established approach toward **3-2**, using LAs and subsequent reflux, to verify the general applicability of this method to these systems. While this strategy did yield the expected results for some of the new species (**3-4** and **3-5**) within reasonable limits, we also encountered surprising outcomes with compounds **3-6** and **3-7**.

The corresponding precursors, pyrrolidinyl-functionalized dithienophospholes **3-4a** and **3-5a**, were synthesized in a similar manner to **3-2a**,²⁴ involving lithiation followed by ring closure using dichloro-*N*-pyrrolidinylphosphane. Compounds **3-4a** and **3-5a** were isolated using column chromatography, resulting in yields of 95% and 74% for the respective products. The purity of these compounds was ascertained through NMR spectroscopy (see SI section 3.1). Subsequently, the *P*-amino-dithienophospholes were subjected to similar conditions as the synthesis of **3-2**,²⁴ leading to the immediate formation of a bright yellow precipitate upon adding BF₃•Et₂O to a solution of **3-4a** in Et₂O (or a pale-yellow cloudy solution in the case of **3-5a**). The experimental data at this stage aligned with those of the corresponding phosphonium intermediate **3-2Int**₁, supporting the formation of a similar species as depicted in Scheme 3-4.²⁴ As evident from the mechanism in Figure 3-2, this stable intermediate was refluxed to drive the reaction forward, resulting in the formation of **3-4** and **3-5** (Scheme 3-4). Both products were isolated using column chromatography with yields of 71% and 44%, respectively. Comprehensive characterization was performed using NMR spectroscopy (see SI section S.3.1).

The successful synthesis of **3-4** and **3-5** suggests that electron-withdrawing modifications and bulky kinetic substitutions do not significantly affect the overall reactivity of the corresponding *P*-pyrrolidinyl-dithienophosphole in forming the respective bi(dithienophosphole) species. Therefore, it is reasonable to assume that the reaction likely follows the same mechanism as outlined as in Figure 3-2.



Scheme 3-5. Synthesis of bi(dithienophosphole)s with electron-donating modification without LA.

The precursors for the targets with extended conjugation, such as **3-6** and **3-7**, were also synthesized using a similar reaction condition as shown in Scheme 3-4. However, unexpected results were observed during the isolation of **3-6a** and **3-7a**. The solution of **3-6a** was heated to reflux in dry THF to selectively precipitate the product at low temperature. During this process, the solution color changed from orange to yellow, indicating the possibility of an unexpected transformation of **3-6a**. $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy of the solution revealed two distinct peaks in a roughly 1:1 ratio: one at 21.3 ppm corresponding to **3-6a** and another peak at -38.0 ppm, later identified as the biphosphole **3-6** (Scheme 3-5a). This serendipitous discovery subsequently led to an intriguing new line of investigation into the formation of these types of bi(phosphole) species (*vide infra*).

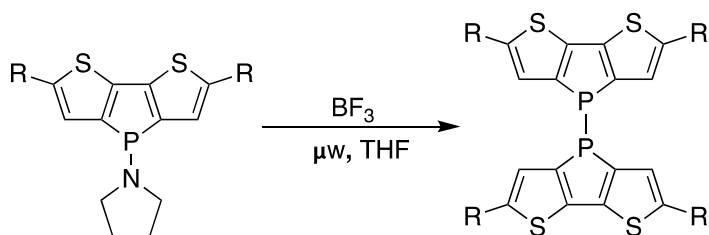
Surprisingly, during the synthesis of the corresponding amino-phosphole **3-7a**, two major peaks (~1:1.5 ratio) were already observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture after stirring for 18 hours at room temperature. The peak at 23.8 ppm aligns with those of the other amino-phosphole precursors and can be assigned to **3-7a**, while the other significant peak at -35.8

ppm suggested the formation of the symmetric biphosphole **3-7**. Complete conversion of **3-7a** to **3-7** was achieved by stirring the solution for an additional 20 hours. This suggests that the P–N bond in **3-7a** is extremely labile and can be effortlessly cleaved to form a P–P bond of **3-7** under ambient conditions in the absence of a LA (Scheme 3-5b). Although the NMR data reveal only one phosphorus peak, some aliphatic impurities are present in the crude mixture of the reaction. However, conventional purification protocols used for isolating similar bi(dithienophosphole) systems have unfortunately not yet proven successful for isolating **3-7** (see SI section 3.1).

These surprising results indicate that the π -extended amino-dithienophospholes favor the formation of biphospholes and confirm that the electronic properties of the main scaffold have a noticeable impact on the stability of the exocyclic P–N bond. It is interesting to note that the transformation requires a thermal impetus in the case of **3-6a** with the heteropentacene scaffold, while the reaction is already triggered at room temperature with **3-7a**. However, the most compelling observation here is that the P–P coupling of *P*-amino-dithienophospholes can be achieved without a LA by a simple modification using an electron-rich π -scaffold.

3.2.3 Synthesis of Bi(dithienophosphole)s Using a Microwave Reactor

Since the P–N bond cleavage in the amino-phosphole precursors is achieved by heat to selectively form the P–P bridged biphospholes (as observed in case of **3-6**) we expected the modified dithienophospholes to react even more rapidly under microwave conditions, i.e., elevated temperature and pressure. This route is also more convenient as it significantly reduces the reaction time and eliminates any accidental exposure to ambient oxygen leading to decomposition of the synthesized bi(dithienophosphole)s.



Scheme 3-6. Synthesis of the functionalized bi(dithienophosphole)s in a microwave reactor.

	Temperature (°C)	Time (minutes)	LA (1 eq BF ₃ •Et ₂ O)	%Yield
3-2	190°C	20	Yes	50%
3-4	190°C	20	Yes	50%
3-5	190°C	20	Yes	57%
3-6	150°C	5	Yes	47%
	190°C	30	No	-----

Table 3-1. General microwave reaction condition for the synthesis of functionalized bi(dithienophosphole)s and their corresponding yield.

To our satisfaction, compounds **3-4a** and **3-5a** converted to the corresponding biphospholes **3-4** and **3-5** when reacted in a microwave reactor under conditions listed in Table 3-1 above. Notably, the same reaction conditions can also be used for the synthesis of the parent system **3-2**. Moreover, none of the reactions proceed in the absence of LA under otherwise identical microwave conditions. This supports the notion that scaffolds with bulky, basic, non- π -extended cores do not impact the overall reactivity of the P–N bond in the amino-phospholes toward P–P bond formation and consequently show similar chemistry to the unfunctionalized parent system **3-2** (Scheme 3-6). However, full conversion of **3-6a** into **3-6** is already observed after 5 min in a microwave reactor at only 150°C with BF₃. This observation suggests that π -extended phospholes show higher reactivity towards P–P coupling in the presence of a LA. This enhanced reactivity was also

suggested by our initial studies, where the formation of **3-6** was already serendipitously observed during the isolation of **3-6a** – in the absence of LA no less. To our satisfaction, 70% conversion of **3-6a** into **3-6** is observed after 30 min without any other by-products on exposing solution of **3-6a** to elevated conditions of temperature and pressure (Scheme 3-6), confirming that a LA is not required to trigger the transformation of **3-6a**. The latter was already established in the case of **3-7a** that even more readily converts into the biphosphole **3-7** at room temperature. The process(es) toward **3-6** and **3-7**, on the other hand, must involve a different mechanism, as the LA in the original mechanism served several purposes and is key for its progression, as determined by our initial studies.²⁴

3.2.4 Mechanism in the Absence of LA

The potentially mechanism that leads to the formation of **3-6** in the absence of a LA was studied via DFT using CPCM(THF) at wB97XD/def2TZVP level of theory. The calculated mechanism theorizes that at elevated reaction temperatures in the absence of BF₃, two molecules of **3-6a** undergo *in-situ* intermolecular de/protonation to form a pyrrolidinide (**3-6a⁻**) and a cationic pyrrolidinium (**3-6aH⁺**) species, respectively. These species then serve as a transition state for **3-6a⁻** that loses a pyrroline moiety to form the phospholide species **3-6Int** as intermediate. The intermediate then attacks the cationic **3-6aH⁺** via a S_N2-type mechanism to expel pyrrolidine to generate **3-6**. The calculations also suggest that the ethynyl-functionalized dithienophosphole **3-7a** appears to undergo similar reaction, but at lower energies. Compound **3-7a**, upon deprotonation, directly dissociates to **3-7P⁻** and the pyrroline, the former of which then reacts with **3-7aH⁺** to form **3-7** (and pyrrolidine) in a similar manner as **3-6** (Figure 3-7).

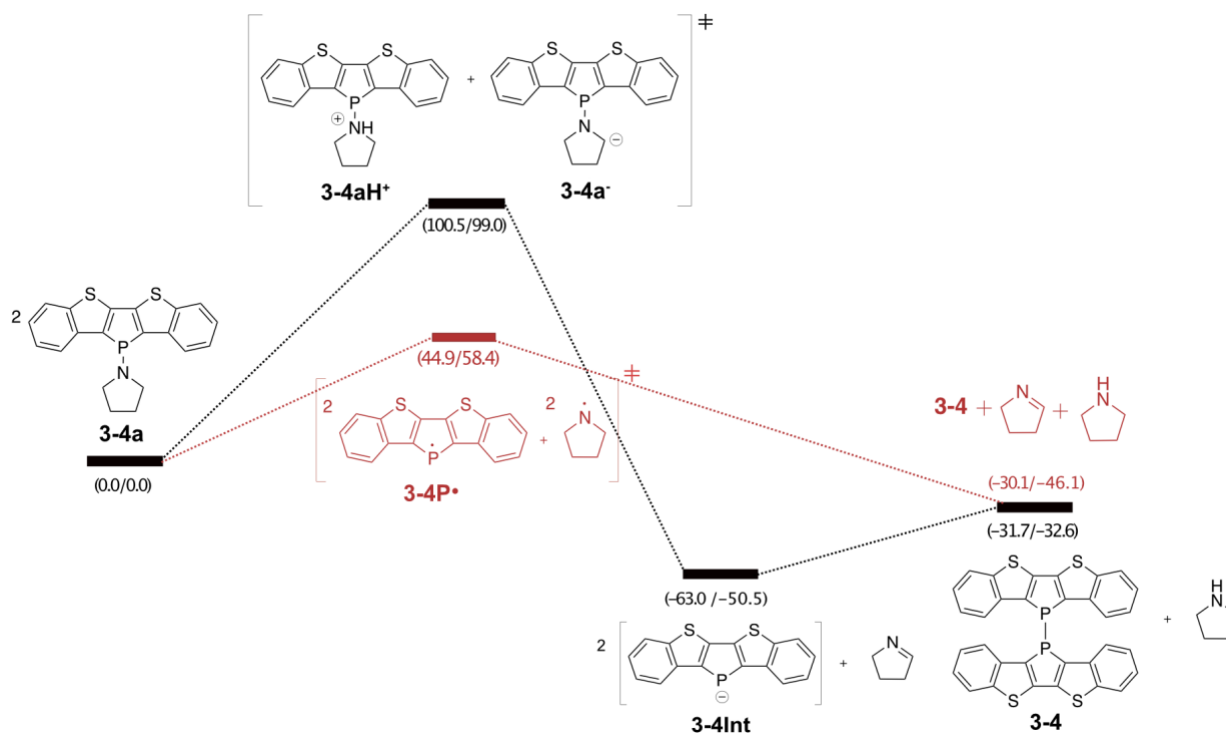


Figure 3-7. Reaction coordinates of the proposed mechanism in the absence of LA; the energies are relative to the starting materials. Gibbs free energies and enthalpies (in parentheses) are given in kcal/mol (Level of theory: wB97XD/def2TZVP; CPCM(THF)).

Alternatively, the reaction could proceed through a low energy radical mechanism, involving the homolytic cleavage of the P–N bond in **3-6a** to generate a P-radical, which then self-reacts to produce **3-6** (see SI section S.3.3). Despite a lower calculated reaction barrier exhibited by this mechanism, we could not experimentally confirm the formation of a radical species within the reaction mixture to date, either directly or indirectly, leading us to consider the heterolytic reaction pathway as more appropriate at this point.

Significantly, the mechanism for the LA-free formation of bi(dithienophosphole) introduces fundamentally distinct intermediate species compared to the original mechanism. While the original pathway involves a positively charged asymmetrically substituted P–P phosphonium intermediate (**3-2Int₁**)²⁴, the LA-free process entails the formation of negatively charged phospholide species¹⁰ (**3-6Int**, **3-7P⁻**). The combination of DFT calculations and experimental

evidence suggests that π -extended cores are more efficient in generating the phospholide intermediate, contrary to the anticipated role of electron-withdrawing modifications in stabilizing these highly reactive anions.³⁶ However, the potential for forming bi(dithienophosphole)s from precursors with electron-donating moieties cannot be simply inferred based solely on the stabilization of the HOMO levels. Instead, the stabilization and/or destabilization of the FMOs should be considered here, which subsequently contributes to the reduction of the HOMO-LUMO gap, thereby influencing several of the processes outlined below.³⁷ Such reductions are only apparent in derivatives **3-6** and **3-7** as shown in Figure 3-6, and not for derivatives with the non-extended core-scaffold such as **3-4** and **3-5**.

The feasibility of this proposed mechanism for **3-6** and **3-7** can be rationalized based on the stability of the P–N bonds in the transition states. The electron-donating nature of the core in **3-6a** weakens the P–N bond and seeks the nearest positively charged entity to mitigate the excess electron density. One of the active species in driving the reaction forward in the LA-mediated mechanism is the α -proton on the pyrrolidine counterpart, as evidenced by the transition state **3-2TS** in Figure 3-2.²⁴ Given the reactivity of this proton and the absence of alternative cationic sources, it is inherently plausible that intermolecular reaction of two molecules of **3-6a** leads to the formation of **3-6aH⁺** through the abstraction of this proton. However, this gives rise to the formation of **3-6a[–]**, characterized by a highly electronically unstable P–N bond that promptly undergoes cleavage, yielding the phospholide intermediate **3-6Int**. In contrast, compound **3-7a** imparts significantly higher electronic density to the P–N bond than **3-6a**, making the formation and computational identification of the corresponding **3-7a[–]** nearly unattainable. Instead, it readily undergoes cleavage to generate the corresponding phospholide species, **3-7P[–]**, thus driving the reaction forward.

This proposed mechanism not only presents an accessible pathway for the efficient synthesis of highly functional bi(dithienophosphole)s but also highlights the potential of these derivatives to serve as synthons for phospholide species.^{1,10} Such species are in high demand within main-group chemistry due to their reactivity, finding applications in catalysis, organometallic chemistry, and material science (see Chapter 4).

3.2.5 Molecular Structure and Solid-State Packing

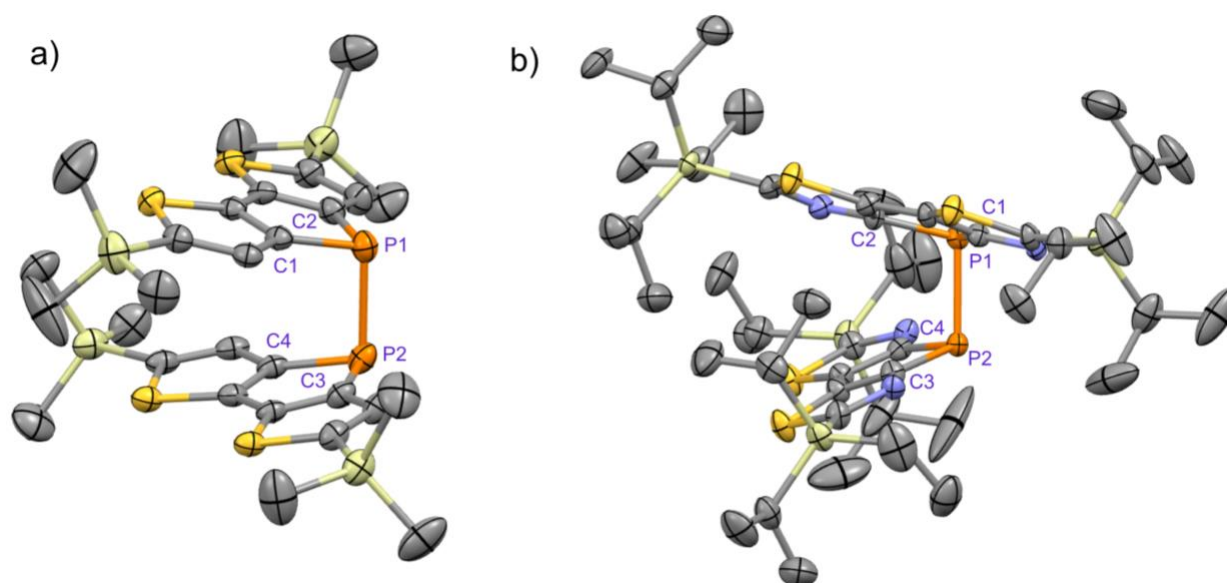


Figure 3-8. Molecular structure for compound a) **3-4** and b) **3-5**. The ellipsoids are set 50% probability, and the hydrogen atoms are omitted for clarity.

We successfully obtained single crystals of compounds **3-4** and **3-5**, suitable for X-ray crystallography, unveiling their distinctive twisted 'gauche-like' configuration reminiscent of **3-1e**.¹⁵ These structures are in line with the computationally optimized geometry of these derivatives, setting them apart from the step-like arrangement adopted by **3-2** (or **3-1c**).^{14,24,28} The P–P bond lengths in these derivatives reside within the range of reported average P–P bond lengths (2.22 Å)²⁶ in diphosphanes, measuring 2.25(10) Å for **3-4** and 2.21(3) Å for **3-5**. Correspondingly, the bond angles in **3-4** (C1–P1–P2: 100.38(8)°, C2–P1–P2: 96.77(9)°, C3–P2–P1: 96.65(9)°, and C4–P1–

P2: 100.81(8)°) and **3-5** (C1-P1-P2: 96.6(2)°, C2-P1-P2: 104.3(2)°, C3-P1-P2: 105.8(2)°, and C4-P1-P2: 97.1(2)°) closely mirror those of **3-2** (C1-P1-P2: 98.49(4)°, C3-P1-P2: 96.88(4)°). Notably, the torsion angles (C1-P1-P2-C4) deviate from the conventional 180°, measuring 35° for **3-4** and 153° for **3-5**, in stark contrast to **3-2** (Figure 3-8).

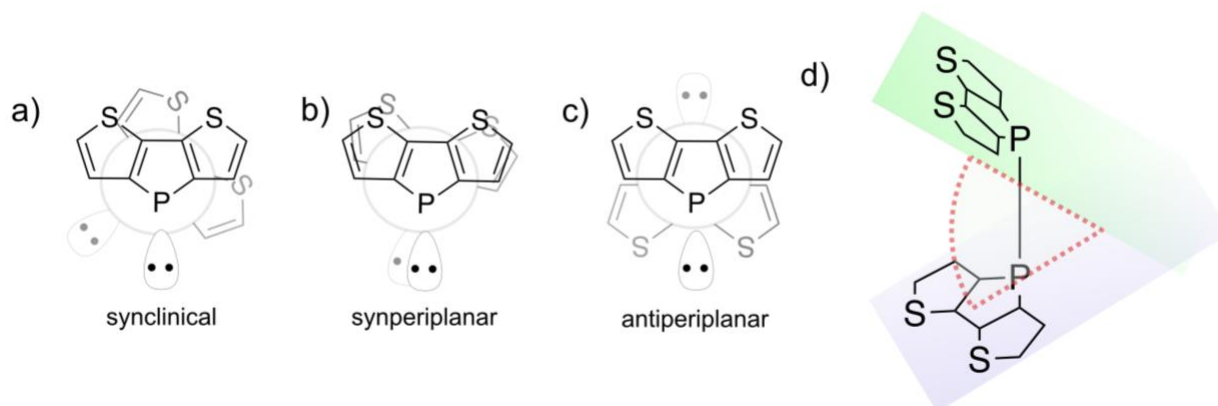


Figure 3-9. a), b) and c) represents various conformation of anticipated bi(dithienophosphole)s and d) angular intersection of dithieno-scaffold planes.

The primary driver of the solid-state structures appears to be the π -stacking interaction, manifesting either intramolecularly or intermolecularly. The step-like or antiperiplanar geometry (Figure 3-9a) in **3-2** fosters robust intermolecular π -stacking, while the substantial TMS or TIPS substituents in **3-4** and **3-5** attenuate such interactions within these derivatives. Simultaneously, potential intramolecular π -stacking interactions that may lead to an eclipsed or synperiplanar geometry (Figure 3-9a), encounter hindrance due to kinetic factors. To accommodate the steric bulk and permit long-range π -interaction, the sole viable scenario is the adoption of a twisted 'gauche-like' structure or synclinal conformation (Figure 3-9c), as revealed by SC-XRD analysis. The kinetic repulsion imparted by this functionalization induces an angular deviation of the π -scaffolds between the subunits (24° for **3-4** and 32° for **3-5**), as illustrated in Figure 3-9d. Notably, despite the typical preference for an antiperiplanar structure in the presence of bulky substituents,

these crystals were grown under low-temperature conditions, prompting the adoption of the favored synclinal conformation.^{2,26,27,29}

The intricate molecular arrangements of **3-4** and **3-5** exert a significant influence on the solid-state packing of these compounds. The steric bulk imposed by the silyl groups within these congeners disrupts the potential for effective π -stacking interactions, precluding the tight head-to-head conformation akin to **3-2**. While achieving such a direct molecular alignment is unfeasible for **3-4**, the presence of the TMS groups nonetheless enables the establishment of extended π -type interactions spanning considerable distances between molecules, culminating in the formation of columnar pillars on a bulk scale (Figure 3-10a,b). In the case of **3-4**, a subtle twist in the π -scaffold of the molecules facilitates their alignment atop one another, featuring a unidirectional orientation of the P–P bonds. Although the nearest molecule within the column maintains a distance of 4.5 Å (lying beyond the customary range of typical π -stacking interactions)²³, analysis of solid-state packing reveals the close proximity of the sulfur (S) atoms, suggesting a potential for orbital overlap akin to the CT observed in **3-2**.²⁴ However, this orbital hybridization is not universally favored across the columns due to a separation of 4.9 Å between them (Figure 3-10a,b).

In the case of **3-5**, the bulkiness of the TIPS group suppresses similar interactions within the solid state, prompting the molecules to exist independently of one another. The closest molecule maintains a separation of 3.5 Å, lying within the range conducive to π -stacking interactions.²³ However, the crystallization pattern mirrors the distorted conformation in **3-1e**, introducing disruptions that impede efficient CT processes on a bulk scale (as depicted in Figure 3-10c,d).¹⁵

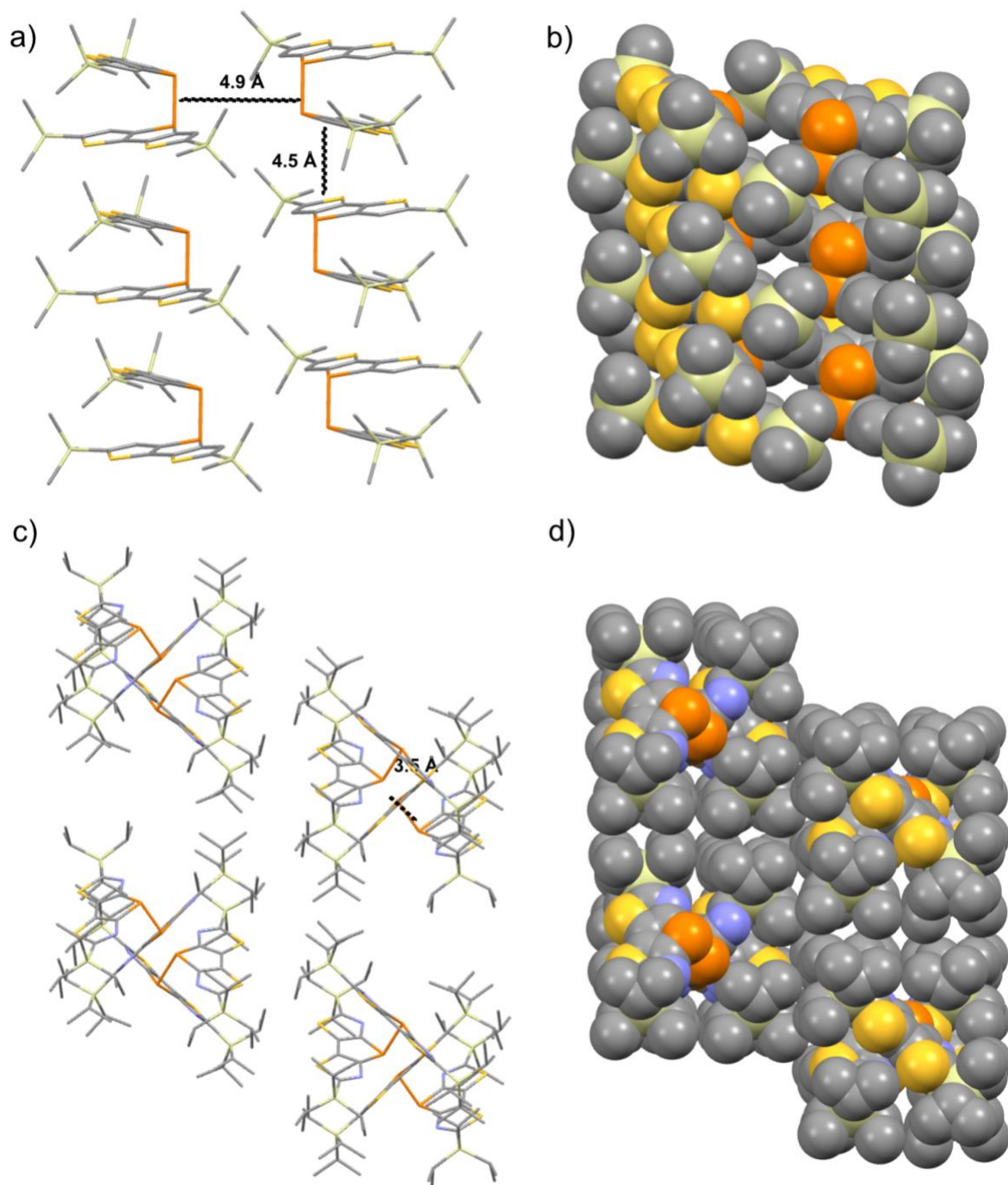


Figure 3-10. Solid-state packing showing a) columnar packing and b) space fill model of **3-4** c) solid-state packing and c) space fill model of **3-5**. Hydrogen atoms are omitted for clarity.

3.2.6 Photophysical Properties

The effect of the various electronic skeletal modifications of bi(dithienophosphole)s on their photophysical properties was studied using absorption and emission spectroscopy.

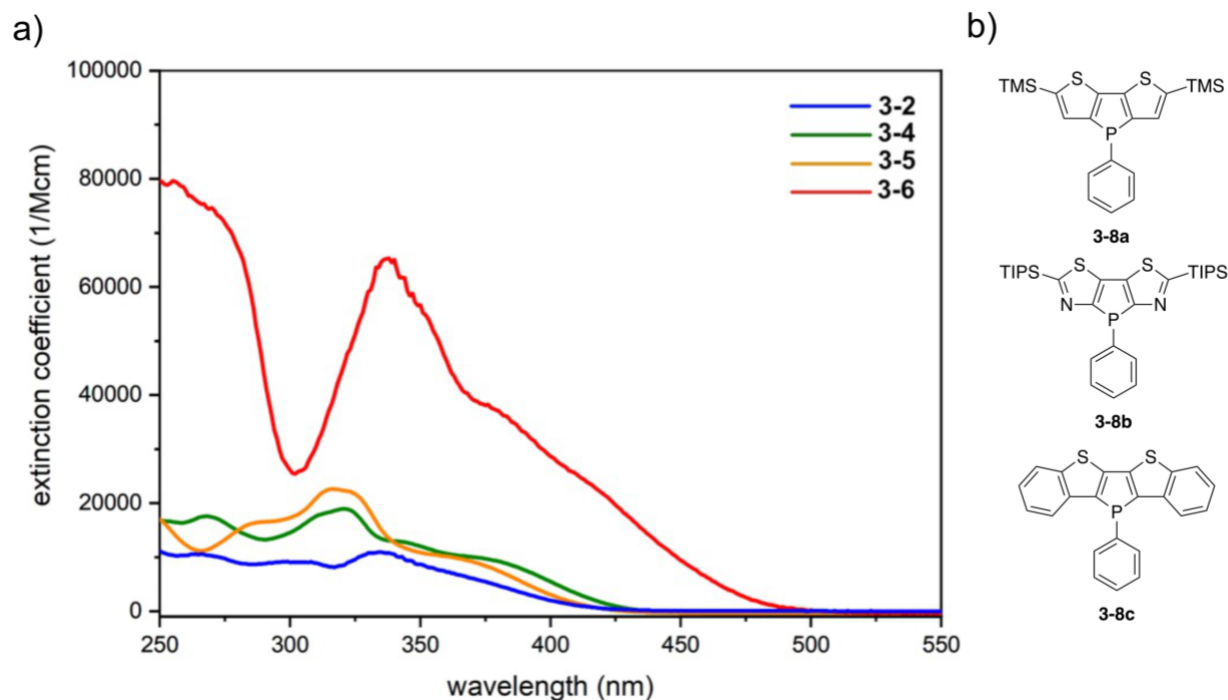


Figure 3-11. a) Absorption spectra of the functionalized bi(dithienophosphole)s in comparison to **3-2** in dry DCM and b) corresponding *P*-phenyl-functionalized monomers of bi(dithienophosphole)s.

Absorption Properties: Regardless of the functionalization, all new derivatives exhibit a broad absorption profile without pronounced, sharp peaks, indicating that the overall symmetry of bi(dithienophosphole)s again significantly influences the photophysical properties of these materials (Figure 3-11a).²⁴ While these derivatives display multiple absorption maxima in DCM (see Table 3-2), the highest values are observed at 335 nm for **3-2**, 321 nm for **3-4**, 319 nm for **3-5**, and 339 nm for **3-6**. Compared to the corresponding phenyl-functionalized ‘monomers’ of these species, the absorption onsets of **3-4** (425 nm vs. 344 nm for **3-8a**), **3-5** (413 nm vs. 344 nm for **3-8b**), and **3-6** (475 nm vs. 385 nm for **3-8c**) are noticeably red-shifted, indicating effective extension

of conjugation through dimerization of the phosphorus center. This is further exemplified by the most red-shifted absorption onset for **3-6** (c.f.: **3-2** at 415 nm), attributed to the pentacene core housing the most extended π -system among all modifications applied in this novel class of bi(dithienophosphole)s. (see SI section 3.5)

	λ_{abs}^a (nm)	λ_{abs}^b (nm)	HOMO-LUMO gap ^a (eV)	Optical bandgap ^b (eV)
3-2	228(<i>f</i> =0.10), 260(<i>f</i> =0.15), 262(<i>f</i> =0.19), 320(<i>f</i> =0.12), 468(<i>f</i> =0.28)	266, 306, 335	3.81	2.99
3-4	336 (<i>f</i> =0.9), 348 (<i>f</i> =0.52,0.48)	268, 312, 321 , 345, 382	3.56	2.92
3-5	---	284, 319 , 329, 370	3.73	3.00
3-6	319(<i>f</i> =0.11), 397 (<i>f</i> =0.22), 432(<i>f</i> =0.20), 439(<i>f</i> =0.16), 484(<i>f</i> =0.12), 549(<i>f</i> =0.13),	264, 339 , 384, 420	3.24	2.61

Table 3-2. Theoretically^a and experimentally^b calculated absorption maxima and bandgap of bi(dithienophosphole)s. The notable transitions are bolded.

Remarkably, the modifications also have a substantial impact on the extinction coefficients (ϵ), with **3-4** and **3-5** exhibiting ϵ values of 19,000 M⁻¹cm⁻¹ and 23,000 M⁻¹cm⁻¹, respectively, compared to **3-2** (11,000 M⁻¹cm⁻¹). The red-shifted absorption is paralleled by a six-fold increase in the extinction coefficient (65,000 M⁻¹cm⁻¹) in **3-6**, underscoring the positive influence of the applied modifications on the photophysical properties of this system. The TD-DFT, B3LYP/6-31G(d) level

of theory, SI section S.3.2) data for these species closely align with the experimental values, revealing numerous transitions with energies that correlate with the broad absorption profile depicted in Figure 3-11a.

Figure 3-12 shows selected orbitals associated with transitions of high oscillator strength (f), leading to absorption in these compounds. In DCM, **3-2** exhibits two main transitions at 262 nm and 468 nm. The former signifies a locally excited transition from one phosphole subunit (HOMO-1) to the entire π -conjugated scaffold of the molecule (LUMO+1), while the latter indicates π - π^* transitions from HOMO to LUMO (Figure 3-12a). Nonetheless, it can be stated that the primary transitions driving effective absorption in bi(dithienophosphole)s are π - π^* transitions, which are computationally diverse in both **3-4** and **3-6**. In **3-4**, a combination of numerous π - π^* transitions are present, primarily at 336 nm involving HOMO-3 to LUMO+1 and HOMO-2 to LUMO+2, and at 348 nm with significant contributions from HOMO-1 to LUMO+1, HOMO to LUMO+2, and HOMO-1 to LUMO+2 transitions (Figure 3-12b). In contrast, π - π^* transitions in **3-6** are represented by a 397 nm transition (HOMO-2 to LUMO+1) and a 432 nm transition (HOMO-1 to LUMO+1) (Figure 3-12c). Many of the calculated transitions are intricately interwoven with transitions of closely matched energies. However, the experimentally determined optical bandgap is smaller than the theoretically calculated HOMO-LUMO gap justifying the discrepancies associated with theoretical and experimental λ_{abs} values in Table 3-2. This can be explained by the fact that DFT calculations generally yield a single-particle HOMO-LUMO gap, while optical methods involve transitions between many-body states, accounting for multiple electronic transitions that contribute to the measured band gap, potentially leading to a smaller value.

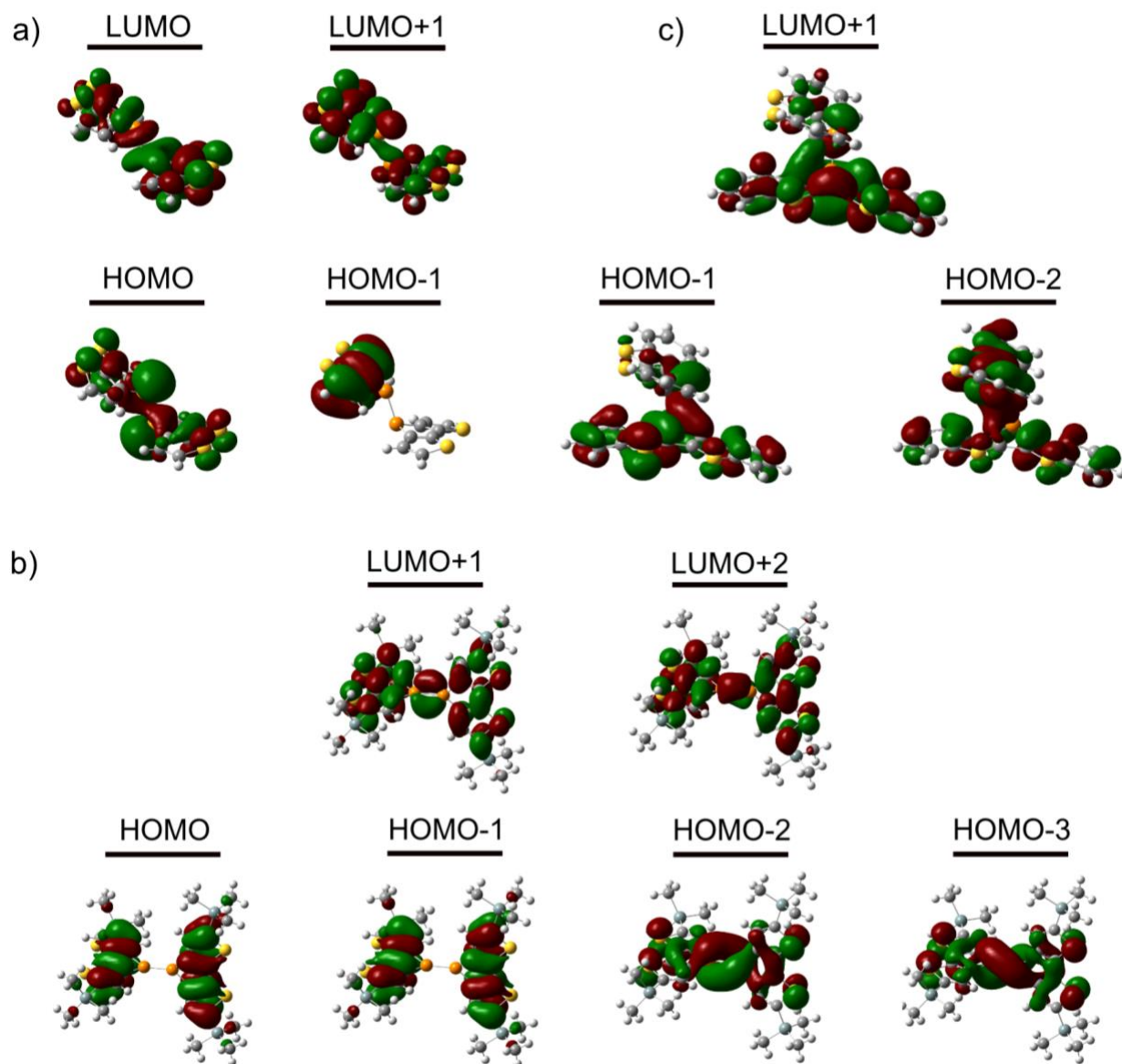


Figure 3-12. Major orbitals leading to notable transitions as calculated by TD-DFT (B3LYP/6-31G(d) level of theory) for a) **3-2**, b) **3-4**, and c) **3-6**.

Emission properties: All new species were found to be luminescent. In our initial study, **3-2** was deemed non-emissive; however, during our investigation, we did observe weak blue emission from this compound as well. Consequently, the emission properties of these bi(dithienophosphole)s were studied in detail. Compounds **3-2**, **3-4**, **3-5**, and **3-6** emit light at wavelengths of 470 nm, 453 nm, 457 nm, and 507 nm, respectively (Figure 3-13). Notably, these bi(dithienophosphole)s exhibit

red-shifted emissions compared to their corresponding phenyl-substituted monomers (**3-3**, **3-8a,b,c**), underscoring the extended conjugation throughout the entire molecular scaffold. Remarkably, the most pronounced bathochromic shift, resulting in green emission at 507 nm, is observed for **3-6**, attributed to its extensively conjugated benzo-fused scaffold.

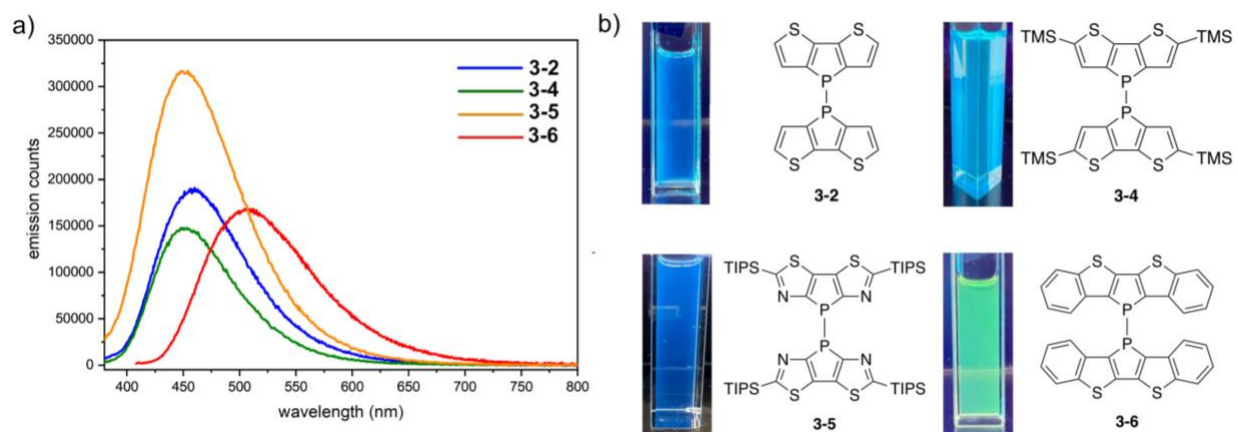


Figure 3-13. a) Emission spectra and b) emission colour of bi(dithienophosphole)s solution in dry DCM (when illuminated under UV-lamp).

Compounds	$\lambda_{\text{ex}}^{\text{b}}$ (nm)	λ_{em} (nm)	QY (%)
3-2	357	470	4.4
3-4	360	453	16
3-5	356	457	3.8
3-6	399	507	29

Table 3-3. Solution state excitation/emission parameters of bi(dithienophosphole)s in DCM, along with the corresponding QYs.

The quantum yields (QY) in solution were determined to be 4%, 16%, and 4% for compounds **3-2**, **3-4**, and **3-5**, respectively, indicating successful enhancement of the emission properties through TMS-functionalization in **3-4**. Particularly noteworthy are the findings for **3-6** that exhibits a

remarkable 7-fold increase in QY (29%) compared to **3-2**. The extended π -scaffold in **3-6** appears to restrict rotation about the P–P bond to some extent, reducing non-radiative transitions and channeling relaxation toward emission. This observation highlights that π -extended scaffolds not only enhance reactivity in P–P coupling but also bolster photophysical attributes in solution.

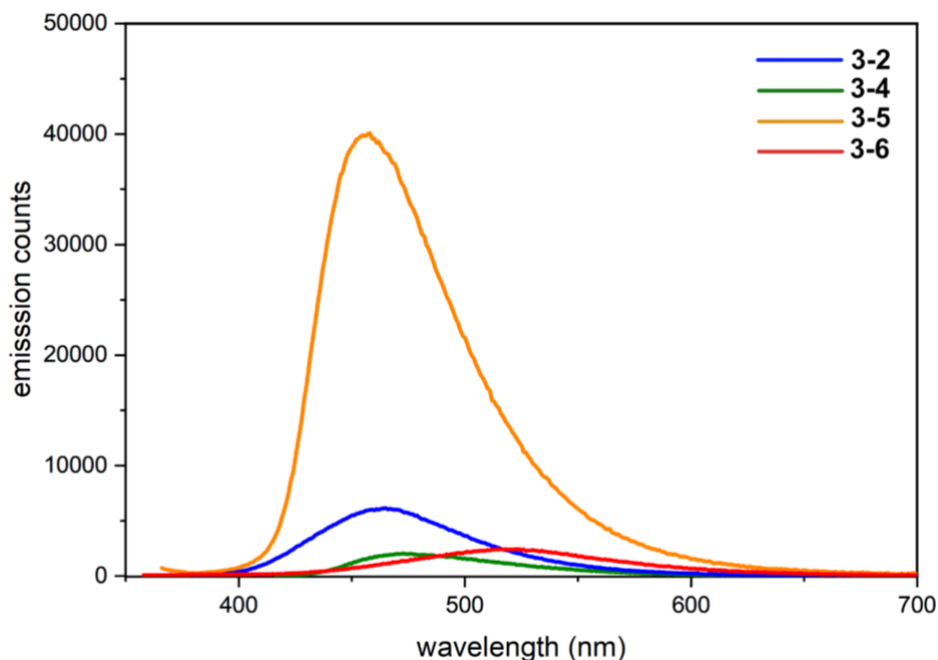


Figure 3-14. Emission spectra of neat films of bi(dithienophosphole)s to study solid-state properties.

To gain insights into the bulk properties of these derivatives, we investigated their solid-state emission characteristics. Compounds **3-2**, **3-4**, **3-5**, and **3-6** exhibit emissions at 460 nm, 500 nm, 457 nm, and 544 nm, respectively (Figure 3-14). The red-shifted emissions for **3-4** and **3-6** imply some degree of aggregation, likely involving π -stacking through a) the columnar arrangement of **3-4** molecules as seen in Figure 3-10a and b) the extended planar scaffold in **3-6**. However, the QY of these derivatives in the solid state is relatively low. The red-shifted λ_{em} suggests ACQ³⁸ as a contributing factor. To verify aggregation in the solid state, we then examined corresponding PMMA films containing 5% weight of these derivatives. The blue-shifted emission exhibited by compounds **3-4** and **3-6** provides a clear indication of substantial separation of the fluorophores in

the PMMA films, in contrast to the densely packed solids. Given that these observed values align closely with data obtained from solution-state measurements, ACQ indeed appears to impair their QY in the bulk. This is further substantiated by the enhanced QY of 4% for the PMMA films of compounds **3-2**, **3-5**, and **3-6**. In contrast, the QY of the PMMA film containing **3-4** experiences a reduction to 3%, suggesting that the intermolecular interactions within the closely packed columnar aggregates contribute to aggregation-induced emission (AIE)³⁹ behavior (See Table 3-3).

Compounds	λ_{ex}^a (nm)	λ_{em}^a (nm)	QY ^a (%)	λ_{ex}^b (nm)	λ_{em}^b (nm)	QY ^b (%)
3-2	315	460	0.5	360	465	4
3-4	336	500	8	385	476	3
3-5	356	457	0	356	457	4
3-6	399	544	0	338	520	4

Table 3-4: Excitation wavelengths, emission wavelengths and quantum yield of bi(dithienophosphole)s neat^a and in PMMA film^b.

3.2.7 Electrochemical Properties: None of these derivatives shows any reversible redox properties, as determined by cyclic voltammetry, but were found to electro-polymerize on the electrode instead. (See SI section S.3.6)

3.3 Conclusion

Our primary objective was to develop and refine the characteristics of the little explored bi(dithienophosphole) system through strategic modifications of its π -scaffold. This endeavor aimed to unravel the interplay between modification strategies and their effects on stability, reactivity, and photophysical attributes. The two parallel approaches employed involved electronic

modifications, encompassing both electron-withdrawing and electron-donating motifs, as well as π -extension and spatial confinement of P–P bond rotation via the introduction of bulky substituents. In pursuit of our objectives, DFT calculations were employed to verify the structures of the targeted bi(dithienophosphole)s, supporting their twisted “gauche-like” conformations. These structural modifications displayed considerable impact on their FMO energies, with considerably reduced energy gaps for the two π -extended species.

Synthetic access to the modified bi(dithienophosphole)s was initially verified by the previously reported LA mediated route. Modifications utilizing bulky TMS functionality and TIPS-protected thiazole core indeed resulted in the synthesis of compounds **3-4** and **3-5**. To optimize reaction efficiency and avert decomposition, the synthesis process was executed under microwave conditions. However, some unexpected but intriguing outcomes were observed during the synthesis of the π -extended species **3-6** and **3-7**, where the derivatives were formed without the involvement of LAs. These contrasting reaction patterns underscored the pivotal role of the electronic nature of the core scaffold in influencing the stability of the exocyclic P–N bond.

The elucidated mechanism behind the LA-free formation of bi(dithienophosphole)s involves *in-situ* de/protonation, culminating in the creation of phospholide intermediates. This mechanism, distinct from the LA-mediated route that proceeds via a phosphonium intermediate, showcased the impact of π -extended (and electron-donating) cores, such as those in **3-6a** and **3-7a**, in weakening the P–N bond and promoting the generation of negatively charged phospholide species. This not only provides an accessible synthetic pathway but also supports the potential of these derivatives as versatile synthons for phospholide species with diverse applications.

Single-crystals X-ray crystallography of compounds **3-4** and **3-5** unveiled their distinctive twisted “gauche-like” configurations, distinct from the reported step-like structure of unmodified **3-2**. The

bulky TMS and TIPS groups in these derivatives impeded both intramolecular and intermolecular π -stacking interactions. Consequently, these modified derivatives exhibited a preference for more relaxed bulk packing compared to **3-2**, resulting in a columnar arrangement of molecules, specifically in **3-4**.

The absorption spectra of the bi(dithienophosphole) derivatives displayed broad profiles lacking distinct peaks. The absorption maxima and bandgap values of these profiles varied across different compounds because of electronic modifications. The close alignment between transition energies calculated through TD-DFT and experimental values underscored the accuracy of the computational approach. The investigation of emission properties demonstrated that the compounds emitted light at varying wavelengths, with largely enhanced QYs in both solution and solid-state environments. This phenomenon was attributed to ACQ and emission processes, which has a pronounced impact on the photophysical behavior of these materials.

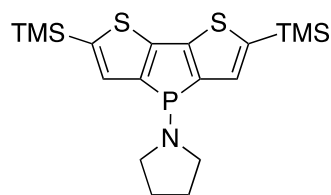
In conclusion, this Chapter advances the understanding of step-conjugated materials derived from bi(dithienophosphole), providing insights into design, synthesis, and properties toward functional materials featuring this unique structural element. Strategic π -scaffold modifications revealed diverse effects on stability, reactivity, and photophysics, highlighting novel synthesis pathways and structural configurations. In addition to the various chemical functionalization of the core scaffold covered herein, post-functionalization is now being explored to further develop the functional properties of these materials. This involves relatively straightforward processes such as oxidation of the phosphorus center or the utilization of click chemistry, particularly relevant in the context of compound **3-7**. This approach holds the promise of providing insights into how such modifications influence the functional characteristics of these materials.

3.4 Experimental Section

General. All reagents were purchased from Sigma Aldrich and Oakwood Chemical. All solvents were purchased from Sigma Aldrich and Fisher chemical. SPS grade solvents (MBraun) from Sigma Aldrich were used for synthesis and characterisations. Compounds **3-2a**, **3-4a'**, and **3-6a'** were prepared according to literature procedures.^{24,32,34} The precursors for the synthesis of compounds **3-5 (3-5a')** and **3-7 (3-7a')** were obtained as synthesized from a previous lab member, Dr. Xiaoming He. ¹H, ³¹P{¹H}, ¹⁹F{¹H}, ¹³C{¹H} NMR spectra were acquired on Bruker NEO 700, 600, 400 and 300 NMR spectrometers on a 5mm ATM probe using TOPSPIN software version 4.0.8. Chemical shifts are reported in parts per million (ppm). Multiplicities are reported as: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), multiplet (m), quartet (q), and broad (br). The solid-state structures of the compound were determined using Bruker DQ Quest eco. The structures were solved and refined using OLEX2 software. All absorption measurements were recorded on an Agilent Technologies Cary 5000 UV-Vis spectrometer at room temperature. All samples for UV-Vis experiments were run in solvents from Sigma Aldrich using 10 mm quartz cuvettes. SPS grade DCM was used as solvent for characterization. All emission measurements were recorded using an Edinburgh FS5 spectrofluorometer and processed using Fluoracle software. QY measurements were collected using integrating sphere; model SC-30 at room temperature. Lifetime measurements (FS5-TCSPC) were conducted using light source EPL405 with an excitation wavelength of 403 nm. All solutions were prepared using solvents from Sigma Aldrich (SPS grade DCM) and measurements were acquired using 10 mm quartz cuvettes. All electrochemical studies were obtained using Metrohm Autolab potentiostat, with 0.1 M n-Bu₄NPF₆ (Sigma Aldrich, electrochemical grade) that was used after recrystallization from THF as electrolyte. The working, reference and counter electrodes used were glassy carbon, silver/silver

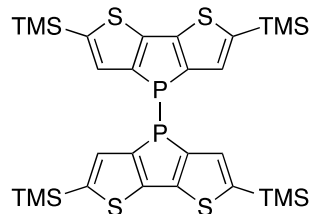
chloride (Ag/Ag^+) and platinum wire, respectively. The electrochemical measurements were carried out at room temperature in dry, degassed THF by bubbling argon through the solution for at least 5 min, and an argon flow was kept over the solution during measurements. The electrochemical cell was recorded using the software NOVA.

Preparation of **3-4a**



Compound **3-4a**³² (2.04g, 5.00 mmol) was dissolved in 100 ml of dry Et_2O and the solution was chilled to -78°C using liquid nitrogen/acetone bath. $n\text{-BuLi}$ (2.05 eq., 0.10 mol, 0.65g) was added to this cold solution with stirring. The solution was stirred for 30 minutes at -78°C and then warmed to room temperature for another 30 minutes. It was cooled again to -78°C and one equivalent of dichloro(pyrrolidiny)phosphane (0.86g, 5.00 mmol) was added with stirring. The cold bath was immediately exchanged for a warm water bath (35°C) and the solution was stirred overnight. The solvent was dried under high vacuum and the brown solid was redissolved in dry pentane and passed through a celite plug. The solution was dried to obtain **3-4a** as a brown oil at 98% yield (2.0g). ^1H NMR (400 MHz, CDCl_3 , ppm): δ 7.25 (s, 2H), 2.91 (m, 4H), 1.74 (m, 4H), 0.35 (s, 18H). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , ppm): δ 20.6. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3 , ppm): δ 148.4 (d, $^2J_{\text{P}}=13.8$ Hz), 146.7 (d, $^2J_{\text{P}}=4.3$ Hz), 141.6 (d, $^3J_{\text{P}}=3.5$ Hz), 133.7 (d, $^1J_{\text{P}}=17.9$ Hz), 49.8 (d, $^3J_{\text{P}}=4.1$ Hz), 26.3 (d, $^2J_{\text{P}}=5.1$ Hz), 0.2 (s). Some residual impurity peaks are also detected.

Preparation of **3-4**



By reflux. One equivalent of etherated BF_3 (0.53g, 3.8 mmol) was added to a solution of **3-4a** (1.54g, 3.76 mmol) in dry ether. After refluxing this mixture for two days, the symmetric **3-4** was formed. The solution was then passed through an alumina plug under argon to yield a yellow oil which is **3-4** (2.55g) at 71% yield.

By microwave reactor. Compound **3-4a** (2.56g, 6.25 mmol) reacted with one equivalence of etherated BF_3 (0.89g, 6.25 mmol) in the microwave reactor for 20 minutes at an elevated temperature of 190°C with one equivalence of BF_3 in dry THF. Compound **3-4** was isolated by passing through a plug of appropriate column material as mentioned early to obtain 50% of **3-4** (4.25g).

^1H NMR (700 MHz, CD_2Cl_2 , ppm): δ 8.48 (s, 4H), 2.29 (s, 32H). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , ppm): δ -39.1. $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CD_2Cl_2 , ppm): δ 149.3 (s), 147.5 (s), 143.8 (s), 133.9 (t, $^1J_{\text{P}}=15.8$ Hz), 1.57 (s).

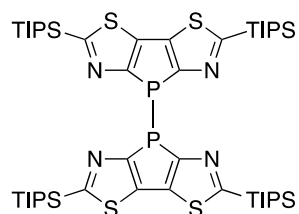
Preparation of **3-5a**



Compound **3-5a**³³ (1.52g, 2.38 mmol) was dissolved in 150 ml of dry Et_2O and was chilled to -78°C using liquid nitrogen/acetone bath. $n\text{-BuLi}$ (2.05 eq., 4.90 mmol, 0.31 g) was added to this cold solution with stirring. The solution was stirred for 30 minutes at -78°C and then warmed to room temperature for another 30 minutes. It was cooled again to -78°C and one equivalent of dichloro(pyrrolidiny)phosphane (0.41g, 2.38 mmol) was added with stirring. The cold bath was immediately switched with a warm water bath (35°C) and the solution was stirred overnight. The

solvent was dried under high vacuum and the brown solid was redissolved in dry pentane and passed through a long celite plug. The orange solution was dried to obtain **3-5a** as a yellow solid at 92% yield (1.26g). ^1H NMR (400 MHz, CDCl_3 , ppm): δ 2.93 (m, 2H), 1.71 (m, 2H), 1.48 (m, 3H), 1.14 (m, 18 H). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , ppm): δ 13.9. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3 , ppm): δ 171.3 (d, $^1J_{\text{P}}=9.8$ Hz), 167.0 (d, $^2J_{\text{P}}=4.6$ Hz), 136.5 (d, $^2J_{\text{P}}=9.5$ Hz), 50.3 (d, $^2J_{\text{P}}=9.1$ Hz), 26.4 (d, $^3J_{\text{P}}=5.1$ Hz), 18.6 (s), 11.6 (s). Some residual impurity peaks are also detected.

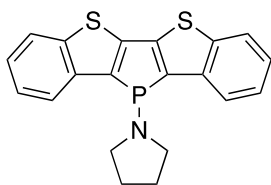
Preparation of **3-5**



By reflux. The amino derivative **3-5a** (0.27g, 0.5 mmol) dissolved in dry ether was then reacted with BF_3 (1 equiv, 0.1g, 0.5 mmol) to give a pale-yellow cloudy solution. On refluxing the solution overnight, **3-5a** converted to **3-5** and was isolated by using an alumina plug under argon to yield 44% of pure product (0.21g).

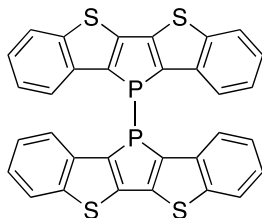
By microwave reactor. Compound **3-5a** (0.55g, 0.95 mmol) reacted in the microwave reactor for 20 minutes at an elevated temperature of 190°C with one equivalence of BF_3 (0.14g, 0.95 mmol) in dry THF. Compound **3-5** was isolated by passing through a plug of appropriate column material as mentioned early to obtain 50% of **3-5** (0.49g). ^1H NMR (700 MHz, CDCl_3 , ppm): δ 1.38 (septet, 12H, $^3J_{\text{H}}=7$ Hz), 1.11 (d, 72H, $^3J_{\text{H}}=7$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , ppm): δ -52.0. $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3 , ppm): δ 171.3 (s), 163.6 (t, $^1J_{\text{P}}=3.5$ Hz), 136.5 (s), 18.6 (d, $^5J_{\text{P}}=19.3$ Hz), 11.7 (s).

Preparation of **3-6a**



Compound **3-6a**³⁴ (0.49g, 1.16 mmol) was dissolved in 450 ml of dry Et₂O and three equivalence of Tetramethylethylenediamine (TMEDA; 0.52 ml, 3.49 mmol) was added to the solution. The solution was chilled to -78°C using liquid nitrogen/acetone bath and n-BuLi (2.05 eq., 2.32 mmol, 0.15 g) was added with stirring. The solution was stirred for 30 minutes at -78°C and then warmed to room temperature for another 30 minutes. It was cooled again to -78°C and one equivalent of dichloro(pyrrolidinyl)phosphane (0.2 g, 1.16 mmol) was added with stirring. The cold bath was immediately switched with a warm water bath (35°C) and the solution was stirred overnight. The solvent was dried under high vacuum and the brown solid was redissolved in dry DCM and passed through a long celite plug. The orange residue after drying the solvent was washed several times with dry pentane. The product **3-6a'** was isolated at 60% yield (0.25 g). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.90 (d, 4H), 7.44(m, 2H), 7.34 (m, 2H), 3.09 (m, 4H), 1.80 (m, 4H). ³¹P{¹H} NMR (162 MHz, CDCl₃, ppm): δ 21.3. ¹³C{¹H} NMR (100.6 MHz, CDCl₃, ppm): δ 143.2 (d, ³J_P=5.0 Hz), 142.1 (d, ²J_P=13.1 Hz), 141.4 (d, ²J_P=5.0 Hz), 138.7 (d, ¹J_P=16.1 Hz), 125.3 (s), 124.1 (s), 50.6 (d, ²J_P=10.0 Hz), 26.8 (d, ³J_P=5.0 Hz).

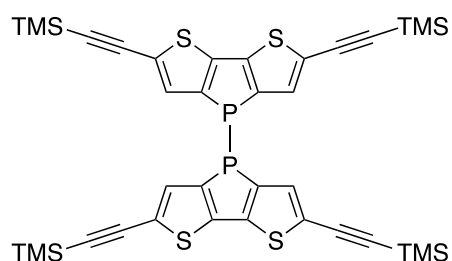
Preparation of **3-6**



By microwave reactor. Compound **3-6a** (0.07g, 0.2 mmol) was reacted in a microwave reactor with one equivalence of BF₃•Et₂O (0.03g, 0.2 mmol) at 150°C for 5 min in dry THF to converts to **3-6**. The solution was dried and redissolved in dry DCM. This solution was then passed through a celite plug to purify **3-6**. The solution was dried under vacuum to yield an orange solid at 47% yield (0.06g). To further

explore this enhanced reactivity, **3-6a** dissolved in dry THF was reacted in a microwave without BF_3 at 190°C for 30 min. The 70% of **3-6a** converted to **3-6** at this condition (1:1; without any other by-products). ^1H NMR (400 MHz, CDCl_3 , ppm): δ 7.78 (q, 4H, $^3J_{\text{H}}=8$ Hz, $^4J_{\text{P}}=4$ Hz), 7.28 (m, 8H), 7.09 (d, 4H, $^3J_{\text{H}}=8$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , ppm): δ -38.0. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CD_2Cl_2 , ppm): δ 133.7 (d, $^1J_{\text{P}}=19.5$ Hz), 128.7 (s), 128.5 (d, $^2J_{\text{P}}=7.1$ Hz), 125.1 (s), 124.4 (s), 123.3 (s), 122.1 (s). Residual solvents identified.

Preparation of **3-7**



Compound **3-7a**³⁵ (0.68g, 1.31 mmol) was dissolved in 400 ml of dry Et_2O . The solution was chilled to -78°C using liquid nitrogen/acetone bath and $n\text{-BuLi}$ (2.05 eq., 2.32 mmol, 0.17 g) was added with stirring. The solution was stirred for 30 minutes at -78°C and then warmed to room temperature for another 30 minutes. It was cooled again to -78°C and one equivalent of dichloro(pyrrolidiny)phosphane (0.23 g, 1.31 mmol) was added with stirring. The cold bath was immediately switched with a warm water bath (35°C) and the solution was stirred overnight. The reaction mixture was then filtered and stirred overnight to observe the formation of **3-7** ($^{31}\text{P}\{^1\text{H}\}$ NMR: δ -35.8 ppm)

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CHAPTER 4: UNLOCKING VERSATILE TRANSFER AGENTS:

SYNTHESIS AND REACTIVITY OF DITHIENO-PHOSPHOLIDE FOR

P-C AND P-P BOND FORMATION

4.1 Introduction

Phospholides are an intriguing class of phosphorus-containing compounds that have garnered significant interest for their distinctive properties. They advance organophosphorus ligands, transition metal complexes, and catalytic processes in academia and industry. Recent years have seen a surge in phospholide chemistry, opening a valuable path for potential solutions in optoelectronics, catalysis, and energy storage. Upon coordination to transition metals, phospholides show promise in enabling greener and more sustainable chemical processes, inspiring innovations across diverse fields.¹⁻⁷

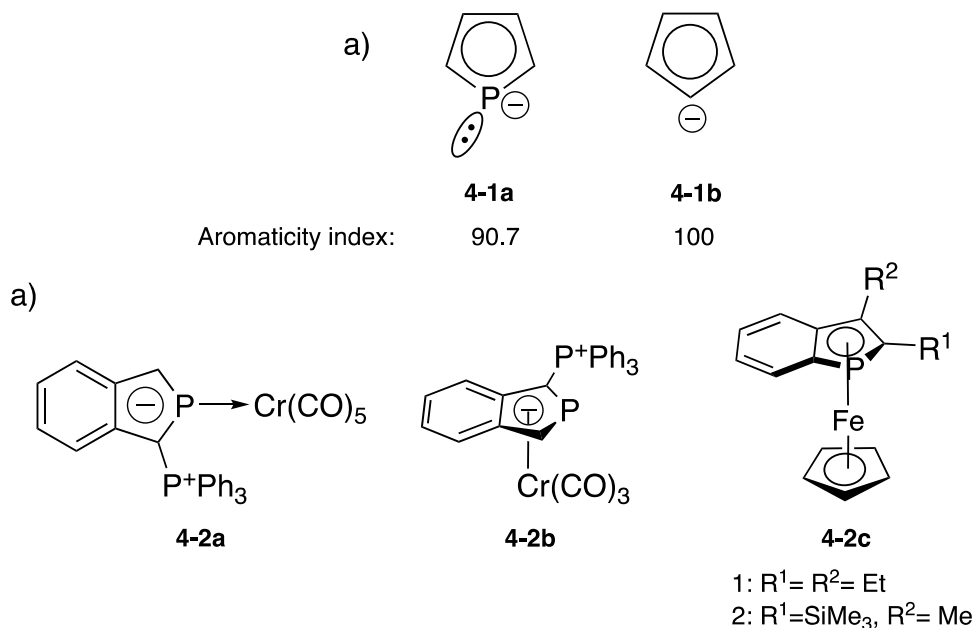


Figure 4-1. a) Aromaticity of phospholide anion and b) amphipathic nature of phospholide⁸.

Phospholide (**4-1a**) is a five-membered cyclic compound containing a negatively charged phosphorus atom. It is characterized by high aromaticity comparable to the cyclopentadienyl anion (**4-1b**).²⁻¹¹ Unlike the neutral trivalent phosphole analogues, phospholides exhibit unique reactivity. They can participate in nucleophilic reactions involving their lone pair while simultaneously exploiting their anionic character, influencing interactions with other charged species. As a result, phospholide anions act as both σ - and π -donors. In the former scenario, they can donate the lone pair of electrons on P atom to vacant metal orbitals (**4-2a**), while in the latter the π -electrons on the phosphole ring are donated in a “side-on” manner to the metal orbitals as in case of **4-2b**. However, they can also accept π -electron density from electron-rich species like metal d-orbitals (**4-2c**), rendering them amphipathic in nature and versatile in coordination chemistry.^{8,12-14} The equivalent anionic heterole species of other group 15 elements, such as pyrrolide¹⁵, arsolide^{16,17}, and stibolide¹⁸, have found applications in pharmaceuticals, agrochemicals, and materials science.^{2,16,19,20-25}

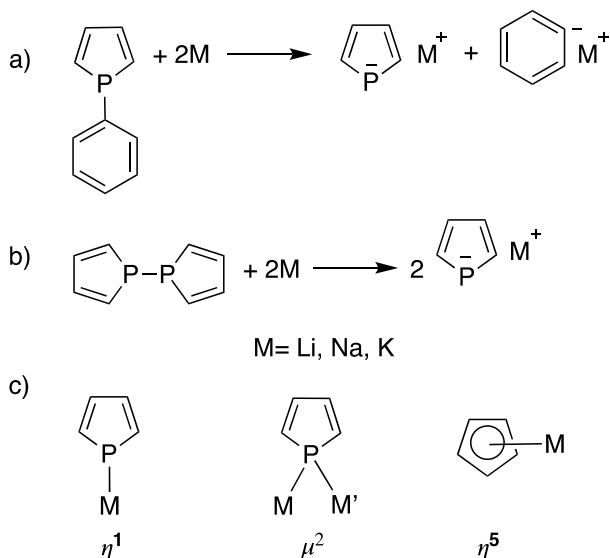


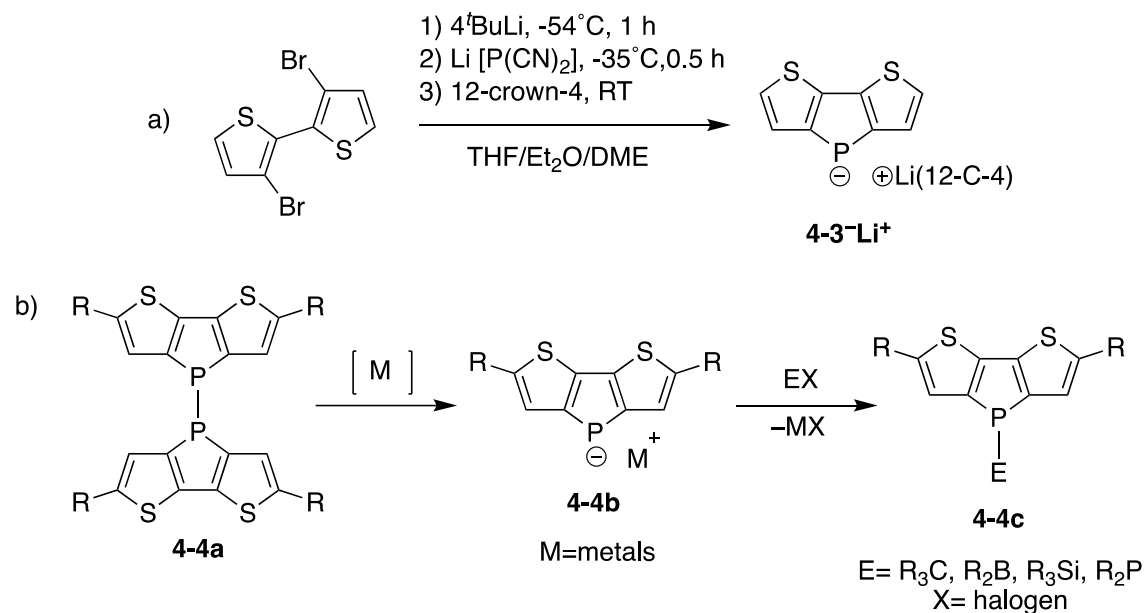
Figure 4-2. Various syntheses (a,b) and c) complexation modes of phospholide.

Phospholide synthesis commonly involves alkali metal-mediated cleavage of the exocyclic P–R bond in trivalent phospholes (Figure 4-2a). This reduction pathway is driven by the aromaticity of the resulting phospholide anion. Another approach involves cleaving the P–P bond of biphosphole via a redox strategy that has been used for the synthesis of unique non-conventional phospholide complexes (Figure 4-2b).^{2,26-32} These species are stabilized by covalent bonds between the phosphorus atom and metal or metalloid atoms, as well as bulky substituents surrounding the central phosphole ring. Phospholide coordination to metals results in highly polarized P–M bonds, with the metal providing electron density to stabilize the negative charge on phosphorus. However, the electronic properties of phospholides can vary based on metal, coordination environment, and phosphorus substituents, affecting their reactivity with certain organic functionalities. Phospholides display diverse complexation modes, with η^1 -P and μ^2 -P complexes being common. Particularly intriguing are the η^5 -complexes of phospholide with an available lone pair, offering additional reactivity possibilities (Figure 4-2c).^{1,5,6,33}

This thesis Chapter focuses on a new dithieno-phospholide, a compound characterized by two thiophene moieties flanking the central phosphole unit. This species offers an intriguing opportunity toward value-added functional conjugated materials by combining the advantageous reactivity properties of phospholide anions with the high luminescence and electron-accepting nature of the dithienophosphole scaffold.³⁴ In this context, these reactive species would exhibit significant potential as highly emissive transfer agents in organic chemistry. Despite their exceptional qualities, dithieno-phospholides have been underexplored to date due to the lack of a readily accessible synthetic route or precursor.

A recent publication by Liu et al. reported a three-step procedure for generating and isolating the dithieno-phospholide complex **4-3**[–]**Li**⁺ via; 1) lithiation of 3,3'-dibromo-2,2'-bithiophene, 2)

bridging with $[P(CN)_2]^-$ anion produced electrochemically from P_4 , and 3) stabilizing the resulting phospholide using a suitable crown ether (Scheme 4-1a). While this method is currently the sole known approach to form dithieno-phospholide, its transferability and applicability to functionalized or modified dithienophospholes remain largely unexplored, none the least due to the highly reactive $[P(CN)_2]^-$ reagent.³⁵



Scheme 4-1. a) Synthesis of **4-3⁻Li⁺** using $[P(CN)_2]^-$ anion³⁵ and b) proposed synthesis of dithieno-phospholides from R-functionalized bi(dithienophosphole)s to generate various P-species.

In this context, bi(dithienophosphole)s (**4-4a**) are promising precursor candidates, since the P–P bond is inherently labile and can be effectively cleaved under appropriate conditions (see Chapter 3), potentially serving as precursors for various functionalized dithieno-phospholide complexes (**4-4b**) through a single-step process (Scheme 4-1b).³⁶ An attractive aspect of the new method discussed in this thesis is the relative stability of the precursor, allowing it to be stored under argon for an extended period. This is in contrast to the conventional precursors used in phospholide chemistry, which are highly reactive; bi(dithienophosphole)s thus offers several advantages such

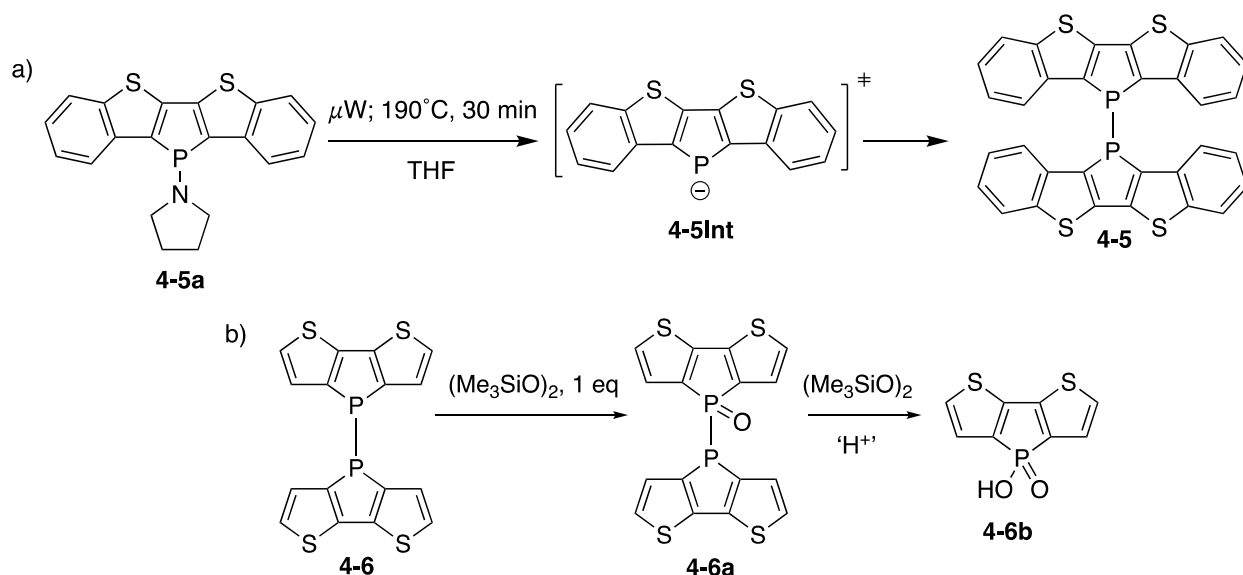
as a long shelf-life, moderate stability, facile synthesis, and emissive properties (See Chapter 3) for details). The dithieno-phospholides thus generated can be judiciously employed as an *in-situ* synthon towards deliberate creation of a diverse spectrum of phosphorus-functionalized species via a straightforward salt metathesis route (Scheme 4-1b). This versatile methodology fundamentally enables the generation of a comprehensive array of derivatives, characterized by P–C, P–B, P–Si, and P–P bonds that may potentially hold significance within the realms of catalysis and material science in principle, which makes it a noteworthy avenue for exploration and advancement.^{20,24,29,37,38}

This thesis Chapter now presents a promising and efficient approach to utilizing bi(dithienophosphole)s as versatile building blocks for the synthesis of functionalized dithieno-phospholides. The initial exploration work discussed in this thesis investigates various reaction conditions leading to the synthesis of dithieno-phospholide. The transient species formed is then reacted with various halide compounds, generating new P–C and P–P bonds toward value-added conjugated organophosphorus materials, and the stability of these compounds is briefly addressed.

4.2 Results and Discussions

Recent work by our group has established the LA-mediated cleavage of the P–N bond of *P*-amino-dithienophosphole, resulting in the formation of bi(dithienophosphole) with a P–P bond.³⁶ This thesis, and specifically Chapter Three, serves as an extension to this initial proof-of-concept work toward a versatile functional platform, exploring the reaction conditions and properties that lead to the formation of more symmetrically functionalized bi(dithienophosphole)s with both electron-donating and -withdrawing substituents. Intriguingly, π -extended bi(dithienophosphole)s are successfully synthesized through a mechanism that can also proceed in the absence of a LA,

invoking a highly transient phospholide intermediate. The latter had not been observed or isolated in the reaction mixture so far (Scheme 4-2a). Notwithstanding, these findings suggest the possibility of accessing dithieno-phospholide species from bi(dithienophosphole)s. Although the conditions for decomposition of bi(dithienophosphole)s by the P–P bond cleavage under acidic conditions are briefly discussed in our earlier publication (Scheme 4-2b)³⁶, the reductive cleavage of this bond to synthesize corresponding dithieno-phospholides had remained unexplored to date.

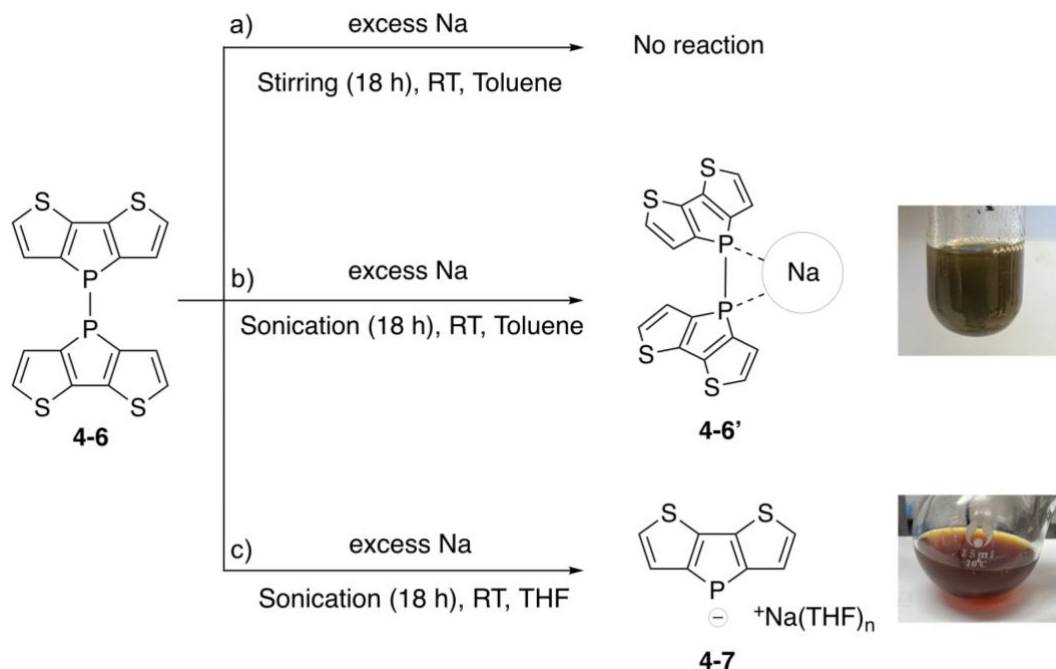


Scheme 4-2. a) Synthesis of π -extended bi(dithienophosphole) **4-5** via phospholide intermediate **4-5Int**, b) P–P bond cleavage leading to decomposition of parent bi(dithienophosphole) **4-6** by oxidation³⁶.

To verify the synthetic accessibility of a dithieno-phospholide anions, the generic reaction conditions, as depicted in Figure 4-2b, originally used for generating phospholide from biphosphole, were explored with the unfunctionalized bi(dithienophosphole) **4-6**.^{31 32} The progress of the reaction was carefully examined using ^{31}P NMR spectroscopy to identify optimal conditions for effectively addressing the P–P bond cleavage. Additionally, we explored the reactivity of this species to form various new phosphorus bonds toward highlighting its stability and potential as a readily transferable agent. To this end, we propose a facile synthesis of dithieno-phospholide from

bi(dithienophosphole) using sodium metal (or equivalent reagents) *in-situ* to observe the formation of derivatives with P–C and P–P bonds.

4.2.1. Synthesis of Dithieno-phospholide Sodium Complex

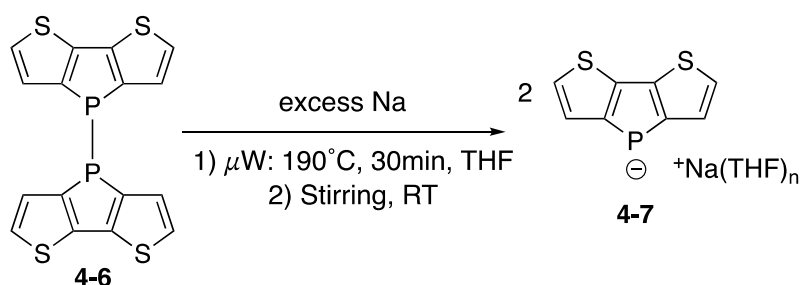


Scheme 4-3. Synthesis of dithieno-phospholide complex, 4-7 using sodium metal.

Synthesis of dithieno-phospholide using sodium metal: The traditional synthetic pathway reported in the literature, which involves stirring a biphosphole solution with elemental sodium under ambient conditions to facilitate the creation of the corresponding phospholide species, does unfortunately not readily extend to bi(dithienophosphole)s (Scheme 4-3a).^{7,6,30} In contrast, subjecting the corresponding solution to sonication led to the emergence of a slightly greenish solution accompanied by the formation of a finely dispersed black precipitate (Scheme 4-3b). Examination of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of this mixture revealed the presence of two distinct

peaks: one at -37 ppm assigned to **4-6** and another at -82.2 ppm, appearing in a ratio of 1:1.3. These shifts in the NMR spectrum, along with the alteration in solution color, suggested a reaction yielding nano-particulate sodium metal, coordinated with the P atoms of **4-6** through an η^1 complexation mode, resulting in the formation of **4-6'**.³⁹

Interestingly, no observable change occurred upon prolonged exposure to similar reaction conditions, implying that the aromatic solvent (toluene) employed is not able to sufficiently stabilize a molecular sodium phospholide species in solution. Consequently, it prevented the extraction of molecular P-species from their nano-particulate state, thus thwarting the generation of the desired dithieno-phospholide species. This hypothesis gained was further confirmed through an experiment where a solution of **4-6** in dry THF underwent sonication for 18 hours. The initial yellow solution transitioned into a brown solution with a discernible violet fluorescence (Scheme 4-3c). Notably, the ^{31}P NMR spectrum exhibited a sole peak at 12.8 ppm (SI), consistent with the analogous species recently reported by Liu et al. that exists as weakly coordinating ion pair, thereby lending support to the creation of the corresponding dithieno-phospholide sodium complex **4-7**, stabilized by THF (See SI section 4.1).³⁵



Scheme 4-4. Synthesis of dithieno-phospholide sodium complex, **4-7** using a microwave reactor.

Based on these observations, it becomes evident that the coordination of the P atom with the metal within a donor solvent environment plays a pivotal role in facilitating the cleavage of the P–P bond

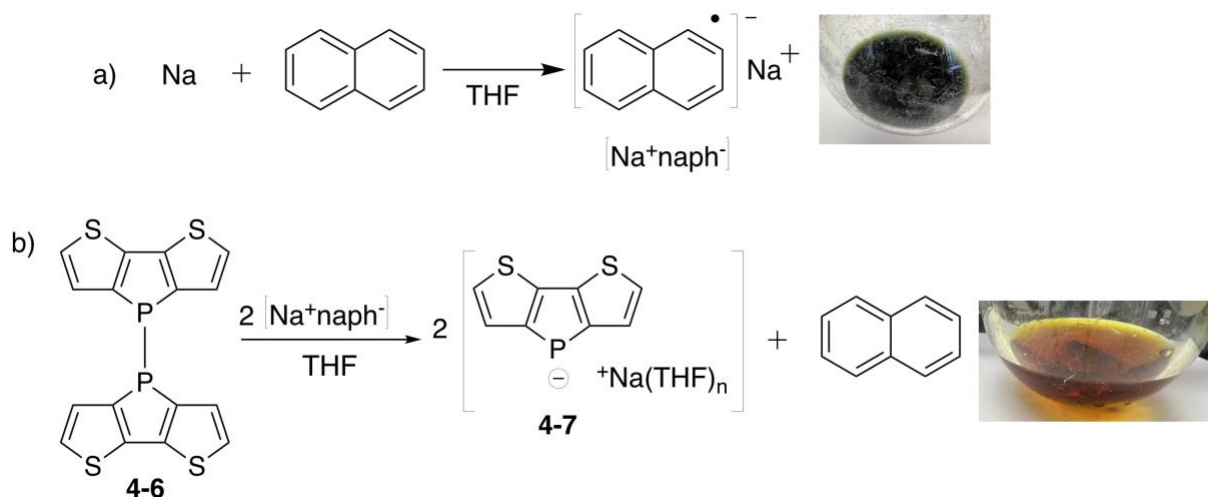
in compound **4-6**.⁵ To enhance metal coordination and expedite the reaction, a solution containing an excess of sodium metal was subjected to microwave irradiation under elevated temperature and pressure conditions (Scheme 4-4). Remarkably, within a 30-minute timespan, the reaction yielded a solution with a green hue, accompanied by the formation of a black precipitate, as previously noted. Capitalizing on the expanded surface area afforded by the activated metal, the solution's colour gradually transitioned to brown overnight at RT, leading to the formation of compound **4-7**. Despite these advancements, attempts to isolate the product from the suspension containing an excess of fine sodium metal particles through a range of filtration and chromatographic techniques conducted under an argon atmosphere proved futile (See SI section 4.1).

During the progress of these studies, the Liu group reported on the synthesis of similar dithieno-phospholide complexes that have been stabilized using various metals and crown ethers.³⁵ As a result, the isolation of the dithieno-phospholide species **4-7** was set aside, redirecting our attention to enhancing the dithieno-phospholide functions through strategic modifications, which were not the focus of the Liu group anyway. However, the attempt to functionalize **4-7** with chlorodiphenylphosphine (Ph_2PCl) was not successful and is attributed to the excess sodium metal present in the reaction mixture (*vide infra*).

Synthesis of dithieno-phospholide using sodium naphthalenide: Considering the detrimental effects of excessive metal presence on subsequent reactions, the use of sodium naphthalenide was explored as it allows to precisely match the stoichiometry of the reaction. Moreover, the formation of **4-7** generates naphthalene as a secondary product, which can be conveniently removed from the reaction mixture.

Sodium naphthalenide was synthesized by a well-established procedure from the literature, employing dry THF as the solvent.^{40,41} Upon the addition of a half equivalent of **4-6** directly into

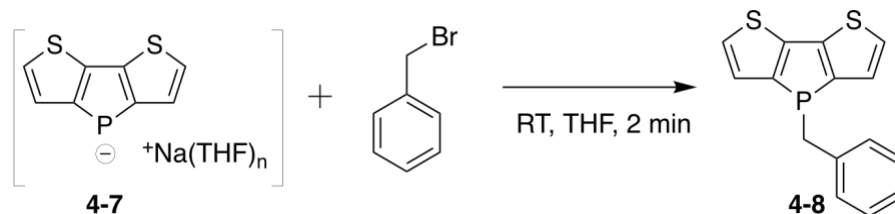
this solution, the initially profound green hue promptly changed to a golden yellowish-brown shade (Scheme 4-5). The visual change suggested the successful formation of **4-7**, which was further confirmed by ^{31}P NMR spectroscopy. Notably, this approach boasts several advantages over the previously discussed reactions, including a remarkable reduction in reaction time, and no need for elevated temperatures or pressure, as well as the absence of any excess reducing agent that could impede subsequent reactions, or additional by-products. (See SI section 4.1)



Scheme 4-5. Two-step synthesis of dithieno-phospholide complex **4-7** using sodium naphthalenide.

4.2.2 Functionalization of Dithieno-phospholide

Having established a convenient pathway for the synthesis of dithieno-phospholide, we then explored its potential as a versatile building block for generating derivatives featuring diverse phosphorus-heteroatom bonds. Our initial approach focussed on reagents with reactive halogen substituents, positioned strategically at targeted heteroatomic sites, to engage in straightforward salt metathesis reactions with **4-7**, as outlined in Scheme 4-1b.

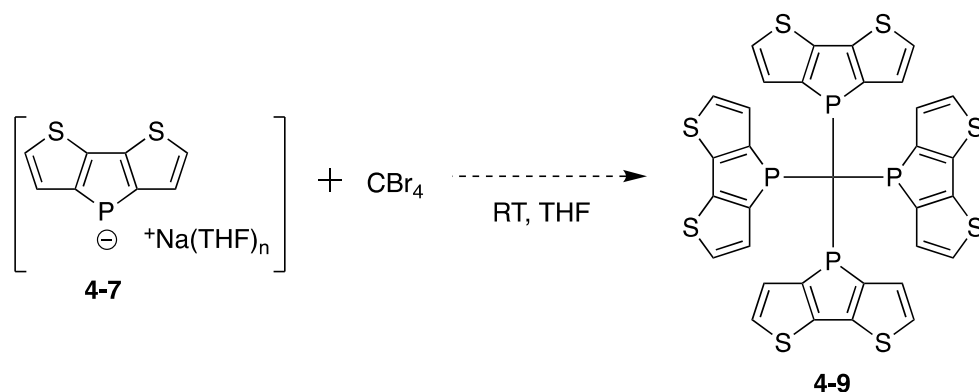


Scheme 4-6. C-Functionalization of **4-7** with benzyl bromide to generate **4-8**.

The first target was the *P*-benzylated species **4-8**, as it had been reported by us previously (but synthesized by our traditional approach via BzPCl_2).⁴² Upon addition of one equivalent of benzyl bromide to a solution of **4-7**, the solution's brown hue rapidly transformed into a lighter appearance (Scheme 4-6). The isolation of the product was achieved via a simple alumina plug under argon to afford pure **4-9**, as determined by multinuclear NMR spectroscopy. The observed singlet peak at -19.6 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum as well as the peaks in the ^1H NMR spectrum closely matched the literature-established values for this compound (See SI Section 4.1 for details).⁴² Remarkably, the absence of any other detectable by-products underscores both the efficiency of the P–C bond formation, and it illuminates the potentially vast spectrum of derivatives that should be accessible by this very simple, straightforward strategy.²⁹ (See SI section 4.1)

To further explore the scope of C-functionalization possibilities of the dithieno-phospholide, the synthesis of **4-9** was attempted (Scheme 4-7). When 0.25 equivalents of carbon tetrabromide (CBr_4) was added directly into the solution of **4-7**, the brown hue of the solution promptly intensified. However, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture revealed few peaks, none of which corresponded to the anticipated product, **4-9**. While CBr_4 provides a $\text{sp}^3\text{-C}$ towards salt metathesis, it is also well-known to undergo Appel⁴³ and Corey-Fuchs reactions⁴⁴ in presence of a phosphine to generate bromine cations. This cation could react with the phospholide to make the corresponding brominated species that eventually gave **4-6** as the major product of the mixture (See SI Section 4.1 for details). In addition to this reactivity, the steric hindrance posed by the four

dithienophosphole moieties could also contribute to the unsuccessful synthesis of **4-9**. (See SI section 4.1)



Scheme 4-7. C-Functionalization of **4-7** with carbon tetrabromide to generate **4-9**.

Formation of a P–P bond: In addition to investigating C-functionalization, a brief exploration of P-functionalization of dithieno-phospholide was also conducted, yielding some intriguing findings. The synthesis of P-functionalized derivatives was also targeted through the same straightforward salt metathesis, as shown in Scheme 4-1b. This method involved the reaction of compound **4-7** with species of type EX = Ph₂PCl, PhPCl₂, and PCl₃ resulting in the creation of new derivatives.

Notably, the derivatives of particular interest, namely **4-10**, **4-11** and **4-12**, were subjected to structural optimization using DFT at the B3LYP/6-31G(d) level of theory, prior to their synthesis. The optimization revealed HOMO-LUMO gaps of 3.86 eV, 3.68, and 3.39 eV for derivatives **4-10**, **4-11**, and **4-12** respectively. Examination of the MOs highlighted the predominant localization of HOMO and HOMO-1 orbitals on the dithieno-phosphole unit, with P-lone pair contribution in HOMO-1 of **4-10**. The LUMO and LUMO+1 levels are delocalized on the π -system of the dithienophosphole involving the σ^* orbitals, except for the LUMO+1 of **4-11**. Strikingly, the structure of compounds with multiple dithienophosphole units (**4-11** and **4-12**) optimizes with

intramolecular π -stacking interaction between these scaffolds, that could presumably lead to stability in these systems.

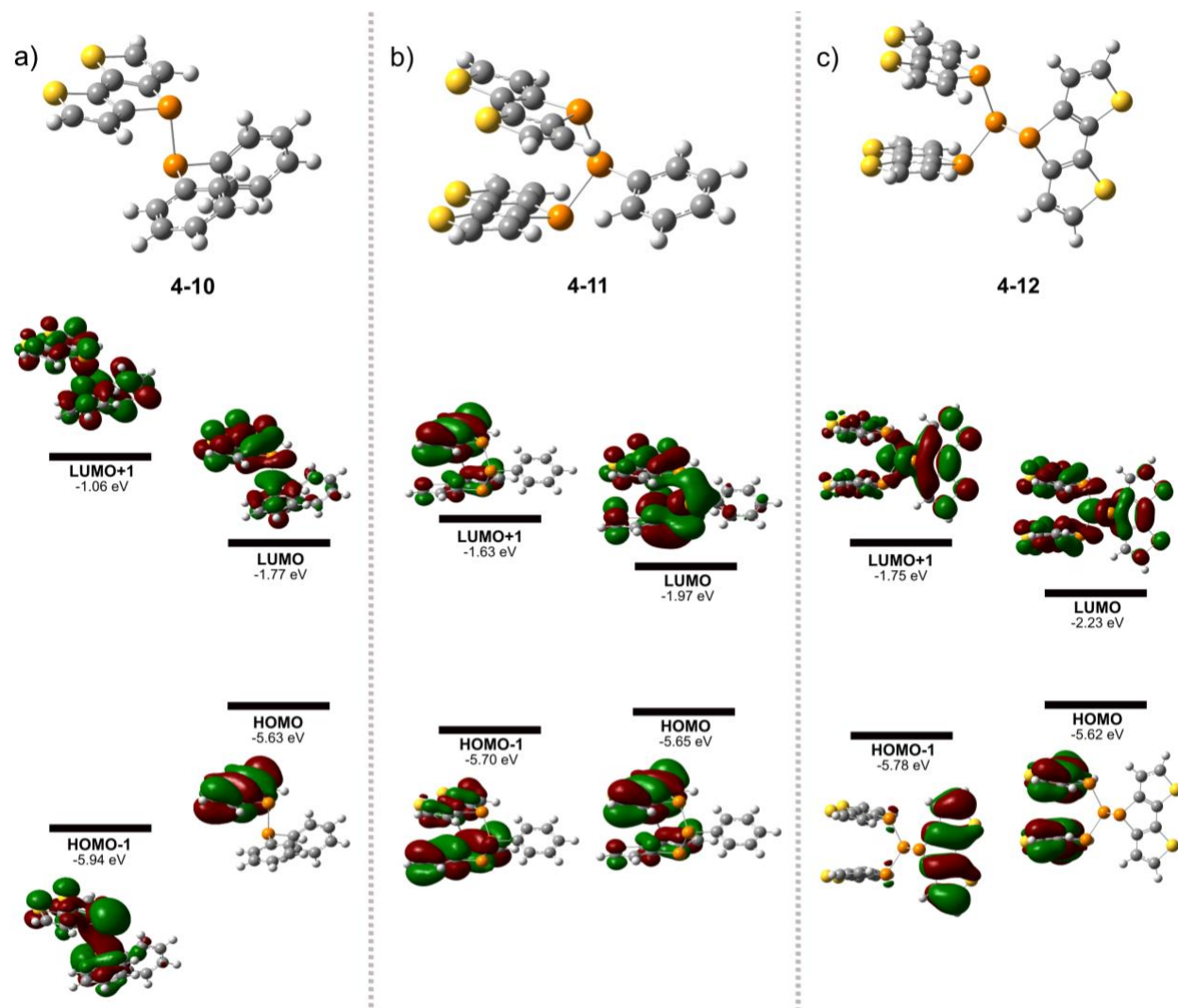
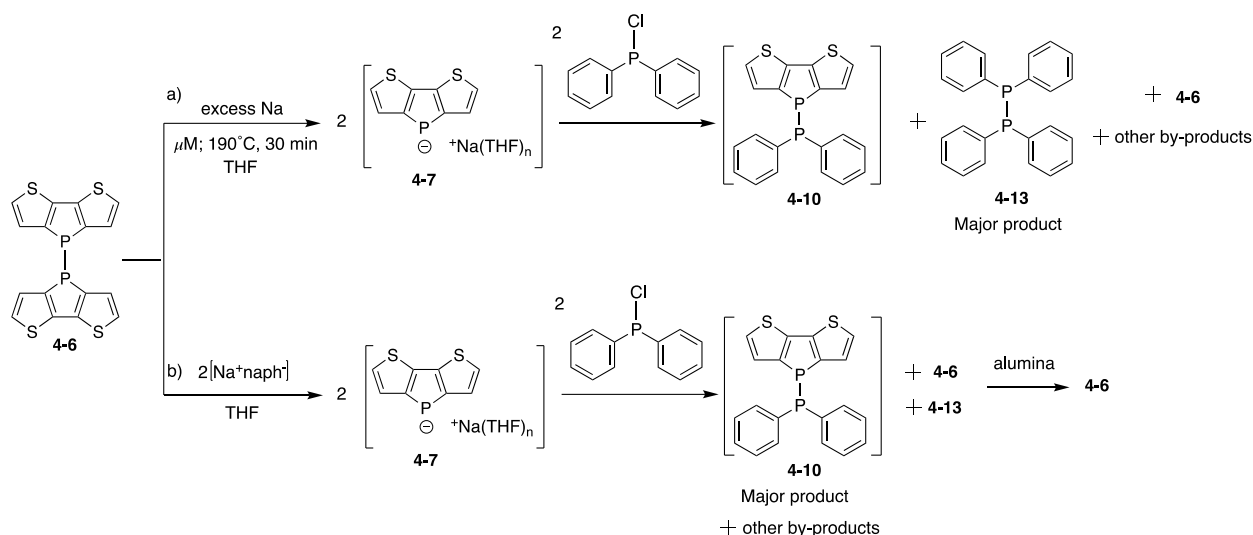


Figure 4-3. FMOs of **4-10**, **4-11** and **4-12** calculated using DFT at the B3LYP/6-31G(d) level of theory.

The *P*-functionalization of dithieno-phospholide was initially attempted by using dithieno-phospholide produces through microwave reaction of **4-6** with excess sodium metal. On addition of an equimolar amount of Ph_2PCl to this mixture, the brown colour of the solution immediately turns to pale yellow with bluish-green fluorescence (Scheme 4-8a). However, $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy revealed the formation of a mixture of products, instead of selective synthesis **4-10**.

The main peak in the spectrum corresponded to unreacted Ph_2PCl , in addition to a significant amount of both **4-6** (-37 ppm) and **4-13** (-15 ppm) in the mixture. Nonetheless, two promising doublets at -3.7 ppm and -38.4 ppm with $^1J_{\text{P-P}}$ of 239 Hz were also present in the spectrum (Figure 4-4), supporting the formation of the desired dithienophosphole **4-10** in principle.^{45,46,47,48}



Scheme 4-8. P- Functionalization of **4-7** with Ph_2PCl to generate **4-10**.

The significant formation of the by-products, specifically **4-13** was assumed to be a side reaction of excess activated Na metal with Ph_2PCl .⁴⁹ This reaction was thus repeated with dithienophospholide synthesized using sodium naphthalenide as this route eliminated the possibility of any unwanted reactivity of excess metals with reagents (Scheme 4-8b). The resulting solution underwent a similar colour change as before – from brown to yellow, though with a much weaker resulting fluorescence. However, the spectral data revealed similar observation as above, even though the ratio of the anticipated product **4-10** was higher in this scenario. In an attempt to optimize the reaction conditions to improve the reaction's selectivity, temperature, reaction time, order of component addition, and the influence of the reducing metal were modified. However, despite these attempts, none led to the selective or preferred synthesis of **4-10**. Interestingly, in an

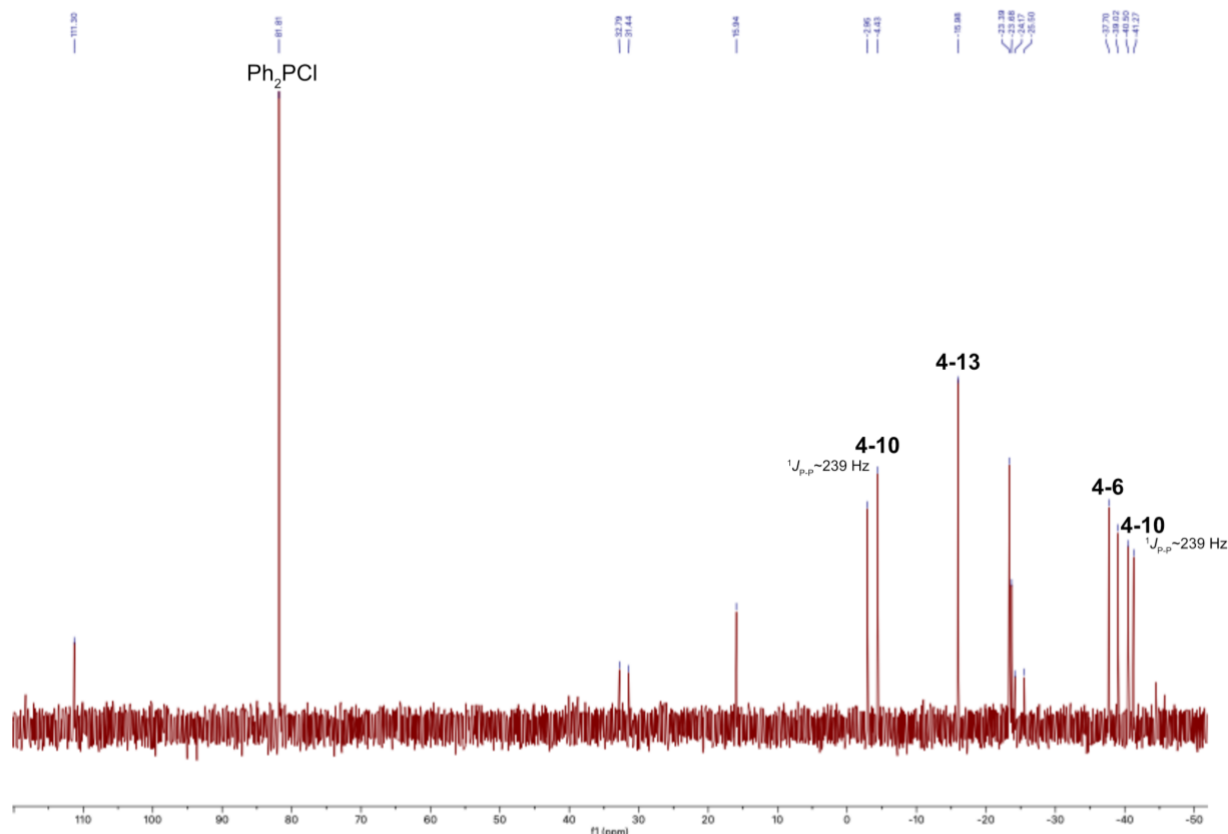
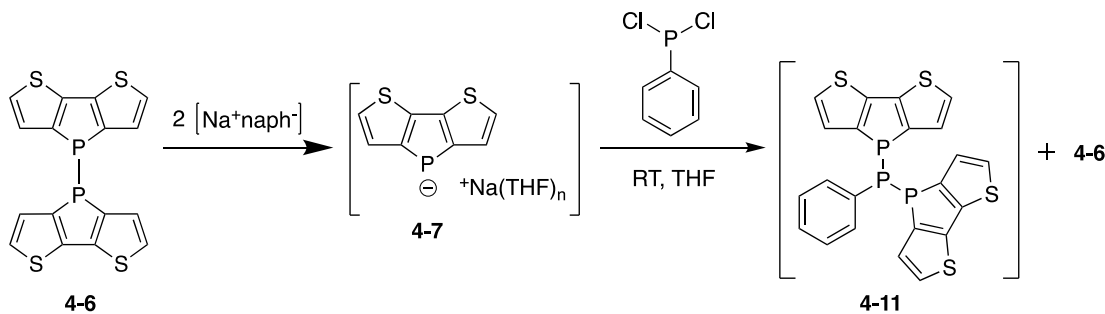


Figure 4-4. ^{31}P NMR (162 Hz, THF) spectroscopy of the reaction mixture in Scheme 4-8a within 15 minutes of reaction.

attempt to isolate the desired product from this mixture via an alumina plug, **4-10** was found to revert back to the precursor **4-6** via P scrambling – a phenomenon documented for related compounds in the literature.^{21,24} This observation supports the notion that the newly formed P–P bond in **4-10** is inherently unstable and quickly breaks down in the solution, seemingly unaffected by the conditions governing its creation or isolation.



Scheme 4-9. P-Functionalization of **4-7** with PhPCl_2 to generate **4-11**.

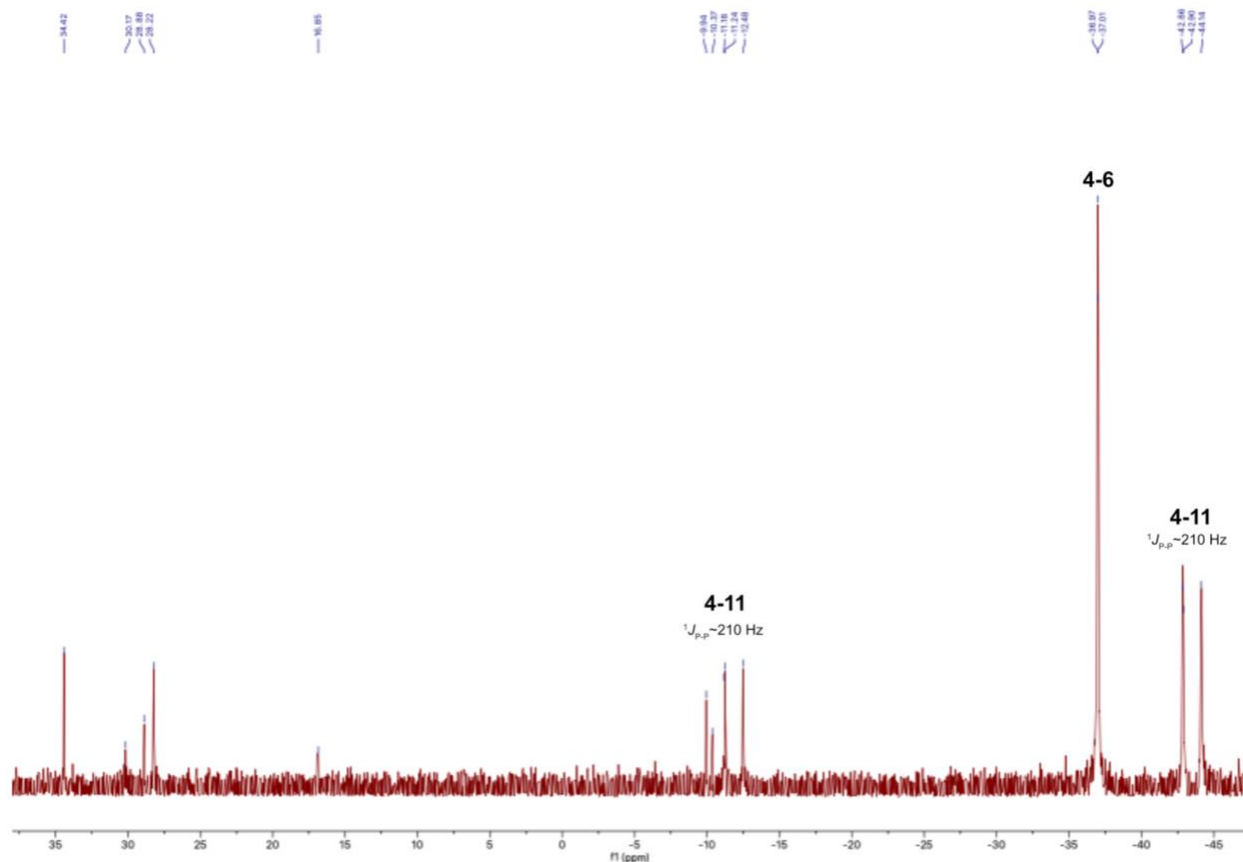


Figure 4-5. ^{31}P NMR (162 Hz, THF) spectroscopy of the reaction mixture shown in Scheme 4-9 within 15 minutes of reaction.

By contrast, the computationally optimized configuration of **4-11** (Figure 4-3b) demonstrates a promising π -stacking interaction between its two dithienophosphole units. We anticipated that this interaction would provide intramolecular stabilization to this derivative by mitigating the proclivity for P-scrambling. Reaction of dichlorophenylphosphane (PhPCl_2) with **4-7** (Scheme 4-9), led the solution change color from brown to yellow. However, immediate ^{31}P NMR spectroscopic analysis revealed a mixture of products within the solution in analogy to the reaction with Ph_2PCl . While the **4-6** remained the dominant constituent, the spectrum exhibited a doublet of doublet (dd) at -11.2 ($^1J_{\text{P-P}} \sim 210$ Hz) ppm, and a doublet (d) at -43.5 ppm ($^1J_{\text{P-P}} \sim 210$ Hz). The distorted doublet of doublets corresponded to the central phenyl-P, asymmetrically coupled to two dithienophospholes, whereas the doublet originated from spatially inequivalent

dithienophosphole-P to show 1:1:2 ratio, suggesting the presence of **4-11** within the mixture (Figure 4-5).^{45,46,47,48}

Despite the envisioned enhancement of stability in **4-11** through the potential π -stacking interactions, as predicted by the DFT calculations, **4-11** displayed behavior reminiscent of **4-10**. Notably, the flexible and still labile P–P bond facilitated P-scrambling, resulting in the decay of **4-11** and the regeneration of **4-6**, in addition to several other, to date unidentified phosphorus-containing species. These reactions support the fleeting nature of *P*-functionalized dithienophospholes and emphasize the dynamic reactivity of **4-7**.

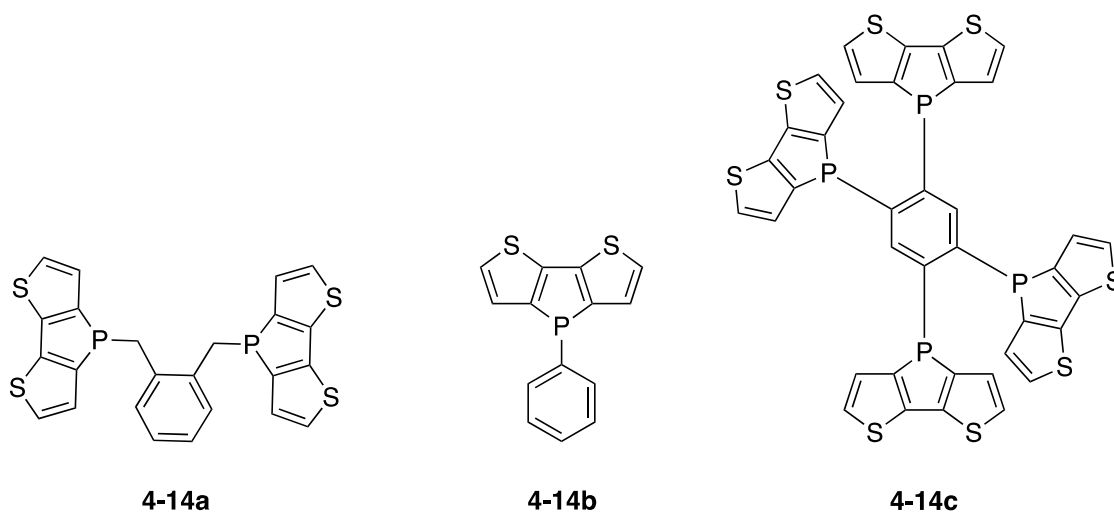


Figure 4-6. Select examples of prospective derivatives for P–C functionalization.

The present findings offer a promising pathway for the synthesis of dithieno-phospholide. They also underscore the adaptable nature of this anion, making it suitable for straightforward salt-metathesis processes. However, the success of this reaction in principle must be complemented by the stability of the targeted species, which is crucial in realizing the full synthetic potential of the phospholide. Consequently, our current focus is directed towards identifying new, stable targets that are resistant to decomposition, particularly through P-scrambling. To this end, we will explore the functionalization of sp^2 -C to enable the simultaneous transfer of multiple dithieno-phospholide

units (**4-14a**).²⁹ Furthermore, we will investigate the reactivity of this anion with sp^3 -C (**4-14b,c**) and conduct comprehensive photophysical and electrochemical characterizations of these systems (Figure 4-6).⁵⁰

4.3 Conclusion

In conclusion, the investigation into the synthetic access of dithieno-phospholides from the corresponding bi(dithienophosphole)s and their reactivity has revealed an intriguing realm of chemical behavior and potential applications. The synthesized dithieno-phospholides, characterized by their unique reactive properties, hold significant promise as versatile building blocks for functional conjugated materials. The successful development of a controlled synthetic pathway for dithieno-phospholide sodium complexes, employing sodium naphthalenide, exemplifies the adaptability of these compounds in crafting precise molecular structures.

The formation of P–C and P–P bonds through strategic functionalization underscores the potentially rich chemistry that dithieno-phospholides offer in principle. The ease with which P–C bonds are created showcases the practical utility of these compounds as effective tools for organic synthesis. Furthermore, the transient nature of P-functionalized derivatives, highlighted by the observed P-scrambling, emphasizes the dynamic character of these phospholides. While the challenge of stabilizing certain *P*-functionalized derivatives remains, the potential for harnessing their unique reactivity in catalytic processes and material science applications is undeniable.

While several aspects still need to be further developed and solidified, this initial proof-of-concept work nonetheless offers invaluable insights into the domain of dithieno-phospholide chemistry, laying a solid groundwork for forthcoming investigations. While the scope of the projects extends to the formation of phosphorus-heteroatom bonds such as P–P, P–B and P–Si bond, a major and

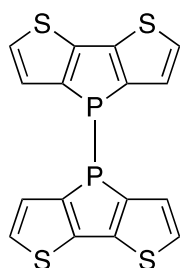
immediate focus will be in broadening dithieno-phospholide functionalization, particularly through the incorporation of P-(sp^2 -C) and P-(sp^3 -C) bonds using the straightforward salt metathesis approach. Simultaneously, the transferability of dithieno-phospholide synthesis to other electronically modified bi(dithienophosphole)s is also under consideration as a short-term goal.

4.4 Experimental section

General. All reagents were purchased from Sigma Aldrich and Oakwood Chemical. All solvents were purchased from Sigma Aldrich and Fisher chemical. SPS grade solvents (MBraun) from Sigma Aldrich were used for synthesis and characterization.

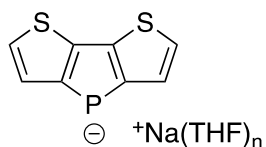
Nuclear Magnetic Resonance (NMR) spectroscopy: ^1H , $^{31}\text{P}\{^1\text{H}\}$, $^{19}\text{F}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$ spectra were acquired on Bruker NEO 700, 600, 400 and 300 NMR spectrometers on a 5mm ATM probe using TOPSPIN software version 4.0.8. Chemical shifts are reported in parts per million (ppm). Multiplicities are reported as: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), multiplet (m), quartet (q), and broad (br).

Synthesis of bi(dithienophosphole) **4-6**



P-pyrrolidinyl-dithienophosphole (**4-6'**) was synthesized according to the literature.³⁶ Compound **4-6a** (3.51g) of was dissolved in 10 ml dry THF. One equivalent of BF_3 was added to the solution and the solution was reacted in a microwave reactor at 190°C for 20 minutes. The solution was passed through a silica plug under argon. The solution was dried to yield a yellow solid at 10% yield (0.5g). The NMR data corresponded to the reported values in ref. 36.

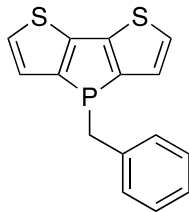
Synthesis of dithieno-phospholide **4-7**



Using sodium metal and microwave reactor. Compound **4-6a** (0.27 g, 0.7 mmol) was dissolved in 15 ml of dry THF, and an excess piece of sodium metal was added to the solution. The mixture was reacted in a microwave reactor at 190°C for 30 minutes, resulting in a green colour solution with a black precipitate. The solution was stirred overnight, yielding a brown suspension with excess metal. The reaction mixture exhibited complete conversion of starting material to **4-6**. $^{31}\text{P}\{^1\text{H}\}$ (162 MHz, THF): δ 12.3 ppm. Attempts to isolate the product from the suspension of excess fine sodium metal particles using various filtration and chromatographic techniques under argon were unsuccessful, leading to the decomposition of the phospholide.

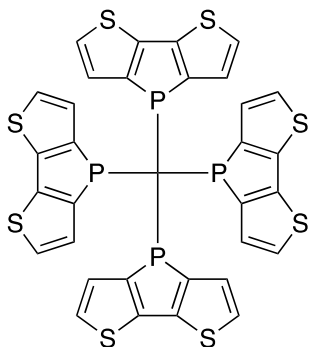
Using sodium naphthalenide. Naphthalene (1 μmol , 0.012g; 2 equiv.) was dissolved in 8 ml of dry THF. Following this, a small excess piece of sodium metal was introduced into the solution. The mixture was left to stir under an argon atmosphere, and within ten minutes of introducing the metal, the color of the solution transitioned from colorless to a deep green, confirming the successful formation of sodium naphthalenide [Na^+naph^-]. Stirring of the reaction mixture continued for two hours to ensure the complete reaction of the naphthalene. Subsequently, the sodium metal fragments were carefully extracted from the solution using tweezers. Continuing the procedure, one equivalent of **4-6** (0.5 μmol , 0.018g) was introduced directly into the solution while stirring. $^{31}\text{P}\{^1\text{H}\}$ (162 MHz, THF): δ 14.8 ppm.

Synthesis of **4-8**



Naphthalene (0.028g, 0.2 mmol) was dissolved in dry THF (5 ml) and a small piece of sodium metal was added to this solution. The solution was stirred for two hours to yield $[\text{Na}^+\text{naph}^-]$. The excess unreacted sodium was removed with a spatula and 0.1 mmol (0.043g) of **4-6** was directly added to this solution with stirring. The solution colour changed to brown immediately. After stirring for ten minutes, one equivalent (0.2 mmol, 0.037 g) of benzyl bromide was introduced directly into the reaction mixture under an argon atmosphere with continuous stirring. Within a mere two minutes of this addition, the solution's brown hue shifted to a pale-yellow translucent appearance. The mixture was stirred for 30 minutes and was meticulously passed through an alumina plug under argon, yielding pure **4-8** at 85% yield (0.051g). $^{31}\text{P}\{^1\text{H}\}$ (162 MHz, THF): δ -19.6 ppm. ^1H NMR (400 MHz, CDCl_3): δ 7.22 (m, 5H), 7.01 (d, $^3J_{\text{H-H}} \sim 4\text{Hz}$, 4H), 3.15 (s, 2H). residual solvent identified.

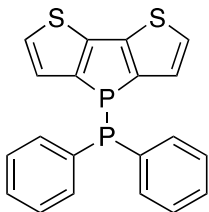
Synthesis of **4-9**



Naphthalene (0.026g, 0.2 mmol) was dissolved in dry THF (5 ml) and a small piece of sodium metal was added to this solution. The solution was stirred for two hours to yield $[\text{Na}^+\text{naph}^-]$. The excess unreacted sodium was removed with a spatula and 0.1 mmol (0.039g) of **4-6** was directly added to this solution with stirring. The solution colour changed to brown immediately. After stirring for ten minutes, half an equivalence (0.05 mmol, 0.017 g) of carbon tetrabromide (CBr_4) was introduced directly into the reaction mixture under an argon atmosphere with continuous stirring. The solution's brown hue intensified with in 3 minutes of

addition. The $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectrum of the reaction mixture do not show peaks corresponding to the anticipated product, **4-9**, but rather shows **4-6** as the major product.

Synthesis of **4-10**



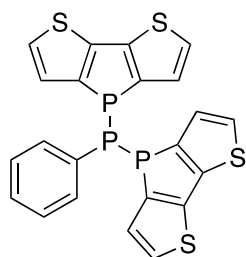
By microwave reaction. Compound **4-6** (0.1 g, 0.3 mmol) was dissolved in 6 ml of dry THF, and an excess piece of sodium metal was added to the solution.

The mixture was reacted in a microwave reactor at 190°C for 30 minutes and was stirred overnight under argon to yielding a brown solution with excess metal. Two equivalences of Ph_2PCl (0.5 mmol, 0.12g) was added with stirring. The solution colour immediately transformed to pale yellow, displaying a distinct bright greenish-blue fluorescence. The ^{31}P NMR spectroscopy of the reaction mixture was obtained within 15 minutes, revealing a mixture of products, with **4-13** being the major product.

Using sodium naphthalenide. Naphthalene (0.018g, 0.1 mmol) was dissolved in dry THF (5 ml) and a small piece of sodium metal was added to this solution. The solution was stirred for two hours to yield $[\text{Na}^+\text{naph}^-]$. The excess unreacted sodium was removed with a spatula and 0.07 mmol (0.027g) of **4-6** was directly added to this solution with stirring. The solution colour changed to brown immediately. After stirring for ten minutes, two equivalence (0.1 mmol, 0.031 g) of Ph_2PCl was introduced directly into the reaction mixture under an argon atmosphere with continuous stirring. The solution colour immediately transformed to pale yellow, displaying an albeit less intense greenish-blue fluorescence. The ^{31}P NMR spectroscopy of the reaction mixture was obtained within 15 minutes, revealing a mixture of products akin to the earlier reaction. However, this mixture shows peaks corresponding to **4-10** at higher intensity, suggesting better

selectivity of reaction by this method. On passing the solution through an alumina plug, **4-10** completely transformed to **4-6**.

Synthesis of **4-11**



Naphthalene (0.024g, 0.2 mmol) was dissolved in dry THF (5 ml) and a small piece of sodium metal was added to this solution. The solution was stirred for two hours to yield $[\text{Na}^+\text{naph}^-]$. The excess unreacted sodium was removed with a spatula and 0.09 mmol (0.036g) of **4-6** was directly added to this solution with stirring. The solution colour changed to brown immediately. After stirring for ten minutes, one equivalence (0.09 mmol, 0.017 g) of PhPCl_2 was introduced directly into the reaction mixture under an argon atmosphere with continuous stirring. The solution colour changed to pale brown and the ^{31}P NMR spectroscopy of this mixture was obtained within 15 minutes, revealing a mixture of products with **4-6** being the major product.

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CHAPTER FIVE: CONCLUSION AND OUTLOOK

5.1 Summary and Conclusions

This thesis focuses on the structural modification of phosphorus atoms in dithienophospholes to tailor their properties for practical material applications. Throughout the Chapters, various methods were explored to manipulate the spatial arrangement of dithienophospholes, shedding light on their characteristics and potential applications.

Chapter Two delved into hypervalency and the synthesis of geometrically constrained pentacoordinate dithienophospholes, showcasing their unique chemical reactivity. These derivatives deviated from their predicted 3BP geometry, adopting 4SQ structures with pronounced Lewis-acidic phosphorus centers. Section 1 of this Chapter introduced these pentacoordinate species as LAs and detailed their intriguing reactivity with ambient moisture, resulting in crystal-to-crystal changes. Additionally, these compounds display fluoride abstraction capabilities, forming hexacoordinate P-species that facilitate challenging organic transformations, such as C–O bond activation in deoxyaryloxylation reactions. The subsequent section explores a novel series of pentacoordinate dithienophospholes as stable and neutral LAs, synthesized through electronic and geometric modifications of the quinone or dithieno-scaffold. The strategic introduction of bulky substituents reduces strong supramolecular interactions, altering the geometry from the conventional 4SQ to a distorted 3BP configuration. Notably, derivatives with dithieno-scaffold modifications exhibit significantly enhanced FIA values, forming hexacoordinated fluoride adducts that accelerate organic transformations. The study also unveiled hydride abstraction reactions mediated by phosphorus, resulting in the formation of the original trivalent

dithienophosphole precursor. The exploration of metal coordination to the quinone moiety significantly amplified the Lewis acidity of the phosphorus center.

Chapter Three aims to enhance less-explored bi(dithienophosphole)s through strategic modifications to their π -scaffold. Two approaches were pursued: electronic modifications and the introduction of bulky substituents to influence P–P bond rotation. Electronic modification of the π -scaffold alleviates the dependence on LAs for cleaving the exocyclic P–N bond of *P*-pyrrolidinyl-dithienophosphole during the formation of bi(dithienophosphole). This Chapter details a new mechanism involving phospholide intermediates. The structure of bi(dithienophosphole)s with bulky substituents was elucidated through X-ray crystallography, revealing twisted configurations that disrupted π -stacking interactions and resulted in more relaxed bulk packing. The absorption spectra of these derivatives display broad profiles with variable absorption maxima and bandgap values, depending on the electronic modifications. Remarkably, these compounds exhibit substantial emission properties with moderate quantum yields in both solution and the solid-state.

Chapter Four investigates the synthesis of dithieno-phospholides from bi(dithienophosphole)s and their reactivity. The successful development of a controlled synthetic pathway for dithieno-phospholide sodium complexes, using sodium naphthalenide, highlights the adaptability of these compounds in crafting precise molecular structures. The functionalization of this anion to form P–C and P–P bonds via a simple salt metathesis process, underscoring their practical utility in organic synthesis. The dynamic nature of *P*-functionalized derivatives, including P-scrambling, emphasizes their unique reactivity potential, although stabilizing some *P*-functionalized derivatives remains challenging. While numerous aspects require further development and

solidification, this initial proof-of-concept work provides invaluable insights into dithienophospholide chemistry, laying a robust foundation for future investigations.

5.2 Ongoing and Future Research

While the preceding Chapters have provided fundamental insights into the synthesis and properties of structurally modified dithienophospholes, the comprehensive understanding of their reactivity and potential real-world applications remains an area ripe for exploration, especially in chapters Three and Four.

5.2.1 Expanding the Reactivity Scope of Hypervalent Dithieno[3,2-*b*:2',3'-*d*]phospholes

Chapter Two extensively examined the synthesis and structural properties of pentacoordinate dithienophospholes. However, Section 1 faced limitations in exploring the Lewis-acidic nature of these species due to inhibitory π -stacking interactions, restricting the accessibility of nucleophiles to the Lewis-acidic P center. Consequently, the work in this section was limited to small nucleophiles like OH^- and F^- .¹ To address this challenge, Section 2 of this chapter aimed to mitigate π -stacking dimers by incorporating bulky substituents onto the π -scaffold. This approach broadened the range of reagents to include other polarizable organic substrates, particularly those with high polarizability.²

Chapter Two unequivocally demonstrated that geometric and electronic modifications to the π -scaffold, along with metal coordination to electron-rich centers, can enhance the Lewis acidity of these species.² Therefore, future research can extend to developing modified hypervalent compounds with even greater Lewis acidity. Preliminary attempts to synthesize such derivatives have yielded promising results (See SI section S.5.1). The reactivity of these species can be further explored by studying their reactions with various polarizable organic substrates, unveiling their

potential as stable and neutral LAs. Moreover, exploring the feasibility of closing the catalytic cycle, as indicated in Chapter Two, could provide insights into the practical utility of these derivatives in catalysis. This could be achieved by addition of appropriate *o*-quinone to the reaction mixture that underwent hydride abstraction to react with the trivalent dithienophosphole that is formed as a by-product to initiate another cycle of reaction (See SI Section S5.1).

5.2.2 Symmetrically and Asymmetrically Functionalized Bi(dithienophosphole)s

Recent advancements in conjugated main-group dimers highlight the significance of Chapter Three within the domain of biphosphole-based materials with practical applications.³⁻⁵ This Chapter provides in-depth insights into various electronically modified bi(dithienophosphole)s and their optical characteristics, yet their stability in the context of further functionalization remains uncharted.

The initial phase of stability analysis involves the post-functionalization of the P center of the synthesized bi(dithienophosphole)s. Compound **3-6** has been chosen for this purpose based on preliminary observations suggesting its potential for ambient oxidation, which opens the door to *P*-functionalization (refer to SI section 5.2). Since symmetric oxidation of unfunctionalized bi(dithienophosphole)s has not been reported previously,⁶ there is a strong aspiration to functionalize the P center of compound **3-6** through straightforward oxidation, generating of symmetric and asymmetric derivatives (Figure 5-1a).

Subsequently, the stability analysis will be complemented by post-functionalization of the π -scaffold of bi(dithienophosphole)s, employing two distinct approaches: 1) the deprotection of bulky groups in **3-5** (Figure 5-1b), and 2) the execution of a click reaction on the ethynyl

functionality of **3-7** (Figure 5-1c). Achieving these objectives will lay a solid foundation for harnessing the extensive potential of bi(dithienophosphole)s with outstanding material properties.

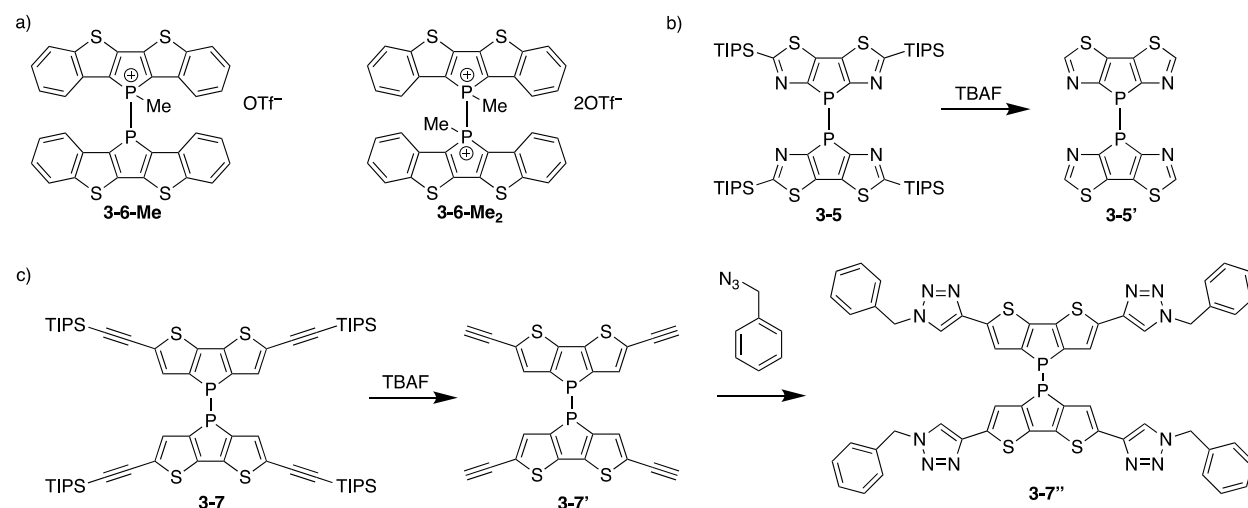


Figure 5-1. Post-functionalization of bi(dithienophosphole)s.

While the derivatives presented in Chapter Three display improved photophysical properties compared to the unfunctionalized system, they are electrochemically unstable. This presents an opportunity for improvement, as these materials are envisioned to be used as electron-acceptors in organic devices.⁷ Consequently, the design of derivatives with improved electrochemical properties is currently in progress. Given that the design of bi(dithienophosphole)s heavily relies on modifying the energy levels of FMOs, thereby reducing the HOMO-LUMO gap, various functionalities have undergone scrutiny using DFT calculations to screen for the most viable modifications. Among the many derivatives under scrutiny, **5-1a** and **5-1b** stand out as potential frontrunners. This distinction is primarily attributed to their small computationally calculated HOMO-LUMO gaps, measuring at just 2.9 eV and 2.86 eV, respectively. Intriguingly, both derivatives share a notable structural resemblance to the parent system, **3-2**, exhibiting a distorted step-like geometry.⁶ This structural feature suggests the possibility of advantageous photophysical

properties, electrochemical stability, and solid-state packing, which could be highly advantageous for practical device applications. (Figure 5-2, See SI Section S5.3)

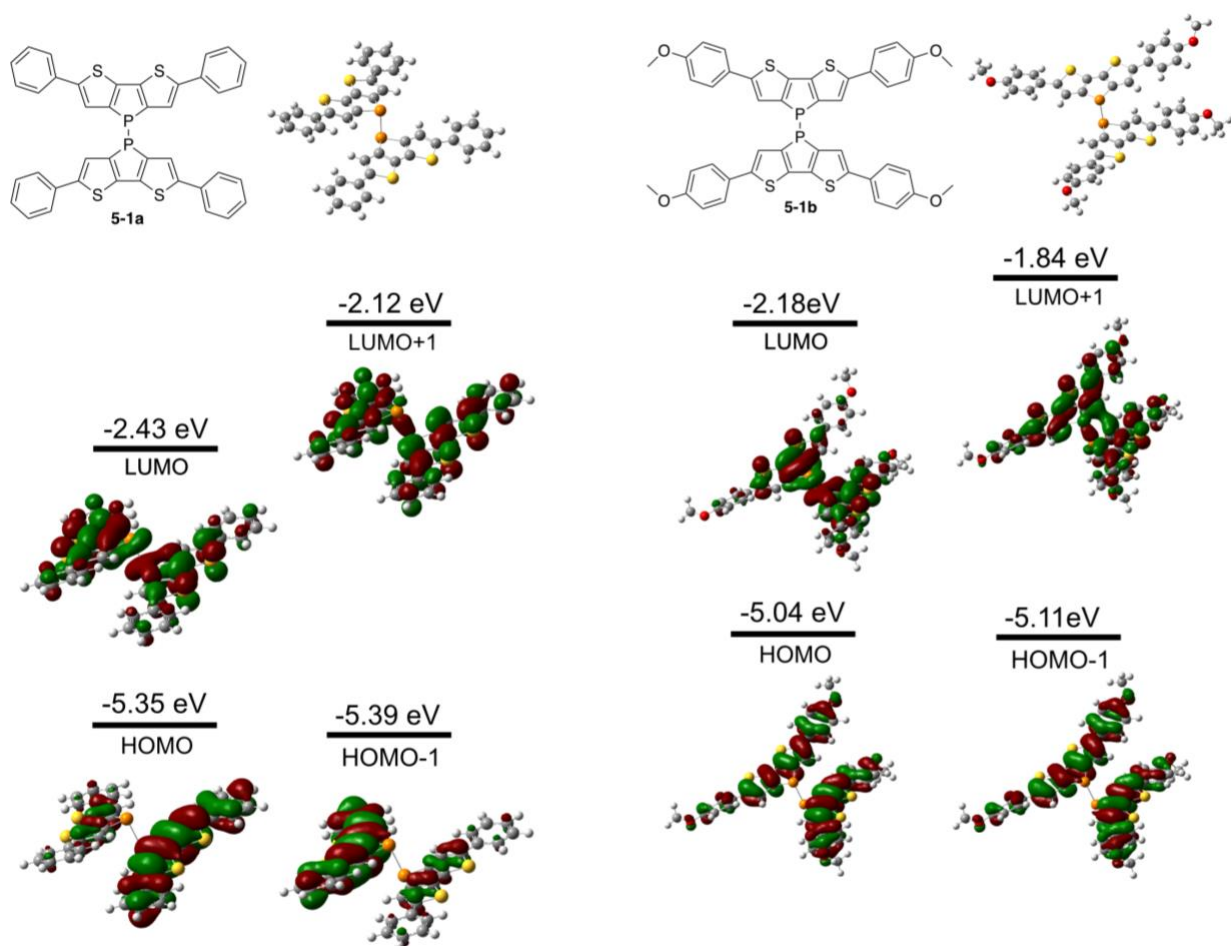


Figure 5-2. Prospective symmetric bi(dithienophosphole)s.

In a similar vein, asymmetrically functionalized π -cores have been shown to directly influence the FMOs of bi(dithienophosphole)s. These systems remain unexplored to date but hold promise for improved photophysical and electrochemical properties. Although our initial efforts to extend the LA-mediated synthesis route for these systems have faced setbacks, the insights derived from Chapter Three lay the groundwork for further exploration.

5.2.3 Exploring the Potential of Dithieno-phospholide Chemistry

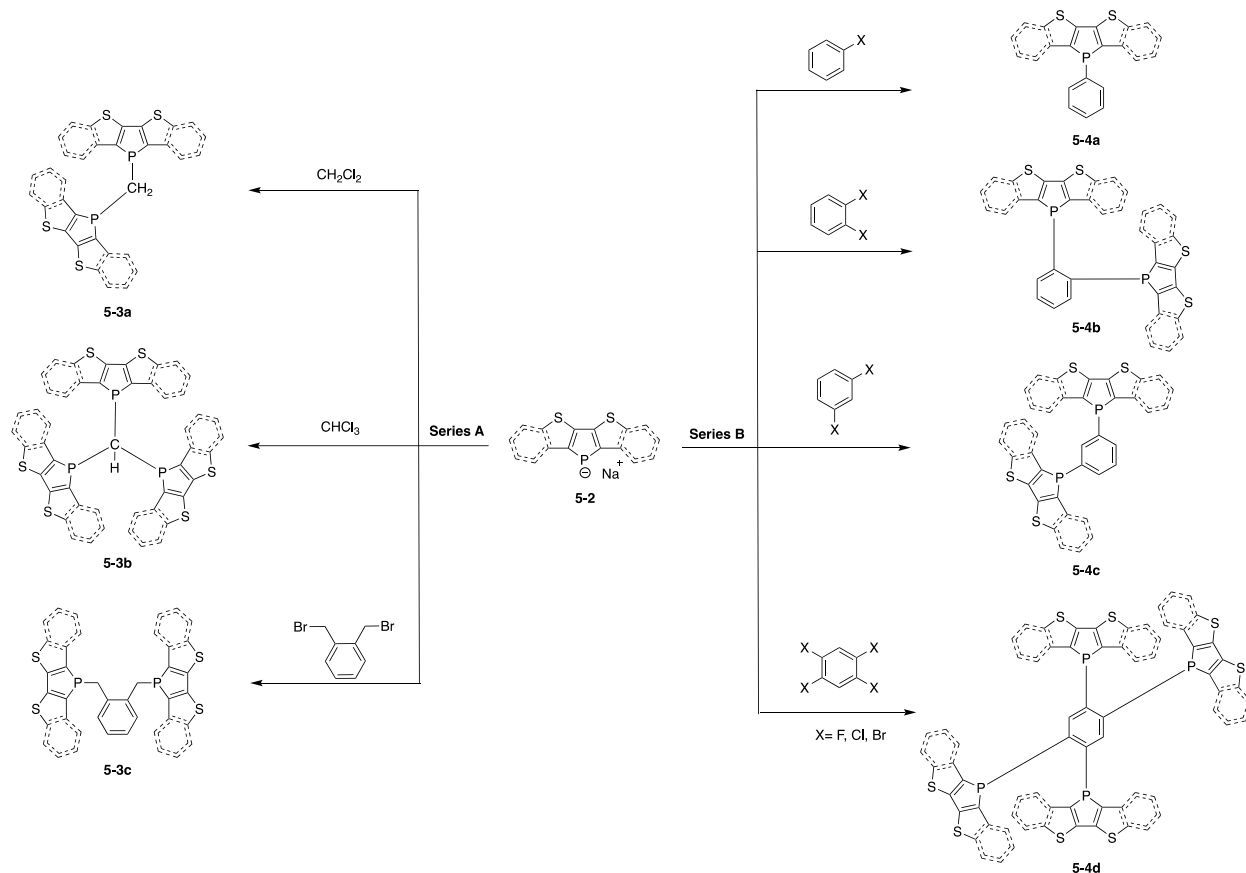


Figure 5-3. Some potential sp^3 -C and sp^2 -C functionalization of modified/unmodified dithieno-phospholide.

Chapter Four delves into bi(dithienophosphole)s as promising stable precursors for dithieno-phospholide synthesis, a compound with limited synthetic accessibility. Preliminary studies show that dithieno-phospholides possess immense potential as easily transferable agents for the synthesis of highly luminescent dithienophosphole derivatives. While Chapter Four examines the reactivity of these anions with stable reagents involving sp^3 -C and various P-Cl derivatives, the functionalization of sp^2 -C is left unexplored, highlighting their untapped potential as valuable synthons.⁸ Immediate research goals involve studying the reactivity of dithieno-phospholides with select sp^2 -carbon compounds while assessing preference/selectivity for various carbon-halogen

bonds. Although initial attempts to introduce multiple dithienophosphole units on sp^3 -C were unsuccessful, further exploration with less sterically encumbered reagents is planned (Figure 5-3). An essential aspect of dithieno-phospholide chemistry is understanding the conditions governing P–P cleavage of electronically modified bi(dithienophosphole)s to generate various dithieno-phospholide species. Investigating the reactivity of these extended/modified dithieno-phospholide species will provide a comprehensive understanding of their potential in both organic and material chemistry (Figure 5-3).

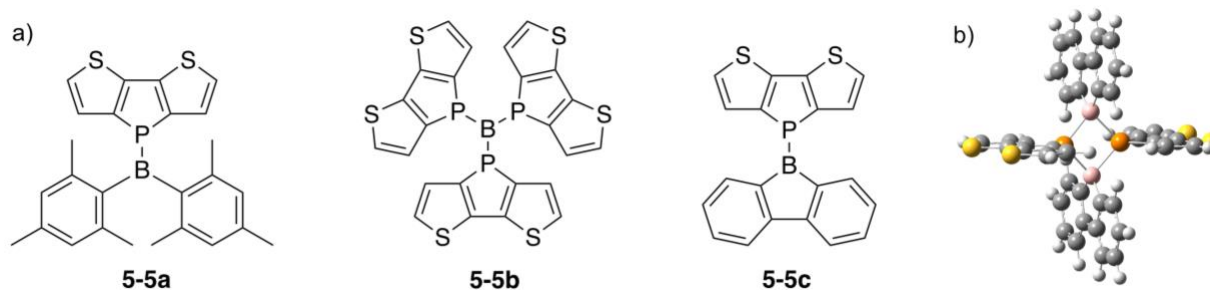


Figure 5-4. a) *B*-functionalization of dithieno-phospholide and b) optimized structure of **5-5c**.

While the discussion has primarily focused on *C*-functionalization and *P*-functionalization, preliminary computational analysis suggests that *B*-functionalization of dithieno-phospholide is another intriguing avenue worthy of exploration. Figure 5-4 shows some potential targets, with the optimized structure of **5-5c** standing out. These derivative exhibits intermolecular stabilization through dimerization and may prove valuable in catalytic and material chemistry.⁹

However, the chapters within this thesis successfully achieve spatial perturbations of dithienophospholes, resulting in materials exhibiting intriguing functional properties, often with unexpected outcomes. Throughout our exploration of diverse methods and strategies for effecting these structural modifications, it becomes apparent that the range of reactivity and properties displayed by these species is extensive, requiring further investigation. Thus, dithienophospholes

remain as a promising building block in the field of material chemistry, holding significant untapped potential.

5.3 References

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Supporting Information

Structural Modifications of Dithienophospholes for Applications as Functional Materials

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A Dissertation submitted to the Faculty of Graduate Studies
in partial fulfilment of the requirements for the degree of Doctor of Philosophy

Graduate Program in Chemistry

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CHAPTER TWO: PENTACOORDINATE HYPERVALENT DITHIENOPHOSPHOLES: A JOURNEY THROUGH REACTIVITY AND STRUCTURAL VARIATIONS

Chemical and experimental details

Materials and Methods: All reagents were purchased from Sigma Aldrich and Oakwood Chemical. Compounds **2-1**^{S1} and **2-2**^{S2} were prepared according to literature procedures. All solvents were purchased from Sigma Aldrich and Fisher chemical. SPS grade solvents (MBraun) from Sigma Aldrich were used for synthesis and characterisations. These solvents were further dried by passing them through neutral alumina, followed by three freeze-pump-thaw cycles.

Nuclear Magnetic Resonance (NMR): ¹H, ³¹P{¹H}, ¹⁹F{¹H}, ¹³C{¹H} spectra were acquired on Bruker NEO 700, 600, 400 and 300 NMR spectrometers on a 5mm ATM probe using TOPSPIN software version 4.0.8. Chemical shifts are reported in parts per million (ppm). Multiplicities are reported as: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), multiplet (m), quartet (q), and broad (br).

Elemental Analysis (EA): Elemental analysis was performed by using Vario EL Cube Elemental Analyzer. All runs were performed with approximately 5 mg of sample. Results were obtained in duplicates.

X-Ray Crystallography (XRD): The solid-state structures of the compound were determined using Bruker DQ Quest eco. The structures were solved and refined using OLEX2 software. Deposition

Number(s) 2044241 (for **2-1a**), 2044242 (for **2-1b**), 2044243 (for **2-2a**), 2044244 (for **2-2b**), 2044245 (for **2-1a • H₂O**), 2235915 (for **2-1c**), 2235916 (for **2-1e**), and 2235917 (for **2-6**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

UV-Visible Spectroscopy (UV-Vis): All absorption measurements were recorded on an Agilent Technologies Cary 5000 UV-Vis spectrometer at room temperature. All samples for UV-Vis experiments were run in solvents from Sigma Aldrich using 10 mm quartz cuvettes.

Emission and Photoluminescence (PL) measurements: All emission measurements were recorded using an Edinburgh FS5 spectrofluorometer. PLQY measurements were collected using integrating sphere; model SC-30 at room temperature. All solutions were prepared using solvents from Sigma Aldrich and measurements were acquired using 10 mm quartz cuvettes.

Electrochemistry measurements: All electrochemical studies were obtained using Metrohm Autolab potentiostat, with 0.1 M n-Bu₄NPF₆ (Sigma Aldrich, electrochemical grade) that was used after recrystallization from THF as electrolyte. The working, reference and counter electrodes used were glassy carbon, silver/silver chloride (Ag/Ag⁺) and platinum wire, respectively. The electrochemical measurements were carried out at room temperature in dry, degassed THF by bubbling argon through the solution for at least 5 min, and an argon flow was kept over the solution during measurements. The electrochemical cell was recorded using the software NOVA.

2.1 Structure-reactivity studies on hypervalent square-pyramidal dithieno[3,2-*b*:2',3'-*d*]phospholes

S.2.1.1 Synthesis and Characterisation

(i) *Compound 2-1a*

Phenyl-dithienophosphole **2-1**^{SI} (1.68 g, 6.2 mmol) was dissolved in dry, degassed DCM (25 ml) and added to one equivalent of *o*-chloranil (1.5g) dissolved in DCM (25 ml). The green-yellow fluorescent solution mixture was stirred overnight at room temperature under argon. The mixture was concentrated to one-third of the original volume and the yellow solution purified by column chromatography (silica, DCM) was dried with roto-evaporation to obtain a bright yellow powder at a yield of 63% (2.0 g, 3.9 mmol). ¹H NMR (600 MHz, CD₂Cl₂, ppm): δ 7.81 (dd, 2H, ³J_P=14.40 Hz, ³J_H=7.20 Hz), 7.48 (dd, 2H, ³J_H=6.00 Hz), 7.45 (dd, 1H, ³J_H=7.20 Hz, ⁵J_P=0.60 Hz), 7.35 (m, 2H), 7.30 (dd, 2H, ³J_P=4.80 Hz, ³J_H=4.20 Hz). ³¹P{¹H} NMR (162 MHz, CD₂Cl₂, ppm): δ -39.1. ¹³C{¹H} NMR (100 MHz, CD₂Cl₂, ppm): δ 144.9 (d, ²J_P=123.8 Hz), 144.4 (d, ¹J_P=36.2 Hz), 141.8 (s), 132.9 (d, ¹J_P=135.9 Hz), 132.2 (d, ⁴J_P=25.7 Hz), 131.9 (d, ²J_P=12.1 Hz), 130.7 (d, ²J_P=9.1 Hz), 129.1 (d, ³J_P=13.6 Hz), 127.0 (d, ³J_P=15.1 Hz), 124.0 (s), 115.1 (d, ²J_P=13.6 Hz) (Figure S2.1-32). E.A. (%) calc'd for C₂₀H₉S₂PO₂Cl₄ (518.20): C 46.36, H 1.74, S 12.37, found: C 46.47, H 1.67, S 12.54.

(ii) *Compound 2-1b*

o-Chloranil was substituted for an electron-rich quinone; 9,10 phenanthrene quinone to generate compound **2-1b**. A 1:1 equiv. solution of compound **2-1**^{SI} (1.78 g, 6.5 mmol) and quinone (1.4 g) in degassed dry THF (70 ml) was refluxed for 20 hours. The ³¹P{¹H} NMR spectrum showed the

complete conversion of **2-1'** (-21 ppm) to product **2-1b** (-43 ppm) after 18 hours. On concentrating the solution and washing with dry, degassed pentane for isolation, product **2-1b** decomposed back to the starting material (**2-1'**) with some amount of phenyl-dithienophosphole oxide **2-1'-O**^{S1} (18 ppm). Further attempts to isolate the remaining product lead to complete decomposition of **2-1b**. (Figure S2.1-1a-c)

After investigating the reactivity of the synthesized class of compound with water, the synthesis of compound **2-1b** was repeated with 1:1 equiv. of **2-1'** (0.25 g, 0.9 mmol) and 9,10 phenanthrene quinone (0.20 g) in the glovebox under dry conditions using DCM (alumina dried and freeze-pump-thaw cycled) (50 ml). The solution was stirred for 24 hours at room temperature and the product was isolated by recrystallization from the reaction mixture at 61% yield (0.50 g, 1 mmol). ¹H NMR (600 MHz, CDCl₃, ppm): δ 8.62 (d, 2H, ³J_H=8.34 Hz), 8.10 (d, 2H, ³J_H=7.80 Hz), 7.85 (dd, 2H, ³J_H=7.38 Hz, ²J_P=0.74 Hz), 7.61 (m, 4H), 7.50 (t, 2H, ³J_H=8.84 Hz), 7.25 (m, 2H), 7.25 (m, 2H), 7.21 (m, 2H), 7.16 (m, 1H). ³¹P{¹H} NMR (121.5 MHz, CDCl₃, ppm): δ -44.1. ¹³C{¹H} NMR (151 MHz, CDCl₃, ppm): δ 146.5 (d, ²J_P=122.3 Hz), 143.1 (d, ¹J_P=34.7 Hz), 135.5 (s), 134.1 (d, ¹J_P=135.9 Hz), 131.4 (d, ²J_P=12.1 Hz), 130.9 (d, ⁴J_P=3.0 Hz), 130.7 (d, ⁵J_P=9.1 Hz), 128.2 (d, ³J_P=13.6 Hz), 126.5 (d, ³J_P=4.5 Hz), 126.5 (s), 125.6 (d, ²J_P=13.6 Hz), 124.2 (s), 123.1 (s), 122.8 (d, ²J_P=10.6 Hz), 120.7 (s) (Figure S2.1-33). E.A. (%) calc'd for C₂₈H₁₇O₂PS₂ (480.54): C 69.99, H 3.57, S 13.34, found: C 68.97, H 3.65, S 11.57.

b) 18 hour/ reflux (THF)

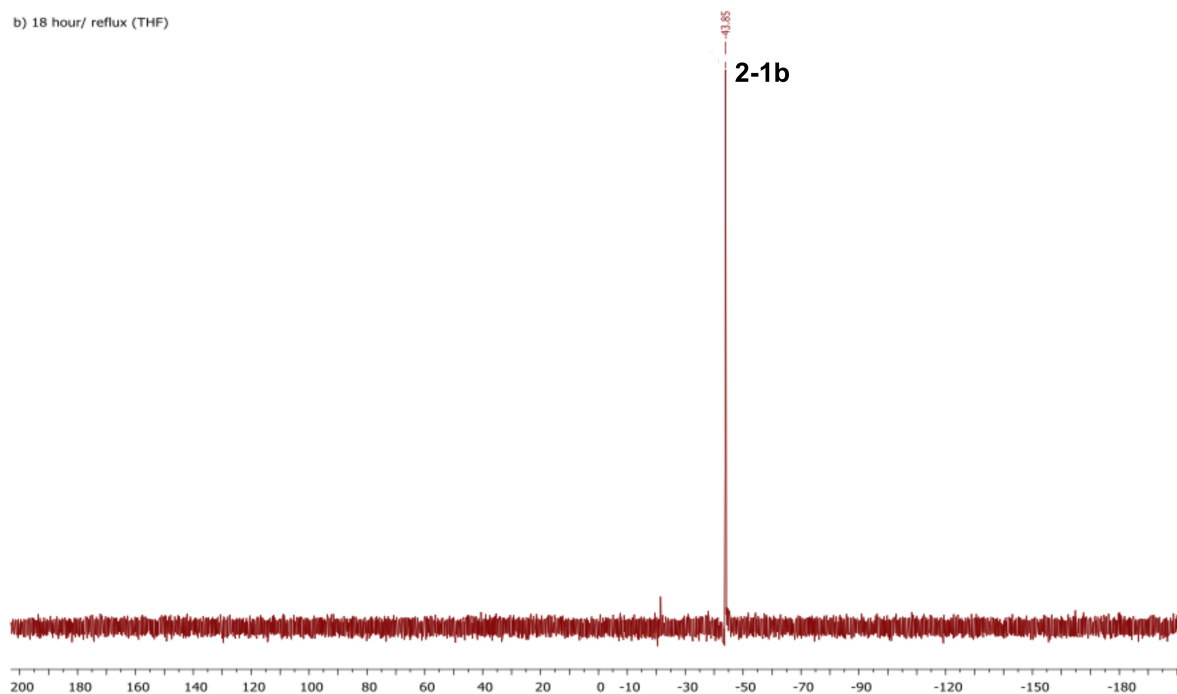


Figure S2.1-1a. Reaction monitoring by $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, showing formation of **2-1b**.

a) 1 hour/ Reflux (THF)

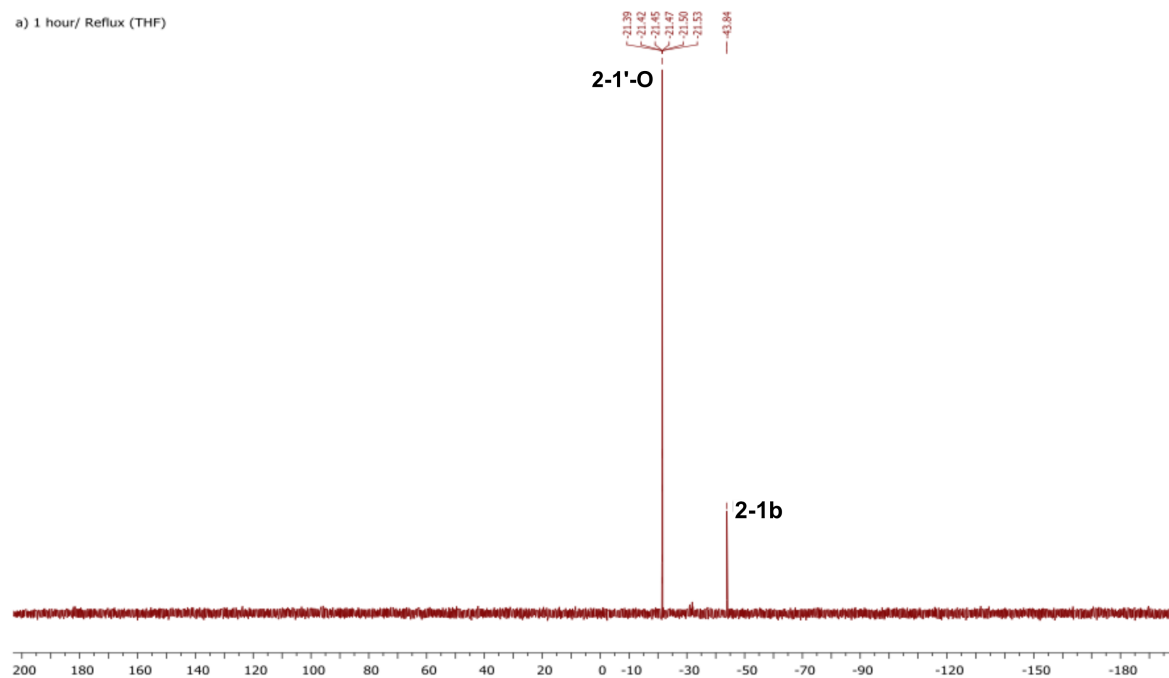


Figure S2.1-1b. Reaction monitoring by $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, showing decomposition of **2-1b** to **2-1'-O**.

c) Isolation from pentane

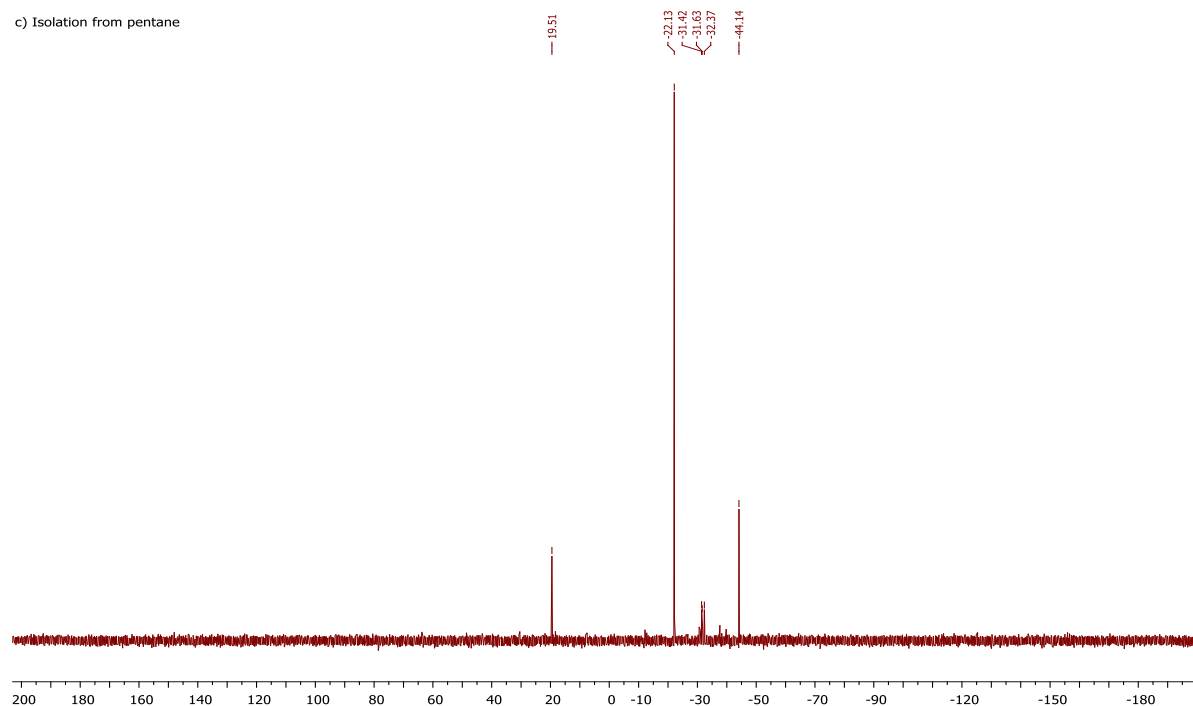


Figure S2.1-1c. Reaction monitoring by $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, showing complete decomposition of **2-1b** to **2-1'-O**.

(iii) Compound **2-2a**

Trivalent phosphole **2-2'**^{S2} (1.56 g, 4.3 mmol) was stirred overnight (16 hours) with *o*-chloranil (1 equiv., 1.06 g) in 30 ml dry, degassed DCM at room temperature to obtain a yellow fluorescent solution of compound **2-2a**. The solution was filtered at 0° C to remove unreacted quinone and dried by roto-evaporation to obtain a bright yellow powder with a yield of 62% (1.61 g, 2.6 mmol). ^1H NMR (400 MHz, CDCl_3 , ppm): δ 7.36 (dd, 2H, $^3J_{\text{H}}=1.60$ Hz, $^4J_{\text{P}}=5.20$ Hz), 7.23 (dd, 2H, $^3J_{\text{H}}=4.04$ Hz, $^3J_{\text{P}}=4.80$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , ppm): δ -50.3. $^{19}\text{F}\{^1\text{H}\}$ NMR (376.5 MHz, CDCl_3 , ppm): δ -132.2 (*o*-F, m), -148.5 (*m*-F, m), -158.9 (*p*-F, m). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3 , ppm): δ 146.4 (d(m), $^2J_{\text{P}}=262.6$ Hz), 144.5 (d, $^2J_{\text{P}}=191.0$ Hz), 143.7 (d, $^1J_{\text{P}}=286.7$ Hz), 143 (d(m), $^4J_{\text{P}}=332.0$ Hz), 141.0 (s), 137.8 (d(m), $^2J_{\text{P}}=260.6$ Hz), 130.3 (d(t), $^2J_{\text{P}}=11.1$ Hz,

$^5J_F=3.0$ Hz)), 128.6 (d, $^2J_P=81.5$ Hz), 126.7 (d, $^3J_P=17.1$ Hz), 124.6 (s), 115.0 (d, $^2J_P=14.1$ Hz) (Figure S2.1-34). E.A. (%) calc'd for $C_{20}H_4S_2PO_2Cl_4F_5$ (608.14): C 39.50, H 0.66, S 10.54, found: C 39.84, H 0.73, S 10.12.

(iv) Compound 2-2b

A similar synthetic protocol as for **2-1a**, was used in synthesis of compound **2-2b**, with 4 mmol of **2-2**^{S2} (1.46 g) and 9,10-phenanthrene quinone (1.0 equiv., 0.84 g) in 70 ml dry, degassed DCM. The orange-yellow powder of **2-2b** was obtained after evaporation of the solvent at a yield of 80% (1.83 g, 3.2 mmol). 1H NMR (300 MHz, $CDCl_3$, ppm): δ 8.66 (d, 2H, $^3J_H=8.10$ Hz), 8.06 (dd, 2H, $^5J_P=8.10$ Hz, $^3J_H=1.29$ Hz), 7.63 (d(t), 2H, $^3J_H=6.00$ Hz, $^6J_P=3.00$ Hz), 7.56 (m, 4H), 7.24 (dd, 2H, $^3J_H=1.11$ Hz, $^3J_P=4.89$ Hz). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, ppm): δ -53.7. $^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$, ppm): δ -132.3 (*o*-F, m), -150.3 (*m*-F, m), -160 (*p*-F, m). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm): δ 207.0 (s), 145.3 (d, $^2J_P=132.0$ Hz), 144.5 (d, $^1J_P=38.3$ Hz), 136.1 (s), 135.3 (s), 130.7 (d(t), $^1J_F=3.8$ Hz, $^4J_P=10.6$ Hz), 130.0 (d, $^1J_P=71.3$ Hz), 126.9 (s), 126.8 (d, $^3J_P=15.8$ Hz), 125.8 (d, $^2J_P=15.8$ Hz), 124.7 (s), 123.1 (s), 122.4 (d, $^2J_P=11.3$ Hz), 120.7 (s) (Figure S2.1-35). E.A. (%) calc'd for $C_{28}H_{12}S_2PO_2F_5$ (570.50): C 58.95, H 2.12, S 11.24, found: C 59.37, H 1.80, S 11.12.

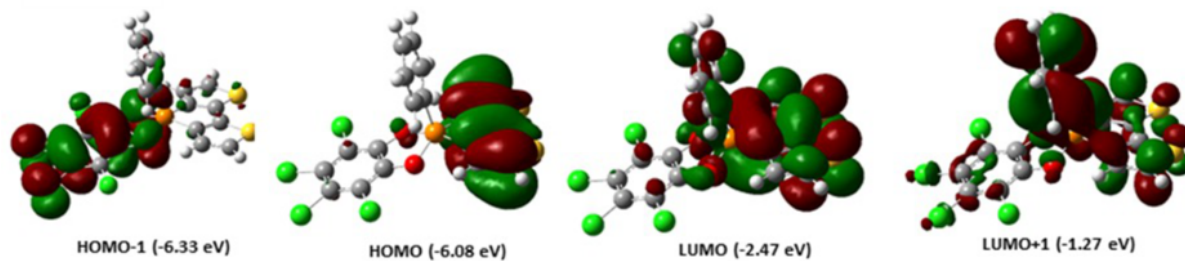
S.2.1.2 Theoretical Calculations

(i) DFT FMO calculations

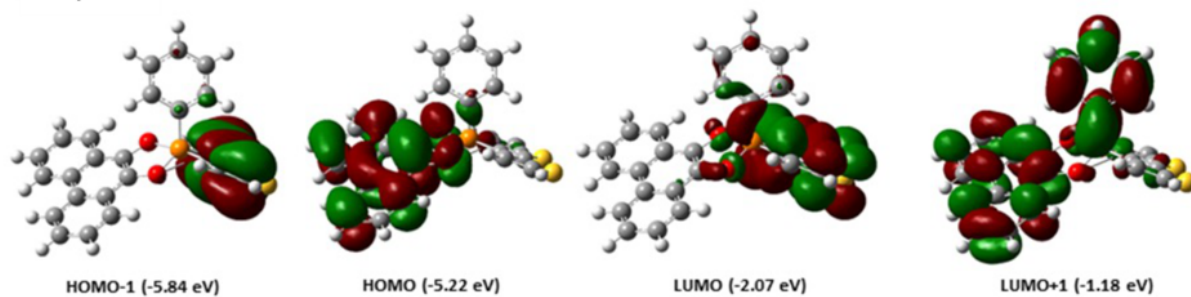
The DFT FMO calculations were conducted at the B3LYP/6-31G+(d) level of theory.^{S3} Compound **2-1a** shows localized π -orbitals of dithienophosphole and *o*-chloranil in the HOMO and HOMO-1, respectively. The π^* -antibonding orbitals of the dithienophosphole and phenyl group host the LUMO and LUMO+1. The dithienophosphole possesses donor character when comparing the electron-accepting *o*-chloranil group. Using an electron-rich quinone reverses the electronics between the substituents. Compound **2-1b** has a HOMO localized on the 9,10-phenanthrene quinone substituent while dithienophosphole moiety hosts the HOMO-1. The LUMO of the compound is localized over the π^* -antibonding orbital of the dithienophosphole, which acts as the acceptor. Both quinone- and perfluorophenyl-groups host the LUMO+1. The DFT calculations for compound **2-2a** consistently failed under the given conditions. Compound **2-2b** shows the similar donor-acceptor separation of HOMO and LUMO as **2-1b** with HOMO-1 localized on dithienophosphole. The LUMO+1 is localized in π^* -antibonding of the perfluorophenyl group and very little over the quinone (Figure S2-2). The Cartesian coordinates for FMOs of the compounds are listed below in Tables S2.1-1a-c.

Figure S2.1-2. DFT calculated (B3LYP/6-31G+(d) level of theory) HOMO-1, HOMO, LUMO, and LUMO+1 levels of **2-1a**, **2-1b**, and **2-2b**.

Compound 2-1a



Compound 2-1b



Compound 2-2b

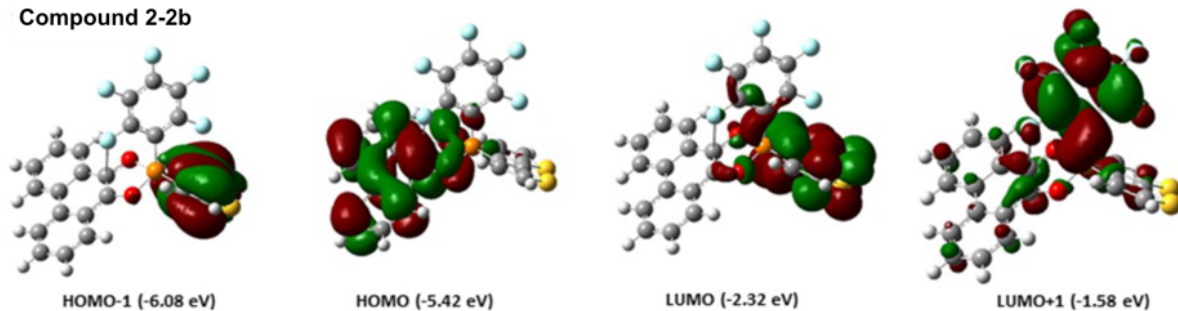


Table S2.1-1a. Cartesian coordinates for the minimized structure of **2-1a**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.726008	-0.245418	-0.220752
2	6	0	-2.038135	-0.054517	-1.493109
3	6	0	-1.190323	1.163927	-1.923216
4	6	0	-0.934213	1.984317	-0.849111
5	16	0	-1.850765	1.467832	0.597581
6	1	0	-0.835529	1.336489	-2.917823
7	1	0	-0.267191	2.820587	-0.874233
8	6	0	-3.173357	-1.207962	0.187567
9	6	0	-3.417187	-1.993087	-0.849918
10	16	0	-3.857628	-1.805942	1.696878
11	6	0	-4.386355	-3.144184	-0.496136
12	6	0	-4.771538	-3.071286	0.822515
13	1	0	-4.721793	-3.889534	-1.186669
14	1	0	-5.524565	-3.688260	1.266579
15	15	0	-2.594770	-1.540777	-2.441661
16	6	0	-3.812514	-3.298566	-3.728640
17	6	0	-3.823463	-2.163279	-4.517018
18	6	0	-4.577462	-4.418486	-4.062995
19	6	0	-4.605715	-2.105133	-5.673742
20	6	0	-5.365835	-4.379726	-5.225429
21	6	0	-5.380211	-3.222847	-6.030526
22	8	0	-2.988190	-3.203502	-2.577119
23	8	0	-3.005792	-1.084843	-4.051160
24	6	0	-0.861055	-2.059507	-2.635449
25	6	0	-0.169986	-2.613895	-1.549632
26	6	0	-0.217166	-1.904544	-3.870485
27	6	0	1.164971	-3.013329	-1.698853
28	1	0	-0.661608	-2.732209	-0.606652
29	6	0	1.117792	-2.303975	-4.019705
30	1	0	-0.744811	-1.481252	-4.699530
31	6	0	1.808859	-2.858371	-2.933891
32	1	0	1.692618	-3.436618	-0.869808
33	1	0	1.609415	-2.185659	-4.962684
34	1	0	2.828127	-3.163349	-3.047825
35	17	0	-4.554352	-5.854080	-3.045087
36	17	0	-6.336766	-5.776740	-5.676258
37	17	0	-6.370039	-3.177337	-7.485094
38	17	0	-4.620841	-0.653859	-6.669319

Table S2.1-1b. Cartesian coordinates for the minimized structure of **2-2b**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	15	0	-1.270431	2.796347	-1.217422
2	6	0	-0.343022	4.126200	-2.055959
3	6	0	0.148408	3.251696	-2.361749
4	6	0	0.790235	2.109553	-2.761126
5	6	0	-0.265117	1.539830	-2.075138
6	6	0	-0.537294	5.517822	-2.198721
7	6	0	0.511500	6.105191	-2.968462
8	16	0	1.808554	4.920507	-3.310698
9	16	0	1.819273	0.914896	-3.531037
10	6	0	0.814063	-0.388269	-2.833678
11	6	0	-0.334488	0.135737	-2.165842
12	8	0	-1.931994	2.217265	0.278287
13	6	0	-2.775925	3.813835	-1.310141
14	6	0	-3.289978	4.214307	-2.553299
15	6	0	-4.472630	4.965426	-2.609662
16	6	0	-5.130980	5.324542	-1.424835
17	6	0	-4.604014	4.938617	-0.184644
18	6	0	-3.425486	4.186676	-0.128608
19	1	0	-1.367492	6.060690	-1.794168
20	1	0	-1.127701	-0.459271	-1.767151
21	1	0	-2.782402	3.945894	-3.456633
22	1	0	-4.874738	5.264255	-3.555242
23	1	0	-6.036895	5.892236	-1.466685
24	1	0	-5.102996	5.217804	0.719702
25	1	0	-3.019563	3.894777	0.816764
26	1	0	0.520422	7.121183	-3.301713
27	1	0	1.049776	-1.429455	-2.903195
28	8	0	0.304577	2.135971	-0.875457
29	6	0	0.342933	1.800239	0.502710
30	6	0	-0.852276	1.909863	1.132964
31	6	0	1.488255	1.392252	1.196835
32	6	0	0.163514	1.345627	3.242645
33	6	0	1.389386	1.151256	2.579300
34	6	0	2.509960	0.714173	3.294109
35	6	0	3.726930	0.506899	2.631036
36	1	0	2.437555	0.535921	4.346465
37	6	0	2.715202	1.219585	0.536066
38	6	0	3.832295	0.765471	1.254498
39	1	0	4.577171	0.153473	3.176365
40	1	0	2.798587	1.429899	-0.510135
41	1	0	4.765223	0.612582	0.752770
42	6	0	-0.966105	1.733596	2.512137
43	6	0	-2.188562	1.943619	3.154504
44	6	0	-2.286228	1.761164	4.537081
45	1	0	-3.047212	2.244631	2.589005
46	6	0	0.066928	1.151756	4.626507
47	6	0	-1.159151	1.364884	5.273287
48	1	0	-3.220942	1.925353	5.030839

49	1	0	0.926110	0.843469	5.187170
50	1	0	-1.236096	1.225540	6.329260

Table S2.1-1c. Cartesian coordinates for the minimized structure of **2-2b**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	15	0	-0.929843	0.145450	-0.154478
2	6	0	-2.278236	-1.172289	-0.315129
3	6	0	-3.234711	-1.033314	0.666850
4	6	0	-2.974644	0.058710	1.585076
5	6	0	-1.816852	0.773991	1.323726
6	6	0	-2.561192	-2.253763	-1.194906
7	6	0	-3.721534	-2.910926	-0.861583
8	16	0	-4.493841	-2.218685	0.541527
9	16	0	-3.810287	0.672970	2.965331
10	6	0	-2.589775	1.905597	3.194793
11	6	0	-1.597451	1.832918	2.252333
12	8	0	0.480795	1.234272	0.276260
13	6	0	-0.812492	0.571100	-1.943871
14	6	0	-1.977471	0.677433	-2.720402
15	6	0	-1.897247	0.999785	-4.076144
16	6	0	-0.650837	1.186130	-4.680569
17	6	0	0.513075	1.065819	-3.918022
18	6	0	0.434344	0.775768	-2.553579
19	1	0	-1.938464	-2.541048	-2.035455
20	1	0	-0.743591	2.497710	2.219046
21	1	0	-4.170906	-3.767787	-1.347203
22	1	0	-2.685189	2.599690	4.019629
23	8	0	0.035398	-1.153615	0.368078
24	6	0	1.520691	-0.747296	-0.074146
25	6	0	1.644395	0.764338	-0.218671
26	6	0	2.609497	-1.655964	-0.144131
27	6	0	4.077806	0.286453	0.449295
28	6	0	3.916283	-1.129123	0.120449
29	6	0	5.002929	-2.032665	0.049623
30	6	0	4.820419	-3.371153	-0.259800
31	1	0	6.010633	-1.680371	0.243175
32	6	0	2.437198	-3.025377	-0.457773
33	6	0	3.528277	-3.872666	-0.514182
34	1	0	5.679601	-4.035350	-0.303579
35	1	0	1.434368	-3.395581	-0.648008
36	1	0	3.389536	-4.923907	-0.753544
37	6	0	2.933037	1.144919	0.515328
38	6	0	3.077725	2.515753	0.830526
39	6	0	4.328327	3.049302	1.082684
40	1	0	2.187813	3.137150	0.865627
41	6	0	5.338292	0.874766	0.712961
42	6	0	5.465589	2.219434	1.022585

43	1	0	4.434622	4.103723	1.324411
44	1	0	6.235988	0.266977	0.673751
45	1	0	6.450965	2.634148	1.219078
46	9	0	1.568934	0.699165	-1.826023
47	9	0	1.722508	1.243055	-4.491049
48	9	0	-0.572583	1.482210	-5.995374
49	9	0	-3.029636	1.118844	-4.801415
50	9	0	-3.188240	0.474288	-2.158912

(ii) Computational methods for structural rationalization and mechanism explorations:

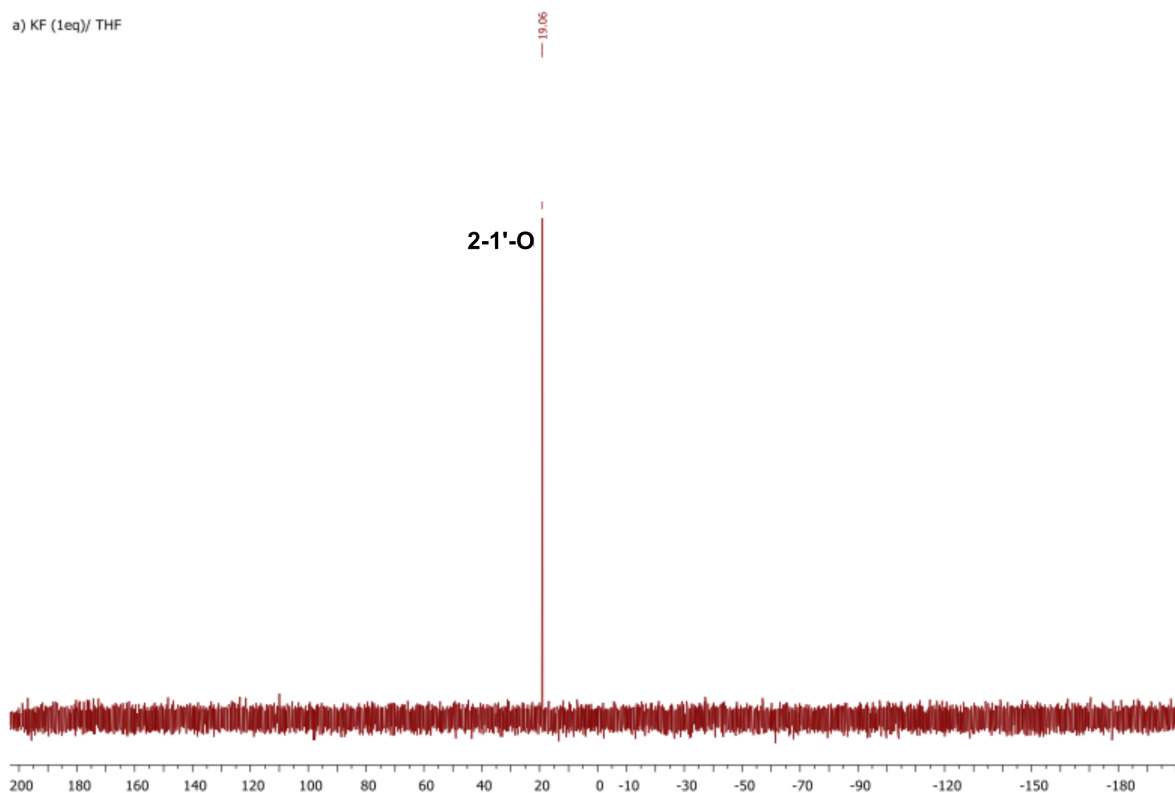
All molecular calculations for Sections 2.1.9 below and Fig. S2.1-25 in the main text were performed using the ORCA 4.2.0 software package,^{S4} at the CAM-B3LYP^{S5}/MA-DEF2-SVP^{S6} level of theory and with the conductor-like polarizable continuum solvent model^{S7} of tetrahydrofuran (THF). After geometry optimizations, Hessian calculations were carried out to assure that the structures are at the minima or saddle points of potential energy surface. Saddle points correspond to transition state (**2-TS**) structures. The addition of electronic energy, solvation free energy, and zero-point vibrational energy results in the energy of a molecular structure, which is used to estimate the relevant energies reported in the main text. As to the FIA calculations, the same method was used, except that the solvent model was not invoked (as a gas phase model was used, as introduced by Greb),^{S8} and the enthalpy correction is included. The Natural Bond Orbital analyses^{S9} were carried out using the GAMESS-US package.^{S10}

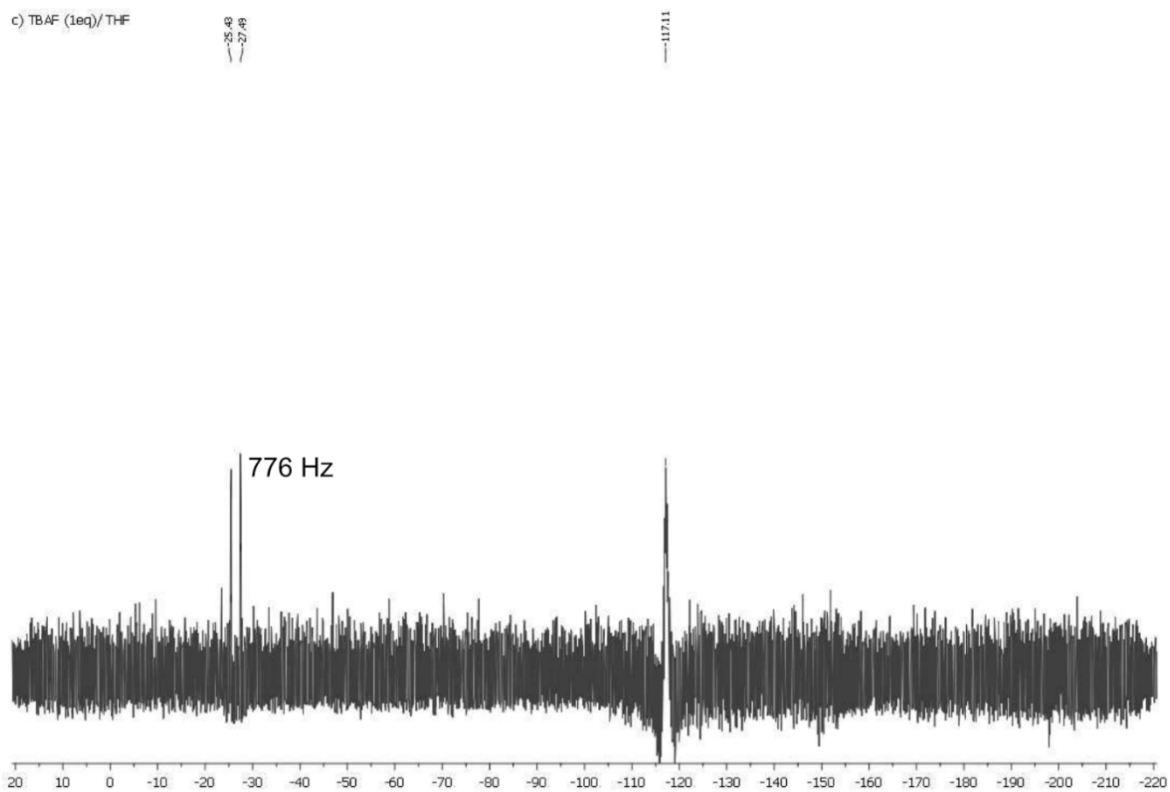
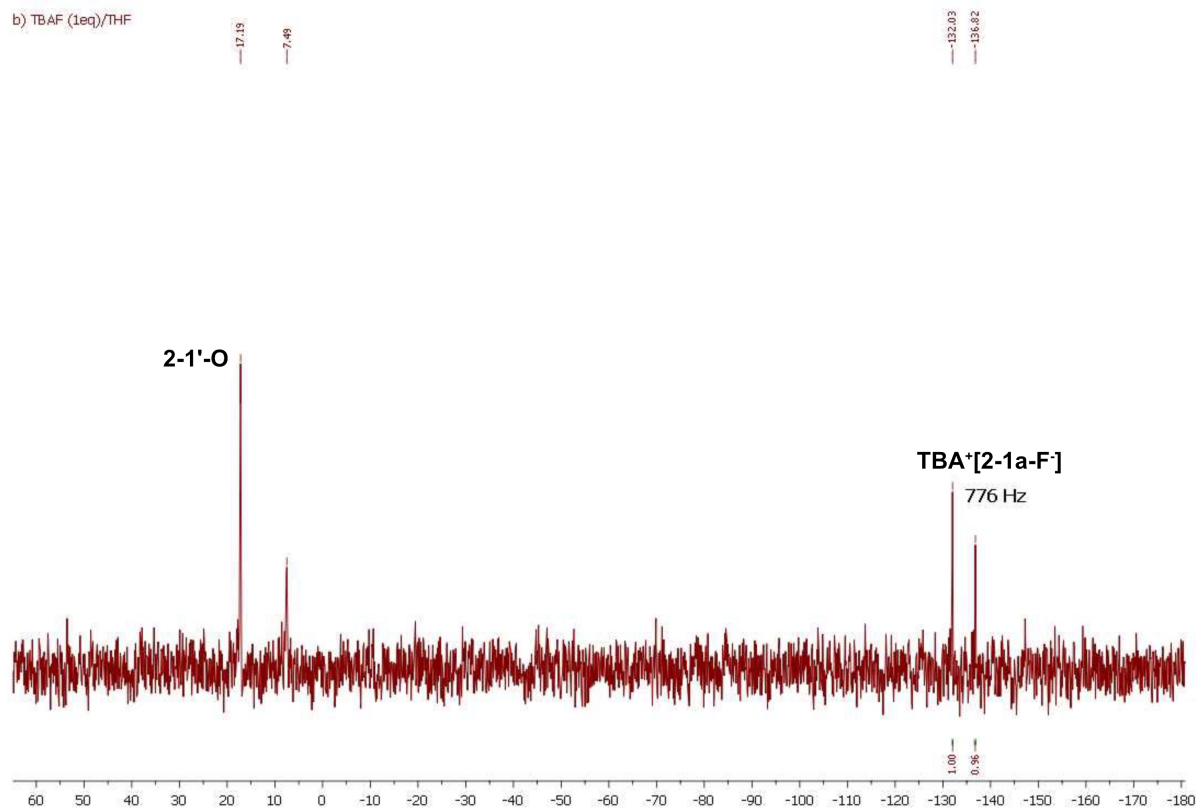
The solid state calculations for exploring crystal-to-crystal dissociations of dithienophospholes compounds were carried out using the Quantum Espresso software package.^{S11} Calculations were performed using the PBE functional^{S12} and PAW pseudopotentials.^{S13} All the solid states calculations were performed with unrestricted spin (nspin = 2), energy cut-off (Ecutwfc) of 40 Ry, density cut-off (Ecutrho) of 400 Ry. K points grids were selected to be $5 \times 4 \times 2$ (except $5 \times 3 \times 3$ for the dissociated crystal), inversely proportional to the lattice parameters a , b , and c .

S.2.1.3 Study of the Lewis acidity with KF and TBAF/THF

For the determination of the Lewis acidity, 0.2 mmol of **2-1a** (0.10 g) was dissolved in 20 ml of dry, degassed toluene to which 1 equiv. of potassium fluoride (KF, 0.01 g) was added with stirring. After 1 hour, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction shows that **2-1a** transforms to **2-1'-O** (19.1 ppm) and does not support the formation of $\text{K}^+[\text{2-1a-F}^-]$ (Figure S2-3). We surmise that crystalline KF contains adventitious water that reacts with **2-1a**, and hence the reaction was repeated with 1 equiv. of TBAF dissolved in 1 M of dry THF (0.2 ml) with 0.025 g of **2-1a**. The reaction was monitored with $^{31}\text{P}\{^1\text{H}\}$ and $^{19}\text{F}\{^1\text{H}\}$ NMR spectroscopy (Figure S2.1-3a-c) to show the presence of $\text{TBA}^+[\text{2-1a-F}^-]$ (doublet at -134.5 ppm and -26.5 ppm respectively) along with **2-1'-O** (17.2 ppm).

Figure S2.1-3. Fluoride abstraction reaction monitoring by (a) $^{31}\text{P}\{^1\text{H}\}$ for reaction with KF (b) $^{31}\text{P}\{^1\text{H}\}$ for reaction with TBAF and (c) $^{19}\text{F}\{^1\text{H}\}$ NMR spectroscopy for reaction with TBAF. (THF).

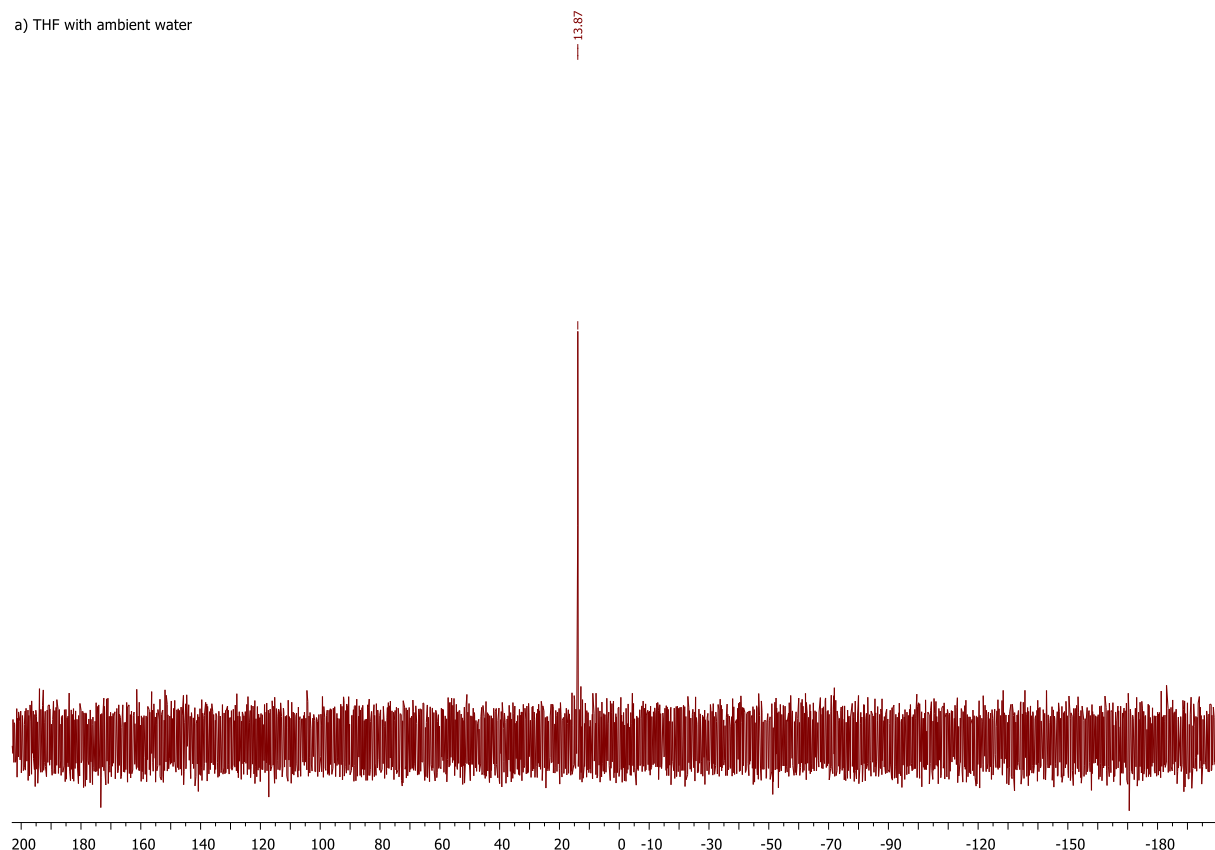




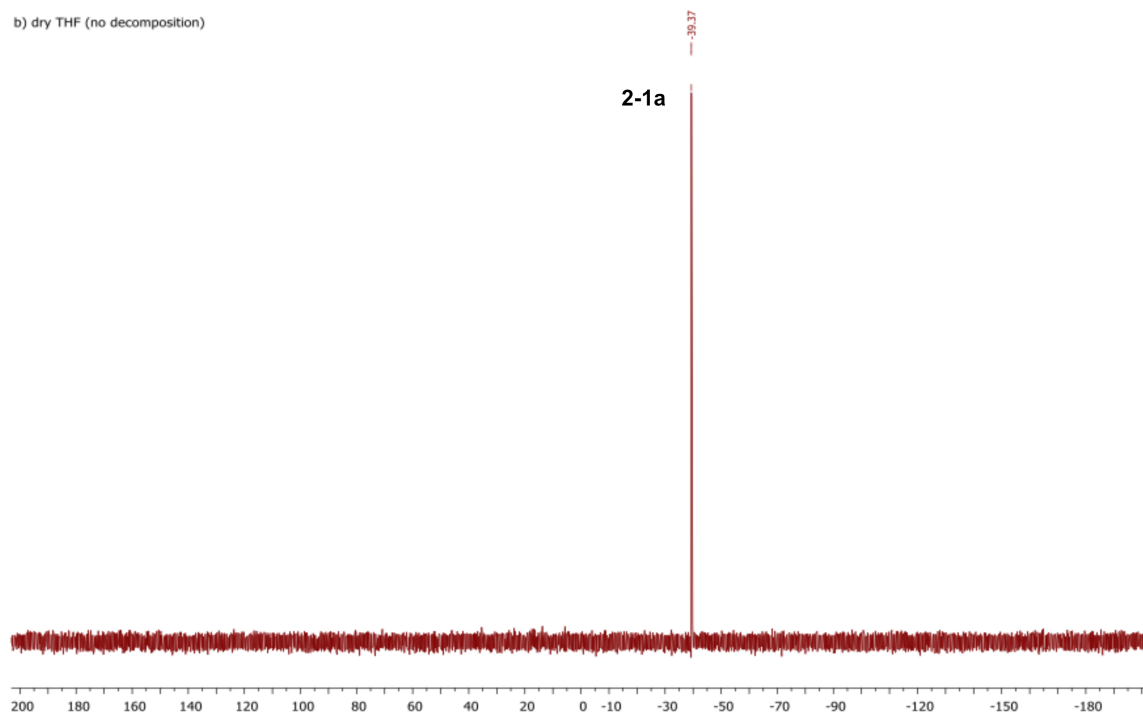
S.2.1.4 Reactivity of compound 2-1a with water

Compound **2-1a** transforms immediately to **2-1'-O** in wet THF, which is evident in an emerging signal at 13.9 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (Figure S2.1-4a). On freeze-pump-thaw-cycled dry, degassed THF, no new NMR signals are detected confirming the stability of the species under these conditions (Figure S2.1-4b). However, the $^{31}\text{P}\{^1\text{H}\}$ NMR peak at -39.4 ppm disappears and a new signal at 20.8 ppm emerges upon addition of degassed water (Figure S2.1-4c).

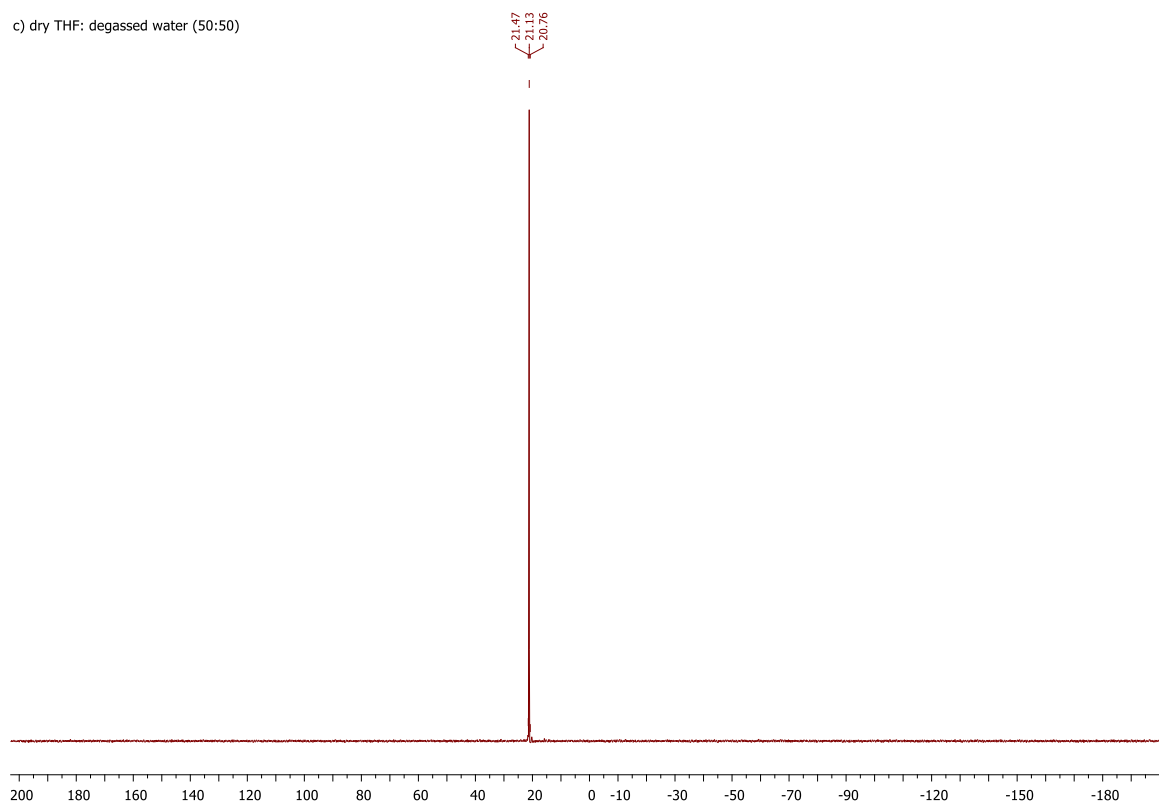
Figure S2.1-4. Transformation of **2-1a** in presence of water monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (a) THF with ambient water (b) dry THF and (c) dry THF: degassed water (50:50)



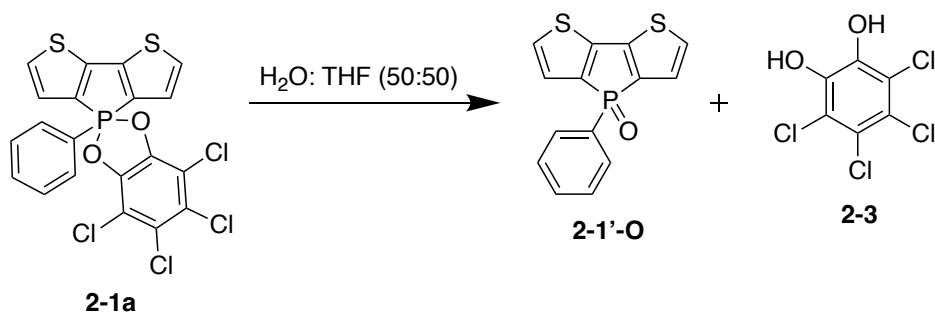
b) dry THF (no decomposition)



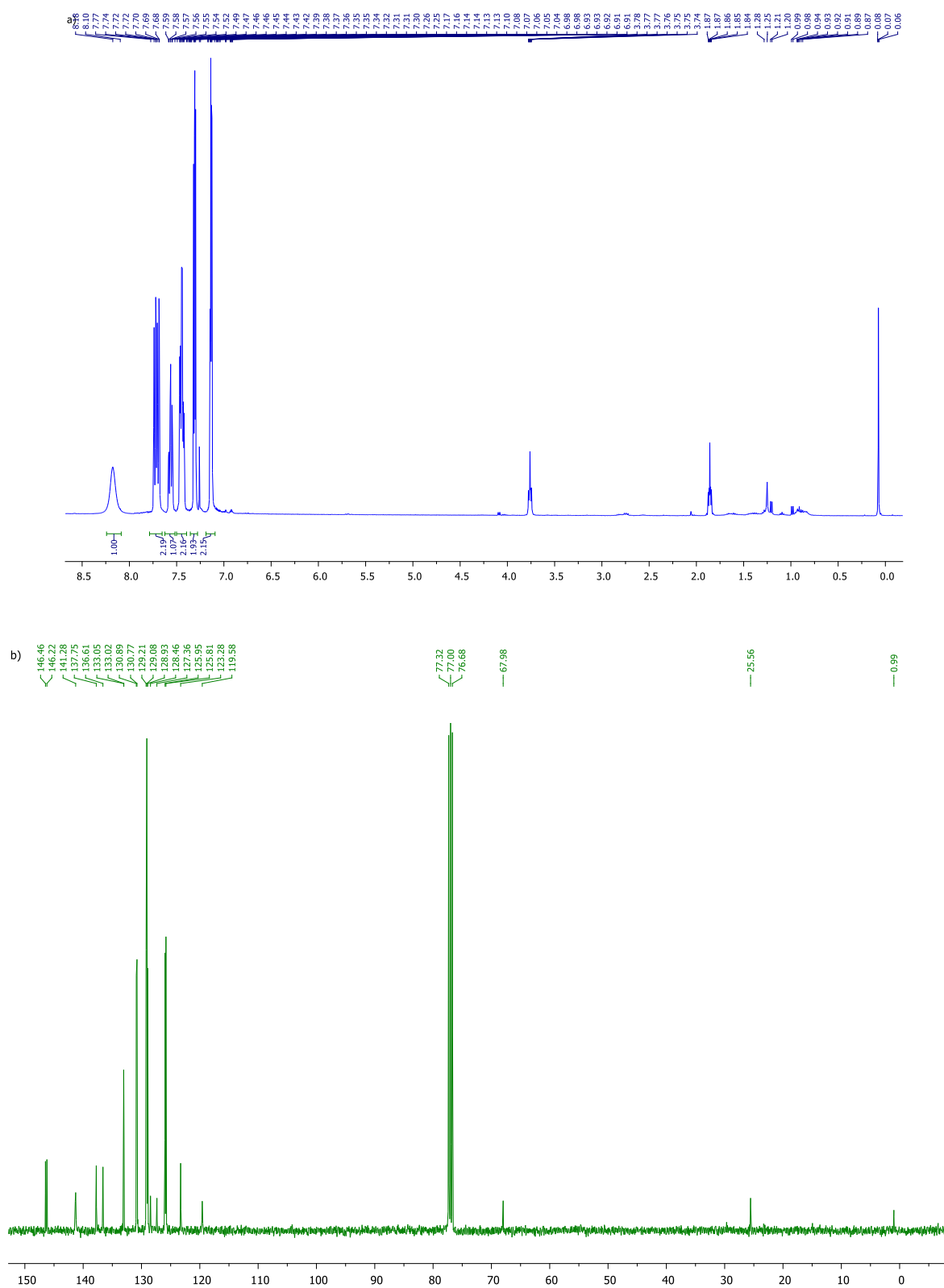
c) dry THF: degassed water (50:50)



Multinuclear NMR spectra of the transformed single crystals of **2-1a** (Scheme S2.1-1) were recorded in dry CDCl_3 . The ^1H NMR spectrum shows the characteristic broad -OH peak of **2-3** at 7.88 ppm, while the remaining proton signals belong to **2-1'-O**. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the reaction mixture indicated that the peaks at 119.5 ppm, 123.4 ppm, and 141.24 ppm belong to **2-3**. The formation of the catechol is evident from the disappearance of a doublet with $^2J_{\text{P-C}}$ coupling at 115.1 ppm, which corresponds to the quinone carbons (Figure S2.1-5).



Scheme S2.1-1. Transformation of **2-1a** in presence of water.

¹H and b) ¹³C{¹H} NMR spectroscopy (CDCl₃).

S.2.1.5 X-ray structures, supramolecular interactions and excimer formation in solution

(i) Compound 2-1a

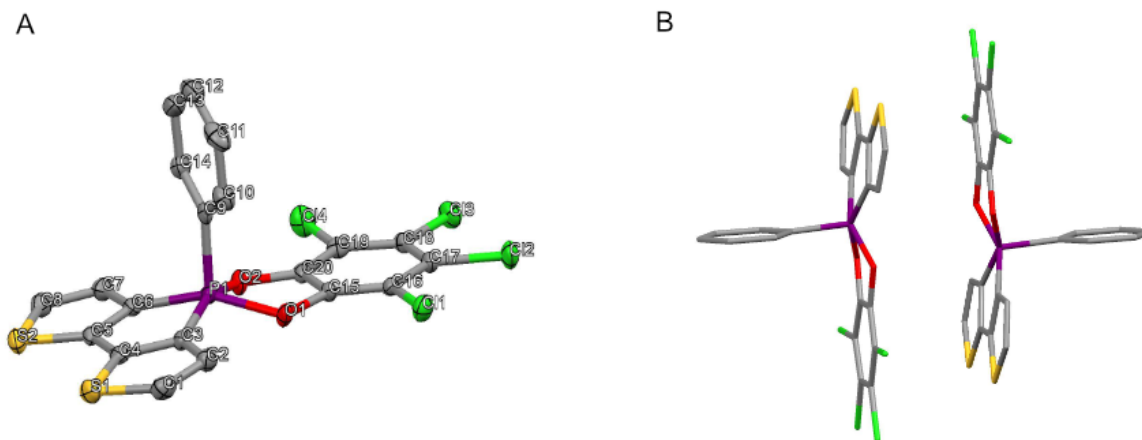


Figure S2.1-6a. Crystallographically determined solid-state structure of compound **2-1a** (left) and its supramolecular dimerization (right). Atomic displacement ellipsoids depicted at 50% probability level. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): P1-C3 1.83(3), P1-C6 1.83(9), P1-O1 1.73(4), P1-O2 1.72(8), P1-C9 1.80(9), C15-O1 1.36(1), C20-O2 1.35(8); C6-P1-C3 88.4(9), C3-P1-O1 86.4(3), O1-P1-O2 87.2(2), O2-P1-C6 87.1(6), C3-P1-C9 103.8(9), C6-P1-C9 103.6(5), C9-P1-O2 100.4(9), O1-P1-C9 101.8(4).

Table S2.1-2a. Crystal data and structure refinement for compound 2-1a.

Identification code	compound A
Empirical formula	C ₂₀ H ₉ O ₂ PS ₂ Cl ₄
Formula weight	518.16
Temperature/K	173.0
Crystal system	Monoclinic
Space group	P2 ₁ /c
a/Å	11.6769(3)
b/Å	8.6815(2)
c/Å	20.2009(5)
α /°	90
β /°	98.1160(10)
γ /°	90
Volume/Å ³	2027.32(9)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.698
μ/mm^{-1}	0.885
F(000)	1040.0
Crystal size/mm ³	0.1 × 0.1 × 0.1
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	5.116 to 55.03
Index ranges	-15 ≤ h ≤ 15, -11 ≤ k ≤ 11, -26 ≤ l ≤ 26
Reflections collected	35560
Independent reflections	4659 [R _{int} = 0.0983, R _{sigma} = 0.0455]
Data/restraints/parameters	4659/0/262
Goodness-of-fit on F ²	1.056
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0458, wR ₂ = 0.0810
Final R indexes [all data]	R ₁ = 0.0626, wR ₂ = 0.0928
Largest diff. peak/hole / e Å ⁻³	0.80/-0.46
CCDC number	2044241

(ii) Compound 2-1b

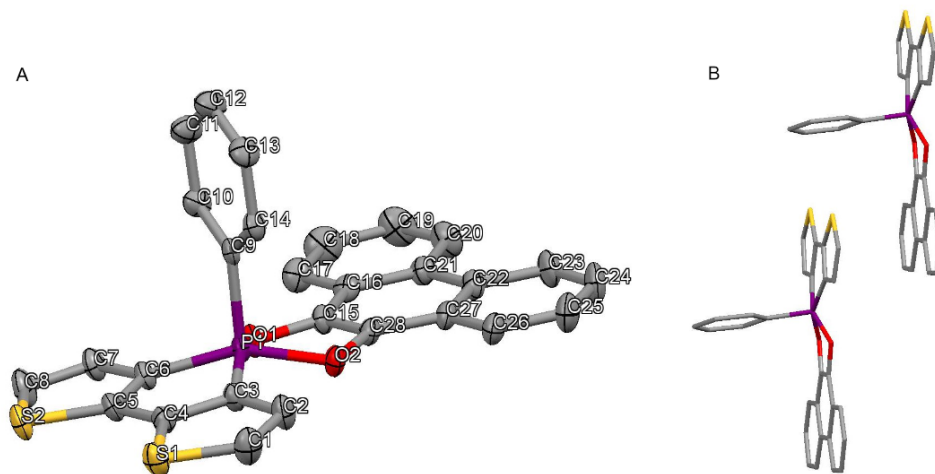


Figure S2.1-6b. Crystallographically determined solid-state structures of **2-1b** (left) and its supramolecular dimerization (right). Atomic displacement ellipsoids depicted at 50% probability level. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): P1-C3 1.84(2), P1-C6 1.83(6), P1-O1 1.72(5), P1-O2 1.72(0), P1-C9 1.82(2), C15-O1 1.36(8), C28-O2 1.37(0); C6-P1-C3 88.0(3), C3-P1-O2 86.7(6), O1-P1-O2 87.3(4), O2-P1-C6 87.7(6), C3-P1-C9 103.7(6), C6-P1-C9 103.6(5), C9-P1-O2 102.1(4), O1-P1-C9 100.4(8).

Compound **2-1b** proved difficult to crystallize and diffraction data resulted in a large number of unique reflections in the low angle data due to the quality of the crystals generated, leading to the B-level error in the cif file. However, the remaining data is complete and redundant. This combined with the consistency of the structure with the related series of compounds in this study affords us confidence in the structural characterization.

Table S2.1-2b. Crystal data and structure refinement for compound 2-1b

Identification code	compound B
Empirical formula	C ₂₈ H ₁₇ O ₂ PS ₂
Formula weight	480.50
Temperature/K	173.00
Crystal system	Triclinic
Space group	P-1
a/Å	8.486(3)
b/Å	9.239(3)
c/Å	16.573(6)
α /°	91.523(14)
β /°	95.534(11)
γ /°	106.919(11)
Volume/Å ³	1235.3(7)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.292
μ/mm^{-1}	0.303
F(000)	496.0
Crystal size/mm ³	0.6 × 0.6 × 0.3
Radiation	Mo K α (λ = 0.71073)
2 Θ range for data collection/°	5.048 to 60.066
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 12, -23 ≤ l ≤ 23
Reflections collected	54729
Independent reflections	7172 [R _{int} = 0.2094, R _{sigma} = 0.0753]
Data/restraints/parameters	7172/0/367
Goodness-of-fit on F ²	1.053
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0549, wR ₂ = 0.1531
Final R indexes [all data]	R ₁ = 0.0584, wR ₂ = 0.1591
Largest diff. peak/hole / e Å ⁻³	0.58/-0.66
CCDC number	20442412

(iii) Compound 2-2a

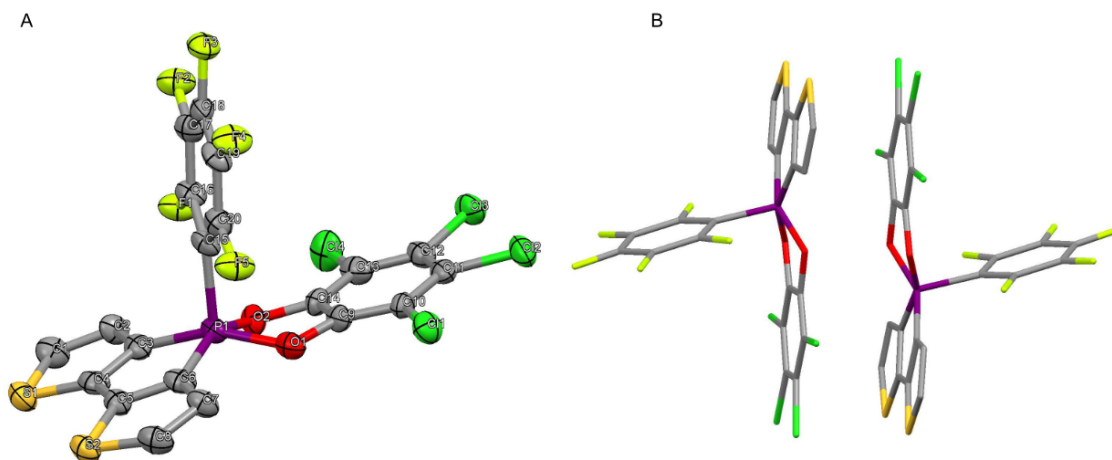


Figure S2.1-6c. Crystallographically determined solid-state structure of **2-2a** (left) and its supramolecular dimerization (right). Atomic displacement ellipsoids depicted at 50% probability level. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°) for **2-2a**: P1-C3 1.85(3), P1-C6 1.83(6), P1-O1 1.72(4), P1-O2 1.70(4), P1-C15 1.84(8), C14-O2 1.36(3), C9-O1 1.35(5); C6-P1-C3 88.0(0), C3-P1-O2 87.5(8), O1-P1-O2 87.1(3), O1-P1-C6 86.7(0), C3-P1-C15 103.9(4), C6-P1-C15 107.2(9), C15-P1-O2 100.0(1), O1-P1-C15 98.3(0).

Table S2.1-2c. Crystal data and structure refinement for Compound 2-2a

Identification code	Compound C
Empirical formula	C ₂₀ H ₄ Cl ₄ F ₅ O ₂ PS ₂
Formula weight	608.12
Temperature/K	173.0
Crystal system	Monoclinic
Space group	P2 ₁ /c
a/Å	10.6116(4)
b/Å	18.4445(7)
c/Å	11.5631(4)
α /°	90
β /°	111.3620(10)
γ /°	90
Volume/Å ³	2107.71(13)
Z	4
ρ_{calc} /cm ³	1.916
μ /mm ⁻¹	0.900
F(000)	1200.0
Crystal size/mm ³	0.5 × 0.5 × 0.3
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	4.122 to 51.362
Index ranges	-12 ≤ h ≤ 12, -22 ≤ k ≤ 22, -13 ≤ l ≤ 13
Reflections collected	12862
Independent reflections	3856 [R_{int} = 0.1372, R_{sigma} = 0.0924]
Data/restraints/parameters	3856/0/307
Goodness-of-fit on F ²	1.100
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0635, wR_2 = 0.1656
Final R indexes [all data]	R_1 = 0.0813, wR_2 = 0.1918
Largest diff. peak/hole / e Å ⁻³	0.69/-1.10
CCDC number	2044243

(iv) Compound 2-2b

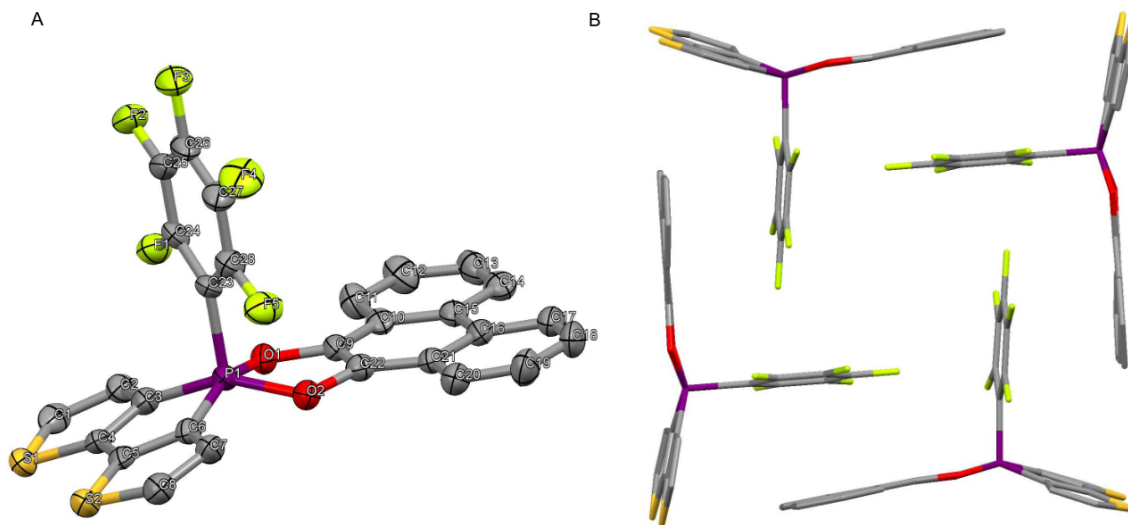


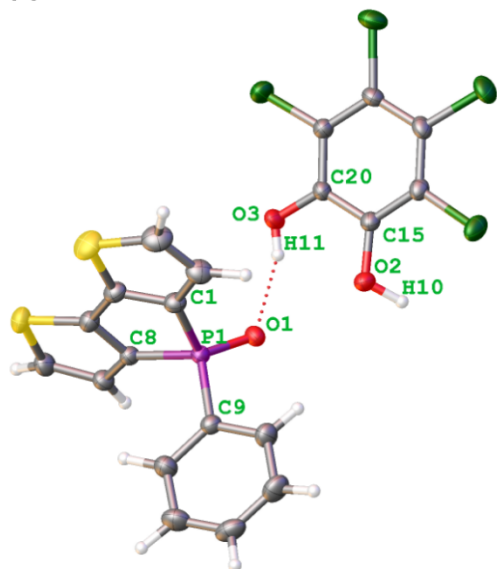
Figure S2.1-6d. Crystallographically determined solid-state structure of **2-2b** (left) and its supramolecular tetramerization (right). Atomic displacement ellipsoids depicted at 50% probability level. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°) for **2-2b**: P1-C3 1.81(7), P1-C6 1.82(5), P1-O1 1.69(2), P1-O2 1.67(0), P1-C23 1.82(2), C22-O2 1.36(4), C9-O1 1.36(8); C6-P1-C3 87.6(8), C3-P1-O1 86.5(2), O1-P1-O2 88.2(8), O2-P1-C6 87.6(5), C3-P1-C23 105.0(7), C6-P1-C23 101.4(1), C23-P1-O2 102.1(8), O1-P1-C23 99.6(8).

Table S2.1-2d. Crystal data and structure refinement for Compound 2-2b

Identification code	Compound D
Empirical formula	C ₅₆ H ₂₄ F ₁₀ O ₄ P ₂ S ₄ Cl _{0.5}
Formula weight	1260.36
Temperature/K	173.00
Crystal system	Triclinic
Space group	P-1
a/Å	11.358(2)
b/Å	14.516(2)
c/Å	16.549(3)
α /°	108.018(5)
β /°	106.995(6)
γ /°	93.965(6)
Volume/Å ³	2442.8(7)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.710
μ/mm^{-1}	0.510
F(000)	1169.0
Crystal size/mm ³	0.1 × 0.1 × 0.1
Radiation	Mo K α (λ = 0.71073)
2 Θ range for data collection/°	4.71 to 51.352
Index ranges	-13 ≤ h ≤ 13, -17 ≤ k ≤ 15, -20 ≤ l ≤ 18
Reflections collected	14683
Independent reflections	7920 [R_{int} = 0.0595, R_{sigma} = 0.0626]
Data/restraints/parameters	7920/0/721
Goodness-of-fit on F ²	1.082
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0539, wR_2 = 0.1296
Final R indexes [all data]	R_1 = 0.0921, wR_2 = 0.1760
Largest diff. peak/hole / e Å ⁻³	1.04/-0.86
CCDC number	2044244

(v) Crystal-to-crystal transformation of 2-1a (Compound 2-1a•H₂O)

A



B

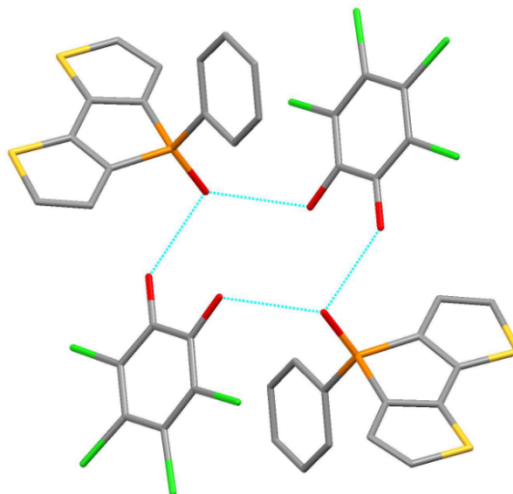


Figure S2.1-6e. Crystallographically determined solid-state structures of transformed crystals of **2-1a•H₂O** in presence of water (left) and its supramolecular interaction by H-bonding (right). Atomic displacement ellipsoids depicted at 50% probability level. Selected bond lengths (Å) and angles (°): P1-C1 1.79(1), P1-C8 1.79(7), P1-C9 1.79(4), O2-C15 1.35(4), O3-C20 1.34(7), P1-O1 1.50(0); C1-P1-O1 115.4(5), C8-P1-O1 119.6(1), C1-P1-C9 106.8(7), C8-P1-C9 108.7(4), C9-P1-O1 111.6(1), O3-C20-C15 121.8(5), C20-C15-O2 116.1(2). H-bonding interaction at 2.66(7) Å

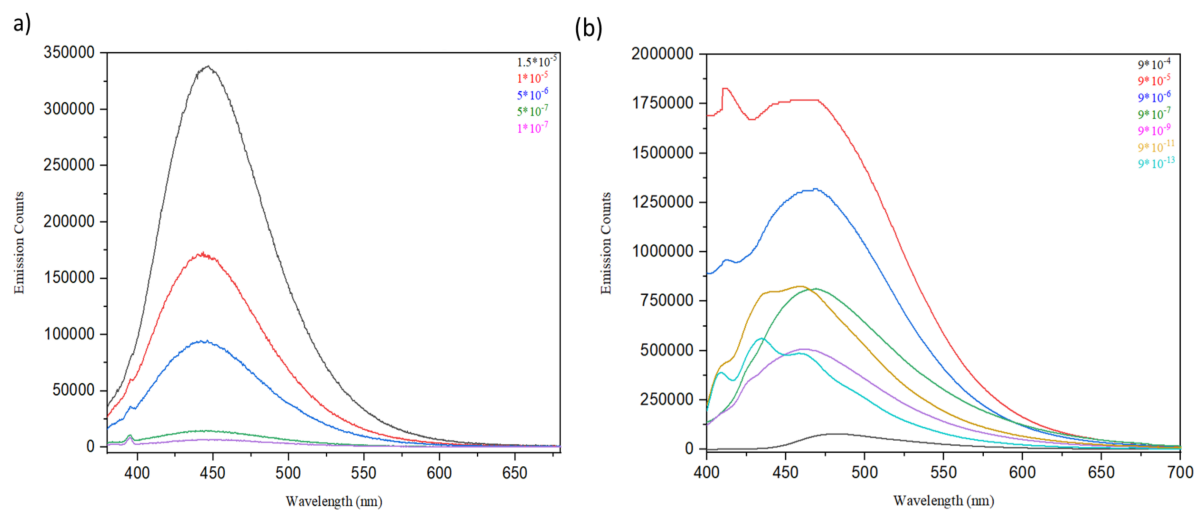
Table S2.1-2e. Crystal data and structure refinement for crystal-to-crystal transformation

Identification code	[A • H ₂ O]
Empirical formula	C ₂₀ H ₁₁ Cl ₄ O ₃ PS ₂
Formula weight	536.18
Temperature/K	173.0
Crystal system	triclinic
Space group	P-1
a/Å	7.4476(7)
b/Å	12.5959(13)
c/Å	13.2064(13)
α/°	116.199(3)
β/°	104.509(3)
γ/°	91.081(3)
Volume/Å ³	1064.13(18)
Z	2
ρ _{calc} /g/cm ³	1.673
μ/mm ⁻¹	0.850
F(000)	540.0
Crystal size/mm ³	0.25 × 0.1 × 0.05
Radiation	MoKα (λ = 0.71075)
2Θ range for data collection/°	5.714 to 61.136
Index ranges	-10 ≤ h ≤ 10, -18 ≤ k ≤ 18, -18 ≤ l ≤ 18
Reflections collected	46942
Independent reflections	6527 [R _{int} = 0.0720, R _{sigma} = 0.0282]
Data/restraints/parameters	6527/0/273
Goodness-of-fit on F ²	1.034
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0306, wR ₂ = 0.0772
Final R indexes [all data]	R ₁ = 0.0370, wR ₂ = 0.0831
Largest diff. peak/hole / e Å ⁻³	0.42/-0.47
CCDC number	2044245

(vi) Comparative discussion of the structures on 2-1a,b-2-2a,b in the solid state

The electron-donating property of the 9,10-phenanthrene quinone in compound **2-1b** reduces the Lewis acidity of P-center compared to that induced by *o*-chloranil substituent. As a result, **2-1b** does not exhibit the planar phase to phase arrangement as seen in **2-1a** and **2-2a**. Here, the quinone and dithieno-moiety of two molecules of **2-1b**, rather exhibit donor to acceptor interactions (3.7 Å) (Figure S2.1-6b). The monomer for compound **2-1b** is detected at 396.5 nm by fluorescence emission-dilution study in toluene (Figure S2.1-7a). Compound **2-2a** shows similar structural features as **2-1a** and likely acquires additional stability from π -stacking interaction of the quinone substituents (3.5 Å), which is closer than that observed in the solid-state structure of **2-1a**. While compounds **2-1a**, **2-1b**, and **2-2a** show supramolecular dimerization, compound **2-2b** forms tetramers in the solid-state, likely due to frequently observed polar F- π interactions (Figure S2.1-6d). Compound **2-2b** is stabilized by the interaction between the orthogonally arranged electron-withdrawing perfluorophenyl group and electron-rich phenanthrene quinone (3.3 Å). The four molecules form the corners of a square and the perfluorophenyl groups are arranged perpendicular to one another at 2.8 Å. The enriched supramolecular interaction makes **2-2b** the most stable among the four as observed experimentally. We surmise that its distinct crystal packing from the other three congeners, also translates to similar intermolecular interaction in solution and can thus explain the different emission properties. By contrast, this derivative exhibit aggregation-caused quenching (ACQ) at higher concentrations, while the peaks resolve to multiple emission maxima (409 nm, 435 nm, and 458 nm) on dilution (Figure S2.1-7b).

Figure S2.1-7. Fluorescence-dilution spectra of (a) compound **2-1b** showing monomer on dilution and (b) compound **2-2b** showing multiple peaks with ACQ.



S.2.1.6 Fluoride abstraction reactions

The hypervalent compounds (a) **2-1a** (0.058 g, 0.001 mmol; CDCl₃, alumina dried and freeze-pump-thaw-cycled) (b) **2-1b** (0.007 g, 0.01 mmol; CDCl₃, alumina dried and freeze-pump-thaw-cycled) (c) **2-2a** (0.06 g, 0.1 mmol; THF, alumina dried and freeze-pump-thaw-cycled) (d) **2-2b** (0.05 g, 0.09 mmol; THF alumina dried and freeze-pump-thaw-cycled) were reacted with 1:1 equiv. of **5** (0.031 g, 0.06 g, 0.025 g, 0.025 g, respectively). The fluoride abstraction reaction of **2-1a**, **2-1b**, **2-2a**, and **2-2b** shows similar doublets confirming the formation of **2-1a-F⁻** ($^1J_{P-F} = 776$ Hz) (Figure S2.1-8a), **2-1b-F⁻** ($^1J_{P-F} = 752$ Hz) (Figure S2.1-8b), **2-2a-F⁻** ($^1J_{P-F} = 795$ Hz) (Figure S2.1-8c), and two sets of doublets of doublets (presumably through long range coupling to C₆F₅ group) coinciding at -140.1 ppm for **2-2b-F⁻** ($^1J_{P-F} = 764$ Hz, 727 Hz) (Figure S2.1-8d) respectively. The doublet of doublet at 137.8 ppm (blue as seen in S2.1-8d) with a coupling constant of 764 Hz (long range coupling of 35 Hz) which corresponds to -56 ppm in ¹⁹F NMR spectrum, is experimentally similar to other P-F type species reported and is assigned to **2-2b-F⁻** species. The doublet of doublet at 142.4 ppm (green as seen in S2.1-8d) with coupling constant, 727 Hz (long range coupling of 35 Hz) corresponds to a species which is structurally similar to **2-2b-F⁻** species, which corresponds to -76 ppm on ¹⁹F NMR spectrum. The precise identification of this species experimentally is cumbersome owing to its transient nature. Compound **2-2b** exhibits different supramolecular interactions in solution and solid state, which could be the reason behind the anomalous behaviours of **2-2b-F⁻** species considering other fluoride species generated. The ³¹P{¹H} (1) and ¹⁹F{¹H} (2) NMR spectra for these reactions after 1 hour of reaction time at room temperature are shown below.

Figure S2-8a. Formation of **2-1a-F⁻** as observed by (1) $^{31}\text{P}\{^1\text{H}\}$ and (2) $^{19}\text{F}\{^1\text{H}\}$ NMR spectroscopy (CDCl_3).

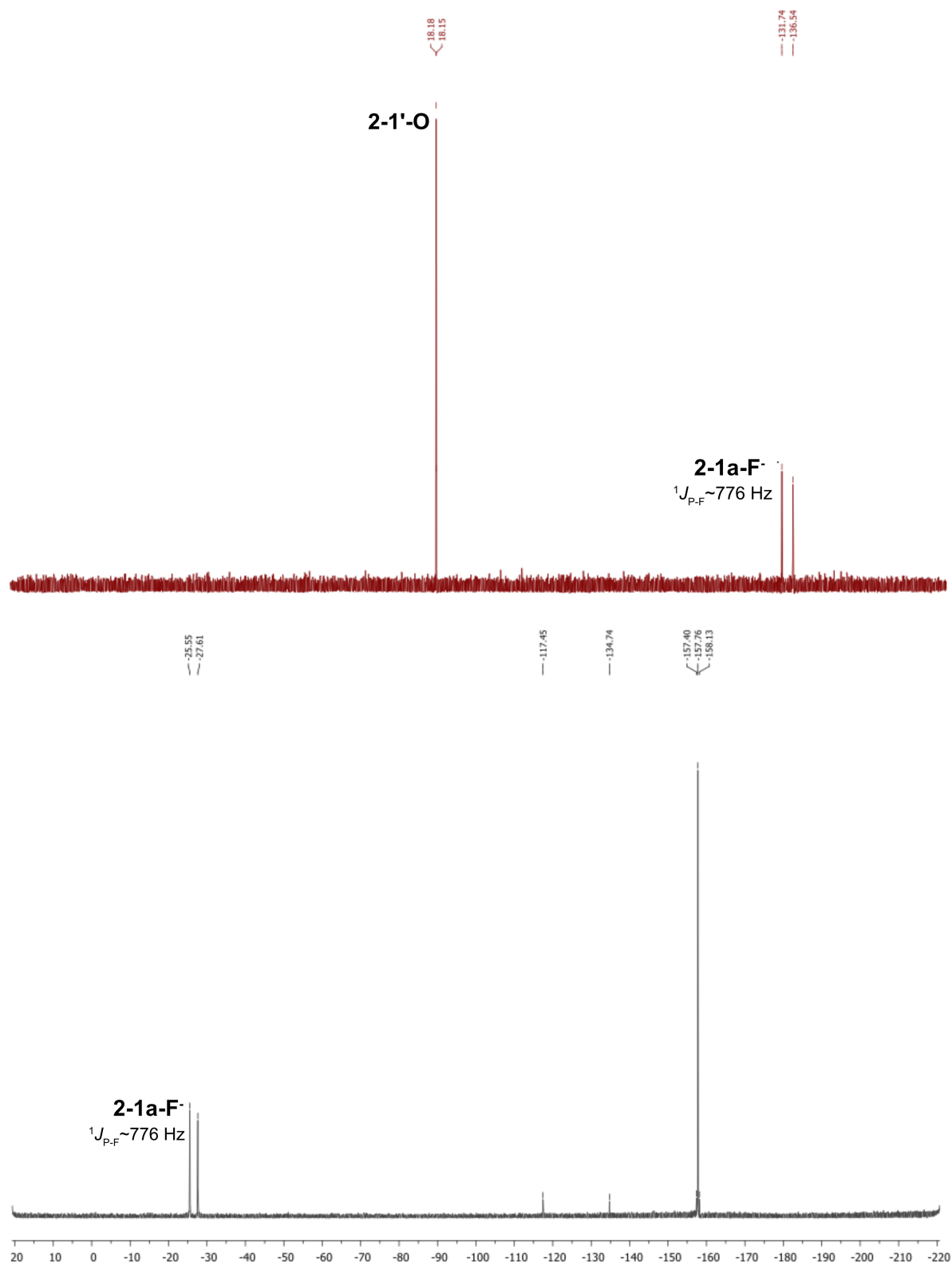


Figure S2-8b. Formation of **2-1b-F⁻** as observed by (1) $^{31}\text{P}\{^1\text{H}\}$ and (2) $^{19}\text{F}\{^1\text{H}\}$ NMR spectroscopy (CDCl_3).

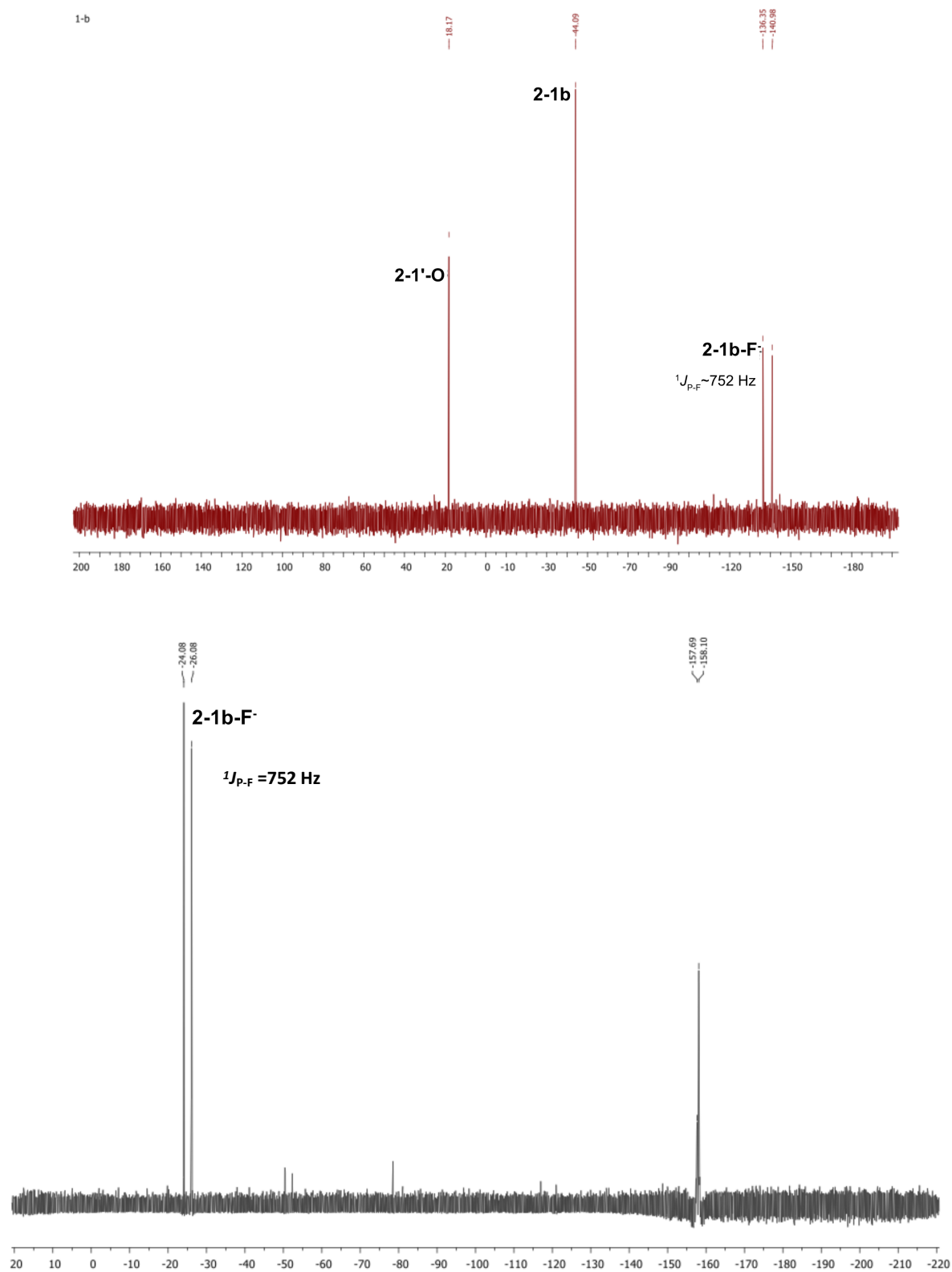


Figure S2-8c. Formation of **2-2a-F⁻** as observed by (1) $^{31}\text{P}\{^1\text{H}\}$ and (2) $^{19}\text{F}\{^1\text{H}\}$ NMR spectroscopy (THF).

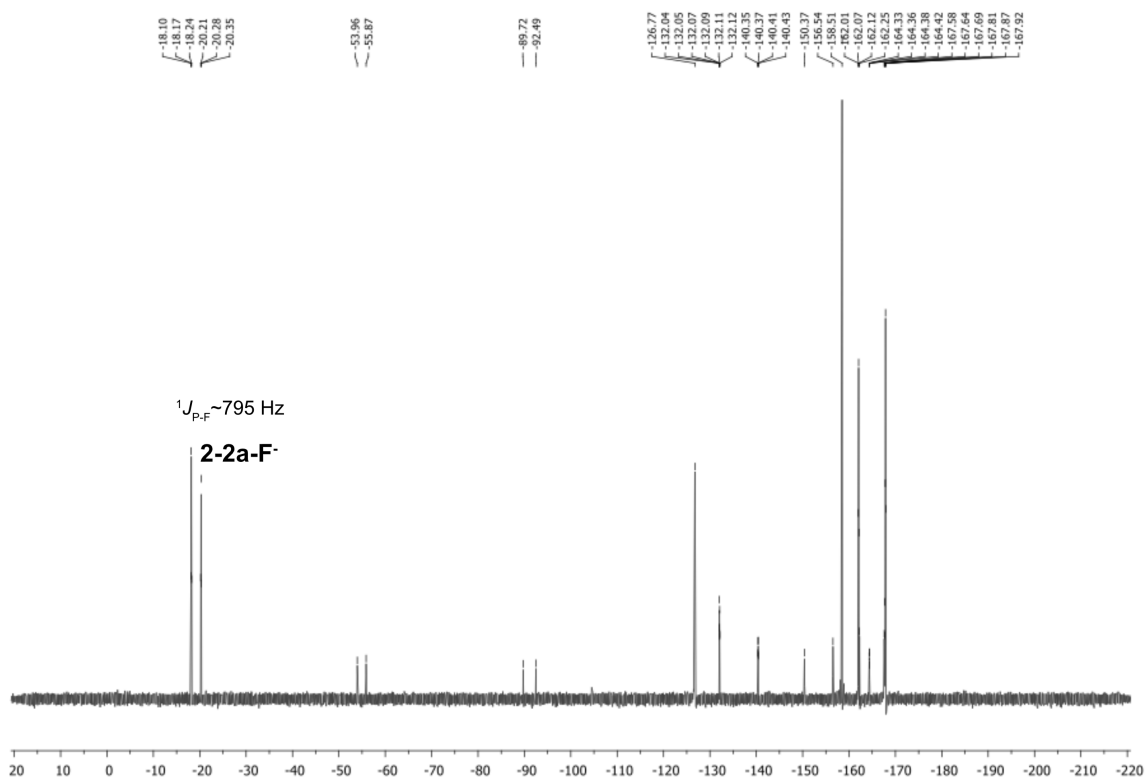
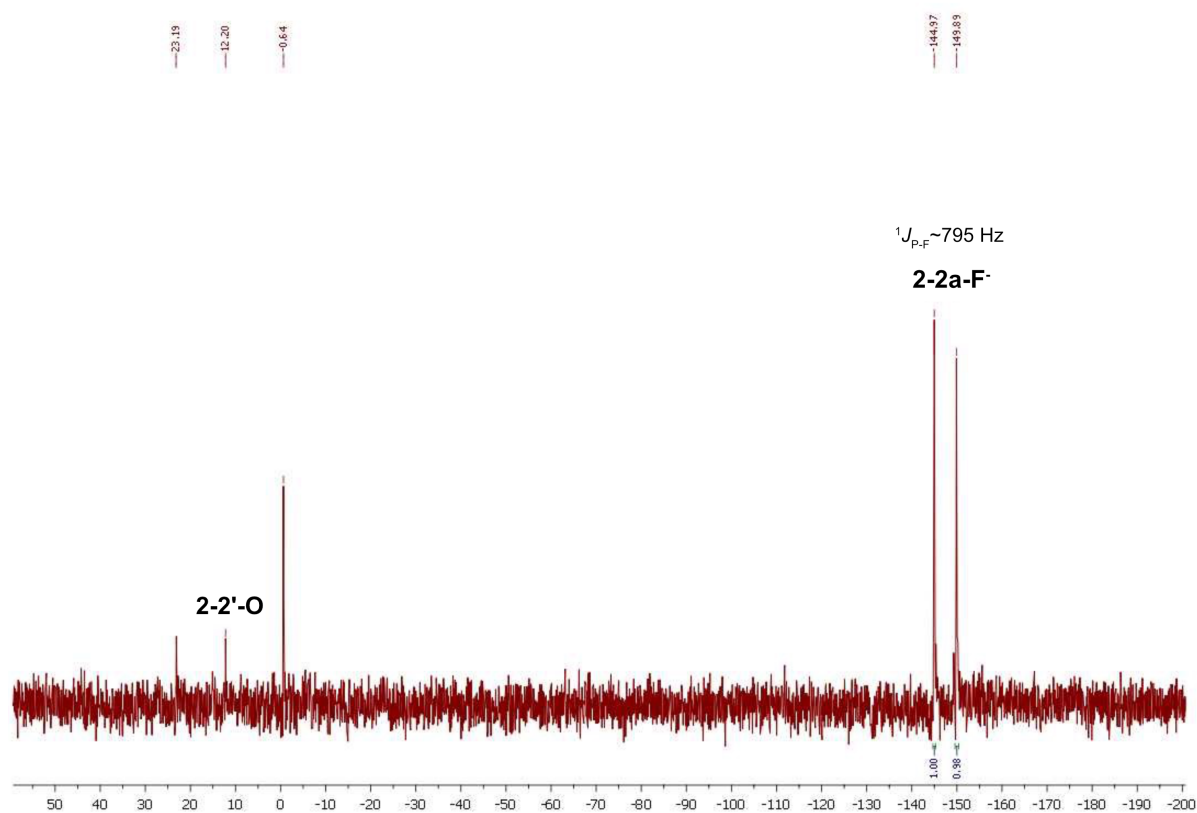
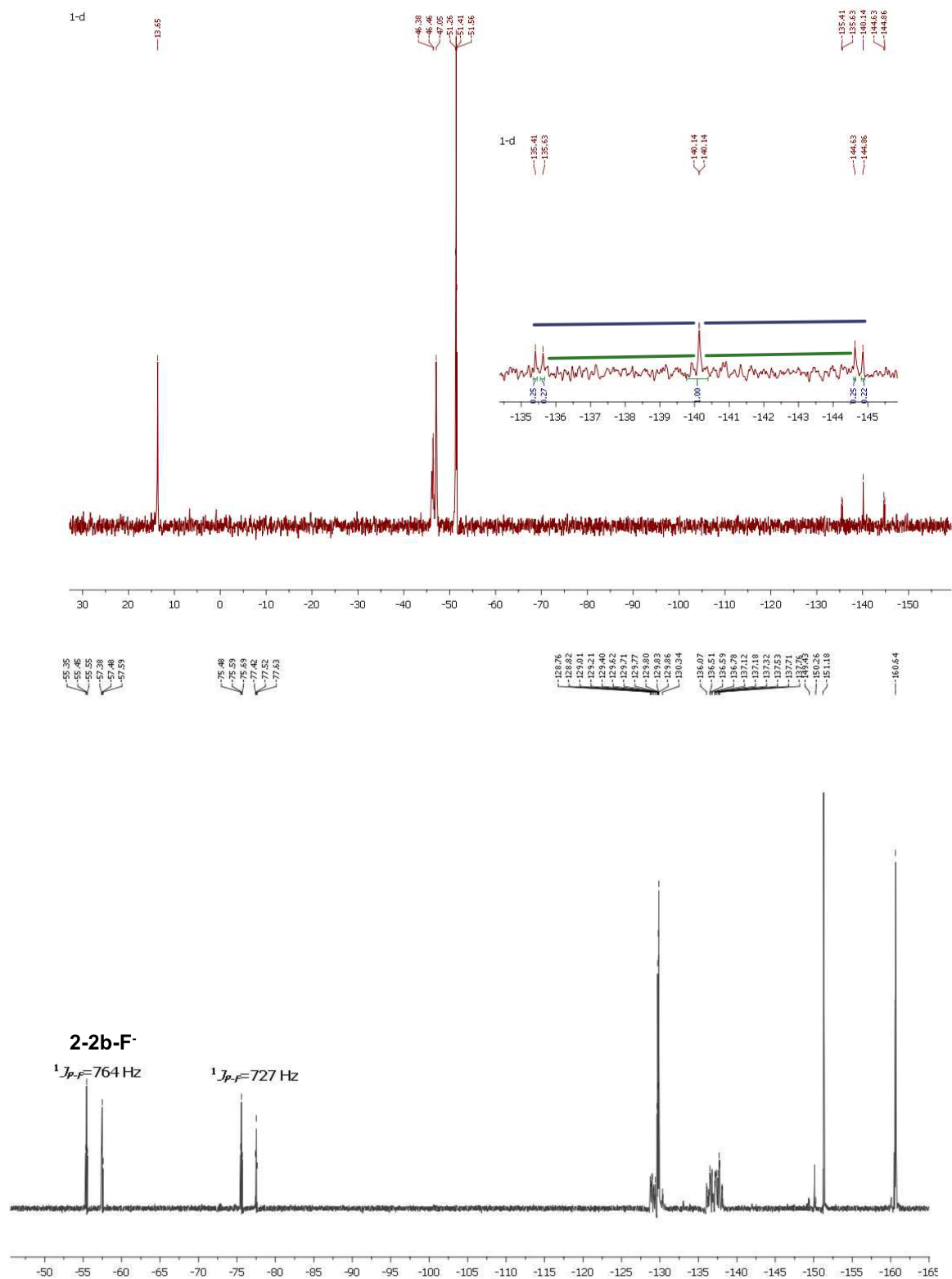
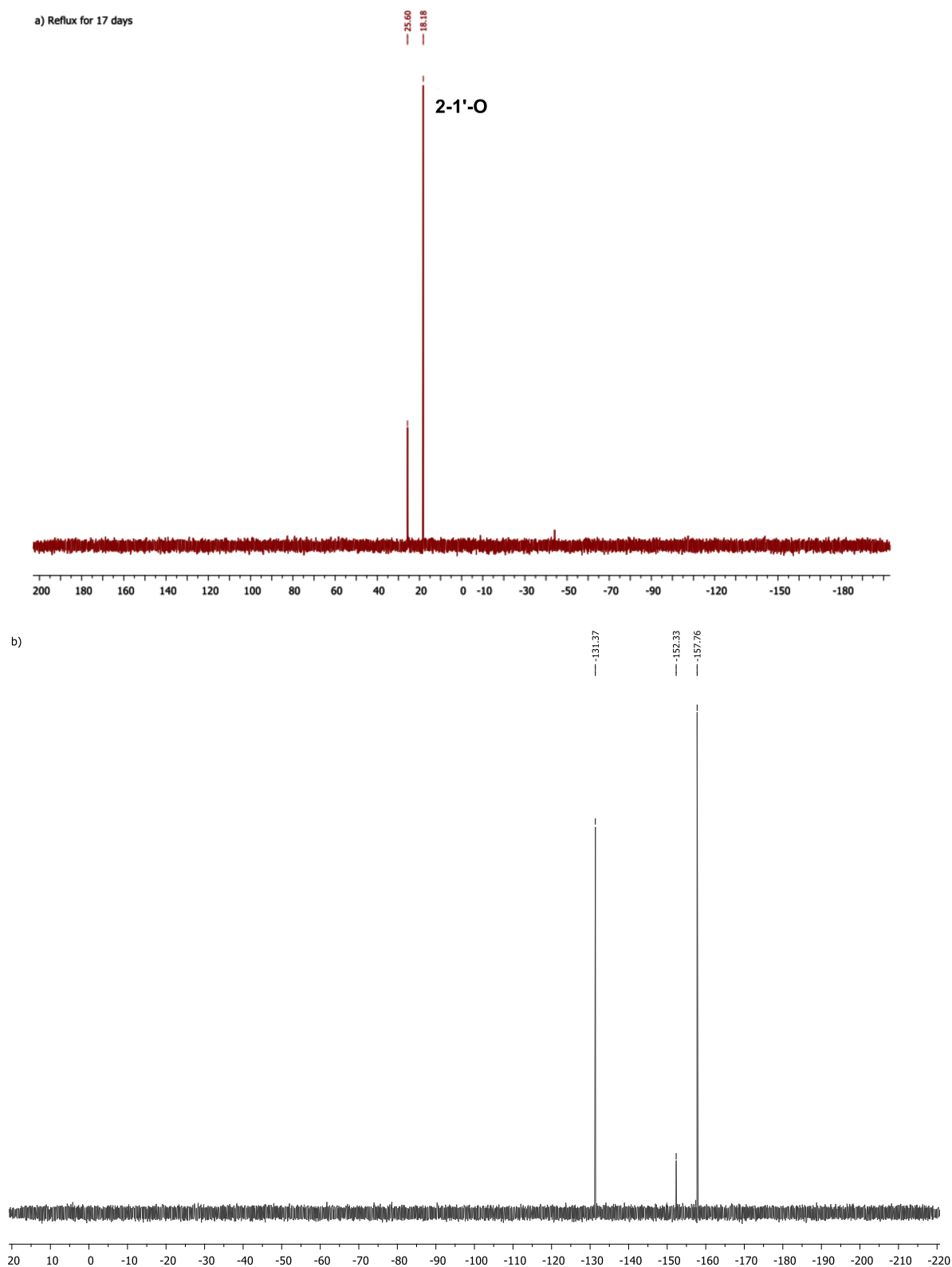


Figure S2-8d. Formation of **2-2b-F⁻** as observed by (1) $^{31}\text{P}\{^1\text{H}\}$ and (2) $^{19}\text{F}\{^1\text{H}\}$ NMR spectroscopy (THF).



All reactions show the formation of an oxide of the parent phosphole (**2-1'-O** for **2-1a** and **2-1b**, **2-2'-O** for **2-2a** and **2-2b**) along with the corresponding fluoride adducts (**R₅P-F⁻**). The reaction of compound **2-1a** in CDCl₃ was initially utilized to study the reaction mechanism for the transformation of **2-1a-F⁻** but the absence of any protons in *o*-chloranil made the identification of by-product difficult. Hence, compound **2-1b** was used instead of **2-1a**. The formed **2-1b-F⁻** was completely converted to **2-1'-O** by refluxing the NMR mixture for 17 days. The ³¹P{¹H} and ¹⁹F{¹H} NMR spectra were recorded to monitor the complete conversion of **2-1b-F⁻** to **2-1'-O** (Figure S2.1-9). The peak at 25.6 ppm in its ³¹P{¹H} NMR spectrum can be attributed to an adduct of the oxide to a Lewis acid.^{S14} ¹³C{¹H} NMR (Figure S2.1-9c) spectrum of this mixture was collected to identify the state of phenanthrene quinone moiety. The blue peaks correspond to **2-1'-O** and the rest of the carbon peaks corresponds to the 7 symmetric carbon atoms of **2-5**.

Figure S2.1-9. Monitoring reaction for complete decomposition of **2-1b-F⁻** by (a) $^{31}\text{P}\{^1\text{H}\}$ and (b) $^{19}\text{F}\{^1\text{H}\}$ NMR spectroscopy followed by the identification of the by-product via (c) $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy. (CDCl_3)



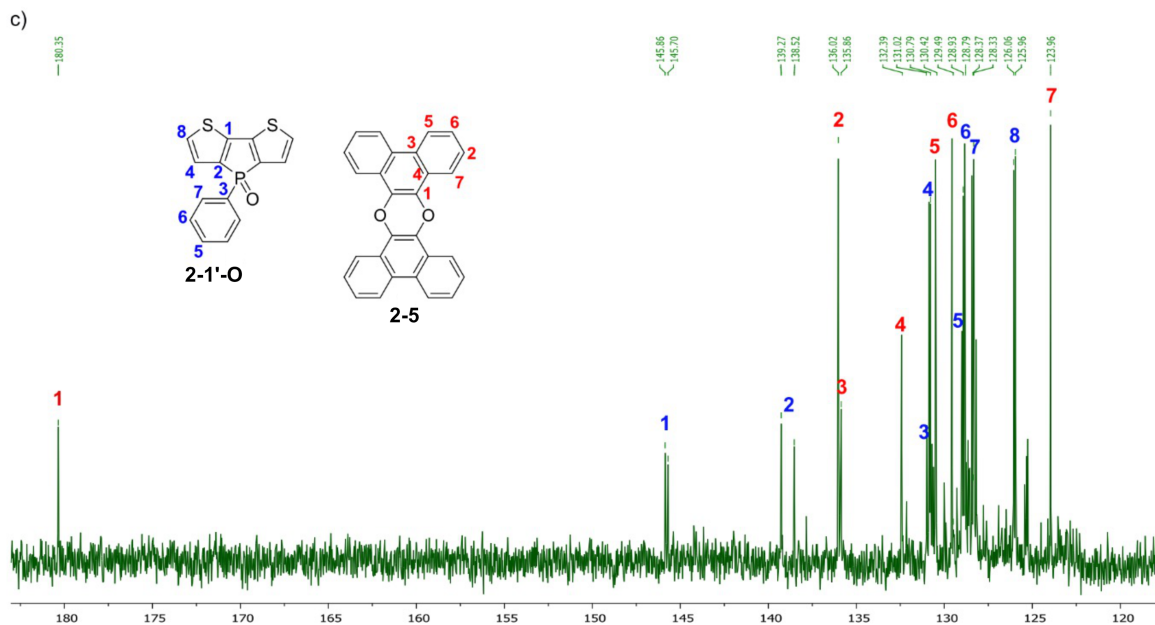
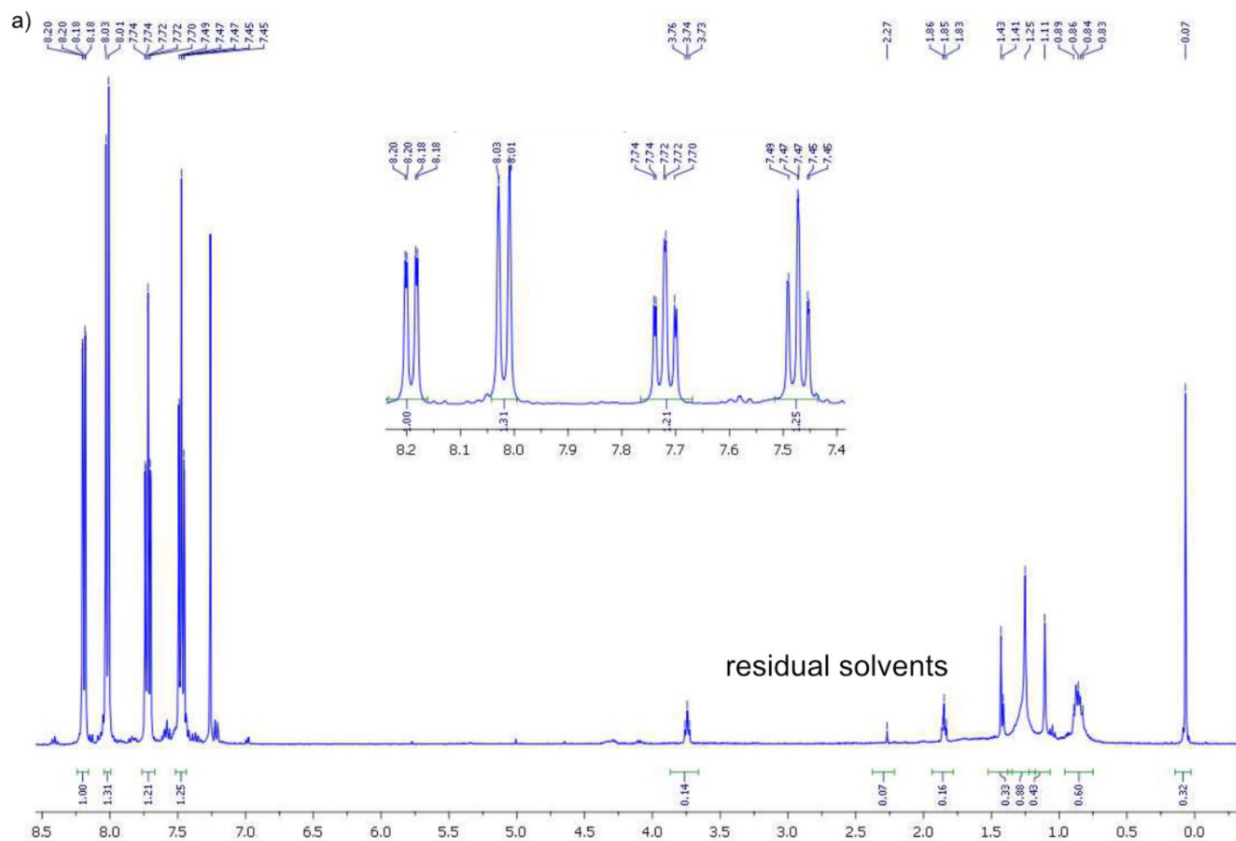
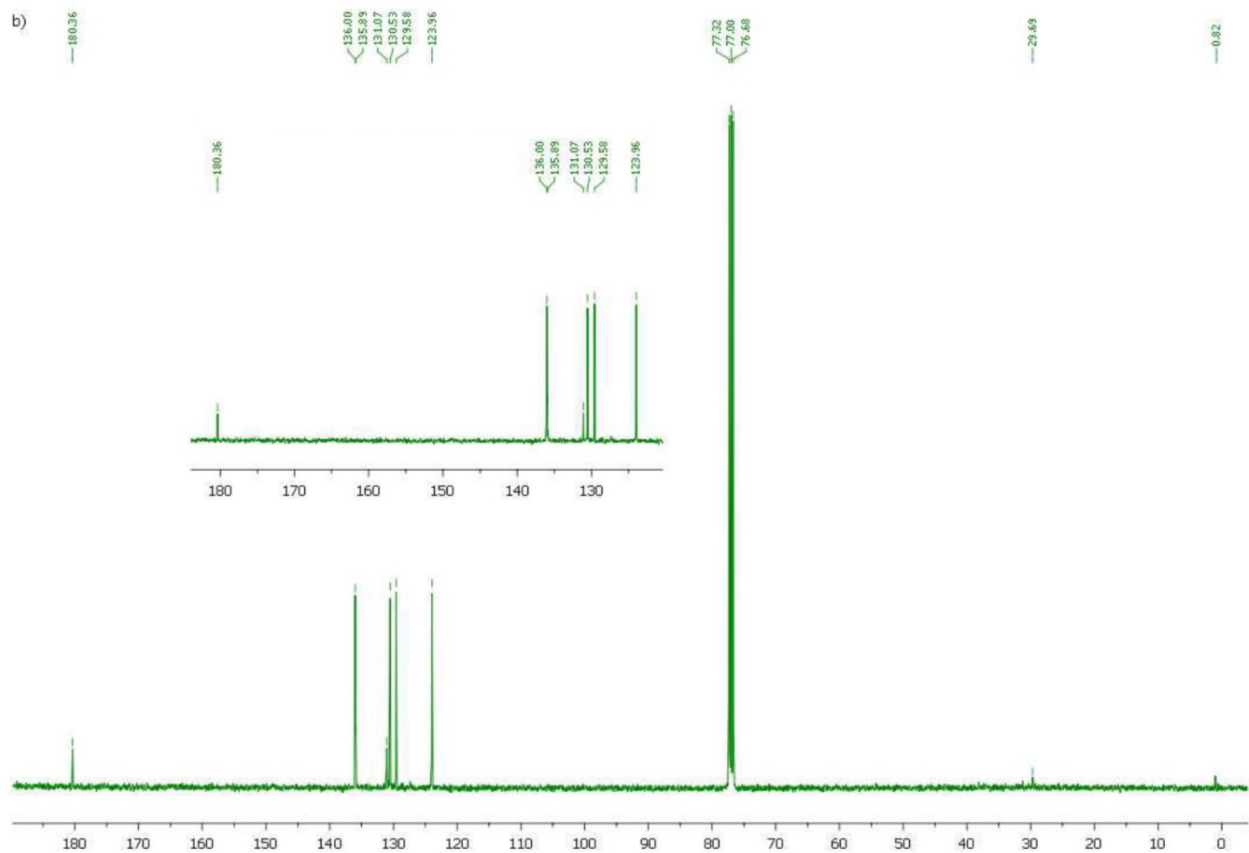


Figure S2.1-20. Isolated compound **2-5** (after complete transformation of **2-1b-F⁻**) by column chromatography (Silica, DCM). (a) ¹H and (b) ¹³C{¹H} NMR spectroscopy for the purified product **2-5** in CDCl₃.



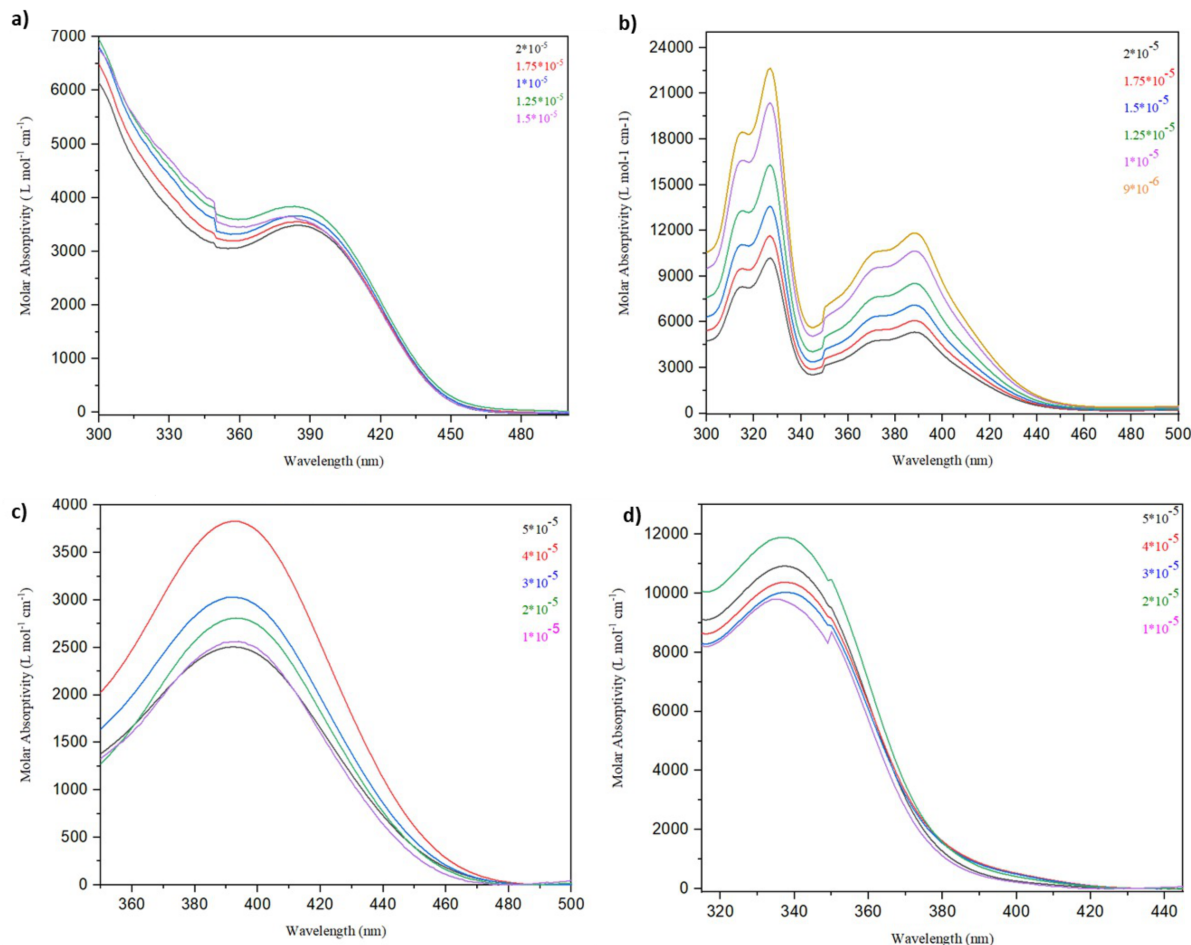


S.2.1.7 Functional properties of synthesized hypervalent compounds

(i) Photophysical Properties

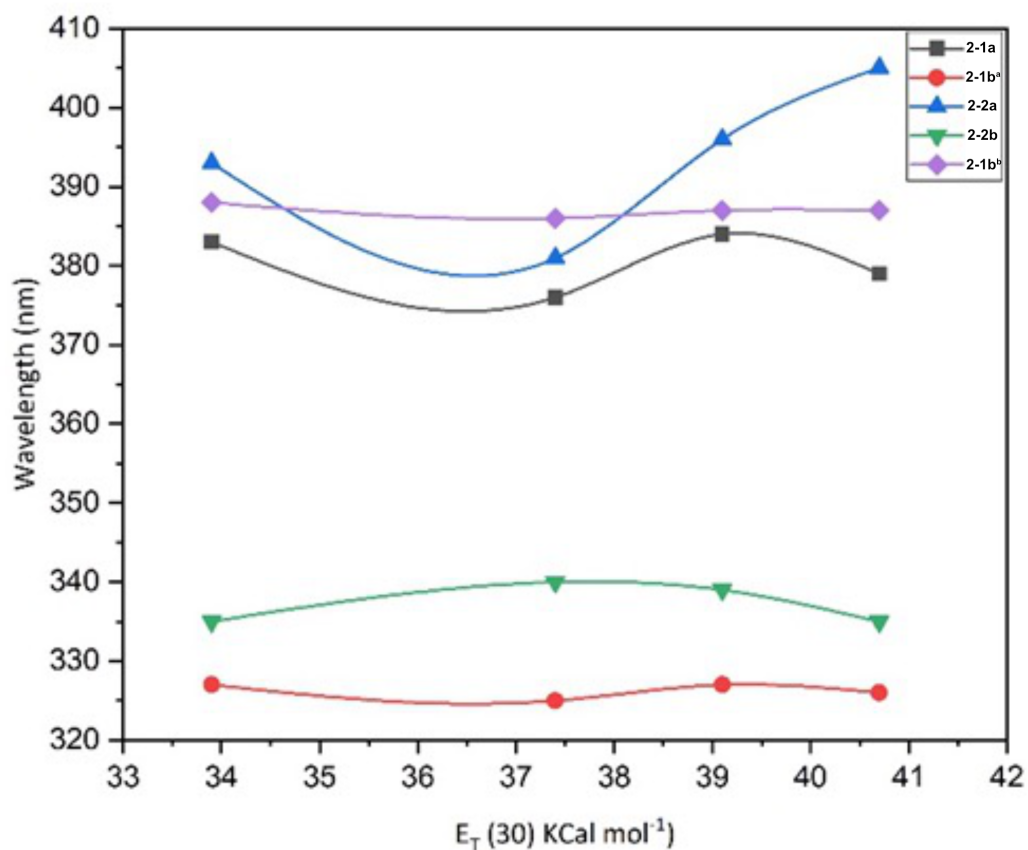
a) UV-Vis spectroscopy: The absorption properties of the compounds were studied in toluene (dried by alumina column and freeze-pump-thaw-cycled). The compounds show aggregation even at a low concentration range of 10^{-5} M as they do not follow Beer-Lamberts law.^{S15} Compound **2-1a** has λ_{max} of 383 nm while the phenanthrene derivative **2-1b** shows two maxima at λ_{max} at 327 nm and 388 nm. Compound **2-1b** exhibits aggregation caused quenching (ACQ) as its absorption increases with a decrease in concentration. Compound **2-2a** and **2-2b** have λ_{max} at 393 nm and 337 nm, respectively (Figure S2.1-21a).

Figure S2.1-21. UV-Vis absorption spectra of a) **2-1a** b) **2-1b** c) **2-2a** and d) **2-2b** in toluene.



b) Solvatochromism: Compound **2-1a** shows a red shift in absorbance in solvents such as toluene, DCM, and chloroform (λ_{max} at 383 nm) in contrast to coordinating solvents such as THF (λ_{max} at 376 nm). The blue-shifted wavelength in THF suggests the coordination of a solvent molecule to the Lewis active site in compound **2-1a**. Similar observations are recorded for compound **2-2a**. Compound **2-1b** has two maxima at λ_{max} (327^a, 388^b nm), both of which are not influenced by the polarity of the solvents. In contrast, compound **2-2b** shows slightly higher absorbance in THF than in non-coordinating solvents, probability due to the interaction with coordinating solvent that breaks the tetrameric interaction (Figure S2.1-22)

Figure S2.1-22. Effect of the solvent polarity (E_T 30 scale)^{S16} on the absorption maxima.



(ii) Emission Spectroscopy

Compounds **2-1a**, **2-2a**, **2-2b** are fluorescent in solution. In toluene, compound **2-1a** emits in the blue-green region at a wavelength of 514.5 nm and compound **2-2a** shows green fluorescence at 532.5 nm; compounds **2-1b** and **2-2b** emit in the blue region at 446 nm and 470.5 nm, respectively. The photoluminescence quantum yield (PLQY) of these compounds is less than 50% in toluene likely due to ACQ, but in non-coordinating solvents such as DCM, the PLQY amount to 6% for **2-1a**, 41% for **2-1b**, 51% for **2-2a**, and 59% for **2-2b**. (Figure S2.1-23)

Figure S2.1-23. Emission spectra a) **2-1a** b) **2-1b** c) **2-2a** and d) **2-2b** in various solvents.

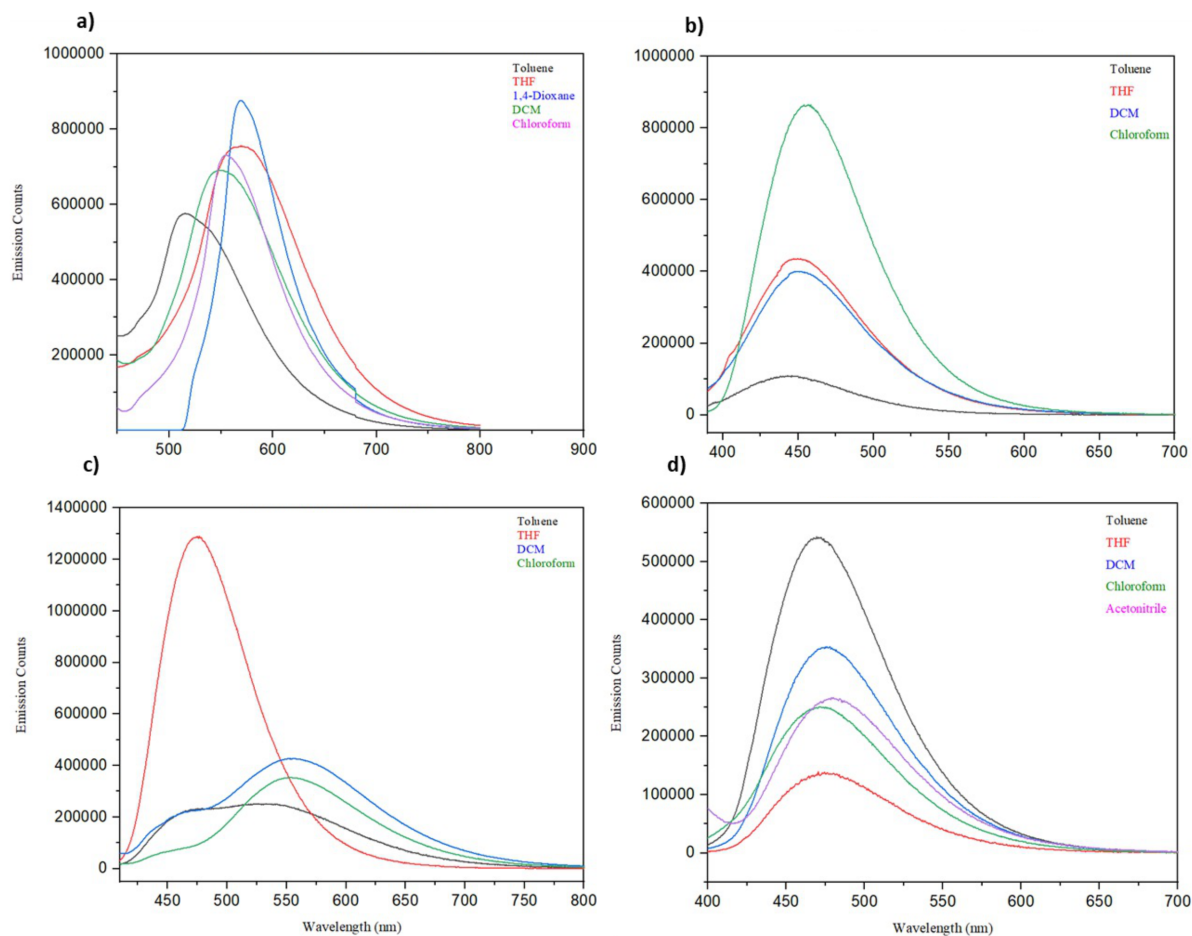


Table S2.1-3. Excitation and emission wavelengths of the synthesized compounds in various solvents with their respective PLQY.

	CH ₃ CN		CHCl ₃		DCM		1,4-Dioxane		THF		Toluene	
(nm)	λ_{ex}	λ_{em}	λ_{ex}	λ_{em}	λ_{ex}	λ_{em}	λ_{ex}	λ_{em}	λ_{ex}	λ_{em}	λ_{ex}	λ_{em}
2-1a			384.5	555.5	390	548	388.5	569	396	570	389.5	514.5
PLQY			7%		6%		16.60%		25%		3%	
2-1b			367	456.5	359	449.5			362	449.5	353.5	446
PLQY			54%		41%				7%		15%	
2-2a			393	552.5	398	556			381	476.5	396	532.5
PLQY			23%		51%				98%		35%	
2-2b	372	479	369.5	471.5	378.5	476			373	470.5	375.5	470.5
PLQY	4%		16%		59%				39%		48%	

(iii) Electrochemical properties

Cyclovoltammetry shows irreversible oxidation and reduction events for all compounds. Compound **2-2a** immediately electro-polymerizes likely due to the presence of highly electron-withdrawing groups. Compounds **2-1a** and **2-1b** show multiple irreversible reduction peaks, but compound **2-1b** shows a reversible oxidation-reduction peak at -1.8 V by differential pulse voltammetry. Compound **2-2b** shows multiple irreversible oxidation peaks in addition to a reduction peak (Figure S2.1-24).

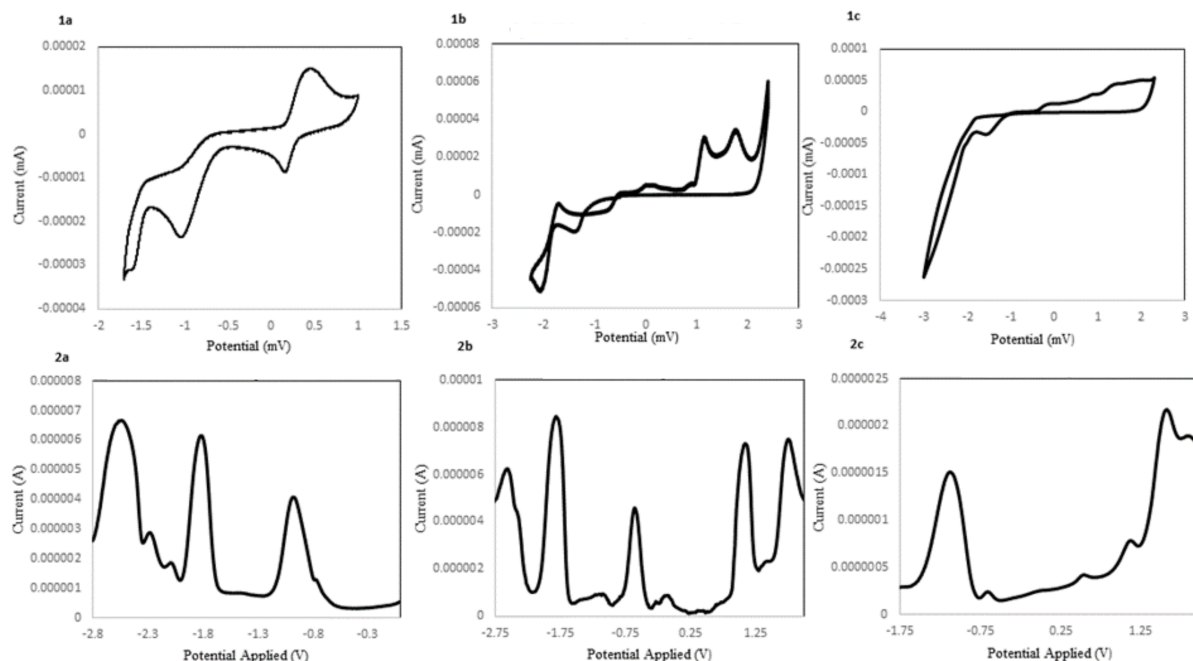


Figure S2.1-24. Electrochemistry (1: cyclic voltammetry, CV, 2: Differential Pulse Voltammetry, DPV) of a) **2-1a** b) **2-1b** and c) **2-2b**.

S.2.1.8 Stability of the hypervalent compounds toward heat and light

Heat: The crystals of compound **2-1a** grown in a wet solvent such as CHCl_3 transformed immediately to **2-1'-O** and **2-3** on slightly heating to 30° C, while the crystals grown from dry solvent in the glovebox are stable to up to 130°C.

Light: All compounds are stable under daylight provided they are stored under dry conditions. The amorphous powder exposed to light shows tarnishing on the surface, if exposed to air. All compounds are also stable under daylight in solution (dry solvents). After a period of 7 days, new decomposition peaks are observed in solution of compound **2-1a** in *d*-chloroform stored under sunlight. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the solution after 2 months of irradiation shows multiple peaks suggesting the formation of unidentified decomposition products.

Given the very long duration required for the decomposition of 50% of the product, these compounds can be considered stable in light.

S.2.1.9 Exploration of structures and reaction mechanisms using computational chemistry

(i) Computational rationale for the observed square pyramidal structures:

We optimized the 3BP and 4SQ structures of compounds **2-1a,b-2-2a,b** using the CAM-B3LYP functional and the ma-def2-svp basis set. Compound **2-1a** is taken as a representative for the following discussion. The two structures of **2-1a** are shown and compared in Figure S2.1-25. Whenever there is ambiguity, atom numbers are given to specify which atom is referred to (e.g., C2, O18, etc.). The other three compounds have similar structures.

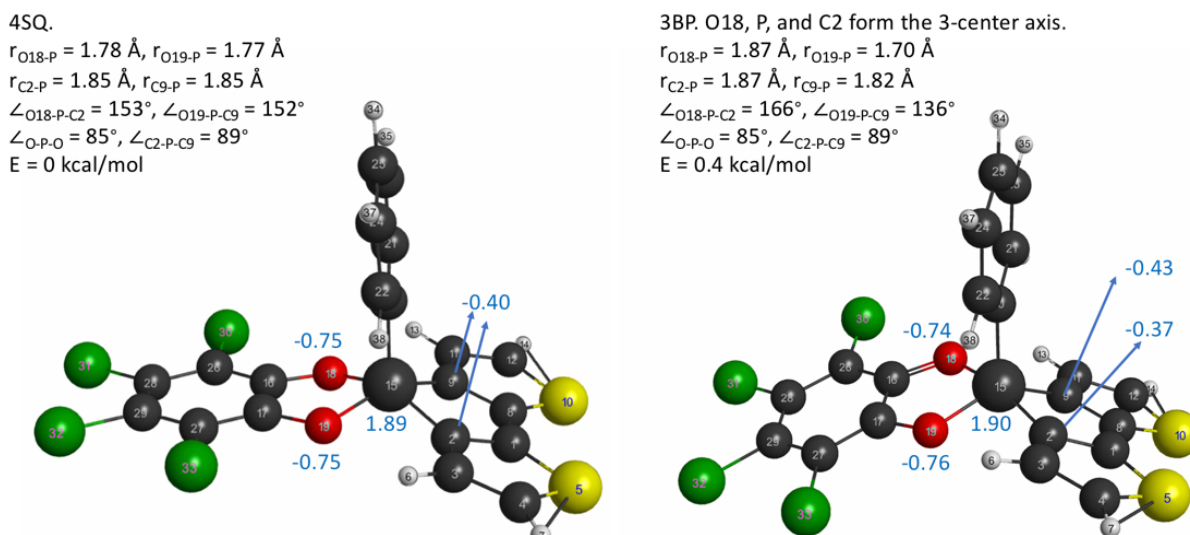


Figure S2.1-25. The comparison of the 4SQ and 3BP structures of compound **2-1a**. The numbers in blue color are natural atomic charges.

The 4SQ and 3BP structures are very close in energy (0 vs. 0.4 kcal/mol). Considering the accuracy of our calculations, we can say that they are isoergic. The 3BP structure has its 3c-4e bond along one O atom (O18) and the opposite C atom (C2) in the dithieno unit. The $\angle_{\text{O-P-C}}$ angle is 166° , not a perfect linear alignment as the typical 3c-4e F-P-F bond in PF_5 . The phenyl group takes an equatorial position in 3BP, and this is also the case when it is replaced by the pentafluorophenyl

group in **2-2a** and **2-2b**. Note that the following two angles in both the 3BP and 4SQ structures are nearly identical; $\angle_{\text{O-P-O}} = 85^\circ$ and $\angle_{\text{C2-P-C9}} = 89^\circ$. These most conserved geometrical parameters are determined by the respective 5-membered rings (P-O-C-C-O and P-C-C-C-C). As explained below, these two angles raise the preference towards the 4SQ structure of this class of compounds.

Since the 3c-4e interaction in 3BP is favored when two electronegative groups are at the termini of the 3c bond, one would like to put the two O atoms at the termini. But this results in $\angle_{\text{O-P-O}} = 180^\circ$, which is impossible given the large resultant strain of the P-O-C-C-O ring. Next, we consider placing one O and the phenyl group at the axial positions (Figure S2.1-26a), where $\angle_{\text{O-P-O}} = 90^\circ$, close to the 85° one in the P-O-C-C-O 5-membered ring. However, $\angle_{\text{C(ipso)-P-C(ipso)}} = 120^\circ$, which is far from the 89° one in the P-C-C-C-C 5-membered ring. There is too much strain for this 3BP arrangement. This 3BP framework is thus unstable. The replacement of phenyl by pentafluorophenyl further favors the 3c-4e interaction due to the enhancement of electronegativity in the axial position. However, this does not alleviate the strain. This is why the pentafluorophenyl in **2-2a** and **2-2b** does not facilitate the 3BP structure either.

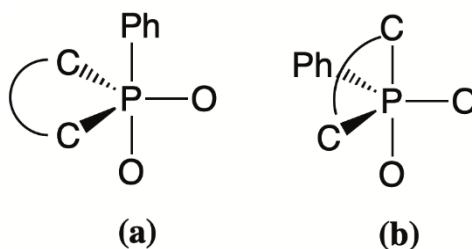


Figure S2.1-26. The two 3BP frameworks discussed.

So, the only possible 3BP structure must adopt the framework in Figure S2.1-26b, with one ipso-carbon and one oxygen atom at the axial positions. The 90° angles for $\angle_{\text{O-P-O}}$ and $\angle_{\text{C-P-C}}$ in the

framework are close to the corresponding 85° and 89° angles in the two 5-membered rings. Indeed, the 3BP in Figure S2.1-25 adopts this framework.

While it is possible to further distort the structure to have a linear O-P-C axial arrangement and an $\angle_{\text{O-P-C}} = 120^\circ$ equatorial arrangement, the 3BP structure in Fig. S2.1-25 adopts an axial $\angle_{\text{O-P-C}} = 166^\circ$ and an equatorial $\angle_{\text{O-P-C}} = 136^\circ$. That is only halfway to the perfect 3BP structure. The C2 atom is not electronegative enough to take an axial position for the 3c-4e interaction. The electronegativities of C, O, and P, are 2.55, 3.44, and 2.19, respectively. Carbon is not much more electronegative than phosphorus, anyway. The natural bond orbital (NBO) analysis shows that it is more appropriate to describe the 3c-4e interaction as the formally O^- donating its lone pair to the $\sigma_{\text{P-C}}^*$ orbital, instead of the typical symmetric case of having two terminal lone pairs interacting through a central empty orbital. The natural population analysis assigns an approx. -0.75 charge to the oxygen atoms, regardless of their position, and a ca. $+1.90$ charge to the phosphorus center. These charges indicate a fairly complete charge transfer from the P atom to the O atoms, consistent with their electronegativities.

The 2nd order perturbation theory analysis of the NBO program indicates a 44.2 kcal/mol strength for the coordinative bonding between the O lone pair and the $\sigma_{\text{P-C}}^*$ orbital along the 3BP axial direction in Figure S2.1-25. This value is of qualitative nature and certainly an overestimation. However, it is indicative enough that the lone-pair-to- σ_{PC}^* coordinative bonding is real. The C2-P bond that is involved in this coordinative bonding is correspondingly elongated to 1.87 Å, when compared to the equatorial $r_{\text{P-C9}} = 1.82$ Å. This coordinative bonding is shown in Figure S2.1-27. The weakening of the axial PC bond further disfavors linear alignment of the O-P-C axial fragment, resulting in the 166° axial O-P-C angle.

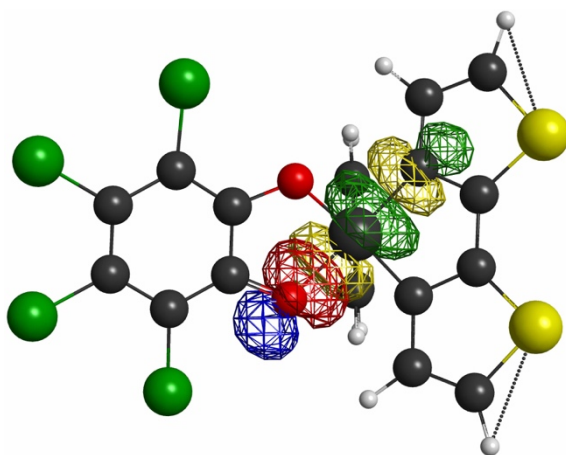


Figure S2.1-27. The coordinative bonding interaction between the oxygen lone pair and the $\sigma_{\text{P-C}}^*$ orbital along the axial direction of the 3BP structure. For a better visualization, the phases of the O lone pair and $\sigma_{\text{P-C}}^*$ orbitals are represented by different colors.

A similar lone-pair- $\sigma_{\text{P-C}}^*$ overlap also occurs between the equatorial O19 and the P-C9 bond, but with a smaller magnitude because of the less linearity ($\angle_{\text{O19-P-C9}} = 136^\circ$). The P-C9 bond is correspondingly shorter than the P-C2 bond (1.82 vs 1.87 Å). The NBO analysis gives a 13.9 kcal/mol strength for this 3c-4e interaction. Clearly, the enhancement of the O18-P-C2 3c-4e interaction is at the cost of weakening the O19-P-C9 3c-4e interaction. The formation of a perfect 3BP structure with linear O18-P-C2 is hence hindered. And there is a tendency to form the 4SQ structure with equivalent O-P-C 3c-4e interactions, with the O18-P-C2 one being weakened and the O19-P-C9 one being strengthened, if the strengthening outweighs the weakening.

In the 4SQ structure, $\angle_{\text{O-P-C}} = 153^\circ$ for the two symmetrically equivalent 3c-4e fragments, and their interaction strengths are 33.8 kcal/mol. The strengthening is indeed larger than the weakening. The 4SQ structure is slightly lower in energy than the 3BP structure by 0.4 kcal/mol. Note that the ~20 kcal/mol enhancement of O19-P-C9 3c-4e interaction and the ~10 kcal/mol decrease of the O18-P-C2 3c-4e interaction are qualitative estimates. They should not be used to argue that the 4SQ structure should be more stable than the 3BP structure by approx. 10 kcal/mol.

The small energy difference between the 4SQ and 3BP structures indicates a shallow potential energy surface connecting the two 3BP structures (there are two such structures due to symmetry) and the 4SQ structure. The molecule thus dynamically adopts the two types of structures through the C₆Cl₄O₂ group rocking with respect to the symmetry plane of the dithienophosphole (similar to Berry pseudorotation). On average, it exhibits as a 4SQ structure.

All four molecules (**2-1a,b** and **2-2a,b**) feature small 3BP-4SQ energy differences. The largest difference is 1.7 kcal/mol for **2-2a**, with the 3BP structure being slightly more stable. This is too small a barrier to trap the molecule at one of the symmetry-connected 3BP structures. It exhibits a 4SQ structure on average. When the molecules form solids, the 4SQ structures lead to parallel arrangement of aromatic moieties between adjacent molecules and thus stronger π - π stacking interactions. The 4SQ structures are consequently further preferred.

(ii) *Proposed mechanisms for the reaction of 2-1a with water.*

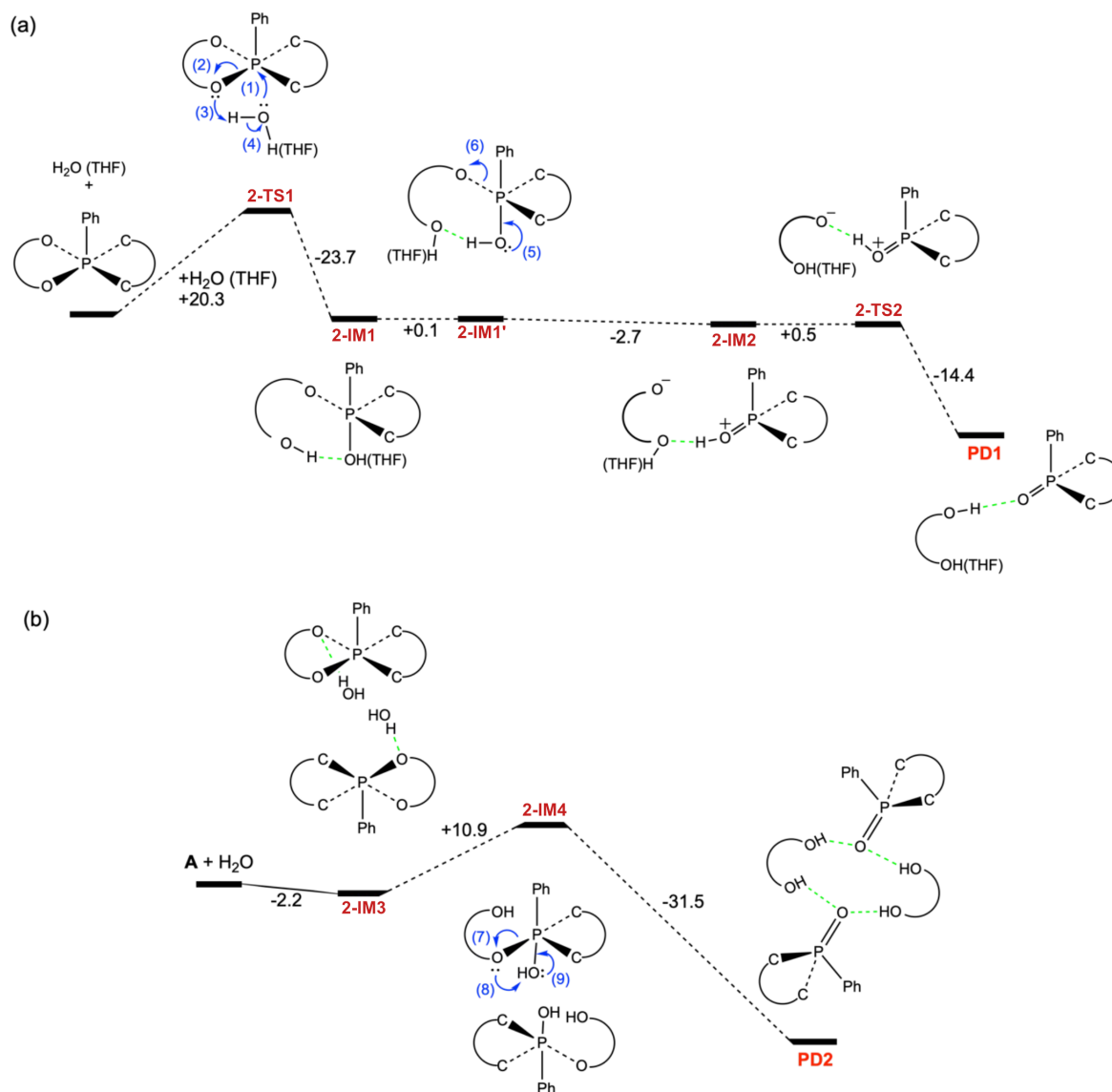


Fig. S2.1-28. Energy landscapes for the reaction of H₂O and **2-1a** in (a) THF solution and (b) crystalline form. In this figure two curves are used to schematically represent the *o*-chloranil and dithieno groups. Key structures for (a) and (b) are shown below in Figure S2.1-29, and S2.1-30, respectively. Energy differences between structures connected by dashed lines are given in kcal/mol. The energy differences in (b) are for each H₂O molecule. The green dashed lines in (a) and (b) indicate hydrogen bonds.

Figure S2.1-28a shows the calculated energy landscape for the reaction $\text{H}_2\text{O}(\text{THF}) + \mathbf{2-1a}$ using solvent model of THF and with one explicit THF solvent molecule. In the figure, “(THF)” is associated to protonic water H atoms via a hydrogen bond. The whole reaction is calculated to be exoergic by 20.0 kcal/mol, and there is essentially only one 20.3 kcal/mol barrier (**2TS1**), which is feasible to overcome under room temperature. As shown, this rate-determining step involves concerted migrations of four electron pairs: (1) the addition of a H_2O lone pair to the acidic phosphorus center, forming the new O-P bond; (2) the heterolytic breakage of one of original O-P bonds and the transfer of the bond pair electrons to a lone pair of the O atom; (3) this O atom donating its lone pair to an H atom of the H_2O molecule to abstract the proton and form a new OH bond; (4) the original OH bond of this H atom in H_2O is broken heterolytically and the bond pair electrons migrate to form a lone pair on O. These four migrations are labelled as (1)-(4) in the Figure S2.1-28a. The experimental data show that changes in electronegativities of the axial (C_6H_5 vs. C_6F_5) and the side group (chloranil vs. phenanthrene quinone) do not result in a clear trend of rates of reaction. This fact is consistent with the calculated mechanism. An electronegative axial group favors electron pair migration (1) but disfavors (2). An electronegative side group favors (2) but disfavors (3). The stochastic rates for the respective reactions of H_2O with **2-1a**, **2-2a**, and **2-2b**, are reflections of these contradictory features.

Once the H_2O -addition intermediate (**2-IM1**) is formed, the subsequent steps are all thermodynamically and kinetically favourable. **2-IM1'** is essentially isoergic with **2-IM1** (only 0.1 kcal/mol higher). They differ in the orientation of the two OH bonds, and to which H atom the explicit THF forms a hydrogen bond. The search of the transition state between **2-IM1** and **2-IM1'** requires two explicit THF molecules, which is computationally costly. Considering the quantum nature of the OH-bond rotations and the large availability of THF solvent molecules, the barrier

between **2-IM1** and **2-IM1'** must be low and easy to overcome. The two intermediates interconvert easily. The remaining O-P bond in **2-IM1'** is long at 1.94 Å bond length (vs. the 1.73 Å summation of the O and P covalent radii). The O-P bond is of pure ionic character and is about to break. In fact, a transition state search starting with the **2-IM1'** structure with a slightly longer O-P distance results in the intermediate **2-IM2**, which is -2.7 kcal/mol lower in energy than **2-IM1'**. This O-P bond breaking must involve a small barrier. It involves two concerted electron pair migrations labelled as (5) and (6). Step (6) is readily achieved because of the aforementioned elongated and ionic nature of the O-P bond. Step (5) is also an easy step due to the cationic nature of the P center. There is a negligible 0.5 kcal/mol barrier between **2-IM2** and the final product (**PD1**; **2-1'-O** and **2-3**). This step is a proton transfer from a positively charged oxygen to a negatively charged oxygen atom. The calculated low energy barrier and large exoergicity are as expected. In the whole process, the phosphorus center acts as a Lewis acid in electron pair migrations (1) and (5) and the aryloxy O-atom acts as a Lewis base in (3).

The calculations show that a similar mechanism is applicable for the solid-state reaction between the crystalline **2-1a** and H₂O (Figure S2.1-28b). The insertion of H₂O in the crystal results in a structure (**2-IM3**) with two H₂O molecules between each pair of **2-1a** dimers. Each H₂O molecule forms a hydrogen bond with one oxygen atom of the *o*-chloranil group, and this process is exoergic by 2.2 kcal/mol per H₂O molecule. **2-IM3** was obtained in a geometry optimization with an initial structure with each H₂O crosslinking the two monomers through forming two hydrogen bonds. However, the result of the optimization indicates unfavorability of the crosslinking. The fact that one H₂O interacts with one **2-1a** molecule and the insertion of H₂O molecules separates the **2-1a** monomers further apart (P-P distance from 5.03 to 6.25 Å) suggests a similar reaction mechanism as in Figure S2.1-28a. With similar electron pair migrations like (1)-(4), **2-IM4** is formed, which

can be viewed as **2-IM1/2-IM1'** embedded in the solid-state environment. Since **2-IM4** cannot freely rotate about the leftover O-P bond as in **2-IM1/2-IM1'**, its formation is 10.9 kcal/mol endoergic. The last step involves concerted electron pair migrations (7)-(9) to form **2-1'-O** and **2-3 (PD2)**. This highly favourable step makes the whole reaction -22.8 kcal/mol exoergic. The exoergicity is comparable to the -20.0 kcal/mol for the reaction in solution. The high energy intermediate **2-IM4** explains the slower rate of the reaction between the **2-1a** crystal and moisture. Given the similar intermediates in the solution and solid-state reactions, no attempt was made to search for transition states in the solid state reactions.

(iii) Key structures of the 2-1a + H₂O reaction in THF solution:

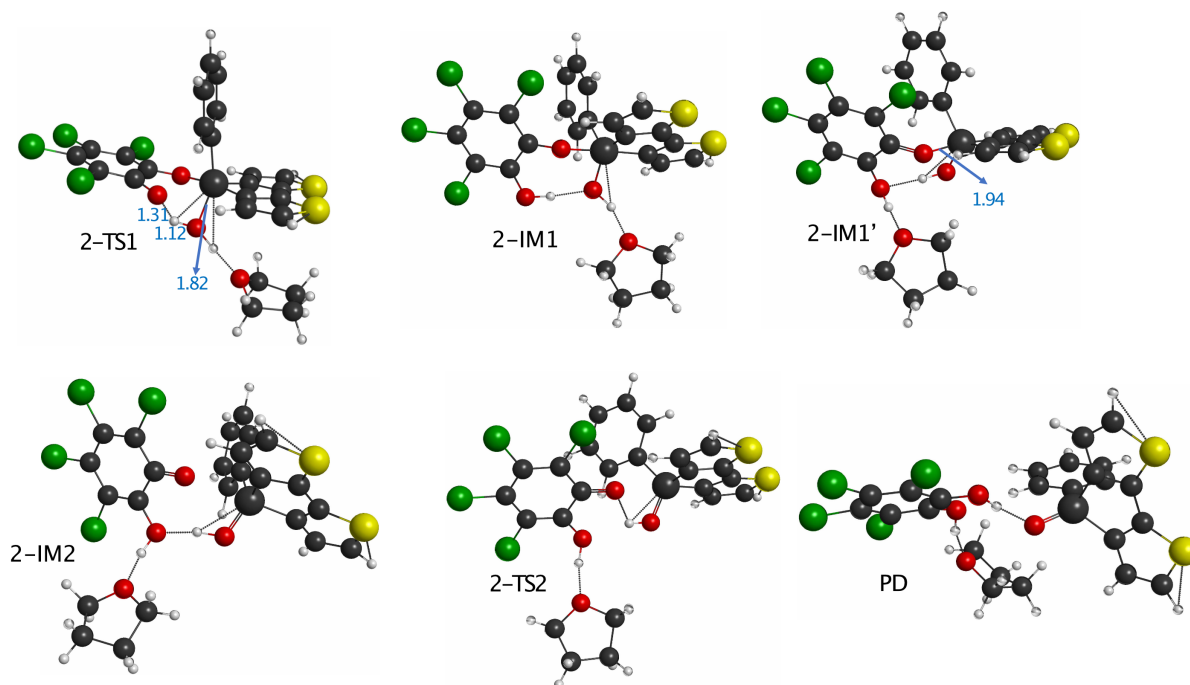


Figure S2.1-29. Pictures of structures mentioned in the energy landscape of the **2-1a** + H_2O reaction in Figure S2.1-28a. Key bond lengths are given in blue color in Å.

(iv) Key structures of the **2-1a** + H₂O reaction via crystal-to-crystal conversion:

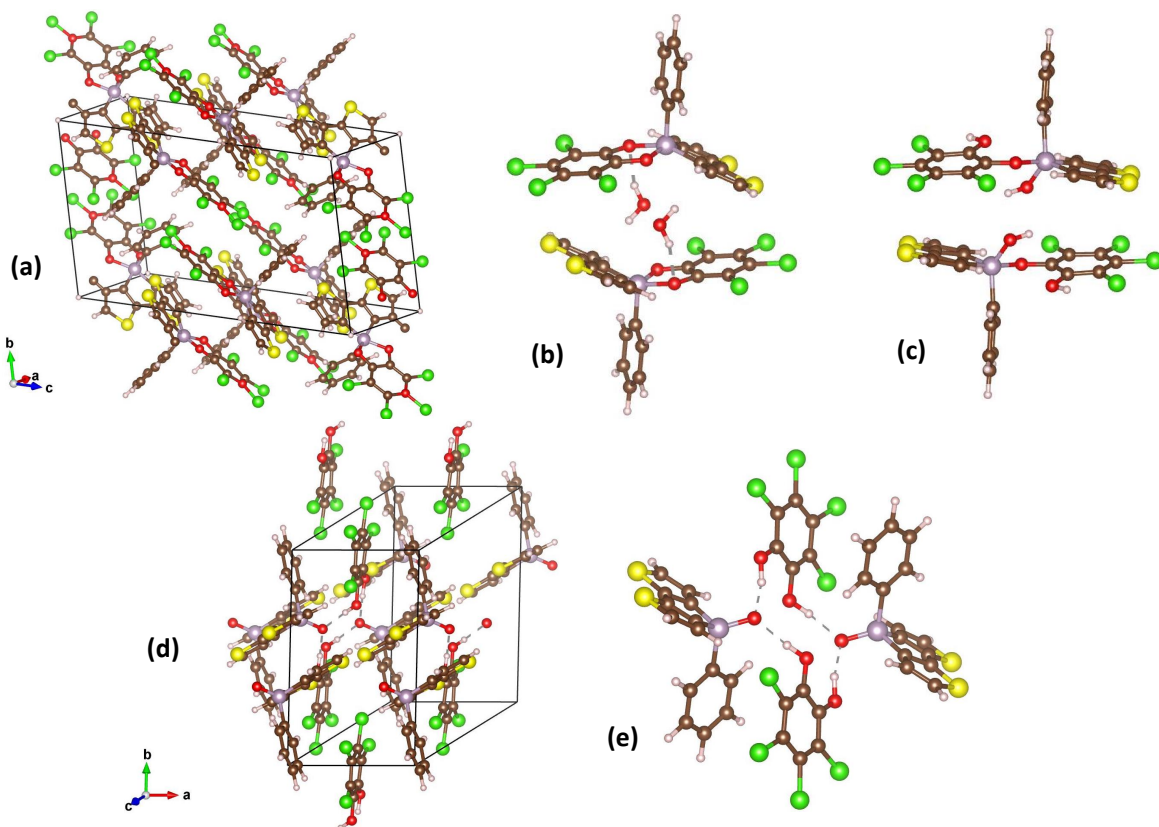


Figure S2.1-30. (a) The P2₁/c unit cell of **2-1a**, which contains two dimers of **2-1a** molecules, (b) the **2-IM3** dimer structure with H₂O molecules being inserted, (c) the **2-IM4** dimer structure, (d) the P1 unit cell of the product (**PD1**) of the **2-1a** + H₂O reaction in crystal, (e) the product dimer structure. The dimer structures in (b), (c) and (e) are taken from the respective unit cells to better illustrate the inter-monomer configurations and the inserted H₂O molecules.

(v) Key structures of the fluorination and deoxyaryloxylation of compound 2-1a:

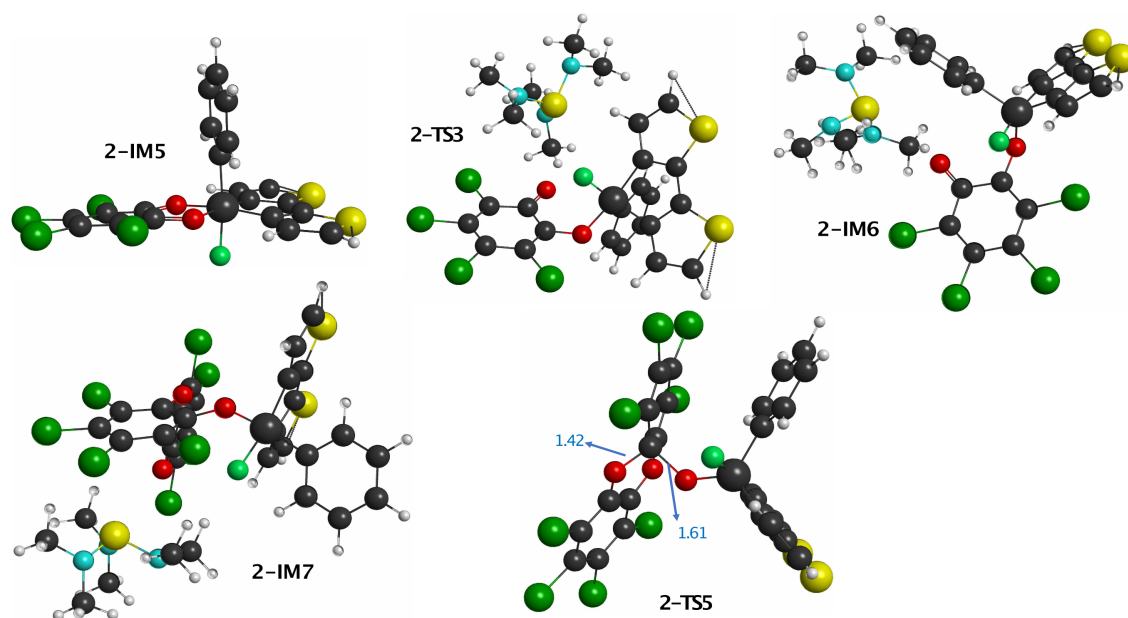


Figure S2.1-31. Pictures of structures mentioned in the energy landscape of the fluorination and deoxyaryloxylation of **2-1A** in Figure 2-8 in the main text. Key bond lengths are given in blue color in Å.

S.2.1.10 Coordinates of all structures discussed in 2.1.9 above and Fig. 2-8 in the main text.

2-1a (3BP):

C	3.36186000	-0.72231800	-0.79878100
C	2.24690200	-1.30768800	-0.25447900
C	2.38523800	-2.72293000	-0.15538600
C	3.60771000	-3.15514500	-0.59425800
S	4.60302700	-1.85339700	-1.14954200
H	1.61728900	-3.40447300	0.21059000
H	3.98712500	-4.17532100	-0.64150000
C	3.24807900	0.71238000	-0.97801000
C	2.04580100	1.25138700	-0.57356600
S	4.28261600	1.88910600	-1.65860200
C	1.96953600	2.65662500	-0.80236300
C	3.11010200	3.13621800	-1.38295600
H	1.10821800	3.27458400	-0.55497800
H	3.34481900	4.15695500	-1.68191100
P	0.96695500	-0.01227400	0.17198400
C	-1.56935700	0.75994200	-0.14577400
C	-1.49480800	-0.59714900	-0.46730300
O	-0.39343600	1.27082000	0.15796700
O	-0.23778800	-1.07773500	-0.39231500
C	1.04608900	-0.03674500	1.98658500
C	1.10335300	1.16009800	2.71090500
C	1.07865500	-1.26125300	2.66424300
C	1.22419300	1.12610000	4.09744900
C	1.17237000	-1.29003300	4.05288000
C	1.25441500	-0.09629900	4.76673700

C	-2.79634300	1.40812800	-0.20134000
C	-2.57967600	-1.30725400	-0.93564100
C	-3.92291700	0.69349500	-0.65021600
C	-3.81612700	-0.64660600	-1.03078600
Cl	-2.87495300	3.07966700	0.22971700
Cl	-5.45473800	1.49310000	-0.73949700
Cl	-5.19301200	-1.49909800	-1.63256900
Cl	-2.37238000	-2.95948800	-1.39008900
H	1.34817700	-0.11928600	5.85485600
H	1.29044900	2.05932800	4.65968300
H	1.06297600	2.11859400	2.19142200
H	1.19062100	-2.24716200	4.57757700
H	1.02489400	-2.20155100	2.11529900

2-1a (4SQ):

C	3.46919200	-0.66451500	-0.94168100
C	2.28978800	-1.25360100	-0.56002400
C	2.36855600	-2.67622100	-0.55544600
C	3.61529100	-3.11667200	-0.90530800
S	4.69746200	-1.81177900	-1.25998200
H	1.54404800	-3.34371100	-0.30637000
H	3.96837600	-4.14291900	-1.00027400
C	3.43721800	0.78681300	-0.94614000
C	2.23281200	1.32717400	-0.56826500
S	4.61614100	1.98399400	-1.26239800
C	2.25313100	2.75205200	-0.56328600
C	3.48279200	3.24311500	-0.90563900
H	1.40123700	3.38415700	-0.31467600
H	3.79653200	4.28204900	-0.99936800

P	1.04665200	0.01406300	-0.04459600
C	-1.46670900	0.66105000	-0.36418700
C	-1.43520300	-0.73432600	-0.36420200
O	-0.24376700	1.18990400	-0.37847500
O	-0.18979900	-1.20720500	-0.38701500
C	1.00788800	0.00022700	1.77479700
C	0.98562300	1.20196400	2.49150300
C	0.93970600	-1.21961900	2.45835400
C	0.88325000	1.18120000	3.88019100
C	0.84174200	-1.23584300	3.84706600
C	0.81372900	-0.03599600	4.55590500
C	-2.66967500	1.34416600	-0.37155500
C	-2.60326500	-1.47324200	-0.36086600
C	-3.86657100	0.60503000	-0.41007300
C	-3.83290800	-0.79120600	-0.40376000
Cl	-2.63894700	3.07042800	-0.32434400
Cl	-5.38163100	1.43611600	-0.43804100
Cl	-5.30520200	-1.69473600	-0.42431600
Cl	-2.49388800	-3.19582000	-0.30147100
H	0.72680700	-0.04985200	5.64491000
H	0.85542100	2.11926200	4.43778900
H	1.03352800	2.15827600	1.96838400
H	0.77974400	-2.18773100	4.37808100
H	0.94646100	-2.16169100	1.90818600

2-TS1:

C	3.52861500	-0.59631500	-0.69664700
C	2.33979300	-1.27250700	-0.54702300
C	2.53024000	-2.67995900	-0.45589900

C	3.85372200	-3.02575000	-0.51791200
S	4.88766800	-1.65101000	-0.69780600
H	1.73097300	-3.41284400	-0.34385000
H	4.29173400	-4.02186900	-0.46452000
C	3.39593400	0.83705100	-0.86634000
C	2.10612000	1.31318500	-0.80834400
S	4.53525800	2.09826000	-1.08013700
C	2.03025300	2.72783500	-0.96558000
C	3.27064600	3.28265500	-1.12218700
H	1.10392400	3.30104000	-0.96478700
H	3.53105500	4.32985200	-1.27105000
P	0.94717800	-0.02536700	-0.45873300
C	-1.70235700	0.48817100	-0.22250300
C	-1.88604900	-0.91555800	-0.17921600
O	-0.49566600	0.96639200	-0.55163200
O	-0.86297400	-1.68583700	-0.50849300
C	0.82322400	-0.09102800	1.39877600
C	0.82751300	1.10645600	2.12451800
C	0.77134300	-1.30803000	2.08772100
C	0.81490800	1.08639900	3.51734100
C	0.74924700	-1.32568800	3.48059700
C	0.77828100	-0.13000200	4.19567800
C	-2.76824000	1.35209000	0.00139900
C	-3.13587800	-1.40113200	0.21674900
C	-4.03221500	0.84391900	0.33208300
C	-4.20698600	-0.53284300	0.46978100
Cl	-2.49698000	3.05390000	-0.15455400
Cl	-5.36745000	1.92940400	0.52960000
Cl	-5.75439300	-1.16638400	0.92716000
Cl	-3.33685700	-3.11863300	0.32534200

H	0.76756700	-0.14768800	5.28804200
H	0.83245600	2.02518600	4.07459800
H	0.85233900	2.06477300	1.60366700
H	0.70737300	-2.27968000	4.01052600
H	0.73306700	-2.24744600	1.53715300
H	-0.31214500	-1.30536200	-1.63260900
O	0.39236400	-0.56985300	-2.10822100
H	1.09299700	-0.85727700	-2.78593900
C	2.75166700	-2.02680300	-4.55671900
C	4.20622800	-1.59723200	-4.76917900
C	4.15363700	-0.05072500	-4.74738600
H	4.60701200	-1.99699900	-5.71018500
H	4.84070600	-1.97338700	-3.95539100
C	2.68134300	0.27756500	-4.47400900
H	4.49255900	0.39772400	-5.69078800
H	4.79527100	0.34900900	-3.95053400
O	2.13435600	-0.91474600	-3.90971700
H	2.13930300	0.52121500	-5.40280600
H	2.52614400	1.09139300	-3.75421700
H	2.62388000	-2.90317200	-3.90961200
H	2.24000600	-2.21525000	-5.51539600

2-IM1:

C	3.89163900	1.72180000	-0.71408300
C	2.53891100	1.56030000	-0.94015900
C	1.95176600	2.69822800	-1.56898600
C	2.86526100	3.68483700	-1.79676400
S	4.45575600	3.24222800	-1.25944500
H	0.90236300	2.77771800	-1.83495600

H	2.70304000	4.65741600	-2.25910500
C	4.53899200	0.61112800	-0.03609200
C	3.68452600	-0.41872600	0.26595100
S	6.14181700	0.33236100	0.52248200
C	4.34247200	-1.46513000	0.97532900
C	5.66945300	-1.19466400	1.18353500
H	3.86470900	-2.38068000	1.32568600
H	6.41091000	-1.81377900	1.68737400
P	1.91869200	-0.00294100	-0.26158400
C	-1.60659800	-1.00079800	-0.80673600
C	-1.02958100	0.28223000	-0.63580500
O	-0.88049900	-2.03486500	-1.25095500
O	0.23015600	0.51408800	-0.97666700
C	1.22304300	0.01807000	1.41330600
C	0.92096300	-1.19592400	2.03726600
C	1.04283000	1.22687700	2.08942900
C	0.42607300	-1.19489600	3.34000600
H	1.06364000	-2.14140800	1.51006900
C	0.56251400	1.21878700	3.39549300
H	1.27600600	2.17429800	1.60087100
C	0.24898300	0.01061500	4.01567100
H	0.16903700	-2.13743800	3.82750900
H	0.41296700	2.16094800	3.92685700
H	-0.14707200	0.00896300	5.03329100
C	-2.95452200	-1.20348100	-0.50950900
C	-1.87520500	1.33231400	-0.23476700
C	-3.78354500	-0.14363800	-0.12899600
C	-3.24140100	1.13488900	-0.00787200
Cl	-5.46430600	-0.42226900	0.18219200
Cl	-4.25441800	2.47381200	0.41811300

Cl	-3.58410200	-2.80785500	-0.69406200
Cl	-1.20822600	2.92698700	-0.12953300
H	0.07581100	-1.79334600	-1.29961400
O	1.68175900	-1.39083800	-1.08619400
H	2.47672800	-1.95026500	-1.35818700
C	2.55179200	-3.79675000	-3.05025400
C	3.38730200	-5.03629200	-3.35392700
C	4.83990200	-4.58165300	-3.07623000
H	3.23269100	-5.38091300	-4.38544800
H	3.10337900	-5.85564300	-2.68133400
C	4.68840100	-3.16413300	-2.50136400
H	5.45571800	-4.57609200	-3.98509200
H	5.32590300	-5.24724000	-2.35062500
O	3.32433000	-3.07876900	-2.08479900
H	4.88028200	-2.39725500	-3.27078000
H	5.32132300	-2.95345000	-1.63070500
H	1.56973000	-4.00777100	-2.60714100
H	2.41514800	-3.16638500	-3.94675900

2-IM1':

C	3.85041500	-1.80101100	-0.60042600
C	2.46934400	-1.86095300	-0.62967000
C	1.98565700	-3.18990000	-0.81927700
C	3.00404500	-4.09043000	-0.93543000
S	4.56273100	-3.34252100	-0.80809700
H	0.93193300	-3.45284300	-0.86066900
H	2.92997300	-5.16491200	-1.09861500
C	4.40245000	-0.46914400	-0.40782300
C	3.44111600	0.50206600	-0.28751500

S	5.99825900	0.16652000	-0.35361400
C	4.00778900	1.80076000	-0.16137700
C	5.37729800	1.77032700	-0.17899400
H	3.43487700	2.72265100	-0.05906600
H	6.07113400	2.60514000	-0.09338900
P	1.71654800	-0.22584000	-0.35626900
C	1.16480900	0.18974900	1.32319300
C	0.44667500	1.37428200	1.51429200
C	1.44029600	-0.63981800	2.41111700
C	-0.00000600	1.72000400	2.78761600
H	0.22324500	2.02925700	0.67013000
C	1.00140200	-0.28263100	3.68380900
H	1.98738200	-1.57339400	2.26693600
C	0.27619100	0.89319900	3.87327700
H	-0.57214100	2.63867300	2.93150000
H	1.22694800	-0.93441300	4.53028700
H	-0.08342700	1.17163700	4.86695900
C	-1.93396400	0.09607100	-0.83188900
C	-1.15564100	-0.91967800	-0.23780400
O	-1.41997100	0.76536200	-1.89842100
O	0.05443400	-1.17504800	-0.68801600
C	-3.18839100	0.42167100	-0.32143300
C	-1.73397400	-1.66256600	0.80552200
C	-3.72461400	-0.28727400	0.76098900
C	-3.00452700	-1.35681500	1.30022500
Cl	-5.26662700	0.14483000	1.41160700
Cl	-3.68057200	-2.29922400	2.58280300
Cl	-4.07237000	1.71100200	-1.05742700
Cl	-0.83756700	-2.98979200	1.45670200
O	-0.90531800	-0.86171300	-3.83444500

C	0.45620600	-1.23467700	-4.09994900
C	0.63470200	-1.02513000	-5.59463500
H	0.61665500	-2.28608000	-3.80548700
H	1.10873300	-0.60544800	-3.48356700
C	-0.75801800	-1.35127400	-6.14494900
H	1.41885100	-1.67033900	-6.01081500
H	0.91035400	0.01968100	-5.80492900
C	-1.69463100	-0.88127800	-5.03383300
H	-0.86274200	-2.43459500	-6.30673500
H	-0.97543700	-0.84856000	-7.09706700
H	-2.55298300	-1.55237500	-4.88604200
H	-2.08208700	0.13412700	-5.21607600
H	-1.24726300	0.10808800	-2.64835500
O	1.23451300	0.87027000	-1.44603100
H	0.26412600	0.84461300	-1.64729500

2-IM2:

C	4.53077600	-1.45544000	-0.12117000
C	3.15563000	-1.60828700	-0.16791300
C	2.75371400	-2.97214600	-0.25867200
C	3.83258200	-3.80930100	-0.29063100
S	5.33824000	-2.96094800	-0.19819500
H	1.71350500	-3.28678300	-0.28920500
H	3.83935900	-4.89553800	-0.37190800
C	4.99949100	-0.08143800	0.01451000
C	3.98780600	0.84699600	0.11962500
S	6.54536000	0.65423100	0.06368800
C	4.46489600	2.17936000	0.24288700
C	5.83249900	2.22592900	0.21498900

H	3.83625800	3.06474300	0.33717400
H	6.47799000	3.10028200	0.28953100
P	2.38240500	0.01461800	0.01435500
C	-1.59632300	-0.27347700	-0.93213200
C	-0.89646400	-1.36898300	-0.33522600
O	-0.83263400	0.63736000	-1.60554900
O	0.36597200	-1.47878400	-0.45525600
C	1.46251700	0.27423500	1.53624800
C	0.68039400	1.42830500	1.64439200
C	1.57242700	-0.61262000	2.61176600
C	-0.00884900	1.68764800	2.82829900
H	0.58784900	2.11899000	0.80383000
C	0.88311800	-0.34300200	3.79132500
H	2.17697400	-1.51754900	2.52663800
C	0.09016700	0.80240900	3.89946000
H	-0.62492100	2.58497800	2.91299100
H	0.96747000	-1.03576200	4.63150000
H	-0.44989100	1.01089100	4.82572300
C	-2.96088100	-0.09714200	-0.76648900
C	-1.70757900	-2.31281400	0.34642300
C	-3.73245300	-1.03911200	-0.06680600
C	-3.08754500	-2.15173200	0.47967500
Cl	-5.43847700	-0.80184300	0.15011500
Cl	-4.01568700	-3.35598400	1.32184800
Cl	-3.70026800	1.33048100	-1.42292000
Cl	-0.89904700	-3.71842500	0.96558400
O	-1.14620900	0.85295700	-4.14480600
C	0.07061300	0.84105100	-4.91304900
C	-0.33217500	1.27055400	-6.32151300
H	0.48410400	-0.17976500	-4.89422600

H	0.79213000	1.52017500	-4.43664500
C	-1.80287100	0.84320800	-6.39574100
H	0.29497300	0.79096500	-7.08516200
H	-0.23365400	2.36049100	-6.43783900
C	-2.29184000	1.09259700	-4.97534900
H	-1.88716100	-0.22504300	-6.64743000
H	-2.38378300	1.41243200	-7.13332800
H	-3.09658600	0.41554800	-4.66051800
H	-2.63047500	2.13208700	-4.83009100
H	-1.05810200	0.69644800	-2.58513900
O	1.70001400	0.75048800	-1.21326400
H	0.72004000	0.53436500	-1.36772900

2-TS2:

C	4.002878	-1.581832	0.919435
C	2.622473	-1.680517	0.886173
C	2.155883	-3.024603	0.889440
C	3.198328	-3.908281	0.910634
S	4.741370	-3.124608	0.932335
H	1.102627	-3.295131	0.877293
H	3.154524	-4.996733	0.906804
C	4.522114	-0.217769	0.977538
C	3.545484	0.755003	1.017249
S	6.090415	0.465008	1.056511
C	4.066060	2.072887	1.109864
C	5.433930	2.066287	1.131340
H	3.465278	2.981399	1.155569
H	6.108936	2.918625	1.198469
P	1.922686	-0.024021	0.961029

C	1.010635	0.369023	2.457032
C	-0.110652	1.199914	2.391441
C	1.485047	-0.097038	3.687929
C	-0.753719	1.576292	3.569616
H	-0.488716	1.552085	1.430877
C	0.833211	0.283522	4.857635
H	2.359190	-0.750444	3.739891
C	-0.282797	1.121607	4.799337
H	-1.632426	2.222566	3.522070
H	1.202481	-0.084323	5.817416
H	-0.792428	1.424511	5.716858
O	1.215416	0.574761	-0.329712
H	0.311313	0.152859	-0.437706
C	-2.273622	-0.365005	-0.139442
C	-1.521744	-1.404275	0.496625
O	-1.536639	0.592580	-0.756283
O	-0.247512	-1.418744	0.410537
C	-3.655551	-0.315677	-0.057853
C	-2.279431	-2.382107	1.188641
C	-4.380342	-1.317392	0.611089
C	-3.677239	-2.351687	1.227842
Cl	-6.114674	-1.253427	0.672310
Cl	-4.549370	-3.630571	2.016102
Cl	-4.477105	1.043262	-0.763412
Cl	-1.395555	-3.684860	1.922141
O	-1.854266	0.936837	-3.294071
C	-0.606079	1.041705	-3.999480
C	-0.960780	1.511289	-5.415566
H	-0.128782	0.050767	-3.984530
H	0.047348	1.749775	-3.467416

C	-2.458146	1.198757	-5.525778
H	-0.357800	0.997711	-6.175964
H	-0.780367	2.591539	-5.520232
C	-2.937150	1.412380	-4.099605
H	-2.620757	0.152256	-5.825949
H	-2.984389	1.844139	-6.241214
H	-3.834074	0.839495	-3.833045
H	-3.121311	2.479676	-3.882744
H	-1.784207	0.730529	-1.715072

PD1:

C	4.10144800	-1.99856500	-0.34209200
C	2.81451800	-1.86413100	0.13429900
C	2.43643300	-2.90454000	1.02616100
C	3.44707600	-3.81173800	1.19346400
S	4.86363300	-3.39582400	0.28825800
H	1.46382900	-2.99695100	1.50954700
H	3.44452000	-4.71682600	1.80009200
C	4.50606000	-0.95240800	-1.28236800
C	3.54390400	0.00261900	-1.52539700
S	5.92492900	-0.66467000	-2.20047200
C	3.95701700	0.98843900	-2.46582000
C	5.22416300	0.74473100	-2.92204800
H	3.34949400	1.82817900	-2.80367800
H	5.80660000	1.32001000	-3.64062600
P	2.07171100	-0.35307100	-0.53318800
C	1.94938000	0.88617400	0.78418500
C	0.67907900	1.35736400	1.13340600
C	3.08858600	1.39153800	1.42068200

C	0.55090500	2.31469400	2.13995400
H	-0.19673200	0.96031900	0.61664200
C	2.95179400	2.34740900	2.42432700
H	4.08284900	1.03587500	1.13931500
C	1.68319800	2.80533400	2.78657000
H	-0.43774800	2.68311700	2.42278900
H	3.83658900	2.74300000	2.92726700
H	1.57708300	3.55433000	3.57455800
O	0.76026500	-0.50593800	-1.28488200
H	-0.50264500	-1.49068600	-1.01769800
C	-2.94105600	-0.84646000	-0.87454200
C	-2.36943400	-2.12626600	-1.05542400
O	-2.11290700	0.13050500	-0.48410700
O	-1.05701400	-2.32241900	-0.96901800
C	-4.31318300	-0.67643200	-1.05853200
C	-3.21513100	-3.21880200	-1.26003700
C	-5.14688300	-1.76728600	-1.33680600
C	-4.59780100	-3.04801200	-1.39540100
Cl	-6.84128600	-1.51904800	-1.59780600
Cl	-5.61426200	-4.42584200	-1.64283700
Cl	-4.96729800	0.91923400	-0.88560500
Cl	-2.50133900	-4.79434200	-1.36034400
O	-1.93648300	2.49246600	-1.54323800
C	-1.81360200	3.60833700	-0.64527900
C	-0.84070200	4.56289100	-1.32367600
H	-1.41498200	3.24396500	0.31403400
H	-2.81168200	4.03442000	-0.47212500
C	0.08053100	3.59647100	-2.06837200
H	-0.31395600	5.20613400	-0.60457600
H	-1.37311300	5.20890900	-2.03999100

C	-0.90282500	2.53849300	-2.54798600
H	0.81314500	3.14971900	-1.37854500
H	0.62895800	4.06624700	-2.89706200
H	-0.46201800	1.53579300	-2.63830100
H	-1.36559800	2.82478600	-3.50677000
H	-2.21878000	1.02299500	-0.92679000

2-IM5:

C	3.541358	-0.647051	-0.659351
C	2.317955	-1.256746	-0.527872
C	2.416795	-2.675524	-0.604428
C	3.709456	-3.102061	-0.757869
S	4.827926	-1.779928	-0.835604
H	1.565970	-3.354373	-0.544269
H	4.079132	-4.122855	-0.847235
C	3.499748	0.801948	-0.658263
C	2.244278	1.340235	-0.526160
S	4.723049	2.006628	-0.797849
C	2.265650	2.764845	-0.566991
C	3.534789	3.263962	-0.694538
H	1.378870	3.394343	-0.492542
H	3.851547	4.304999	-0.747598
P	0.966964	0.006493	-0.336476
C	-1.567761	0.669458	-0.394970
C	-1.545745	-0.739348	-0.274494
O	-0.373819	1.225646	-0.411018
O	-0.337029	-1.262022	-0.301593
C	0.965095	-0.006111	1.560750
C	0.981830	1.169794	2.320058

C	0.936610	-1.226875	2.251548
C	0.982769	1.128623	3.716098
C	0.948430	-1.277015	3.644099
C	0.970633	-0.094793	4.382399
C	-2.775585	1.343818	-0.474289
C	-2.733071	-1.445622	-0.181517
C	-3.983468	0.623383	-0.404260
C	-3.960763	-0.760270	-0.260446
Cl	-2.742264	3.063148	-0.696008
Cl	-5.495213	1.469484	-0.455720
Cl	-5.445474	-1.651714	-0.191886
Cl	-2.650570	-3.161211	0.055170
H	0.974502	-0.129398	5.475016
H	0.992338	2.059555	4.288035
H	0.987481	2.139145	1.819268
H	0.930773	-2.242820	4.155361
H	0.899071	-2.161139	1.691296
F	0.776112	-0.042076	-2.087619

2-TS3:

C	2.937817	-0.288622	-1.221072
C	1.891794	-1.045120	-0.764258
C	2.162220	-2.437710	-0.873531
C	3.406300	-2.694827	-1.385256
S	4.268565	-1.242010	-1.755487
H	1.464286	-3.219422	-0.587021
H	3.876898	-3.660394	-1.565740
C	2.663714	1.136591	-1.269106
C	1.385918	1.489836	-0.893749

S	3.641621	2.504378	-1.602707
C	1.189792	2.902132	-0.892844
C	2.325931	3.574472	-1.251199
H	0.249138	3.389740	-0.641949
H	2.472354	4.648266	-1.361940
P	0.404057	0.053803	-0.346172
C	-2.303760	0.481574	-0.566112
C	-2.708406	-0.746516	0.065655
O	-1.068133	0.965774	-0.314773
O	-1.899174	-1.390639	0.794222
C	0.573627	0.026349	1.496672
C	-0.168616	0.932274	2.275880
C	1.558108	-0.744399	2.127501
C	0.104410	1.093250	3.629406
C	1.821169	-0.587748	3.490186
C	1.112408	0.344902	4.239752
C	-3.123869	1.140262	-1.472381
C	-4.041890	-1.160280	-0.223305
C	-4.407958	0.657061	-1.784170
C	-4.854160	-0.500971	-1.148883
Cl	-2.534641	2.611766	-2.186494
Cl	-5.432322	1.532945	-2.882878
Cl	-6.450671	-1.101996	-1.492022
Cl	-4.605117	-2.604508	0.571185
H	1.344726	0.494958	5.296939
H	-0.472426	1.814575	4.212743
H	-0.950994	1.525805	1.809987
H	2.595870	-1.196277	3.962112
H	2.141574	-1.469066	1.563513
F	-0.356424	-0.857711	-1.537094

S	-0.644184	-4.568976	0.558444
N	0.439813	-5.888028	0.405708
N	-1.119193	-4.801312	2.103744
N	-1.779060	-4.975736	-0.537777
C	0.814955	-6.218068	-0.969954
H	1.407946	-7.141208	-0.934081
H	-0.070243	-6.409947	-1.584871
H	1.428180	-5.435260	-1.451333
C	1.594564	-5.769002	1.294832
H	1.274215	-5.547648	2.319929
H	2.117386	-6.734686	1.298913
H	2.305240	-4.989992	0.965614
C	-1.324267	-3.611079	2.929379
H	-1.243510	-2.706991	2.313178
H	-0.589504	-3.590491	3.749251
H	-2.337607	-3.633025	3.357233
C	-1.391093	-6.096374	2.714035
H	-0.801477	-6.187700	3.638929
H	-2.459080	-6.188082	2.966021
H	-1.104523	-6.909729	2.040752
C	-2.089993	-3.990689	-1.571137
H	-1.835150	-4.404260	-2.559800
H	-3.156969	-3.734245	-1.540324
H	-1.516008	-3.071776	-1.402021
C	-2.603163	-6.169732	-0.436708
H	-3.517006	-5.974505	0.146838
H	-2.895101	-6.477926	-1.450076
H	-2.045821	-6.995582	0.019952

2-IM6:

C	3.149448	-0.196711	-1.152181
C	2.062099	-0.960504	-0.797538
C	2.259362	-2.348953	-1.057687
C	3.487950	-2.597645	-1.601892
S	4.418201	-1.144247	-1.802594
H	1.520101	-3.122152	-0.854963
H	3.912924	-3.550171	-1.916511
C	2.983041	1.227738	-0.919645
C	1.772586	1.567590	-0.373338
S	3.980357	2.589402	-1.249178
C	1.636129	2.982462	-0.246215
C	2.753791	3.655868	-0.661158
H	0.750771	3.492427	0.134280
H	2.933422	4.730474	-0.673206
P	0.743468	0.022792	-0.004051
C	-1.792273	0.202090	-0.942686
C	-2.777022	0.324499	0.100286
O	-0.559251	0.763189	-0.723993
O	-2.536409	0.899746	1.191444
C	0.855054	0.033439	1.823563
C	0.843784	1.234831	2.541168
C	0.950196	-1.175498	2.527359
C	0.934946	1.228871	3.931070
C	1.032791	-1.178955	3.916479
C	1.025294	0.023047	4.621016
C	-2.030108	-0.470481	-2.126455
C	-4.033813	-0.290808	-0.222721
C	-3.251764	-1.116054	-2.364182

C	-4.245884	-1.024603	-1.388721
Cl	-0.741355	-0.583066	-3.289205
Cl	-3.530036	-1.987711	-3.843178
Cl	-5.769012	-1.825960	-1.648410
Cl	-5.294263	-0.129924	0.968445
H	1.096453	0.017636	5.711001
H	0.935826	2.172990	4.478997
H	0.762143	2.187240	2.020644
H	1.114405	-2.127234	4.451888
H	0.948283	-2.120794	1.985796
F	-0.187070	-1.442225	0.070912
S	-2.547129	2.323141	4.483408
N	-1.890149	3.084832	5.832199
N	-3.534868	3.416377	3.754380
N	-3.427579	1.099098	5.194660
C	-2.368684	2.932694	7.197602
H	-3.232681	3.576806	7.433826
H	-2.621713	1.885418	7.397116
H	-1.542258	3.218291	7.863383
C	-1.206625	4.329658	5.505363
H	-0.749842	4.268011	4.506771
H	-1.882376	5.201689	5.530209
H	-0.399380	4.489286	6.232387
C	-3.274833	3.695770	2.338888
H	-2.828555	2.816080	1.853703
H	-2.627159	4.581758	2.226239
H	-4.236658	3.899032	1.846349
C	-4.424386	4.329805	4.449802
H	-4.149406	5.366584	4.197963
H	-5.468514	4.155751	4.145137

H	-4.351819	4.210873	5.535805
C	-3.286918	-0.196982	4.505960
H	-3.559727	-0.979257	5.227357
H	-3.935955	-0.266551	3.619344
H	-2.247319	-0.347933	4.191833
C	-4.784577	1.365234	5.669981
H	-5.485203	1.531958	4.835246
H	-5.114988	0.483037	6.234373
H	-4.816503	2.222043	6.351028

2-IM7:

C	4.348665	1.189266	-0.024060
C	3.021462	1.492370	-0.219228
C	2.805974	2.365442	-1.322102
C	3.975315	2.687004	-1.949276
S	5.349028	1.952739	-1.187679
H	1.833650	2.744765	-1.628976
H	4.127530	3.346631	-2.802149
C	4.605434	0.294695	1.091033
C	3.481449	-0.055730	1.798877
S	6.037550	-0.365085	1.773339
C	3.782985	-0.888005	2.914620
C	5.122928	-1.149822	3.017605
H	3.043607	-1.281003	3.612013
H	5.639564	-1.754017	3.762624
P	1.941767	0.654611	0.999083
C	0.051460	2.743446	3.380531
C	0.204058	1.385779	3.050972
O	1.395424	0.928766	2.607719
C	1.169446	-0.820845	0.255669

C	1.585316	-2.114981	0.589726
C	0.128602	-0.666225	-0.669687
C	0.968534	-3.225112	0.015807
C	-0.479107	-1.775481	-1.252448
C	-0.063307	-3.060280	-0.909647
C	-1.160584	3.195524	3.916574
C	-0.831125	0.494043	3.362659
C	-2.214239	2.308277	4.153872
C	-2.033960	0.945246	3.915160
Cl	-1.302559	4.857606	4.356671
Cl	-3.714170	2.879325	4.798365
Cl	-3.298123	-0.176220	4.274285
Cl	-0.576353	-1.195446	3.109495
H	-0.545645	-3.928629	-1.364069
H	1.304469	-4.224157	0.302214
H	2.389194	-2.271877	1.305845
H	-1.283250	-1.628800	-1.976999
H	-0.203212	0.330713	-0.951728
F	0.680009	1.701259	0.526109
O	1.119759	3.561471	3.466673
C	1.904240	4.010511	2.435573
C	3.264709	4.098459	2.670537
Cl	3.907503	3.463104	4.153463
C	4.114795	4.751779	1.763389
Cl	5.813443	4.909863	2.097352
C	3.551130	5.327409	0.620707
Cl	4.582357	6.126162	-0.527113
C	2.176308	5.278655	0.405777
Cl	1.476422	6.003614	-1.012442
C	1.262802	4.657307	1.319744

O	0.010852	4.657522	1.198725
S	-2.746048	4.709045	0.433516
N	-2.517057	3.466951	-0.714141
N	-4.351966	4.438025	0.751348
N	-2.486467	6.053818	-0.464324
C	-1.282387	3.568370	-1.495379
H	-1.379114	2.864928	-2.333679
H	-1.161543	4.575412	-1.904321
H	-0.399977	3.324539	-0.888692
C	-2.675688	2.136298	-0.114896
H	-3.643529	2.047738	0.391454
H	-2.648902	1.406626	-0.935039
H	-1.860535	1.901816	0.589911
C	-4.814849	4.970896	2.029462
H	-3.976430	5.028983	2.734039
H	-5.571994	4.292458	2.446739
H	-5.262120	5.973828	1.921448
C	-5.365192	4.288347	-0.283799
H	-6.176594	3.664792	0.117358
H	-5.791582	5.260263	-0.585448
H	-4.943746	3.787488	-1.162096
C	-1.823234	7.148996	0.242648
H	-1.185288	7.690377	-0.469670
H	-2.549983	7.853168	0.680642
H	-1.174902	6.725640	1.020127
C	-3.171238	6.361711	-1.711133
H	-4.022215	7.042138	-1.544574
H	-2.460330	6.851823	-2.393096
H	-3.532400	5.446518	-2.192670

2-TS5:

C	1.684140	0.229420	-3.349080
C	0.329190	0.172410	-3.113910
C	-0.438280	0.318740	-4.306800
C	0.349530	0.489770	-5.408530
S	2.040610	0.464200	-5.011130
H	-1.526380	0.300550	-4.341120
H	0.042310	0.638720	-6.442680
C	2.511390	0.044330	-2.172290
C	1.800340	-0.220620	-1.029460
S	4.217310	0.070670	-1.925500
C	2.670090	-0.368580	0.093890
C	3.992840	-0.254140	-0.240650
H	2.342170	-0.530860	1.120640
H	4.858860	-0.325910	0.416530
P	-0.082210	-0.201260	-1.368550
C	-0.385790	0.480700	2.160190
C	-1.272340	0.900140	1.080250
O	-0.345050	0.923170	-0.238340
C	-0.388770	-1.976410	-1.041350
C	0.147670	-2.615470	0.080030
C	-1.168490	-2.722450	-1.938710
C	-0.137470	-3.956100	0.337120
C	-1.427220	-4.069050	-1.697860
C	-0.929070	-4.681920	-0.547560
C	-0.543450	-0.686370	2.855300
C	-2.495180	0.126490	1.054890
C	-1.661080	-1.521870	2.647680
C	-2.641150	-1.055310	1.769740

Cl	0.674140	-1.118180	4.017040
Cl	-1.786550	-3.062930	3.436550
Cl	-4.125480	-1.946470	1.612720
Cl	-3.829530	0.812630	0.170330
H	-1.166020	-5.727930	-0.337800
H	0.259820	-4.431660	1.235120
H	0.774420	-2.068180	0.780830
H	-2.032180	-4.639170	-2.406790
H	-1.589940	-2.241310	-2.820990
F	-1.770480	-0.047220	-1.837330
O	0.718040	1.278100	2.392840
C	0.628860	2.578330	2.056830
C	1.694180	3.429660	2.345150
Cl	3.119240	2.751920	3.047060
C	1.583700	4.802830	2.098460
Cl	2.921520	5.846500	2.426520
C	0.390360	5.324310	1.596000
Cl	0.200140	7.027620	1.369970
C	-0.658430	4.459920	1.260700
Cl	-2.130180	5.040160	0.570080
C	-0.531380	3.089420	1.461880
O	-1.554640	2.289700	1.125350
S	-3.059592	4.306353	-2.921441
N	-3.154348	3.842220	-4.527581
N	-4.636872	4.103392	-2.471938
N	-2.639646	5.890230	-2.998711
C	-2.607752	4.642193	-5.613016
H	-3.396503	5.140137	-6.200796
H	-1.919414	5.406100	-5.233848
H	-2.031358	3.984986	-6.279509

C	-3.523697	2.454606	-4.771784
H	-3.420023	1.860116	-3.852877
H	-4.562092	2.359458	-5.129955
H	-2.852243	2.029594	-5.530267
C	-4.894569	3.908988	-1.047859
H	-4.029410	3.446874	-0.562130
H	-5.751224	3.228619	-0.942038
H	-5.136814	4.858317	-0.541240
C	-5.778401	4.504126	-3.282897
H	-6.578630	3.767831	-3.123652
H	-6.156238	5.499542	-2.999123
H	-5.511848	4.499119	-4.346185
C	-1.302462	6.276487	-2.544664
H	-0.699063	6.635347	-3.393462
H	-1.377791	7.078258	-1.795916
H	-0.793369	5.418611	-2.089860
C	-3.477721	6.928771	-3.589253
H	-3.885637	7.585713	-2.805953
H	-2.878659	7.536310	-4.284287
H	-4.308271	6.494667	-4.153873

2-1b:

C	3.258212	-0.984983	-0.822530
C	2.098709	-1.479804	-0.283749
C	2.147203	-2.895902	-0.120198
C	3.353099	-3.418424	-0.504030
S	4.431813	-2.204170	-1.103127
H	1.332909	-3.503045	0.275444
H	3.678454	-4.458050	-0.492874
C	3.263757	0.457766	-0.984540
C	2.099307	1.078933	-0.601722
S	4.457120	1.570492	-1.499592
C	2.170345	2.496627	-0.738876
C	3.388573	2.904570	-1.206448
H	1.360082	3.180798	-0.491122
H	3.731029	3.917122	-1.417887
P	0.890177	-0.109267	0.120549
C	-1.592906	0.674201	-0.203895
C	-1.610513	-0.674049	-0.349544
O	-0.349645	1.163945	-0.066750
O	-0.364566	-1.216199	-0.313420
C	1.055913	0.013999	1.945544
C	0.465860	1.084107	2.637219
C	1.852670	-0.895198	2.659124
C	0.701209	1.259251	3.999295
H	-0.158401	1.797745	2.101665
C	2.075606	-0.722941	4.023976
H	2.320001	-1.737756	2.153160
C	1.518022	0.365788	4.691514
H	0.243488	2.101926	4.521790

H	2.702169	-1.437452	4.562045
H	1.720185	0.520161	5.754093
C	-2.785568	1.457303	-0.246383
C	-2.808473	-1.406238	-0.573575
C	-4.019899	0.775788	-0.433849
C	-4.030003	-0.673319	-0.621091
C	-5.200210	1.553387	-0.421777
C	-5.220570	-1.408929	-0.817208
C	-2.760876	2.856880	-0.058753
C	-2.807988	-2.807242	-0.753686
C	-5.164817	2.920532	-0.230143
C	-5.209678	-2.782709	-0.955172
C	-3.934163	3.580200	-0.054424
C	-3.992905	-3.488302	-0.927589
H	-6.166331	1.070625	-0.563991
H	-6.176187	-0.887721	-0.860179
H	-6.095430	3.491184	-0.217349
H	-6.147172	-3.321160	-1.106462
H	-3.911739	4.660525	0.104095
H	-3.987411	-4.571666	-1.064693
H	-1.800214	3.351346	0.095615
H	-1.855446	-3.339656	-0.737498

2-2a:

C	3.045642	-0.588300	-1.105508
C	1.897867	-1.121751	-0.562472
C	1.715952	-2.498440	-0.879407
C	2.732185	-2.967213	-1.661854
S	3.911623	-1.745116	-2.014693

H	0.877328	-3.102800	-0.538418
H	2.873076	-3.968975	-2.064979
C	3.228189	0.829909	-0.861280
C	2.217925	1.410402	-0.131919
S	4.404266	1.962770	-1.380596
C	2.389608	2.819290	-0.011474
C	3.531334	3.252201	-0.630314
H	1.700558	3.491608	0.496360
H	3.914625	4.269493	-0.702162
P	0.957089	0.120423	0.342672
C	-1.469156	0.495808	-0.493816
C	-1.521957	-0.782639	0.054916
O	-0.264466	1.088805	-0.302994
O	-0.389856	-1.121137	0.642113
C	1.196113	0.102074	2.166775
C	1.020141	1.244372	2.939486
C	1.471983	-1.084831	2.852060
C	1.074133	1.221914	4.327180
F	0.728069	2.410632	2.367289
C	1.537250	-1.133211	4.237290
F	1.681726	-2.221721	2.200604
C	1.334777	0.025387	4.978470
F	0.868348	2.329616	5.025770
F	1.791936	-2.278346	4.856705
F	1.394394	-0.010556	6.298088
C	-2.500973	1.016248	-1.247919
C	-2.669163	-1.553790	-0.072228
C	-3.659988	0.235719	-1.402031
C	-3.744994	-1.027222	-0.808229
Cl	-2.343509	2.587728	-1.939360

Cl	-4.982414	0.866024	-2.320062
Cl	-5.193700	-1.954182	-0.979499
Cl	-2.677983	-3.142195	0.602763

2-2b:

C	2.543607	-0.364536	-1.311386
C	1.431951	-0.908103	-0.695688
C	1.100292	-2.201423	-1.189929
C	1.973400	-2.609985	-2.158144
S	3.193255	-1.422459	-2.485664
H	0.263873	-2.801069	-0.833526
H	1.972755	-3.542215	-2.721038
C	2.936287	0.942385	-0.808549
C	2.108784	1.428263	0.173487
S	4.213432	2.032781	-1.176870
C	2.518490	2.702424	0.653848
C	3.640162	3.152841	0.008750
H	2.011235	3.273148	1.432234
H	4.174922	4.089168	0.165686
P	0.764941	0.190715	0.564549
C	-1.643916	0.758993	-0.123663
C	-1.749334	-0.483575	0.401706
O	-0.395196	1.305508	0.072824
O	-0.611213	-0.902384	0.985915
C	1.376459	-0.137110	2.286191
C	0.794506	0.500247	3.373608
C	2.393420	-1.040377	2.565274
C	1.186835	0.249781	4.680646
F	-0.180550	1.390832	3.175541

C	2.806492	-1.322305	3.863850
F	3.018957	-1.699788	1.590917
C	2.199784	-0.669569	4.929203
F	0.598009	0.883347	5.688774
F	3.763696	-2.218158	4.075671
F	2.586296	-0.919410	6.170769
C	-2.676391	1.399973	-0.868959
C	-2.966479	-1.229606	0.318038
C	-3.873317	0.653659	-1.082917
C	-4.014641	-0.675016	-0.478138
C	-4.886657	1.255749	-1.858234
C	-5.209086	-1.424544	-0.577891
C	-2.542112	2.702683	-1.392285
C	-3.129699	-2.470410	0.968031
C	-4.741962	2.530885	-2.372195
C	-5.362956	-2.633671	0.073859
C	-3.564170	3.262101	-2.130678
C	-4.321190	-3.158699	0.860675
H	-5.810857	0.715985	-2.062618
H	-6.038908	-1.046490	-1.173926
H	-5.547910	2.971528	-2.962749
H	-6.302292	-3.182152	-0.019556
H	-3.456766	4.269984	-2.536213
H	-4.453650	-4.110582	1.378616
H	-1.623405	3.258926	-1.199324
H	-2.304382	-2.867252	1.562478

2-1b-F⁻:

C	3.511368	-0.757368	-0.694823
C	2.269170	-1.325967	-0.560834
C	2.329616	-2.749274	-0.607706
C	3.610344	-3.217622	-0.742072
S	4.766883	-1.930178	-0.840405
H	1.460181	-3.402594	-0.535082
H	3.952099	-4.250397	-0.800714
C	3.518056	0.691367	-0.709533
C	2.280515	1.273262	-0.593242
S	4.786966	1.850620	-0.851501
C	2.355628	2.695611	-0.649806
C	3.642144	3.150367	-0.774844
H	1.491897	3.357832	-0.590798
H	3.994011	4.179267	-0.841064
P	0.947683	-0.018174	-0.384682
C	-1.557547	0.680631	-0.351675
C	-1.566235	-0.687449	-0.319362
O	-0.339242	1.230664	-0.418749
O	-0.355091	-1.255330	-0.367060
C	0.993845	0.011819	1.516998
C	0.995331	1.220738	2.226387
C	1.009058	-1.175786	2.261646
C	1.027745	1.246229	3.621309
H	0.963743	2.164257	1.680189
C	1.040553	-1.160185	3.656619
H	0.988756	-2.135132	1.743145
C	1.052847	0.053488	4.341817
H	1.028982	2.202920	4.149865

H	1.052125	-2.101287	4.212287
H	1.077750	0.070137	5.434705
C	-2.767994	1.435230	-0.349400
C	-2.787937	-1.422136	-0.290263
C	-4.015004	0.744524	-0.331707
C	-4.024405	-0.712399	-0.294347
C	-5.194771	1.522927	-0.331222
C	-5.215355	-1.473775	-0.265139
C	-2.746079	2.849950	-0.366972
C	-2.786638	-2.836668	-0.252801
C	-5.157736	2.903103	-0.344641
C	-5.198157	-2.854188	-0.233312
C	-3.918947	3.573440	-0.360890
C	-3.969427	-3.542849	-0.227024
H	-6.165577	1.028019	-0.316369
H	-6.179224	-0.965305	-0.267290
H	-6.088376	3.474094	-0.341072
H	-6.136833	-3.411477	-0.210197
H	-3.889255	4.665442	-0.369135
H	-3.956034	-4.634770	-0.196219
H	-1.778538	3.354849	-0.378035
H	-1.826192	-3.354930	-0.243171
F	0.780141	-0.048751	-2.150430

2-2a-F⁻:

C	3.519040	-0.688899	-0.712895
C	2.296640	-1.288455	-0.540328
C	2.356494	-2.695025	-0.758233
C	3.625009	-3.126623	-1.031892
S	4.766981	-1.820959	-1.069883
H	1.495552	-3.360167	-0.701662
H	3.966429	-4.142540	-1.227089
C	3.493863	0.759400	-0.689727
C	2.249645	1.307030	-0.505853
S	4.714863	1.951310	-0.906323
C	2.275018	2.730854	-0.570413
C	3.538157	3.217820	-0.774613
H	1.395157	3.363971	-0.465881
H	3.857388	4.255456	-0.865194
P	0.967814	-0.013173	-0.280852
C	-1.546141	0.676901	-0.372716
C	-1.552485	-0.719552	-0.177557
O	-0.341486	1.210087	-0.296861
O	-0.343620	-1.245277	-0.076481
C	1.049317	0.004396	1.665870
C	0.827698	1.140023	2.445897
C	1.200174	-1.173273	2.405217
C	0.780254	1.121921	3.838483
C	1.185399	-1.224860	3.794506
C	0.964092	-0.067459	4.522708
C	-2.724996	1.365177	-0.598250
C	-2.752423	-1.409634	-0.141256
C	-3.944160	0.662477	-0.583191

C	-3.957771	-0.711888	-0.358720
Cl	-2.645742	3.068234	-0.903819
Cl	-5.431752	1.524816	-0.794593
Cl	-5.462176	-1.572396	-0.344831
Cl	-2.720659	-3.110988	0.181262
F	0.929037	-0.098728	5.850542
F	0.557319	2.246410	4.519176
F	0.638674	2.345387	1.902490
F	1.374624	-2.382261	4.429253
F	1.382363	-2.357768	1.816284
F	0.674781	-0.105189	-1.994345

2-2b-F⁻:

C	3.549296	-0.776832	-0.640295
C	2.304490	-1.351068	-0.610634
C	2.369202	-2.768641	-0.745014
C	3.654790	-3.229002	-0.824726
S	4.814931	-1.939176	-0.775940
H	1.497767	-3.421550	-0.761737
H	4.000871	-4.257619	-0.918498
C	3.551488	0.671610	-0.634978
C	2.306556	1.246840	-0.605301
S	4.820326	1.833801	-0.716240
C	2.376388	2.669117	-0.680554
C	3.665168	3.127709	-0.734162
H	1.507424	3.324737	-0.685099
H	4.015411	4.157407	-0.795173
P	0.968840	-0.052427	-0.533907
C	-1.521323	0.651385	-0.465935

C	-1.539837	-0.711020	-0.410979
O	-0.297453	1.176643	-0.611285
O	-0.326298	-1.278962	-0.512646
C	0.923660	-0.001492	1.443337
C	0.733747	1.181429	2.163671
C	1.051399	-1.133575	2.251364
C	0.689558	1.246937	3.554383
F	0.566203	2.360978	1.557676
C	1.042285	-1.104175	3.643067
F	1.190388	-2.360377	1.737773
C	0.858101	0.096709	4.306200
F	0.485586	2.414450	4.168915
F	1.210621	-2.227295	4.344239
F	0.836292	0.140737	5.635087
C	-2.710059	1.430424	-0.369501
C	-2.764217	-1.433171	-0.300845
C	-3.959921	0.755807	-0.272081
C	-3.987813	-0.701551	-0.234295
C	-5.127190	1.551296	-0.207040
C	-5.187435	-1.444283	-0.152634
C	-2.663889	2.844026	-0.384512
C	-2.782707	-2.846799	-0.262236
C	-5.069347	2.930697	-0.234444
C	-5.191265	-2.825036	-0.137433
C	-3.823984	3.583955	-0.315442
C	-3.975395	-3.533225	-0.187849
H	-6.102718	1.071936	-0.130238
H	-6.141978	-0.920996	-0.102333
H	-5.989858	3.515469	-0.181046
H	-6.136875	-3.367466	-0.075774

H	-3.779281	4.675399	-0.324229
H	-3.979567	-4.625272	-0.163344
H	-1.689912	3.332414	-0.443964
H	-1.831489	-3.380408	-0.298792
F	0.895862	-0.093696	-2.273194

SiMe₃F₂⁻:

Si	-0.067035	0.737187	-0.056265
F	1.534738	1.600009	-0.044706
F	-1.670515	-0.120996	-0.010534
C	0.560051	-0.423399	-1.423128
H	-0.257752	-0.941980	-1.946616
H	1.171103	0.122502	-2.158846
H	1.208977	-1.196272	-0.975200
C	0.179946	0.267914	1.768147
H	-0.485933	0.874912	2.402218
H	-0.093976	-0.784976	1.944449
H	1.211501	0.440776	2.109251
C	-0.939866	2.361580	-0.523407
H	-1.803228	2.187070	-1.182353
H	-1.325080	2.844350	0.391681
H	-0.253113	3.069276	-1.010569

SiMe₃F:

Si	-0.492109	0.521603	-0.076373
F	-1.990074	-0.212799	-0.121988
C	0.440512	-0.356343	-1.426655
H	0.476048	-1.441443	-1.242522
H	-0.086905	-0.187413	-2.379763
H	1.470231	0.016780	-1.535694
C	0.076342	0.254089	1.674426
H	-0.529233	0.876651	2.350236
H	-0.051743	-0.797554	1.973059
H	1.131747	0.538816	1.809157
C	-0.696416	2.335810	-0.439876
H	-1.062384	2.521641	-1.461637
H	-1.384222	2.819762	0.268574
H	0.286469	2.825420	-0.333482

(Me₂N)₃S⁺:

S	-4.246463	2.299313	2.946902
N	-2.862300	1.597398	3.562163
N	-3.858931	2.940508	1.482457
N	-4.601369	3.479022	4.064465
C	-1.984946	2.172738	4.572138
H	-1.247349	2.880785	4.157733
H	-2.573025	2.656936	5.358515
H	-1.437056	1.338008	5.030357
C	-2.260606	0.650087	2.627792
H	-3.037109	0.103235	2.073923
H	-1.588754	1.145386	1.905830

H	-1.679859	-0.080146	3.205828
C	-4.700721	2.570597	0.345724
H	-5.527154	1.934156	0.684620
H	-4.107505	2.013221	-0.395570
H	-5.122717	3.469183	-0.128617
C	-2.660553	3.721670	1.207686
H	-2.075281	3.229392	0.415699
H	-2.924594	4.738015	0.876882
H	-2.032916	3.797239	2.101977
C	-6.052225	3.704423	4.153882
H	-6.271098	4.130153	5.142379
H	-6.401721	4.409251	3.381952
H	-6.591457	2.754601	4.051266
C	-3.835968	4.727885	4.131962
H	-4.032064	5.369996	3.258114
H	-4.166728	5.259859	5.033981
H	-2.761641	4.548370	4.223661

(Me₂N)₃SF:

S	-4.336087	2.282766	2.928920
N	-2.865209	1.663832	3.392899
N	-4.056442	2.730524	1.374231
N	-4.477819	3.567043	3.959955
C	-2.389826	1.709409	4.769260
H	-1.487671	2.339912	4.809974
H	-3.153208	2.118413	5.438601
H	-2.144684	0.688532	5.102695
C	-1.984275	1.000433	2.443094
H	-2.482683	0.842186	1.480499

H	-1.085775	1.620663	2.297857
H	-1.698835	0.016324	2.845423
C	-5.125317	2.471844	0.414635
H	-5.921194	1.881619	0.887062
H	-4.731873	1.903812	-0.441907
H	-5.560005	3.415627	0.047261
C	-2.913937	3.528492	0.938216
H	-2.151395	3.603118	1.731987
H	-2.458028	3.044828	0.059626
H	-3.244444	4.539791	0.649567
C	-5.850205	4.007001	4.190554
H	-5.920448	4.421923	5.206887
H	-6.150461	4.790674	3.475619
H	-6.544114	3.159904	4.106157
C	-3.449450	4.598754	4.067058
H	-3.700452	5.455789	3.419833
H	-3.417219	4.948354	5.110035
H	-2.454746	4.209036	3.786707
F	-0.676557	3.721506	3.129314

R₃P=O...SiMe₃F:

C	10.733357	-1.429074	-1.290255
C	10.017025	-2.607010	-1.315319
C	10.145892	-3.313123	-2.543941
C	10.960241	-2.649337	-3.420790
S	11.574673	-1.170524	-2.761880
H	9.655225	-4.258262	-2.778106
H	11.260219	-2.956257	-4.422303
C	10.566802	-0.641616	-0.067993

C	9.697942	-1.192921	0.845152
S	11.201909	0.852885	0.487609
C	9.558497	-0.414740	2.026924
C	10.316313	0.723615	1.972113
H	8.925703	-0.678072	2.874812
H	10.412416	1.512058	2.718263
P	9.017984	-2.749118	0.193848
O	7.520170	-2.793461	-0.012565
C	9.607003	-4.088702	1.266350
C	10.967368	-4.361803	1.457166
C	8.647711	-4.802273	1.990339
C	11.357532	-5.338534	2.371376
C	9.043698	-5.776079	2.907926
C	10.397278	-6.042492	3.100665
H	10.711270	-6.802001	3.820197
H	12.417271	-5.556717	2.522332
H	11.726685	-3.810997	0.896022
H	8.289460	-6.325210	3.474512
H	7.589126	-4.583144	1.836495
Si	5.439837	0.305842	-0.978862
C	4.583746	-0.847715	0.201477
H	5.310945	-1.582224	0.581518
H	4.151833	-0.295562	1.050634
H	3.775342	-1.395300	-0.307940
C	6.787376	1.311995	-0.180311
H	6.376839	1.907309	0.650145
H	7.575310	0.657585	0.221689
H	7.252027	2.001442	-0.903140
C	5.998484	-0.555087	-2.536475
H	5.157327	-1.045959	-3.051171

H	6.482562	0.144639	-3.235511
H	6.728985	-1.332033	-2.259771
F	4.285490	1.441354	-1.419746

R₂(PFP)P=O...SiMe₃F:

C	10.659030	-1.476675	-1.283511
C	9.922750	-2.641864	-1.275522
C	10.006065	-3.370795	-2.493511
C	10.810533	-2.733765	-3.398697
S	11.466613	-1.257010	-2.777898
H	9.491856	-4.309716	-2.699660
H	11.080946	-3.060765	-4.402228
C	10.532785	-0.668603	-0.070795
C	9.683194	-1.192162	0.878298
S	11.199972	0.823512	0.442054
C	9.578906	-0.391723	2.047451
C	10.347400	0.736473	1.948099
H	8.963898	-0.630923	2.915338
H	10.472715	1.538663	2.674854
P	8.952226	-2.721393	0.245717
O	7.458277	-2.752187	0.077861
C	9.568640	-4.091360	1.304584
C	10.903402	-4.150605	1.717513
C	8.716678	-5.081429	1.800473
C	11.374227	-5.129865	2.582760
C	9.167285	-6.071585	2.669136
C	10.499106	-6.098627	3.058245
F	10.934999	-7.042421	3.874971
F	12.649033	-5.150947	2.950025

F	11.782097	-3.253398	1.274833
F	8.328440	-6.992681	3.127165
F	7.435078	-5.128955	1.464828
Si	5.467093	0.381253	-1.013018
C	4.613752	-0.733220	0.204476
H	5.333111	-1.469935	0.594728
H	4.201150	-0.152736	1.044421
H	3.790089	-1.278944	-0.281832
C	6.849341	1.375813	-0.258351
H	6.458255	2.021240	0.543731
H	7.612955	0.713733	0.176974
H	7.337479	2.016153	-1.010223
C	5.978627	-0.511797	-2.569281
H	5.116884	-0.991749	-3.059569
H	6.459726	0.171076	-3.286759
H	6.700407	-1.300587	-2.303830
F	4.319822	1.523889	-1.452358

(C₁₂Cl₈O₂)₂:

C	1.636912	1.282481	-0.000061
C	1.586641	-0.113967	-0.000683
C	0.350315	-0.770179	-0.001002
C	-0.823325	-0.027793	-0.000066
C	0.448224	2.023118	0.000098
C	-0.774257	1.363032	-0.000139
O	-2.007946	-0.693269	0.000738
C	-3.145390	0.051658	0.001278
O	-1.911674	2.107988	-0.000120
C	-3.096284	1.442506	0.000305

C	-4.367881	-0.608571	0.001737
C	-5.556569	0.132126	0.000871
C	-5.506238	1.528597	-0.000261
C	-4.269940	2.184836	-0.000292
Cl	3.155473	2.095689	0.001131
Cl	3.041798	-1.033874	-0.000380
Cl	0.221902	-2.487343	-0.002819
Cl	0.440678	3.745299	0.001709
Cl	-4.360267	-2.330760	0.001840
Cl	-7.075181	-0.680922	-0.000390
Cl	-6.961311	2.448623	-0.001986
Cl	-4.141649	3.902045	-0.001509

2-5:

C	-1.422481	0.622917	-0.499778
C	-1.440522	-0.723439	-0.333954
O	-0.292959	-1.473846	-0.389226
C	-2.636740	1.391620	-0.510989
C	-2.670220	-1.434709	-0.144637
C	-3.880338	0.724884	-0.374472
C	-3.894582	-0.717140	-0.166367
C	-5.055186	1.506617	-0.405341
C	-5.089953	-1.451108	-0.005637
C	-2.598638	2.795435	-0.659454
C	-2.674232	-2.835113	0.041290
C	-5.006616	2.878412	-0.553304
C	-5.082725	-2.822269	0.152007
C	-3.766542	3.528957	-0.671589
C	-3.863377	-3.519912	0.176756

H	-6.026187	1.024737	-0.300027
H	-6.046879	-0.931153	-0.012988
H	-5.931996	3.457360	-0.570339
H	-6.023685	-3.362349	0.272426
H	-3.727097	4.614295	-0.784635
H	-3.856101	-4.602403	0.319604
H	-1.634383	3.292962	-0.760926
H	-1.724483	-3.368975	0.063501
O	-0.259546	1.311699	-0.738168
C	0.890449	0.563482	-0.777484
C	2.122145	1.278125	-0.944560
C	3.347386	0.563455	-0.903600
C	3.331848	-0.878357	-0.691982
C	2.087913	-1.548233	-0.570888
C	0.872254	-0.782618	-0.606343
C	2.125608	2.677873	-1.134175
C	3.315032	3.364633	-1.256177
C	4.543334	1.299063	-1.051243
C	4.535420	2.669495	-1.215623
C	2.050896	-2.952120	-0.424516
C	3.220074	-3.683543	-0.401416
C	4.459913	-3.030134	-0.505292
C	4.507680	-1.657841	-0.648073
H	1.175232	3.209803	-1.170902
H	3.307383	4.446673	-1.402472
H	5.501101	0.781024	-1.029179
H	5.476681	3.211007	-1.327015
H	1.086434	-3.451765	-0.336246
H	3.181721	-4.769246	-0.291754
H	5.386058	-3.607265	-0.479802

H	5.478950	-1.174022	-0.741428
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2-1'-0:

C	3.447788	-0.722752	-0.970265
C	2.192510	-1.131319	-0.572271
C	2.040108	-2.546492	-0.606114
C	3.191687	-3.168868	-1.006903
S	4.456313	-2.047280	-1.371823
H	1.130986	-3.083276	-0.332560
H	3.372939	-4.233949	-1.147421
C	3.668081	0.717864	-0.913294
C	2.594243	1.444374	-0.445407
S	4.991374	1.721495	-1.332349
C	2.842107	2.845658	-0.440137
C	4.100808	3.139610	-0.890698
H	2.131347	3.605750	-0.115487
H	4.567242	4.117936	-1.000551
P	1.223198	0.314568	-0.044541
O	-0.095298	0.604868	-0.726463
C	1.040706	0.179135	1.758846
C	0.017395	0.900743	2.385101
C	1.849250	-0.681262	2.516115
C	-0.220982	0.736043	3.748720
C	1.608278	-0.841236	3.878578
C	0.564621	-0.146661	4.490381
H	0.354207	-0.303912	5.551096
H	-1.027709	1.290463	4.232856
H	-0.618497	1.566988	1.798344
H	2.228984	-1.524470	4.461929

H	2.649774	-1.250109	2.039079
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Dithienopentafluorophenylphosphole, $R_2(PFP)P=O$:

C	3.556547	-0.889172	-0.971575
C	2.339916	-1.402686	-0.575166
C	2.278055	-2.820665	-0.683835
C	3.461471	-3.341089	-1.128147
S	4.644991	-2.118877	-1.444264
H	1.411858	-3.431434	-0.429445
H	3.719678	-4.383861	-1.310019
C	3.650423	0.564112	-0.944195
C	2.509110	1.206511	-0.516158
S	4.875541	1.670146	-1.385952
C	2.613921	2.623398	-0.572782
C	3.845528	3.013455	-1.023925
H	1.823654	3.321971	-0.298037
H	4.217014	4.024976	-1.184131
P	1.262332	-0.031717	-0.090016
O	-0.096624	0.089918	-0.726612
C	1.122300	-0.012750	1.748629
C	0.440677	1.059867	2.331869
C	1.560860	-1.012860	2.615688
C	0.174397	1.132292	3.691017
F	0.026928	2.076238	1.578271
C	1.315622	-0.959365	3.983667
F	2.222703	-2.078341	2.176436
C	0.598453	0.101076	4.520644
F	-0.472886	2.172767	4.200225
F	1.759978	-1.929270	4.772271

F 0.334982 0.139429 5.815074

2-1a Crystal:

Dimer Crystal

1.0

8.766156904	-0.000000037	-0.000000091
-0.000000046	11.800955868	0.061710046
-0.000000185	-3.097969152	20.545328310

S P Cl O C H

8 4 16 12 80 44

Cartesian

4.231063130	-0.623727710	16.221871229
4.535093382	9.326714331	4.385168124
0.152014844	0.925256618	5.949207372
8.614141963	7.777729937	14.657832040
1.065539338	9.725534914	2.883658105
7.700617450	-1.022548562	17.723380955
5.448617873	0.526435652	7.450717403
3.317538915	8.176551156	13.156321907
3.807117051	1.132915293	2.174561490
4.959039626	7.570071228	18.432477761
0.575961240	-0.416068275	12.447226739
8.190195368	9.119054943	8.159812780
1.339459577	6.279449794	1.212384718
7.426697566	2.423536528	19.394654760
3.043618758	4.730464993	11.485049192
5.722537698	3.972521611	9.121990375
2.229146659	0.796715289	19.121593395
6.537010389	7.906271166	1.485445571

2.153931859	2.345700077	8.848929992
6.612224637	6.357286686	11.758109513
4.186190719	6.011234660	2.482587128
4.579966413	2.691751703	18.124452071
0.196887167	4.462249861	12.755251178
8.569269101	4.240736444	7.851788258
7.923873525	3.436600792	1.177402526
0.842283312	5.266385730	19.429636898
5.225361175	1.887616689	11.450066914
3.540795496	6.815369674	9.156972676
3.210932496	1.927736581	0.715961169
5.555224361	6.775249701	19.891077846
1.172145961	0.378753333	10.988625984
7.594010624	8.324233303	9.618413503
5.419967698	1.732667696	1.707454062
3.346188911	6.970318841	18.899585366
1.036889761	8.519302336	8.626920593
7.729266853	0.183684265	11.980118937
3.895998038	7.194119463	1.261339030
4.870158900	1.508866994	19.345700249
0.487080040	5.645134384	11.534002974
8.279076428	3.057851961	9.073036488
4.947977888	8.032866081	0.836644591
3.818179067	0.670120366	19.770394353
0.564899108	2.219105525	9.497730673
8.201257337	6.483880930	11.109308721
2.477752457	10.695058273	2.866868099
6.288404215	-1.992071822	17.740171142
6.860830937	-0.443087730	7.467507067
1.905325850	9.146074464	13.139532332

2.619957064	7.303412257	0.685117126
6.146199913	1.399574211	19.921922257
1.763121342	5.754427146	10.957780737
7.003035062	2.948559318	9.649258656
4.084650792	2.828726265	0.212697650
4.681505993	5.874260101	20.394341770
0.298427550	1.279742185	10.485362481
8.467729023	7.423244193	10.121676862
4.675812976	-0.230779349	3.062136136
4.090343637	8.933766054	17.544903424
0.292734660	10.482750049	7.272238920
8.473421995	-1.779763361	13.334800795
0.995904697	0.157903909	1.526748667
7.770252166	8.545082514	19.080290571
3.387173565	-1.391079684	11.799412892
5.378983003	10.094066456	8.807626649
4.402966128	2.690317537	4.423105561
4.363190355	6.012669310	16.183933244
0.019888318	7.561653214	5.911267909
8.746268497	1.141333737	14.695771871
3.416419289	2.332235100	3.492975883
5.349737530	6.370751473	17.114063370
0.966659445	0.783251276	13.765641069
7.799497212	7.919735329	6.841398300
5.965837118	-0.443012719	3.613437419
2.800319456	9.145999102	16.993602060
7.183398294	-1.991996789	13.886102315
1.582758572	10.694983418	6.720937593
4.969147863	-1.834020149	17.184730445
3.797008728	10.537006882	3.422309048

8.180086854	-0.285035980	6.912066257
0.586069656	8.988022519	13.694973120
6.390567371	3.554654874	0.396183367
2.375589398	5.148331322	20.210855915
2.007489052	6.697315021	9.938191518
6.758667404	2.005671443	10.668847852
5.354701415	2.717392672	0.789314236
3.411455473	5.985593938	19.817724918
0.971623027	7.534577907	9.545059988
7.794533518	1.168408436	11.061979487
2.297699303	0.065279622	2.082773084
6.468457330	8.637706912	18.524266138
2.085379090	-1.483703849	12.355437615
6.680777570	10.186690556	8.251601933
2.127923872	2.868217093	3.613747736
6.638232338	5.834769414	16.993291207
2.255153917	1.319233430	13.886413401
6.511002860	7.383753448	6.720626214
2.728039805	-1.477447303	16.224344496
6.038116672	10.180433832	4.382694800
1.655038308	0.071537241	5.951680274
7.111118406	8.631449394	14.655359294
0.216430414	10.869424215	1.906805314
8.549726390	-2.166437873	18.700233557
4.599508830	-0.617453454	8.427570357
4.166647888	9.320440442	12.179469235
1.828581557	3.740745862	4.659329059
6.937575208	4.962240984	15.947710363
2.554496806	2.191761618	14.931993674
6.211659915	6.511225080	5.675045391

2.809903811	4.083599073	5.592705225
5.956252601	4.619387688	15.014333151
1.573173591	2.534615149	15.865371393
7.192983172	6.168371943	4.741668164
4.098134069	3.557314706	5.472099408
4.668022560	5.145672372	15.134939670
0.284944253	2.008330415	15.744764768
8.481212419	6.694656356	4.862274360
0.633739889	0.977567962	0.911933314
8.132416743	7.725418535	19.695105903
3.749338286	-0.571415613	11.184597900
5.016818416	9.274402442	9.422441665
5.407468904	2.277364564	4.334711063
3.358687830	6.425622587	16.272328045
1.024390343	7.974606412	5.999662715
7.741766443	0.728380276	14.607376844
6.814162592	0.225498124	3.486541519
1.951993842	8.477488588	17.120498209
6.335072445	-1.323486154	13.759206434
2.431084318	10.026472910	6.847833111
1.353287428	2.588372662	2.899783629
7.412869162	6.114613714	17.707255630
3.029790779	1.039388745	13.172448487
5.736365895	7.663598010	7.434590941
1.876226819	-1.043304804	15.710557476
6.889929999	9.746291279	4.896481661
2.506851209	0.505679876	5.437893233
6.259305379	8.197306817	15.169146463
0.810537472	-1.953086504	18.980567534
7.955619444	10.656072792	1.626471287

3.572540965	-0.404102462	8.707904542
5.193615783	9.107089299	11.899135112
0.819555109	4.139493642	4.757158588
7.946601252	4.563493253	15.849880628
5.202634201	6.112477431	5.577215664
3.563522529	2.590509540	15.029823676
2.565421872	4.745884759	6.424262167
6.200734817	3.957102263	14.182776846
1.817656220	3.196900225	16.696927653
6.948500562	5.506086639	3.910111611
4.865286686	3.803693964	6.207408231
3.900870032	4.899293065	14.399630480
0.482208570	6.448277454	4.126965057
8.283948044	2.254709788	16.480074269

2-IM3:

H₂O inserted

1.0

8.768658569	-0.000000096	-0.000000038
-0.000000126	11.773690124	0.045487182
-0.000000070	-2.060739597	21.571619007

S P Cl O C H

8 4 16 12 80 44

Cartesian

4.014491129	0.154570316	17.165821303
4.754167233	9.558380185	4.451285106
0.369838271	1.184939674	6.380010991
8.398820255	8.528011014	15.237095533

1.274490386	9.850658086	2.985188922
7.494168294	-0.137707557	18.631917496
5.658819913	0.892661972	7.846107330
3.109838634	8.820288518	13.770999204
3.752333052	1.543254679	2.652171661
5.016325384	8.169695856	18.964934585
0.631995737	0.512884939	13.437980945
8.136662410	9.200065560	8.179125281
1.307302774	6.392638690	1.335979354
7.461355656	3.320311955	20.281126881
3.077026135	5.362269055	12.121789295
5.691632278	4.350681587	9.495317070
2.203978775	1.858059914	20.299456135
6.564679653	7.854890531	1.317650180
2.180350189	2.888429192	9.513646108
6.588308023	6.824521374	12.103460197
4.148322291	6.259726867	2.636057844
4.620336137	3.453223716	18.981048471
0.236006647	5.229357988	13.421868268
8.532651725	4.483592446	8.195238125
7.920198311	3.632514912	1.304732747
0.848460105	6.080435607	20.312373444
5.232789488	2.602145728	12.090542403
3.535868864	7.110804884	9.526563967
3.124313916	2.359689382	1.215451686
5.644344467	7.353261264	20.401654486
1.260014938	1.329319491	12.001260683
7.508643329	8.383630895	9.615845430
5.361429295	2.197456657	2.161667553
3.407229153	7.515493622	19.455438510

0.977099930	8.545863028	8.669629171
7.791558304	1.167087554	12.947477134
2.639212628	-1.688022317	20.692330512
6.129447692	11.400972560	0.924776000
1.745119300	-0.657655064	9.906522044
7.023541289	10.370605431	11.710583910
3.899457556	7.211519859	1.220005451
4.869200912	2.501430912	20.397100850
0.484871571	6.181150288	12.005815560
8.283786742	3.531800407	9.611290880
4.983938681	7.909714820	0.644136437
3.784719651	1.803235791	20.972969819
0.599609383	2.833605087	10.187159745
8.169048872	6.879345194	11.429946414
2.590740257	10.937517630	3.116650771
6.177918221	-1.224566939	18.500455559
6.975069955	-0.194197506	7.714645820
1.793588501	9.907147934	13.902460478
2.619267887	7.269682118	0.646215806
6.149390566	2.443268380	20.970890400
1.765060939	6.239312524	11.432025907
7.003597418	3.473638064	10.185080502
4.019899423	3.121930832	0.554989503
4.748758977	6.591019650	21.062116789
0.364429502	2.091561245	11.340798554
8.404228809	7.621389230	10.276307737
4.691729372	0.193851349	3.494165459
4.076929088	9.519099145	18.122940771
0.307400370	10.549469036	7.337131650
8.461257983	-0.836518592	14.279974603

0.999673863	0.435653597	1.935600425
7.768984549	9.277296830	19.681505696
3.384655221	-0.594716098	12.721409972
5.384003150	10.307666728	8.895696228
4.291736619	3.015203066	4.957889941
4.476921887	6.697747309	16.659216327
8.676065717	7.728117479	5.873407202
0.092592500	1.984832908	15.743698880
3.335781325	2.708057771	3.980223603
5.432877202	7.004892828	17.636882599
1.048547482	1.677687891	14.766033331
7.720110800	8.035262694	6.851072827
5.999560905	0.011828669	4.014154445
2.769097629	9.701121792	17.602951777
7.153426482	-1.018540949	14.799963802
1.615231988	10.731491446	6.817142592
4.858892963	-1.117554284	17.938079156
3.909765415	10.830504844	3.679027282
8.294095113	-0.087184850	7.152269406
0.474563343	9.800135422	14.464836925
6.369552600	3.733461396	0.557525017
2.399105702	5.979489224	21.059581177
1.985223383	7.009858656	10.273771896
6.783434989	2.703091829	11.343334310
5.299287687	3.046218657	1.112629755
3.469370794	6.666732014	20.504476358
0.914958305	7.697101487	9.718667141
7.853699964	2.015849121	11.898439206
2.308479299	0.394829147	2.493699183
6.460179148	9.318121435	19.123407050

2.075849589	-0.635540696	13.279508457
6.692808691	10.348491168	8.337597674
2.054993187	3.267492250	4.060445731
6.713665196	6.445458318	17.556660520
2.329336247	2.237121915	14.846254464
6.439322217	7.475828398	6.770851992
2.592524628	-0.815192369	17.029670232
6.176133733	10.528142810	4.587436034
1.791804857	0.215177040	6.243860210
6.976853590	9.497773615	15.373246352
0.320478586	11.021936978	2.147770724
8.448179961	-1.308986768	19.469335214
4.704808028	-0.278616761	8.683525622
4.063850392	9.991567405	12.933580830
1.736112069	4.124961168	5.111575721
7.032546608	5.587989449	16.505530482
2.648216853	3.094591107	15.897385806
6.120441337	6.618359166	5.719720582
2.688803924	4.429058306	6.085721722
6.079854460	5.283892123	15.531384639
1.695525403	3.398687632	16.871530648
7.073132656	6.314262853	4.745575785
3.965020490	3.868983722	6.009975030
4.803637982	5.843966788	15.607131175
0.419308461	2.838613663	16.795785123
8.349349590	6.874336506	4.821321012
0.569686493	1.289752317	1.417085076
8.198971866	8.423198058	20.200020973
3.814642371	0.259382460	12.202894153
4.954015864	9.453568167	9.414211863

5.286099999	2.573922371	4.903615852
3.482558572	7.139028009	16.713490468
0.901770475	8.169398124	5.927680729
7.866887568	1.543552255	15.689425188
6.792659386	0.755302031	3.984335174
1.975999231	8.957648318	17.632771017
6.360327977	-0.275067476	14.770144218
2.408330470	9.988018059	6.846962086
1.304377530	3.020343502	3.310263539
7.464280916	6.692607127	18.306842548
3.079951545	1.989973387	14.096072787
5.688706861	7.722976974	7.521033464
1.702127073	-0.390585584	16.578620208
7.066531267	10.103535883	5.038485980
2.682202330	0.639783750	5.792809886
6.086456171	9.073166860	15.824296850
0.688596212	-1.063973604	19.800339205
8.080062297	10.776924013	1.816766728
3.695733087	-0.033603882	9.014529451
5.072925276	9.746554360	12.602577002
0.734057476	4.543925395	5.180086081
8.034600961	5.169025169	16.437020204
5.118386467	6.199395362	5.651210940
3.650271709	3.513554905	15.965895659
2.429981601	5.085784384	6.916328603
6.338676854	4.627166205	14.700777807
1.954347564	4.055413749	17.702138356
6.814310518	5.657536418	3.914968089
4.707042969	4.081740548	6.778867438
4.061615470	5.631209807	14.838238865

0.322713408	6.661580320	4.052429123
8.445944677	3.051370169	17.564676973
6.126747157	0.527955184	1.256129829
2.641909349	9.184995320	20.360976366
1.742418240	10.215363545	9.575167620
7.026238412	-0.502413347	12.041938809
6.335066819	9.453219480	21.548950780
2.433591476	0.259731212	0.068155355
1.950737877	-0.770640825	10.853965748
6.817920396	10.483590597	10.763140639

2-IM4:

OH on P, H on O

1.0

8.849550692	-0.001478231	-0.002248098
0.012492793	11.479555014	0.042786513
0.039507561	-4.303191514	21.627201548

S P Cl O C H

8 4 16 12 80 44

Cartesian

5.560588066	-1.307646052	16.975188578
3.340963546	8.482531640	4.692551787
7.757957901	0.835756770	6.167474081
1.143592347	6.339129086	15.500266335
0.223963975	9.858617993	2.975925456
8.677587539	-2.683732594	18.691814722
4.638968217	-0.539067622	7.879726198
4.262582356	7.713953100	13.788014092
3.741337263	0.653935698	2.432844754

5.160213826	6.520950034	19.234895309
0.723745239	-1.484972987	13.247383125
8.177805492	8.659858970	8.420357079
2.028467703	5.763344274	1.894556007
6.873083407	1.411541419	19.773184417
2.444993175	3.624279347	12.711016831
6.456557652	3.550606496	8.956723050
2.105014347	-1.024696667	20.612187290
6.796536954	8.199582313	1.055552880
2.387664541	1.139745069	9.794978603
6.513886292	6.035140612	11.872761520
5.057409073	6.139093596	2.652149524
3.844142127	1.035792087	19.015590514
8.265285663	3.986469792	13.471528224
0.636265149	3.188416077	8.196212120
7.972596413	4.218365337	0.685412968
0.928954499	2.956520395	20.982327240
5.332108104	2.063040952	11.507185194
3.569442851	5.111845138	10.160554996
3.375547396	2.017567878	1.206197698
5.526003815	5.157317780	20.461542305
1.088349025	-0.119010360	12.023810879
7.813201634	7.293896418	9.643929447
6.035281770	2.573601471	2.087675683
2.866269441	4.601284102	19.580064082
1.621356923	6.743376454	8.757143776
7.280193940	0.431509985	12.910596920
3.971659490	7.044666624	20.253243194
4.929891755	0.130218839	1.414497364
0.515779222	9.184365404	9.443400856

8.385771263	-2.009479343	12.224339578
4.373999090	7.028150202	1.343390584
4.527551908	0.146735505	20.324349579
0.091815887	4.874779392	12.159825816
8.809734745	2.300106406	9.507914249
5.155499546	7.931015618	0.609174025
3.746051595	-0.756129732	21.058566099
0.747326892	1.404649636	10.245572584
8.154223898	5.770236398	11.422167539
1.859276680	10.367551977	3.033974314
7.042274566	-3.192666941	18.633766501
6.273307276	-1.050765724	7.821392063
2.628243499	8.225650759	13.846347986
3.031573568	6.832247036	0.991349507
5.869977388	0.342638654	20.676390421
1.434082228	4.683264501	11.804976474
7.467468534	2.491621682	9.862763840
4.203607353	2.855244608	0.563847874
4.697943875	4.319641026	21.103892214
0.256066818	0.714808461	11.381691989
8.645483975	6.460077697	10.286048373
4.148448908	10.659251941	3.564126795
4.753102621	-3.484366521	18.103613702
8.562273015	-1.344274834	7.291667793
0.339277478	8.519160602	14.376072779
0.858396810	0.503900117	1.612235825
8.043154746	6.670985513	20.055504426
3.607275376	-1.637353578	12.427854520
5.294275027	8.812239221	9.239885807
4.571051709	1.844210858	4.870590101

4.330499532	5.330674701	16.797150182
0.149374171	7.478204039	5.977846793
8.752176666	-0.303317957	15.689893259
3.680161396	1.894738537	3.795248396
5.221389676	5.280146961	17.872491765
0.788087213	-0.246797080	14.612567119
8.113464281	7.421682749	7.055173139
5.291275692	10.089333237	4.177303209
3.610275165	-2.914447648	17.490437123
8.044996344	7.947955272	14.985305549
0.856554808	-0.773069590	6.682434703
5.886372160	-2.710986525	17.921433909
3.015180718	9.885872113	3.746306349
7.430091155	-0.569214097	7.110540576
1.471458216	7.744099800	14.557199734
6.336258867	3.979969434	0.167264178
2.565292208	3.194916276	21.500475979
1.933778478	5.346140000	10.682388078
6.967772341	1.828745838	10.985352147
5.540302885	3.130658699	0.946832004
3.361248209	4.044227190	20.720907893
1.132232250	6.189124308	9.901747285
7.769318542	0.985761865	11.765993086
2.050973815	0.037570958	2.225222593
6.850577486	7.137314279	19.442518130
2.413733254	-2.102549785	13.039701730
6.487817543	9.277435210	8.628039083
2.633615154	2.829849261	3.822274346
6.267936415	4.345036742	17.845465783
1.833131246	0.690210166	14.637340283

7.068419726	6.484675551	7.030400132
3.898816274	-1.741801639	16.829000148
5.002735006	8.916687521	4.838739840
0.569740313	0.401384428	6.023309011
8.331810490	6.773501989	15.644431554
8.629880872	-0.299844883	1.900678307
0.271670148	7.474730481	19.767061686
4.217752641	9.616859700	8.950277521
4.683798268	-2.441973662	12.717462983
2.477684126	3.684049668	4.913452640
6.423866998	3.490835801	16.754287556
1.993286258	1.540969020	15.730460759
6.908264812	5.633916793	5.937279459
3.376413342	3.629466129	5.980104980
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2-PD2:

Dissociated product

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Cartesian

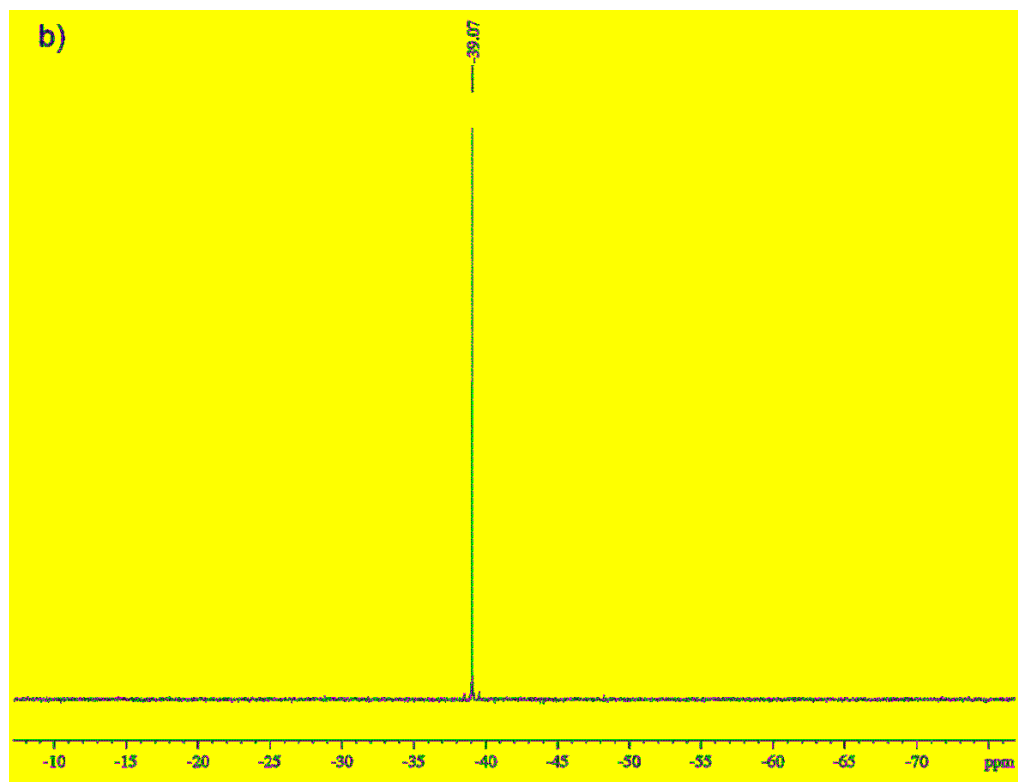
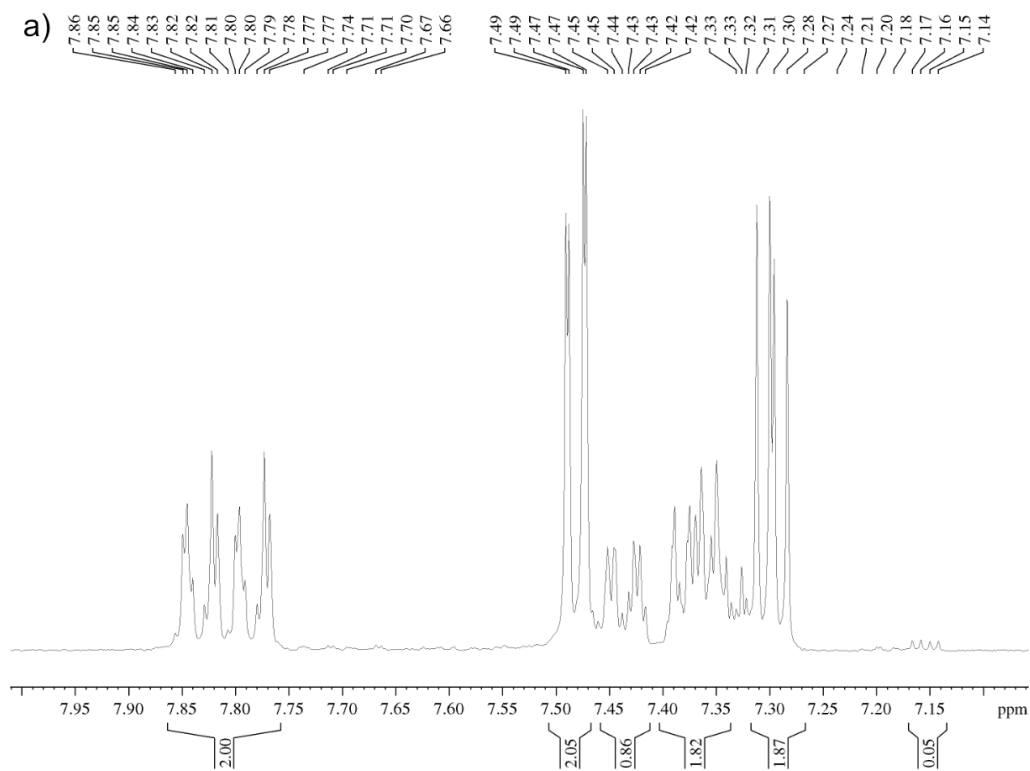
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Figure S2.1-32. NMR spectroscopic characterization of **2-1a** in CD₂Cl₂; a) ¹H NMR spectrum b) ³¹P{¹H} NMR spectrum c) ¹³C{¹H} NMR spectrum.



c) DEPT-135

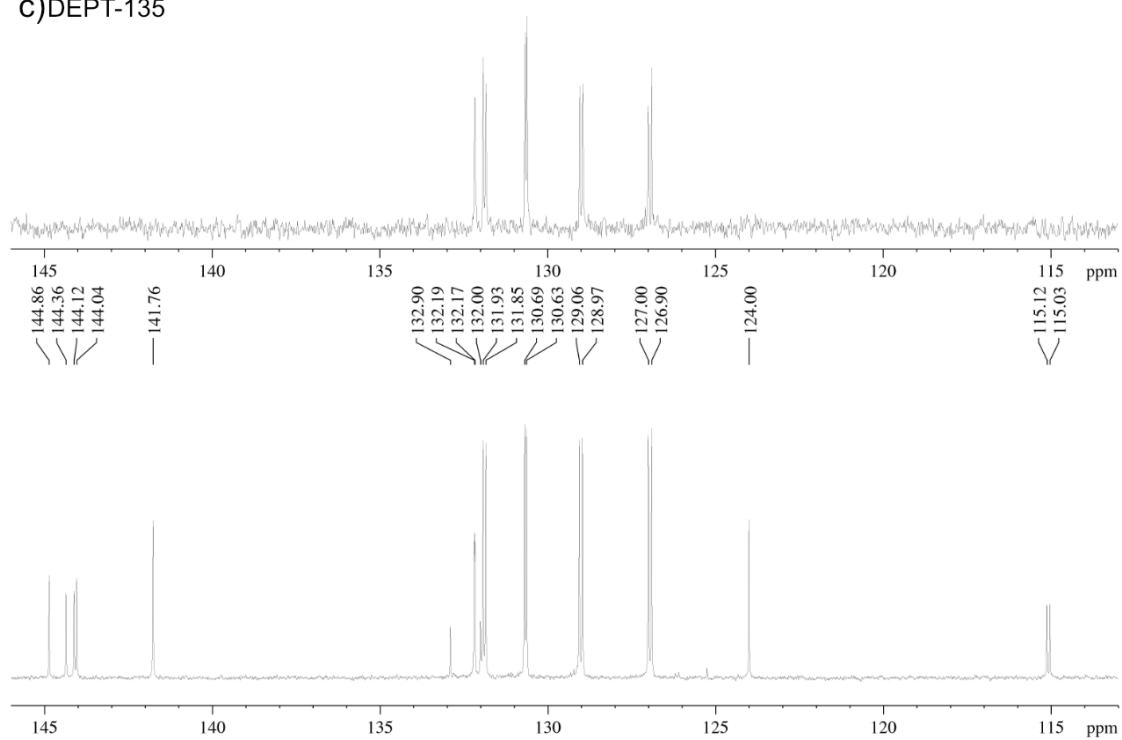
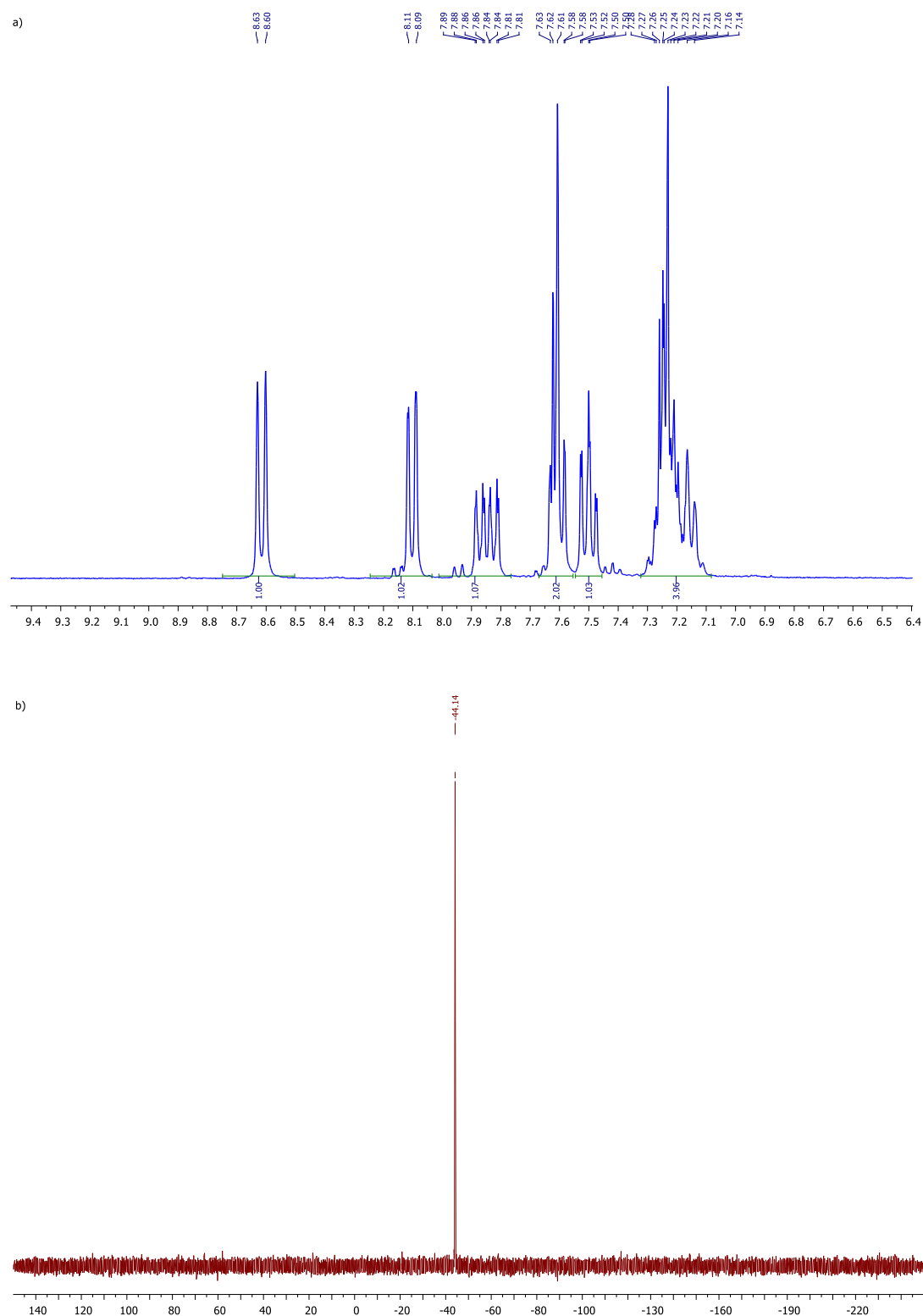


Figure S2.1-33. NMR spectroscopic characterization of **2-1b** in CDCl₃; a) ¹H NMR spectrum b) ³¹P{¹H} NMR spectrum c) ¹³C{¹H} NMR spectrum.



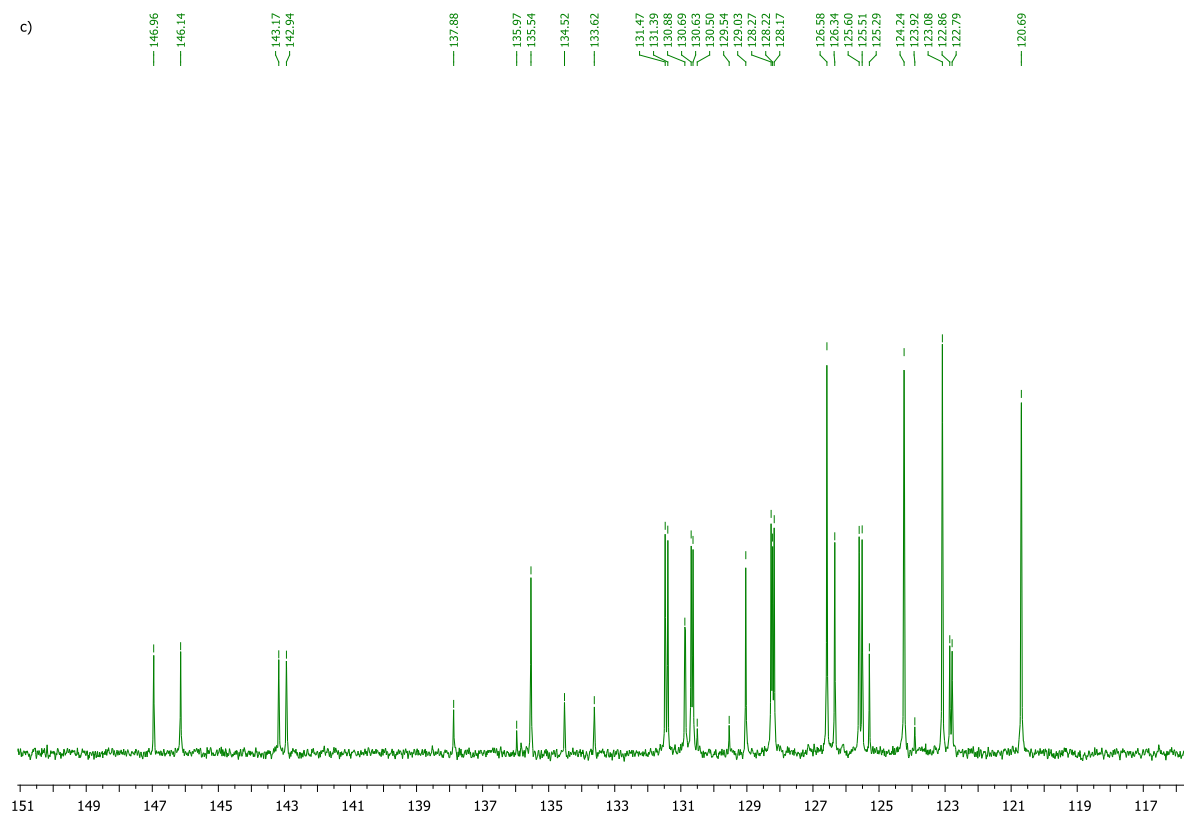
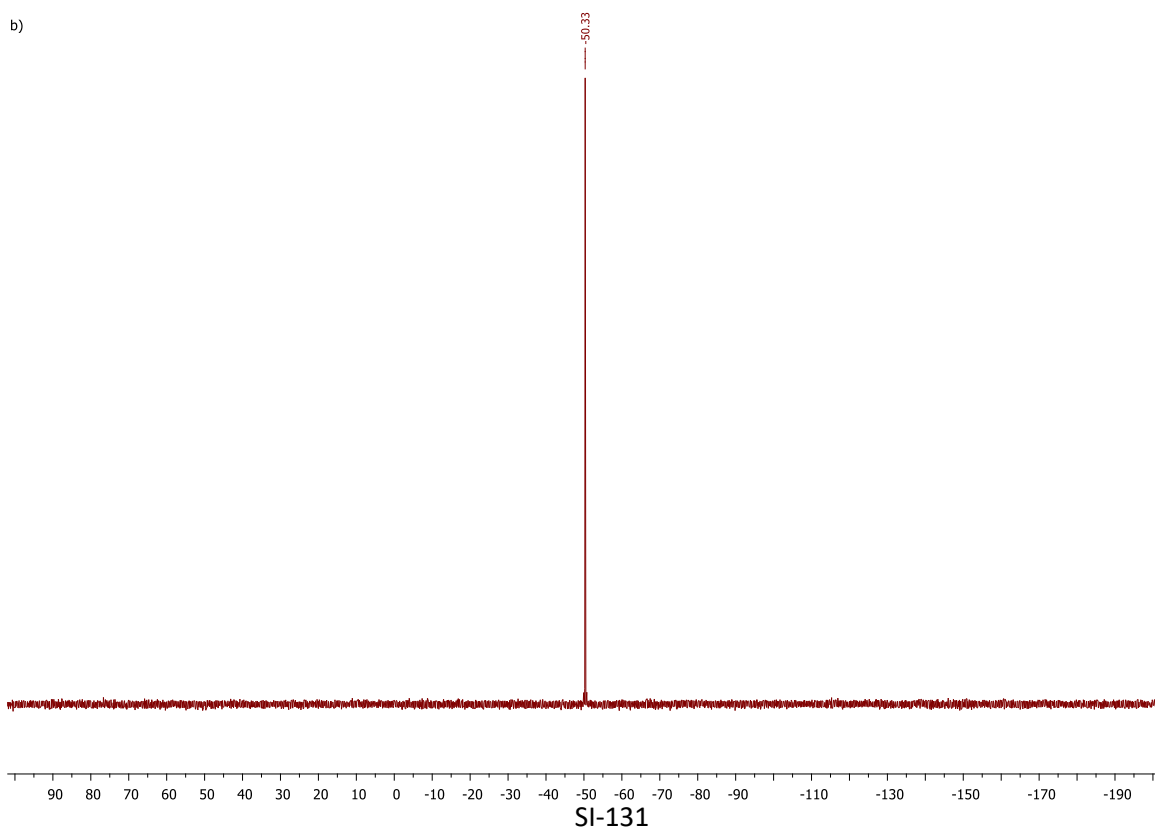
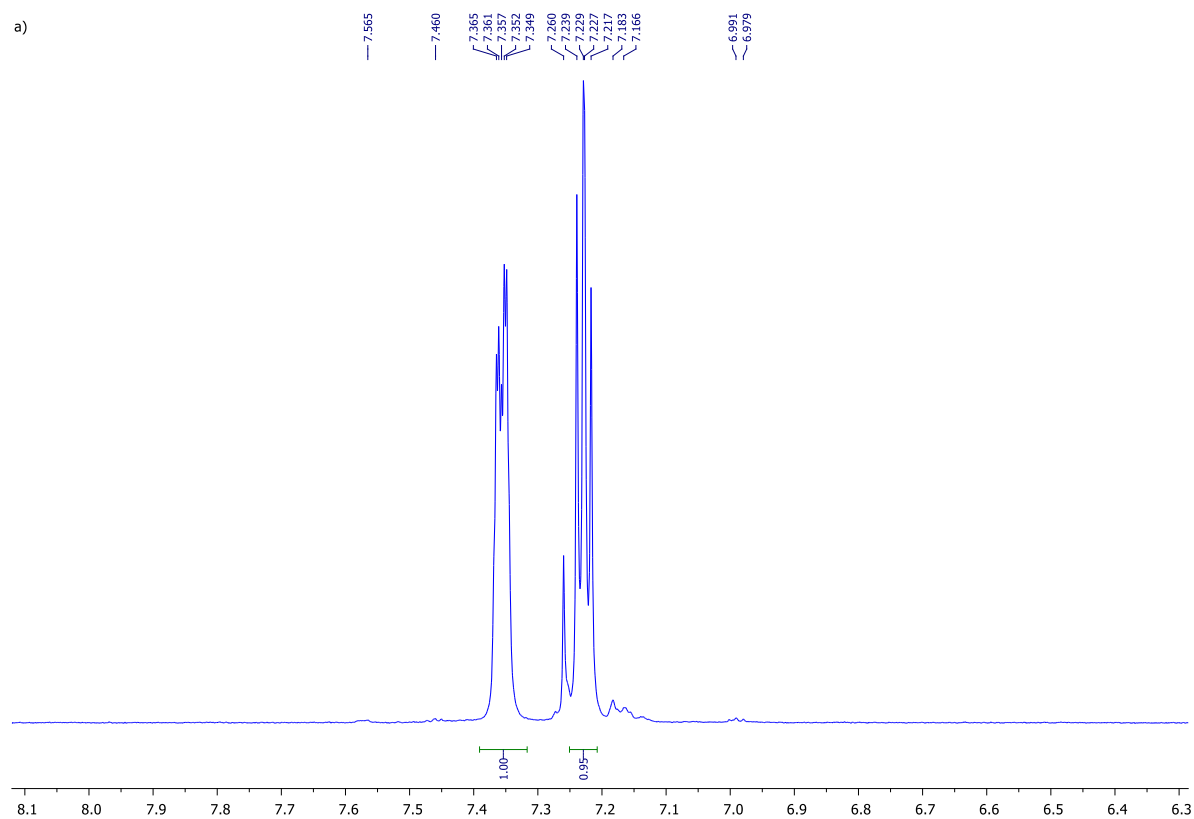


Figure S2.1-34. NMR spectroscopic characterization of **2-2a** in CDCl₃; a) ¹H NMR spectrum b) ³¹P{¹H} NMR spectrum c) ¹⁹F{¹H} NMR spectrum d) ¹³C{¹H} NMR spectrum.



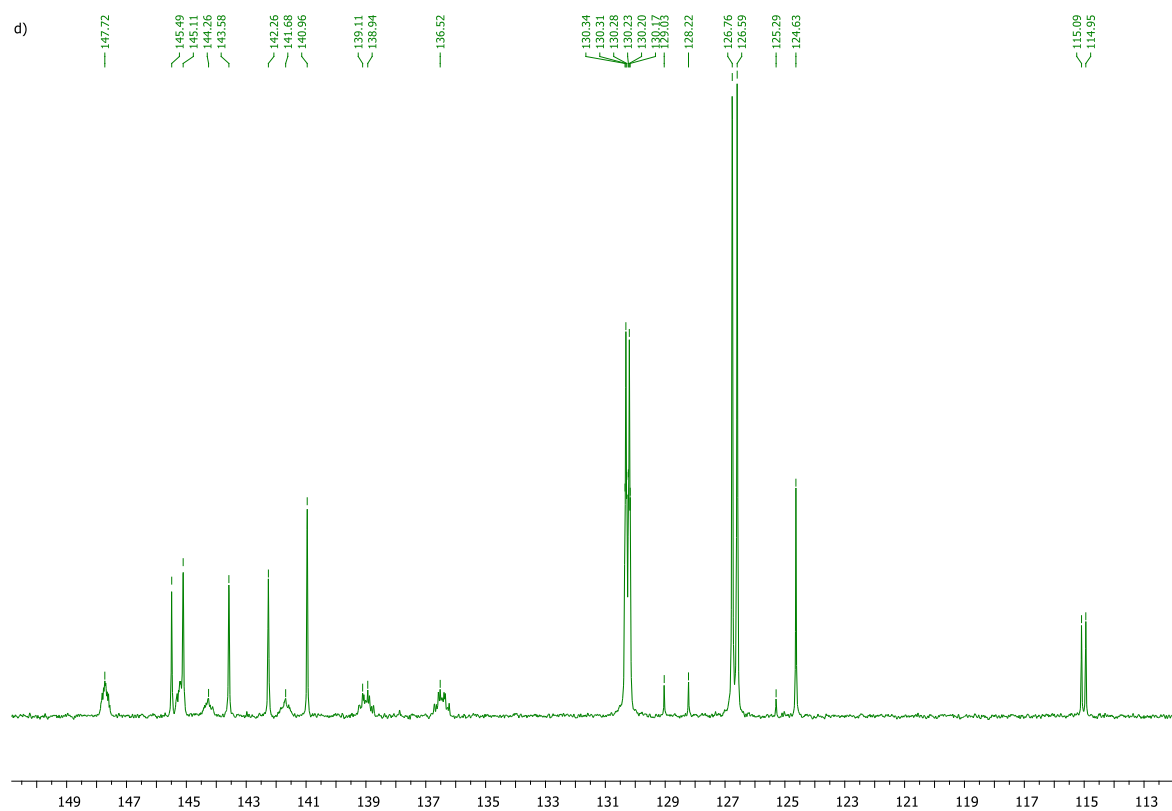
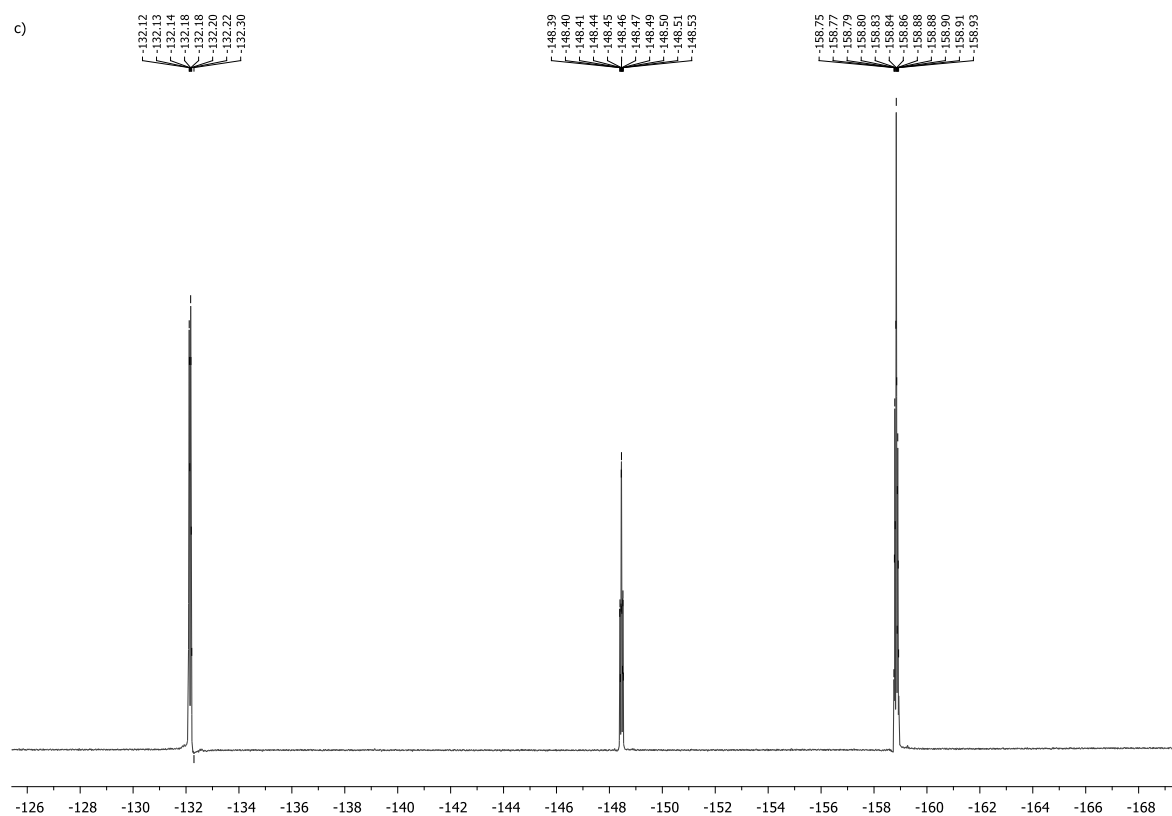
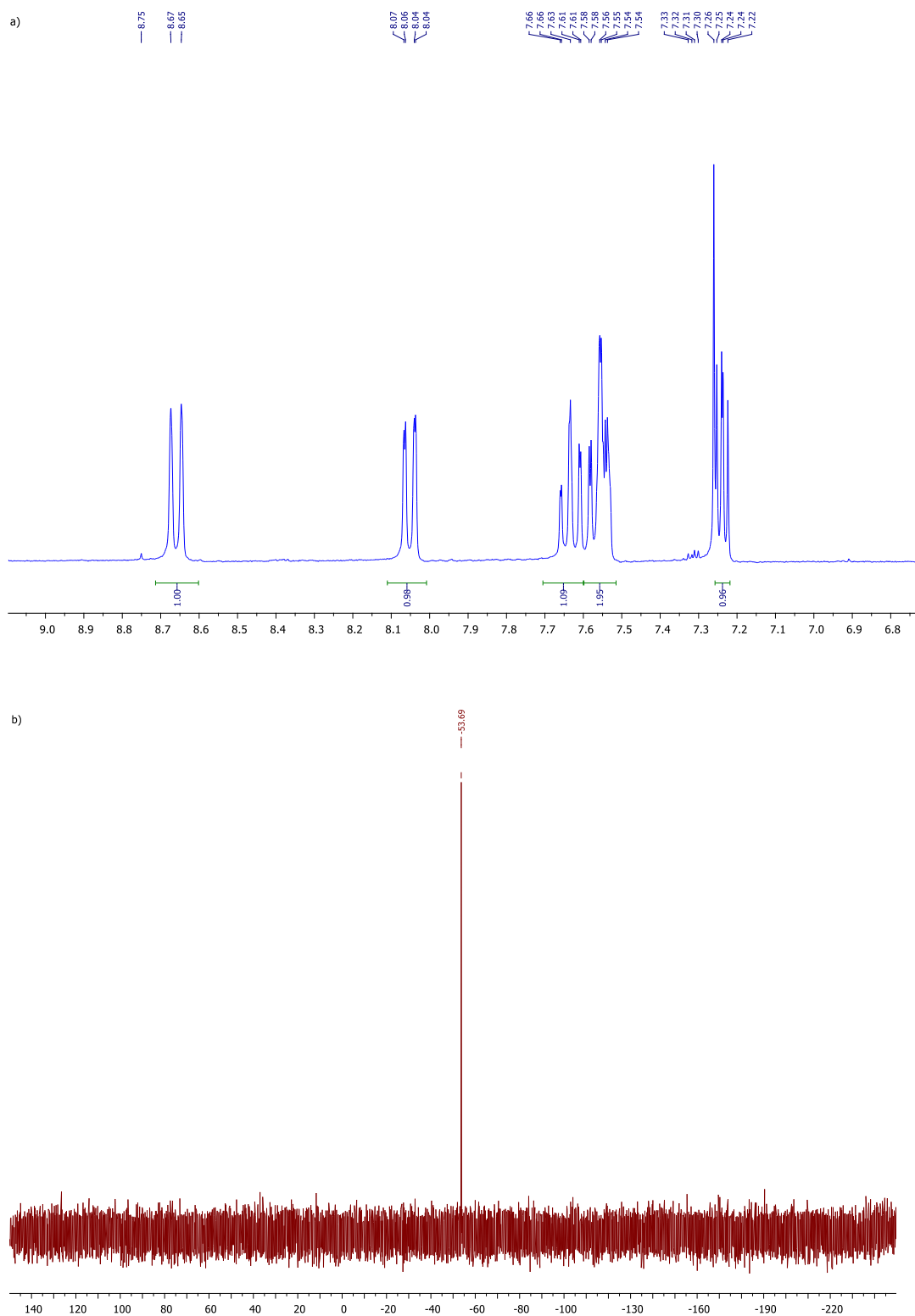
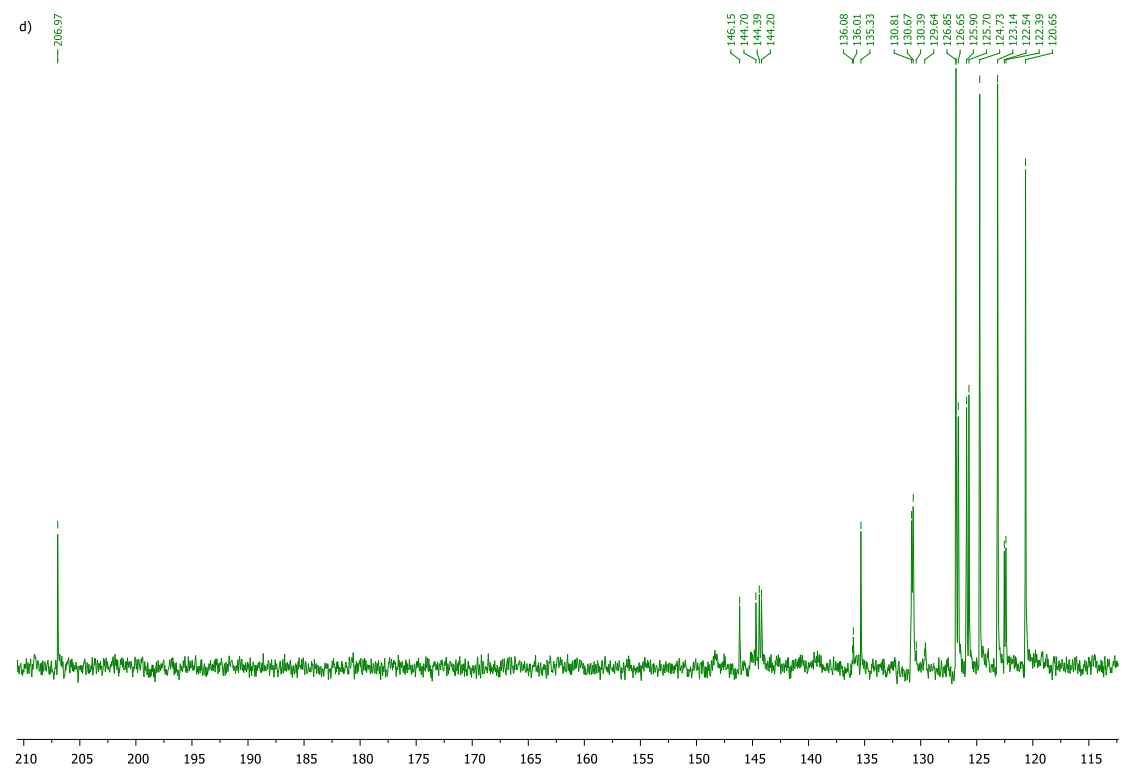
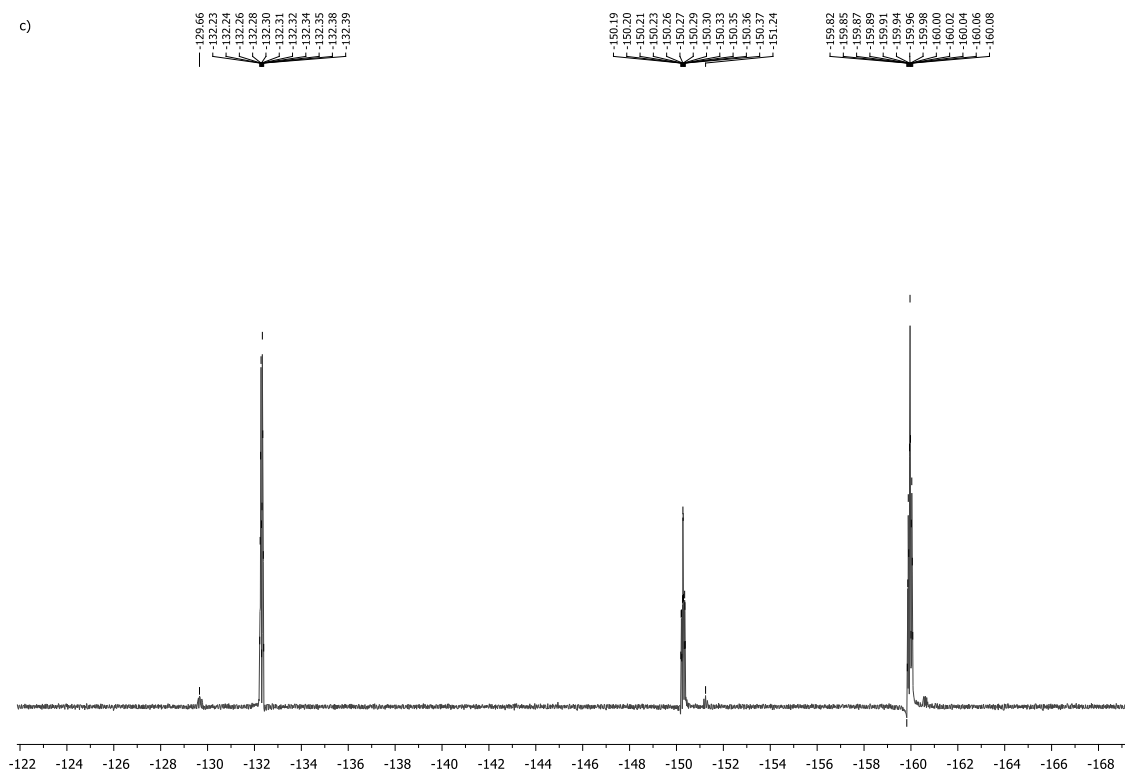


Figure S2.1-35. NMR spectroscopic characterization of **2-2b** in CDCl₃; a) ¹H NMR spectrum b) ³¹P{¹H} NMR spectrum c) ¹⁹F{¹H} NMR spectrum d) ¹³C{¹H} NMR spectrum.





2.2 Exploring the Lewis Acidity and Reactivity of Neutral Pentacoordinate Dithienophospholes

S.2.2.1: Synthesis and NMR Spectroscopy Characterization

(i) *Compound 2-1c*

One equivalent of 3,5-di-*tert*-butyl-1,2-benzoquinone (0.5g, 2.30 mmol) dissolved in dry CH₂Cl₂ (10 ml) was added to a solution of phenyl-dithienophosphole (**2-1'**; 0.62 g, 2.30 mmol)^{S1}. The solution turned dark brown immediately on mixing and was stirred for 16 hours in the glove box. The mixture was dried and the product was isolated by passing through a micro-pipette column of dry alumina by eluting with 50:50 mixture of dry hexane to dry CH₂Cl₂ in the glove box. The bright yellow solution was dried under high vacuum to yield **2-1c** (0.82 g, 73% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.86 (dd, 2H, ³J_P=14.08 Hz, ³J_H=7.00 Hz), 7.53 (d, 2H, ³J_H=4.64 Hz), 7.33 (3H, m), 7.24 (2H, s), 6.94 (1H, s), 6.85 (1H, s), 1.50 (9H, s), 1.33 (9H, s). ³¹P{¹H} NMR (162 MHz, CDCl₃ ppm): δ -47.5. ¹³C NMR (151 MHz, CDCl₃, ppm): δ 147.3 (d, ¹J_P=130 Hz), δ 146.5 (d, ¹J_P=124.4 Hz), 144.6 (s), 143.0 (s), 142.8 (d, ²J_P=35.3 Hz), 142.4 (d, ²J_P=35.5 Hz), 139.7 (s), 134.9 (d, ¹J_P=136.7 Hz), 132.4 (d, ³J_P=9.9 Hz), 131.5 (d, ²J_P=11.7 Hz), 130.7 (d, ²J_P=8.3 Hz), 130.5 (d, ⁴J_P=2.4 Hz), 130.2 (d, ²J_P=8.3 Hz), 128.1 (d, ³J_P=14.1 Hz), 125.3 (d, ³J_P=13.6 Hz), 125.2 (d, ³J_P=13.7 Hz), 114.5 (s), 105.8 (d, ³J_P=12.4 Hz), 34.7(s), 34.6(s), 31.7(s), δ 29.7(s) (Figure S2.2-11). E.A. (%) calc'd for C₂₈H₂₉S₂PO₂ (492.63): C 68.27, H 5.93, S 13.02, found: C 68.34, H 6.45, S 11.25.

(ii) Compound 2-1d

The synthesis of compound **2-1d** was conducted in the glovebox with 1:1 eq. of **2-1**^{S1} (0.66 g, 2.40 mmol) and 1,2-pyrenedione^{S17} (0.56 g, 2.40 mmol) dissolved in 25 ml of dry CH₂Cl₂. The mixture was stirred for 6 days and the solvent was dried under high vacuum. The yellow solid was purified by washing with dry pentane several times to yield **2-1d** (0.84 g, 69% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.38 (d, 2H, ⁴J_H=6.72 Hz), 8.07 (m, 6H), 7.95 (dd, 2H, ³J_H=7.16 Hz, ²J_P=14.24 Hz), 7.74 (2H, ³J_H=4.76 Hz), 7.29 (m, 5H). ³¹P{¹H} NMR (162 MHz, CDCl₃, ppm): δ -43.9. ¹³C{¹H} NMR (100.6 MHz, CDCl₃, ppm): δ 146.6 (d, ¹J_P=123.1 Hz), 143.1 (d, ²J_P=35.28 Hz), 136.3 (s), 134.1 (d, ¹J_P=135.8 Hz), 131.5 (s), 131.4 (d, ²J_P=4.7 Hz), 130.9 (d, ⁴J_P=2.34 Hz), 130.7 (d, ²J_P=8.48 Hz), 128.2 (d, ³J_P=14.3 Hz), 127.5 (s), 125.8 (s), 125.6 (d, ³J_P=13.7 Hz), 123.2 (s), 121.9 (d, ²J_P=10.8 Hz), 120.6 (s), 117.7(s) (Figure S2.2-12). E.A. (%) calc'd for C₃₀H₁₇S₂PO₂ (504.56): C 71.42, H 3.40, S 12.71, found: C 68.31, H 3.17, S 12.55.

(iii) Compound 2-1e

One equivalent of 1,10-phenanthroline 5,6-dione^{S17} (0.55g, 2.02 mmol) dissolved in 12 ml dry CH₂Cl₂ was added to a stirring solution of **2-1**^{S1} (0.69 g, 2.02 mmol) in 15 ml dry CH₂Cl₂ in the glove box. The reaction was stirred for 2.5 days until the ³¹P NMR showed completely conversion of starting material to the desired product. The reaction mixture was passed through a micro-pipette column of dry alumina and washed with dry CH₂Cl₂ to isolate a yellow solution. The solution was dried under high vacuum and the residue was washed with dry pentane to yield **2-1e** at 19% yield (0.24g). ¹H NMR (700 MHz, CDCl₃, ppm): δ 8.36 (s, 2H), 8.1 (s, 2H), 8.00 (s, 2H), 7.93 (dd, 2H, ³J_H=7.70 Hz, ³J_P=14.28 Hz), 7.71 (d, 2H, ³J_H=4.62 Hz) 7.33 (m, 3H), 7.27 (m, 2H), 1.64 (s, 18H). ³¹P{¹H} NMR (162 MHz, CDCl₃, ppm): δ -44.5. ¹³C{¹H} NMR (176 MHz, CDCl₃, ppm): δ 148.6 (s), 146.9 (d, ¹J_P=122.5 Hz), 143.1 (d, ²J_P=34.8 Hz), 136.5 (s), 134.5 (d, ¹J_P=136.2 Hz), 131.2 (s),

131.2 (d, $^2J_P=38.1$ Hz), 130.8 (d, $^4J_P=2.2$ Hz), 130.8 (d, $^3J_P=8.7$ Hz), 128.3 (d, $^3J_P=14.6$ Hz), 127.6 (s), 125.6 (d, $^2J_P=13.5$ Hz), 121.5 (d, $^2J_P=10.4$ Hz), 120.5 (s), 118.9 (s), 114.5 (s), 35.3 (s), 32.0 (s). grease and impurity (less than 4%) (Figure S2.2-13). E.A. (%) calc'd for $C_{38}H_{33}S_2PO_2$ (616.77): C 74.00, H 5.39, N 0.00, found: C 73.31, H 5.49, N 0.00.

(iv) Compound 2-1f

The synthesis of compound **2-1f** was conducted in the glovebox with 1:1 eq. of **2-1**^{SI} (0.14 g, 0.52 mmol) and 1,10-phenanthroline-5,6-dione (0.11 g, 0.52 mmol) dissolved in 25 ml of dry CH_2Cl_2 . The mixture was stirred for 2 hours and the mixture was dried under high vacuum. The yellow solid was purified by washing with dry pentane several times to yield **2-1f** (0.10 g, 42% yield). 1H NMR (700 MHz, $CDCl_3$, ppm): δ 9.06 (d, 2H, $^2J_H=2.80$ Hz), 8.46 (d, 2H, $^2J_H=7.77$ Hz), 7.85 (dd, 2H, $^3J_H=7.77$ Hz, $^3J_P=14.49$ Hz), 7.63 (dd, 2H, $^3J_H=4.2$ Hz, $^3J_P=9.38$ Hz), 7.61 (d, 2H, $^2J_H=20.65$ Hz), 7.34 (m, 1H), 7.30 (m, 2H). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, ppm): δ -41.3. $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$, ppm): δ 147.9 (s), 145.7 (d, $^1J_P=123.1$ Hz), 143.5 (d, $^2J_P=34.7$ Hz), 142.2 (s), 134.8 (s), 133.5 (d, $^1J_P=135.9$ Hz), 131.2 (s), 131.2 (d, $^2J_P=12.4$ Hz), 130.4 (d, $^3J_P=8.9$ Hz), 128.4 (d, $^3J_P=14.2$ Hz), 128.4 (s), 126.0 (d, $^2J_P=14.0$ Hz), 122.7 (s), 119.7 (d, $^2J_P=10.1$ Hz). residual CH_2Cl_2 , H_2O and grease (Figure S2.2-14). E.A. (%) calc'd for $C_{26}H_{15}S_2PO_2N_2$ (482.51): C 64.72, H 3.13, N 5.81, found: C 64.02, H 3.12, N 5.80.

(v) Compound 2-6

Compound **2-6'** was synthesized as mentioned in S18 and was isolated at 18% yield (0.18g). Compound **2-6'** (0.03g, 8.6×10^{-5} mol) dissolved in dry CH_2Cl_2 and one equivalent of *o*-chloranil (0.02 g, 8.6×10^{-5} mol) in dissolved in dry CH_2Cl_2 was added to the above solution with stirring. The mixture was stirred for 16 hours and the mixture, dried under high vacuum and residue was washed dry pentane and dried to yield 32% of **2-6** (0.016g). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$,

ppm): δ -30.2. ^1H NMR (400 MHz, CDCl_3 , ppm): δ 8.82 (d, 2H, $^3J_{\text{H}}=8.40$ Hz), 7.91 (dd, 2H, $^1J_{\text{H}}=7.63$ Hz, $^3J_{\text{P}}=14.98$ Hz), 7.87 (d, 2H, $^2J_{\text{H}}=7.98$ Hz), 7.58 (t, 2H, $^2J_{\text{H}}=7.42$ Hz), 7.39 (m, 3H), 7.29 (m, 2H). ^{13}C NMR (176 MHz, CDCl_3 , ppm): δ 145 (d, $^2J_{\text{P}}=39.5$ Hz), 143.1 (d, $^2J_{\text{P}}=15.3$ Hz), 141.5 (s), 138.6 (d, $^1J_{\text{P}}=122.2$ Hz), 138.5 (d, $^4J_{\text{P}}=10.1$ Hz), 132.2 (s), 132 (d, $^2J_{\text{P}}=13$ Hz), 131.3 (d, $^1J_{\text{P}}=132.2$ Hz), 128.9 (d, $^3J_{\text{P}}=15.0$ Hz), 126.4 (s), 126.1 (s), 124.8 (s), 124.3 (s), 123.5 (s), 121.9 (d, $^2J_{\text{P}}=14.3$ Hz). Residual acetone and grease from the NMR tube (Figure S2.2-15). E.A. (%) calc'd for $\text{C}_{28}\text{H}_{13}\text{Cl}_4\text{S}_2\text{PO}_2$ (618.30): C 54.39, H 2.12, N 0.00, found: C 53.87, H 2.28, N 0.00.

(vi) Compound 2-7

Compound **2-7'** was synthesized as reported in S19 and was isolated at 89% yield (1.12g). Compound **2-7'** (0.37g, 6.35×10^{-4} mol) was dissolved in dry CH_2Cl_2 and one equivalent of *o*-chloranil (0.16 g, 6.35×10^{-4} mol) dissolved in dry CH_2Cl_2 was added to the above solution with stirring. The mixture was stirred for 16 hours. The ^{31}P NMR spectroscopy shows that the mixture completely transformed from starting material (**2-7'**, -31.6 ppm) to product (**2-7**, -54.3 ppm). Any purification attempts including column chromatography with alumina/DCM or washing with dry pentane decomposes **2-7** to the oxide of **2-7'**. The reaction was repeated and **2-7** was isolated in the crude mixture and used in further reactions without purification. ^1H NMR (700 MHz, CDCl_3 , ppm): δ 8.34 (dd, 2H, $^3J_{\text{H}}=13.30$ Hz, $^3J_{\text{P}}=25.41$ Hz), 7.43 (m, 1H), 7.35 (m, 2H), 1.45 (q, 6H, $^3J_{\text{H}}=12.95$ Hz), 1.22 (d, 36H, $^3J_{\text{H}}=13.02$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , ppm): δ -54.3. $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, CDCl_3 , ppm): δ 171.9 (d, $^2J_{\text{P}}=30.7$ Hz), 160.9 (d, $^1J_{\text{P}}=249.9$ Hz), 141.5 (s), 138.8 (d, $^1J_{\text{P}}=75.3$ Hz), 134.5 (d, $^1J_{\text{P}}=11.95$ Hz), 132.1 (d, $^3J_{\text{P}}=3.4$ Hz), 130.3 (s), 128.1 (d, $^2J_{\text{P}}=25.5$ Hz), 123.8 (s), 115.0 (d, $^2J_{\text{P}}=24.3$ Hz), 18.5 (s), 11.7 (s). (some starting material and corresponding oxide identified in the mixture). (Figure S2.2-16)

(vii) Compound 2-10

Compound **2-1f** (0.046 g, 9.5×10^{-5} moles) was dissolved in dry CH_2Cl_2 and 1.0 eq of ZnCl_2 in etherated (0.0195 g, 9.5×10^{-5} moles) dropwise to the solution with stirring. An yellow solid precipitate out of the solution with 2 hours of reaction time. The solid was isolated by filtration in the glove box and washed with dry pentane to wash away impurities. The bright yellow solid was dried to isolate **2-10** at 29% yield (0.017g). ^1H NMR (700 MHz, CDCl_3 , ppm): δ 9.17 (d, 2H, $^3J_{\text{H}}=1.26$ Hz, $^7J_{\text{P}}=4.69$ Hz), 8.75 (d, 2H, $^3J_{\text{H}}=1.26$ Hz, $^5J_{\text{P}}=8.33$ Hz), 7.96 (dd, 2H, $^3J_{\text{H}}=4.69$ Hz, $^3J_{\text{P}}=8.33$ Hz), 7.79 (dd, 2H, $^3J_{\text{H}}=7.42$ Hz, $^3J_{\text{P}}=14.84$ Hz), 7.56 (d, 2H, $^3J_{\text{H}}=4.83$ Hz), 7.39 (m, 1H), 7.34 (m, 2H), 7.31 (m, 2H). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , ppm): δ -36.1. $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, CDCl_3 , ppm): δ 207 (s), 144.4 (d, $^2J_{\text{P}}=34.0$ Hz), 143.9 (d, $^1J_{\text{P}}=55.2$ Hz), 136.0 (d, $^4J_{\text{P}}=9.3$ Hz), 132.7 (s), 131.84 (br, s), 130.9 (s), 130.8 (d, $^2J_{\text{P}}=12.3$ Hz), 130.1 (d, $^3J_{\text{P}}=9.5$ Hz), 128.8 (d, $^3J_{\text{P}}=15.1$ Hz), 126.7 (d, $^2J_{\text{P}}=14.3$ Hz), 125.3 (s), 120.4 (d, $^2J_{\text{P}}=11.4$ Hz) (Figure S2.2-17). E.A. (%) calc'd for $\text{C}_{26}\text{H}_{15}\text{Cl}_2\text{N}_2\text{S}_2\text{PO}_2\text{Zn}$ (618.79): C 50.47, H 2.44, N 4.53, found: C 47.60, H 2.01, N 4.28.

S.2.2.2 Theoretical Calculations

DFT FMO calculations

The DFT FMO calculations were conducted at the B3LYP/6-31G+(d) level of theory.^{S3} Compound **2-7** was optimised used SiH₃ as functionality on the thiazole framework, rather than the experimentally preferred TIPS as this bulky functionalization hindered geometrical optimization. The FMOs of all the compounds reported are shown in the figure S2.2-1, with corresponding energies of orbitals and HOMO-LUMO gap in electron volt (eV). The Cartesian coordinates for FMOs of the compounds are listed below in Table S2-4.

Figure S2.2-1. DFT calculated (B3LYP/6-31G+(d) level of theory) HOMO-1, HOMO, LUMO, and LUMO+1 levels of **2-1c-f**, **2-6**, **2-7** and **12-10**. The numerical values in the figure represents the corresponding orbital energy and bandgap in electron volts.

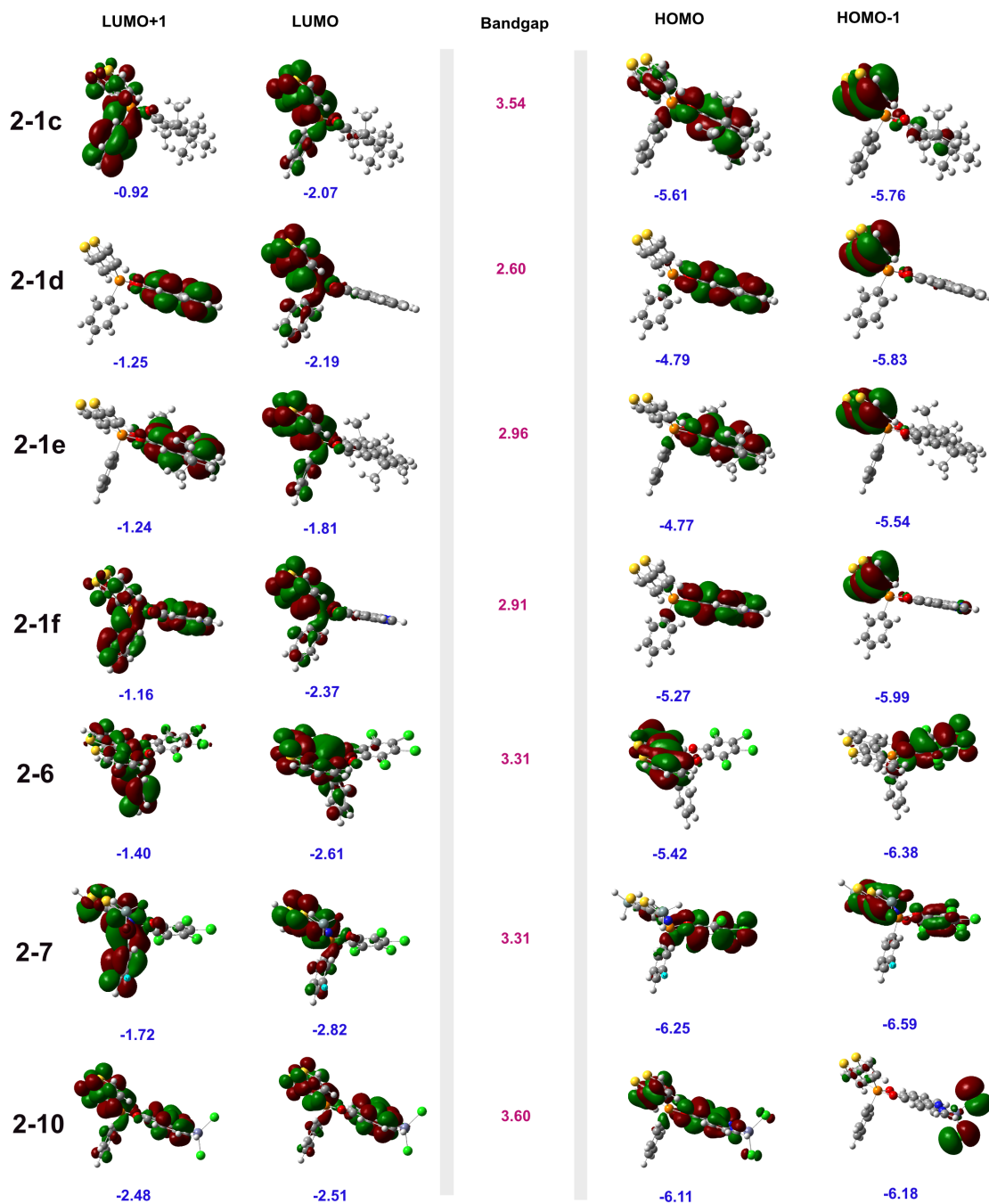


Table S2.2-1a. Cartesian coordinates for the minimized structure of **2-1c**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	15	0	-1.080436	0.369609	0.079552
2	6	0	-2.517541	-0.697100	-0.589316
3	6	0	-3.468704	-0.768200	0.364663
4	6	0	-3.130654	-0.197099	1.641572
5	6	0	-1.865752	0.342326	1.712474
6	6	0	-2.831857	-1.365047	-1.840830
7	6	0	-4.088734	-1.952737	-1.796621
8	16	0	-4.805161	-1.636284	-0.226745
9	16	0	-3.878520	-0.164232	3.186960
10	6	0	-2.446160	0.501691	3.930575
11	6	0	-1.462564	0.703620	3.030675
12	8	0	0.302906	1.305701	0.725316
13	6	0	-1.419156	1.708250	-1.174663
14	6	0	-2.590036	2.481019	-1.127519
15	6	0	-2.816226	3.472908	-2.080648
16	6	0	-1.887384	3.695767	-3.099595
17	6	0	-0.724486	2.927308	-3.154236
18	6	0	-0.483073	1.944422	-2.192893
19	1	0	-0.494240	1.129221	3.286633
20	1	0	-3.330076	2.310424	-0.342441
21	1	0	-3.729262	4.071667	-2.029632
22	1	0	-2.069754	4.469785	-3.849452
23	1	0	0.009740	3.097132	-3.945964
24	1	0	0.440719	1.362973	-2.244913
25	1	0	-2.408176	0.643207	5.007010
26	8	0	-0.004319	-0.885453	-0.269196
27	6	0	1.345440	-0.559102	-0.108368
28	6	0	1.512936	0.705054	0.496643
29	6	0	2.426199	-1.362874	-0.454549

30	6	0	3.899664	0.457847	0.476601
31	6	0	3.685425	-0.802132	-0.125333
32	6	0	2.764791	1.226679	0.787310
33	6	0	2.188617	-2.761657	-1.099553
34	6	0	2.020387	-3.794551	0.048116
35	6	0	0.909183	-2.743139	-1.972882
36	6	0	3.337266	-3.243099	-2.031378
37	1	0	2.930467	-3.852222	0.671393
38	1	0	1.176743	-3.523365	0.707119
39	1	0	1.821803	-4.802540	-0.363618
40	1	0	1.004822	-2.023714	-2.806744
41	1	0	0.751206	-3.747226	-2.407321
42	1	0	0.010060	-2.473910	-1.394144
43	1	0	3.070024	-4.231660	-2.446829
44	1	0	3.487050	-2.546136	-2.874837
45	1	0	4.303797	-3.370904	-1.526211
46	6	0	5.336817	0.964634	0.820062
47	6	0	6.403054	0.418032	-0.165706
48	6	0	5.438664	2.511383	0.759749
49	6	0	5.688384	0.490543	2.257149
50	1	0	6.468268	-0.680914	-0.164415
51	1	0	6.195937	0.743304	-1.200820
52	1	0	7.401600	0.797280	0.118851
53	1	0	4.765208	3.016375	1.469259
54	1	0	6.466806	2.826811	1.015494
55	1	0	5.206903	2.888588	-0.252315
56	1	0	6.701952	0.830200	2.544389
57	1	0	4.971700	0.892052	2.995541
58	1	0	5.663290	-0.611313	2.331023
59	1	0	2.818592	2.206877	1.254213
60	1	0	4.559465	-1.390111	-0.350104
61	1	0	-4.591249	-2.562584	-2.545868
62	1	0	-2.193645	-1.395642	-2.729961

Table S2.2-1b. Cartesian coordinates for the minimized structure of **2-1d**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.508653	0.939869	3.724922
2	6	0	1.683071	1.158102	2.658322
3	6	0	2.069760	0.411816	1.504651
4	6	0	3.175009	-0.400532	1.675166
5	16	0	3.839038	-0.239826	3.333076
6	1	0	2.479701	1.364611	4.715737
7	1	0	0.833823	1.826885	2.669150
8	6	0	3.525707	-1.231022	0.552596
9	6	0	2.683811	-1.138262	-0.533405
10	16	0	4.907149	-2.340921	0.242888
11	6	0	3.087503	-1.935227	-1.645549
12	6	0	4.236540	-2.643228	-1.414561
13	1	0	2.547156	-1.991324	-2.581954
14	1	0	4.758201	-3.330964	-2.061549
15	15	0	1.335898	0.181972	-0.188622
16	8	0	-0.199671	1.362263	0.337165
17	8	0	0.064588	-0.998599	-0.592502
18	6	0	-1.372771	0.677423	0.202348
19	6	0	-2.659219	1.213630	0.548937
20	6	0	-1.260840	-0.588362	-0.302002
21	6	0	-3.803449	0.372060	0.354168
22	6	0	-2.822025	2.511613	1.060282
23	6	0	-2.360910	-1.467348	-0.504962
24	6	0	-5.102440	0.873475	0.688883
25	6	0	-3.659462	-0.953437	-0.166171
26	6	0	-4.096412	2.985694	1.382123
27	1	0	-1.944479	3.133836	1.193344
28	6	0	-2.240471	-2.776070	-1.009314
29	6	0	-5.223508	2.179701	1.200315
30	6	0	-6.242981	0.016901	0.489078
31	6	0	-4.811184	-1.781519	-0.351590

32	1	0	-4.211953	3.990725	1.775670
33	6	0	-3.377240	-3.569159	-1.181896
34	1	0	-1.257001	-3.157120	-1.258200
35	1	0	-6.210100	2.557478	1.453141
36	6	0	-6.104010	-1.247607	-0.006392
37	1	0	-7.225719	0.402950	0.744635
38	6	0	-4.647991	-3.084158	-0.860765
39	1	0	-3.269974	-4.577101	-1.570671
40	1	0	-6.974861	-1.880930	-0.149978
41	1	0	-5.523626	-3.711132	-1.000708
42	6	0	1.794633	1.440206	-1.507226
43	6	0	2.626900	2.523167	-1.206831
44	6	0	1.297067	1.258107	-2.804395
45	6	0	2.966062	3.431198	-2.217307
46	1	0	2.999540	2.669027	-0.198603
47	6	0	1.636242	2.173478	-3.806301
48	1	0	0.637862	0.425235	-3.028628
49	6	0	2.472894	3.258117	-3.515386
50	1	0	3.610070	4.273520	-1.986090
51	1	0	1.245353	2.040161	-4.809852
52	1	0	2.735571	3.965453	-4.295281

Table S2.2-1c. Cartesian coordinates for the minimized structure of **2-1e**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-6.054559	-0.448106	0.811458
2	6	0	-5.062745	-0.656248	-0.113043
3	6	0	-3.687432	-0.269410	0.447135
4	6	0	-3.782069	0.128184	1.705801
5	16	0	-5.428462	0.370798	2.264715
6	1	0	-7.077231	-0.742405	0.685118
7	1	0	-5.227817	-1.045687	-1.098368
8	6	0	-2.457907	0.231188	2.333884
9	6	0	-1.477300	-0.096552	1.483358
10	16	0	-1.966340	0.660748	3.966966
11	6	0	-0.155912	-0.202656	2.300847
12	6	0	-0.331297	0.076850	3.632798
13	1	0	0.792854	-0.472320	1.909736
14	1	0	0.423473	-0.047658	4.384882
15	15	0	-2.010418	-0.312541	-0.365805
16	8	0	-1.075278	1.070264	-0.714036
17	8	0	-0.793505	-1.507697	-0.490045
18	6	0	0.211343	0.704073	-0.222050
19	6	0	1.360059	1.465540	-0.456257
20	6	0	0.387529	-0.776992	-0.190223
21	6	0	2.640069	0.909203	-0.280240
22	6	0	1.211279	2.858744	-0.558499
23	6	0	1.667976	-1.323179	-0.256896
24	6	0	3.766020	1.741967	-0.205814
25	6	0	2.793340	-0.483054	-0.182573
26	6	0	2.334979	3.695611	-0.486040
27	1	0	0.235042	3.282553	-0.692214
28	6	0	1.823560	-2.714623	-0.158668
29	6	0	3.611738	3.133652	-0.309711
30	6	0	5.045124	1.170659	-0.028913
31	6	0	4.072167	-1.034468	-0.011910

32	6	0	3.100940	-3.270939	0.005636
33	1	0	0.962964	-3.352930	-0.210239
34	1	0	4.473857	3.767571	-0.255616
35	6	0	5.194046	-0.181130	0.065466
36	1	0	5.907217	1.807233	0.031295
37	6	0	4.222790	-2.427513	0.079890
38	1	0	6.172659	-0.601929	0.198074
39	1	0	5.200952	-2.845926	0.206633
40	6	0	-2.923504	-0.619605	-1.914194
41	6	0	-3.472546	0.455212	-2.625705
42	6	0	-3.067885	-1.926930	-2.398501
43	6	0	-4.160112	0.223417	-3.823114
44	1	0	-3.366145	1.456571	-2.253032
45	6	0	-3.755830	-2.157279	-3.595470
46	1	0	-2.651290	-2.751276	-1.851473
47	6	0	-4.299815	-1.082370	-4.308816
48	1	0	-4.579010	1.046728	-4.368922
49	1	0	-3.865368	-3.158126	-3.967128
50	1	0	-4.823557	-1.259355	-5.228170
51	6	0	2.155232	5.226771	-0.600628
52	6	0	1.372556	5.520563	-1.869355
53	6	0	1.395477	5.708057	0.623888
54	6	0	3.526038	5.878149	-0.663318
55	1	0	1.921923	5.145224	-2.761306
56	1	0	0.375656	5.028271	-1.836795
57	1	0	1.217506	6.616562	-1.988567
58	1	0	1.961378	5.469525	1.551863
59	1	0	1.240857	6.809802	0.580893
60	1	0	0.398935	5.216877	0.682865
61	1	0	3.429045	6.983905	-0.746915
62	1	0	4.111078	5.647580	0.254191
63	1	0	4.093636	5.508935	-1.546209
64	6	0	3.257301	-4.805559	0.104622
65	6	0	2.450135	-5.289441	1.297531
66	6	0	2.735573	-5.420154	-1.183187
67	6	0	4.727667	-5.137642	0.291406

68	1	0	2.820831	-4.818586	2.235160
69	1	0	1.375604	-5.029400	1.173699
70	1	0	2.532584	-6.394589	1.403828
71	1	0	3.314202	-5.044371	-2.056261
72	1	0	2.827193	-6.529294	-1.152917
73	1	0	1.663932	-5.161804	-1.333323
74	1	0	4.872427	-6.238732	0.366726
75	1	0	5.324933	-4.764720	-0.569903
76	1	0	5.118875	-4.669329	1.221661

Table S2.2-1d. Cartesian coordinates for the minimized structure of **2-1f**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.117617	-3.481269	-2.021388
2	6	0	-0.441962	-2.352717	-1.640183
3	6	0	-1.307115	-1.446258	-0.815212
4	6	0	-2.532068	-1.960893	-0.604339
5	16	0	-2.751674	-3.582813	-1.281395
6	1	0	-0.744065	-4.226094	-2.700186
7	1	0	0.577652	-2.136826	-1.903362
8	6	0	-3.409815	-1.045352	0.159828
9	6	0	-2.761401	0.065467	0.558773
10	16	0	-5.105216	-1.127066	0.670851
11	6	0	-3.620644	0.910307	1.457830
12	6	0	-4.852463	0.346489	1.663080
13	1	0	-3.308345	1.842831	1.888529
14	1	0	-5.595352	0.715861	2.346454
15	15	0	-0.984909	0.256325	-0.090103
16	8	0	0.062847	0.040541	1.282358
17	6	0	1.545094	0.230600	-0.542812

18	6	0	1.390571	-0.082377	0.767508
19	6	0	2.827664	0.304309	-1.131658
20	6	0	2.484113	-0.485624	1.563626
21	6	0	3.959895	-0.049316	-0.357054
22	6	0	3.012883	0.712443	-2.465700
23	6	0	2.325661	-0.895783	2.901431
24	6	0	3.783615	-0.471352	0.998748
25	1	0	2.163968	0.982989	-3.070450
26	6	0	4.283623	0.758208	-2.971712
27	6	0	3.432555	-1.272044	3.612497
28	1	0	1.346989	-0.911369	3.350466
29	6	0	5.371034	0.393678	-2.143885
30	1	0	4.457899	1.068230	-3.989232
31	6	0	4.700828	-1.237303	2.987542
32	1	0	3.342826	-1.592251	4.637794
33	1	0	6.374491	0.428583	-2.536828
34	1	0	5.576441	-1.533689	3.542416
35	8	0	0.340875	0.466749	-1.256536
36	7	0	4.850904	-0.852152	1.738148
37	7	0	5.199435	0.009787	-0.896872
38	6	0	-1.277933	2.090859	-0.157403
39	6	0	-1.620289	2.712801	-1.367877
40	6	0	-1.150806	2.862894	1.006580
41	6	0	-1.842945	4.094646	-1.411875
42	1	0	-1.713092	2.126888	-2.267417
43	6	0	-1.370126	4.245863	0.960640
44	1	0	-0.880412	2.392057	1.937449
45	6	0	-1.717932	4.862550	-0.247493
46	1	0	-2.107726	4.567338	-2.343588
47	1	0	-1.269756	4.835357	1.857400
48	1	0	-1.886316	5.926570	-0.281658

Table S2.2-1e. Cartesian coordinates for the minimized structure of **2-6**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-3.086033	3.408542	-0.758030
2	6	0	-1.856189	2.863586	-0.360925
3	6	0	-1.947048	1.354502	-0.230882
4	6	0	-3.186508	0.910555	-0.510175
5	16	0	-4.365839	2.175557	-0.821511
6	6	0	-3.280981	-0.564706	-0.468889
7	6	0	-2.100585	-1.118551	-0.168292
8	16	0	-4.576646	-1.731705	-0.745033
9	6	0	-2.138409	-2.618945	-0.260354
10	6	0	-3.410429	-3.074640	-0.637948
11	15	0	-0.698279	0.043409	0.202052
12	8	0	0.504407	1.272553	-0.192193
13	8	0	0.332117	-1.160761	-0.515897
14	6	0	1.718167	0.697470	-0.335081
15	6	0	2.960163	1.325232	-0.318337
16	6	0	1.618050	-0.727452	-0.543300
17	6	0	4.116413	0.536509	-0.524601
18	6	0	2.753659	-1.503437	-0.746193
19	6	0	4.014451	-0.861249	-0.740271
20	6	0	-0.363143	-0.083299	1.991214
21	6	0	-0.806875	-1.202391	2.711731
22	6	0	0.337537	0.935451	2.655428
23	6	0	-0.546642	-1.305508	4.082639
24	1	0	-1.349213	-1.984192	2.213259
25	6	0	0.594970	0.831612	4.027259
26	1	0	0.675785	1.797665	2.111243
27	6	0	0.155116	-0.289491	4.741394
28	1	0	-0.888406	-2.166628	4.629292
29	1	0	1.131956	1.614821	4.532353

30	1	0	0.354969	-0.369588	5.795430
31	6	0	-0.758244	3.703316	-0.154987
32	6	0	-0.902869	5.076802	-0.414491
33	6	0	-2.103732	5.595618	-0.869656
34	1	0	-0.065787	5.734975	-0.259737
35	1	0	-2.183955	6.646623	-1.084061
36	6	0	-3.220938	4.764113	-1.050137
37	17	0	2.628772	-3.078732	-0.980593
38	17	0	5.337303	-1.724929	-0.977321
39	17	0	5.554377	1.233104	-0.515628
40	17	0	3.065795	2.900290	-0.073184
41	1	0	0.177599	3.307690	0.189927
42	1	0	-4.157088	5.164248	-1.397531
43	6	0	-3.651151	-4.427850	-0.876210
44	6	0	-2.600653	-5.335456	-0.663290
45	6	0	-1.334671	-4.885514	-0.221162
46	1	0	-2.762352	-6.384804	-0.835409
47	1	0	-0.549169	-5.598263	-0.042651
48	6	0	-1.096476	-3.518170	-0.016937
49	1	0	-0.134982	-3.165459	0.311723
50	1	0	-4.615488	-4.769524	-1.207960

Table S2.2-1f. Cartesian coordinates for the minimized structure of **2-7**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.963750	0.397027	-0.895942
2	6	0	2.269503	-0.598382	-0.307914
3	6	0	3.996736	-1.801842	-1.123621
4	16	0	4.495669	-0.134715	-1.515333
5	6	0	2.198637	1.664608	-0.918025
6	6	0	0.983060	1.547929	-0.336287
7	16	0	2.449158	3.234436	-1.600408
8	6	0	0.770380	3.637394	-1.139353
9	7	0	0.110878	2.662395	-0.525244
10	7	0	2.853823	-1.895504	-0.448292
11	15	0	0.706819	-0.042321	0.566573
12	8	0	-0.148214	-1.428409	0.002156
13	6	0	-1.514015	-1.146904	-0.040498
14	6	0	-1.861827	-0.011425	0.646519
15	6	0	-2.462357	-1.909522	-0.713808
16	6	0	-3.180717	0.433187	0.693379
17	6	0	-3.803613	-1.489541	-0.677852
18	6	0	-4.161870	-0.318810	0.024172
19	8	0	-0.780176	0.603358	1.246126
20	17	0	-3.576895	1.888086	1.574516
21	17	0	-5.831788	0.199281	0.062840
22	17	0	-5.028964	-2.423426	-1.505949
23	17	0	-1.970372	-3.350281	-1.572512
24	6	0	1.425200	-0.306242	2.224290
25	6	0	1.669605	-1.612969	2.668499
26	6	0	1.731419	0.785684	3.050444
27	6	0	2.216441	-1.823798	3.937533
28	1	0	1.436802	-2.455693	2.032930
29	6	0	2.282512	0.569193	4.316628

30	1	0	1.540175	1.794468	2.711991
31	6	0	2.524366	-0.735158	4.761000
32	1	0	2.402899	-2.832184	4.279973
33	1	0	2.518033	1.411380	4.952576
34	1	0	2.948735	-0.901997	5.741570
35	14	0	4.992310	-3.340973	-1.666033
36	1	0	5.700944	-3.026177	-2.924336
37	1	0	5.974646	-3.696692	-0.619021
38	1	0	4.054252	-4.460548	-1.878188
39	14	0	-0.016731	5.347196	-1.473931
40	1	0	-0.675401	5.338751	-2.797521
41	1	0	-1.006319	5.632785	-0.417300
42	1	0	1.054874	6.365428	-1.457631

Table S2.2-1g. Cartesian coordinates for the minimized structure of **2-10**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.953478	-2.289276	3.156180
2	6	0	2.324669	-1.233188	2.557216
3	6	0	2.899847	-0.923111	1.282356
4	6	0	3.942035	-1.753408	0.918415
5	16	0	4.279231	-2.930233	2.165082
6	1	0	2.761845	-2.739478	4.118647
7	1	0	1.496896	-0.691628	2.994208
8	6	0	4.514621	-1.497373	-0.384104
9	6	0	3.863820	-0.535857	-1.137335
10	16	0	5.935712	-2.155980	-1.175560
11	6	0	4.661228	-0.159519	-2.269616
12	6	0	5.748145	-0.969342	-2.465054
13	1	0	4.437138	0.665403	-2.933418
14	1	0	6.475038	-0.943788	-3.263410
15	15	0	2.531899	0.273214	-0.037699
16	8	0	1.287326	-0.202148	-1.122187
17	6	0	-0.064446	0.662772	0.555779
18	6	0	-0.003431	-0.020740	-0.632536
19	6	0	-1.330546	0.960262	1.156946
20	6	0	-1.142205	-0.528734	-1.303826
21	6	0	-2.499687	0.486490	0.512267
22	6	0	-1.488963	1.706586	2.343310
23	6	0	-1.132298	-1.262939	-2.513295
24	6	0	-2.403784	-0.279259	-0.702297
25	1	0	-0.609052	2.084993	2.850857
26	6	0	-2.761367	1.936645	2.830074
27	6	0	-2.329649	-1.688376	-3.055619
28	1	0	-0.186925	-1.475459	-2.998916
29	6	0	-3.872500	1.430582	2.127796

30	1	0	-2.918240	2.501044	3.741413
31	6	0	-3.538495	-1.402796	-2.390054
32	1	0	-2.351885	-2.241577	-3.987040
33	1	0	-4.885039	1.579292	2.484859
34	1	0	-4.501310	-1.699146	-2.790976
35	8	0	1.119220	1.067571	1.030118
36	7	0	-3.557785	-0.735601	-1.241308
37	7	0	-3.742021	0.740294	1.000201
38	6	0	3.192040	1.993753	-0.112954
39	6	0	3.724289	2.611943	1.024882
40	6	0	3.148524	2.674656	-1.336415
41	6	0	4.236185	3.907963	0.928748
42	1	0	3.733235	2.093207	1.976932
43	6	0	3.643528	3.978298	-1.417839
44	1	0	2.713100	2.206454	-2.213161
45	6	0	4.194813	4.591983	-0.289536
46	1	0	4.656814	4.385112	1.807778
47	1	0	3.597251	4.511787	-2.361468
48	1	0	4.584172	5.602331	-0.357946
49	30	0	-5.210617	-0.227501	-0.143705
50	17	0	-6.515703	0.801190	-1.652682
51	17	0	-6.139293	-1.570404	1.423229

S.2.2.3 Xray Crystallography

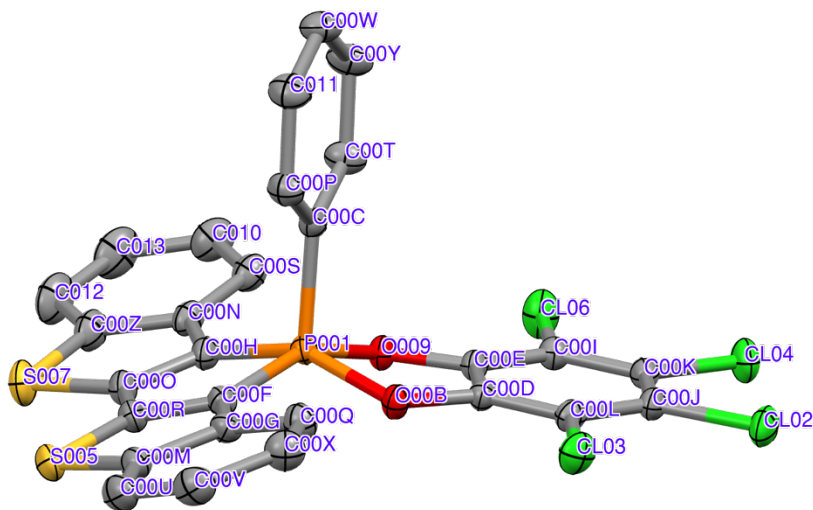


Figure S2.2-2. Crystallographically determined solid-state structure of compound **2-6**. Atomic displacement ellipsoids depicted at 50% probability level. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): P001-C00H 1.85(0), P001-C00F 1.84(8), P001-O009 1.74(5), P001-O00B 1.72(8), P001-C00C 1.81(2), C00E-O009 1.35(4), C00D-O00B 1.35(5); C00H-P001-C00F 88.9(6), C00H-P001-O009 86.4(7), O009-P001-O00B 87.0(0), O00B-P001-C00F 86.1(6), C00C-P001-O009 99.3(1), C00C-P001-O009 103.7(1), C00C-P001-C00F 105.3(1), C00C-P001-C00H 106.2(1).

Table S2.2-2. Crystal data for compounds **2-1c**, **2-1e** and **2-6**.

Parameters	2-1c	2-1e	2-6
Identification code	BAZ_06_03_a_a	NA_P4_17a_2_Om_a	NA_P4_21a_a
Empirical formula	C ₂₈ H ₂₉ O ₂ PS ₂	C ₃₈ H ₃₃ O ₂ PS ₂	C ₂₉ H ₁₃ Cl ₆ O ₂ PS ₂
Formula weight	492.60	616.73	701.18
Temperature	173 K	180 K	173 K
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	C 1 2/c 1	P -1	P 1 21/n 1
a/ Å	35.3984(15)	8.9361(4)	8.7511(3)
b/ Å	9.0963(4)	12.7570(6)	13.1886(4)
c/ Å	18.1185(8) Å	14.7944(7)	24.4618(7)
$\alpha/^\circ$	90	79.460(2)	90
$\beta/^\circ$	119.843(3)	82.087(2)	92.485(1)
$\gamma/^\circ$	90	73.890(2)	90
Volume/ Å ³	5060.4(4)	1586.20(13)	2820.60(15)
Z	8	2	4
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	1.293	1.291	1.651
$\mu(\text{mm}^{-1})$	0.297	0.252	0.844
F(000)	2080.0	648.0	1408.0
Crystal size/ mm ³	0.1*0.1*0.1	0.2*0.2*0.05	0.15*0.15*0.05
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)

2 Θ range for data collection/ $^{\circ}$	27.561 to 2.248	27.547 to 2.021	33.189 to 1.755
Index ranges	$-46 \leq h \leq 46$ $-11 \leq k \leq 11$ $-23 \leq l \leq 23$	$-11 \leq h \leq 11$ $-16 \leq k \leq 16$ $-19 \leq l \leq 19$	$-13 \leq h \leq 13$ $-20 \leq k \leq 20$ $-37 \leq l \leq 37$
Reflections collected	51581	33540	115654
Independent reflections	5841	7317	10814
Data/restraints/ parameters	5841/0/304	4529/0/394	10814/3/441
Goodness-of-fit on F^2	1.310	1.041	1.042
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.1272$ $wR_2 = 0.2412$	$R_1 = 0.1065$ $wR_2 = 0.1405$	$R_1 = 0.0783$ $wR_2 = 0.1113$
Final R indexes [all data]	$R_1 = 0.1083$ $wR_2 = 0.2333$	$R_1 = 0.0507$ $wR_2 = 0.1083$	$R_1 = 0.0458$ $wR_2 = 0.0956$
Largest diff. peak/hole $\text{\AA}^{-3}$	0.452/-0.581	0.529/-0.406	0.726/-0.506
CCDC number	2235915	2235916	2235917

S.2.2.4 Photophysical Characterization

(i) UV-Vis Characterization

Compounds **2-1c-e** and **2-6** were characterized in CH₂Cl₂, which was dried by several freeze-pump-thaw cycles under argon. Due to the low solubility of **2-1f** and **2-10** in CH₂Cl₂, these compounds were characterized in chlorobenzene, which was dried in similar manner.

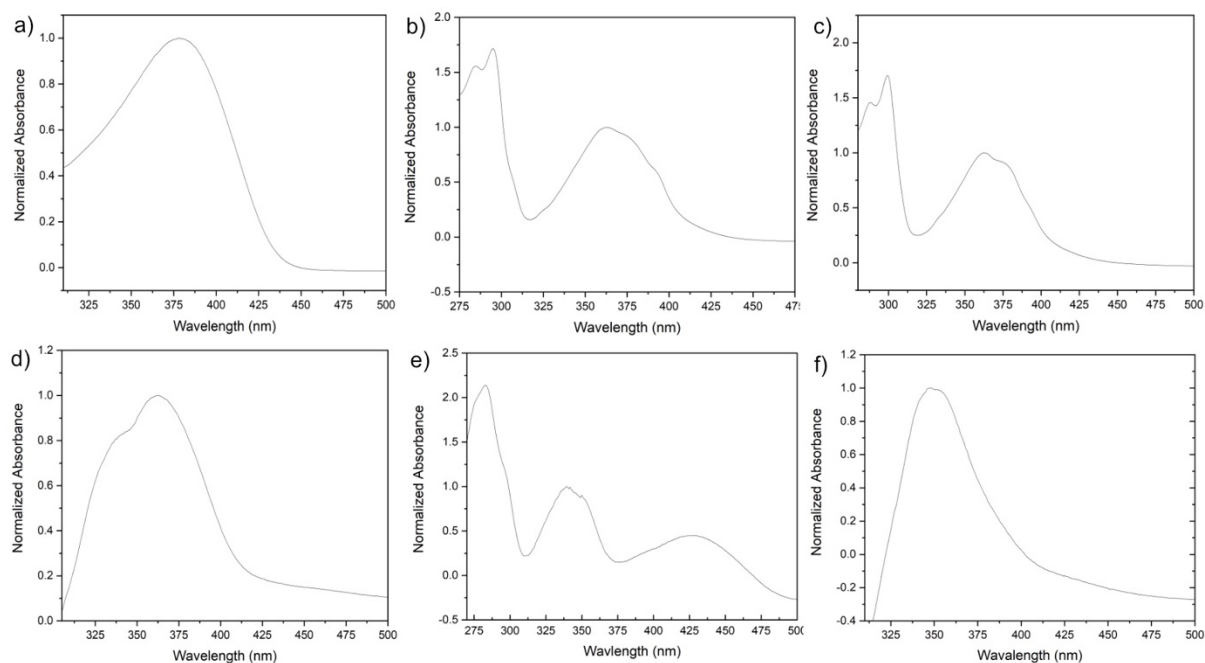


Figure S2.2-3. UV-Vis absorption spectra of a) **2-1c** in CH₂Cl₂ b) **2-1d** in CH₂Cl₂ c) **2-1e** and in CH₂Cl₂ d) **2-1f** in C₆H₅Cl e) **2-6** in CH₂Cl₂ and f) **2-10** in C₆H₅Cl.

Table S2.2-3. Absorption maxima, λ_{max} and molar absorptivity, ϵ of the hypervalent compounds

Compounds	Absorption maxima, λ_{max} (nm)	Molar Absorptivity, ϵ (L mol ⁻¹ cm ⁻¹)
2-1c	378	~4700
2-1d	363	~14000
2-1e	363	~17200
2-1f	336,363	~7800, ~9800
2-6	283,342,428	~12000, ~5500, ~2500
2-10	348	~1706

(ii) Emission Spectroscopy and QY

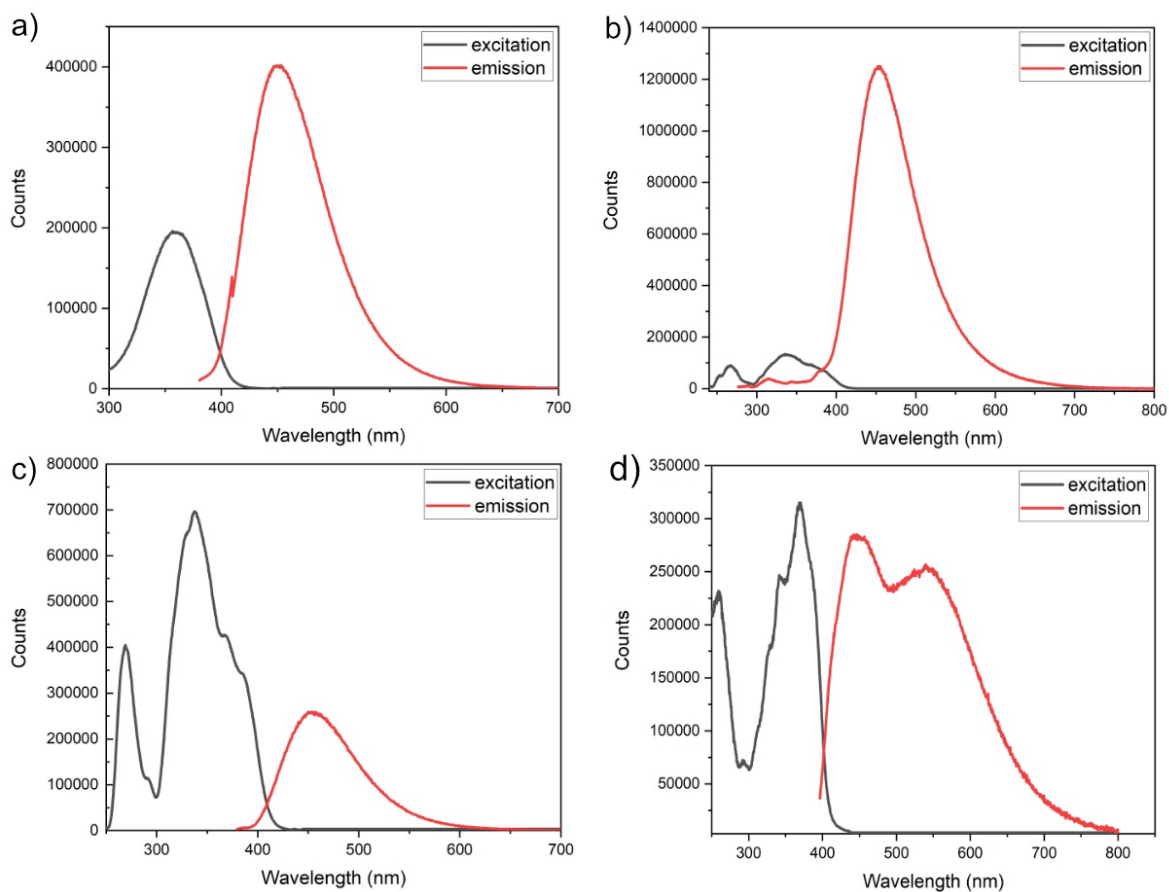


Figure S2.2-4. Excitation and emission spectra a) 2-1c b) 2-1d c) 2-1e and d) 2-6 in CH_2Cl_2 .

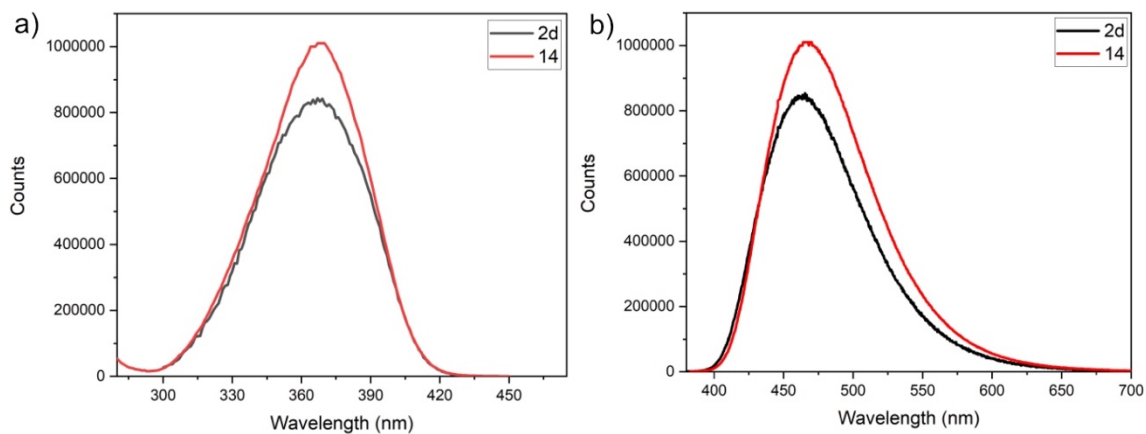


Figure S2.2-5. a) Excitation and b) emission spectra of 2-1f and 2-10 in $\text{C}_6\text{H}_5\text{Cl}$.

Table S2.2-4. Excitation (λ_{ex}) and emission wavelengths (λ_{em}) and quantum yield (QY) of the hypervalent compounds. The excitation that corresponds to the highest quantum yield is given in bold.

Compounds	Excitation Wavelengths, λ_{ex} (nm)	Emission Wavelengths, λ_{em} (nm)	QY (%)
2-1c	340	460	3
2-1d	254, 267, 375	454	26
2-1e	269, 329, 338, 370 , 386	451	19
2-1f	366	460	76
2-6	260, 293, 328, 342, 370, 387	553	28
2-10	368	460	55

(iii) Concentration-dependent fluorescence study

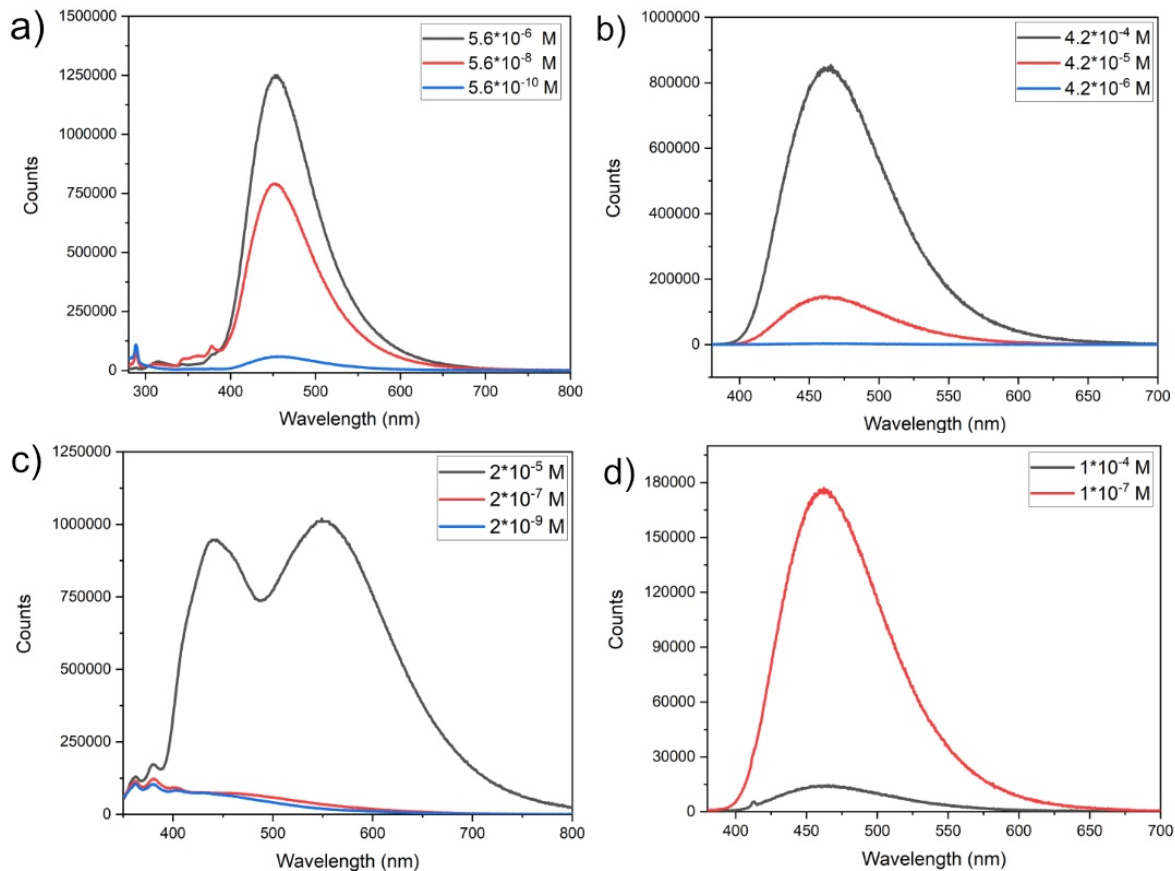


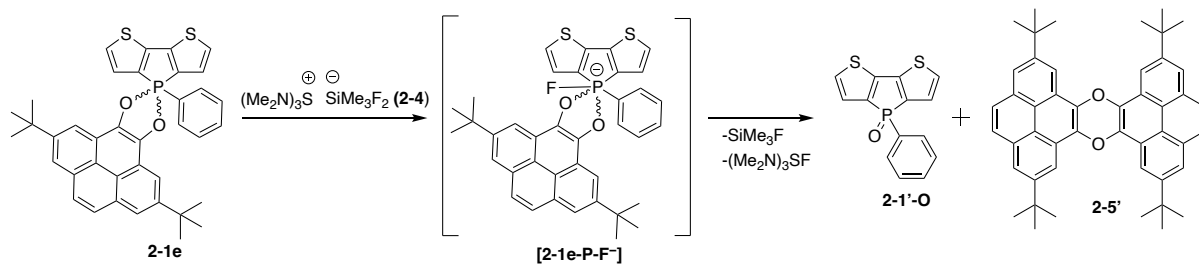
Figure S2.2-6. Fluorescence emission spectra showing monomer and excimer for a) **2-1d**, b) **2-1f** in CH₂Cl₂ and c) **2-6**, d) **2-10** in C₆H₅Cl.

Table S2.2-5. Concentrations at excimers and monomers identified for hypervalent compounds.

Compounds	Excitation Wavelengths, λ_{ex} (nm)	Concentration (M, presence of excimer)	Excimer Wavelengths, λ_{E} (nm)	Concentration ($\times 10^{-4}$ M, presence of monomer)	Monomer Wavelengths, λ_{M} (nm)	Raman Scattering Wavelengths, λ_{R} (nm)
2-1c	340	5×10^{-4}	447,503	5×10^{-6}	417	-
2-1d	267	5.6×10^{-4}	454	5×10^{-10}	318,343,360,376	290
2-1e	269	6×10^{-4}	451	6×10^{-6}	310,347,380	293,370
2-1f	366	4.2×10^{-4}	460	4.2×10^{-6}	No monomer	-
2-6	260	0.2×10^{-4}	553	2×10^{-9}	363,380,405,443	-
2-10	368	1×10^{-4}	460	1×10^{-7}	No monomer	417

S.2.2.5 Fluoride Abstraction

Fluoride abstractions were conducted with all derivatives reported. The reaction monitoring of **2-1e** with **2-4** is given here as a representative example here.



Scheme 2.2-1. Fluoride abstraction reaction.

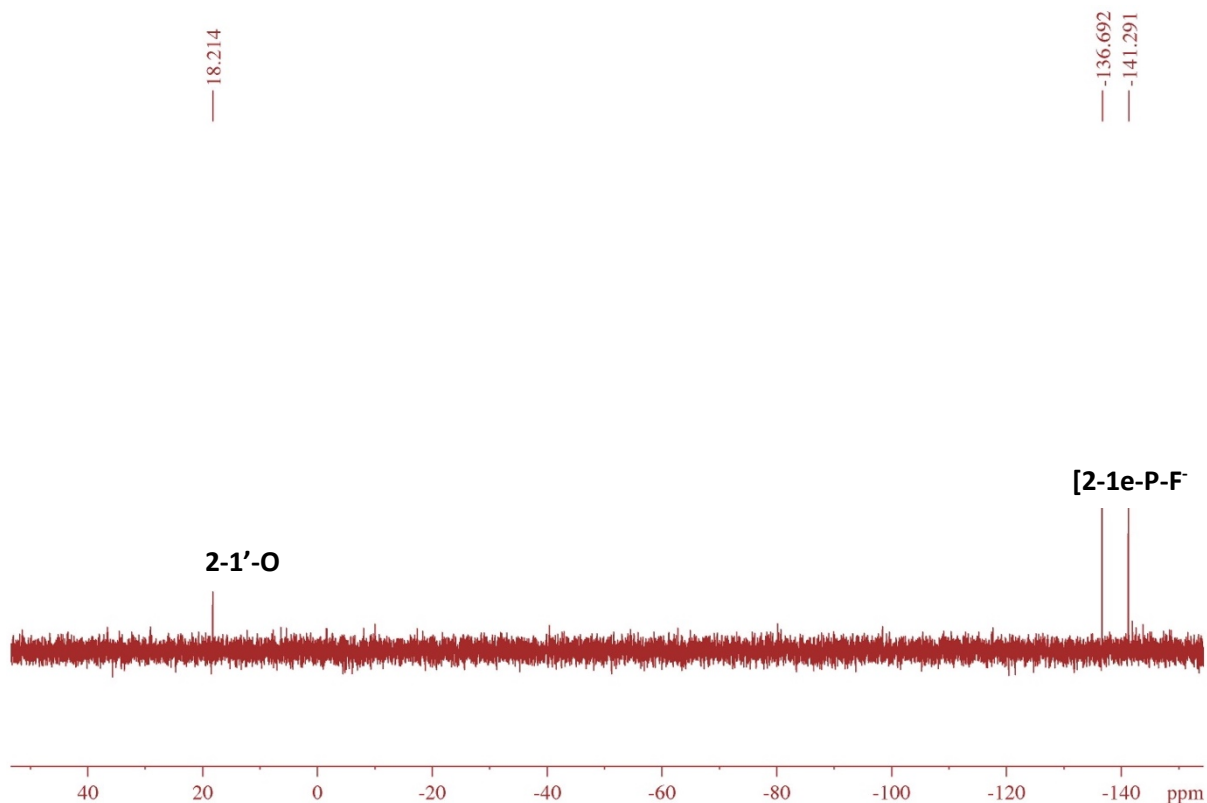


Figure S2.2-7a. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, CDCl_3) for **2-1e** + **2-4** within 1 hour of reaction time, showing formation of **[2-1e-P-F $^-$]** and **2-1'-O**.

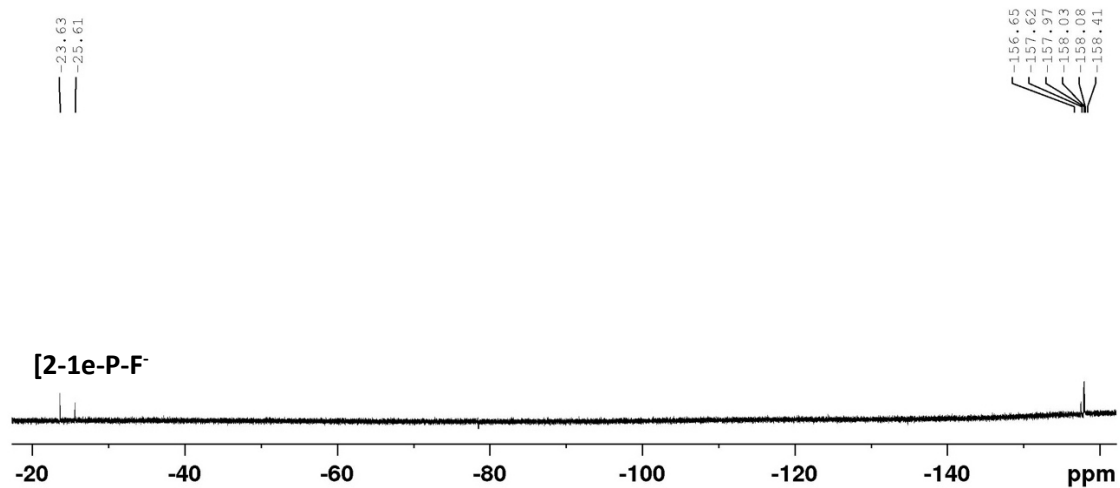


Figure S2.2-7b. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (376.5 MHz, CDCl_3) for **2-1e** + **2-4** within 1 hour of reaction time, showing formation of **[2-1e-P-F]**.

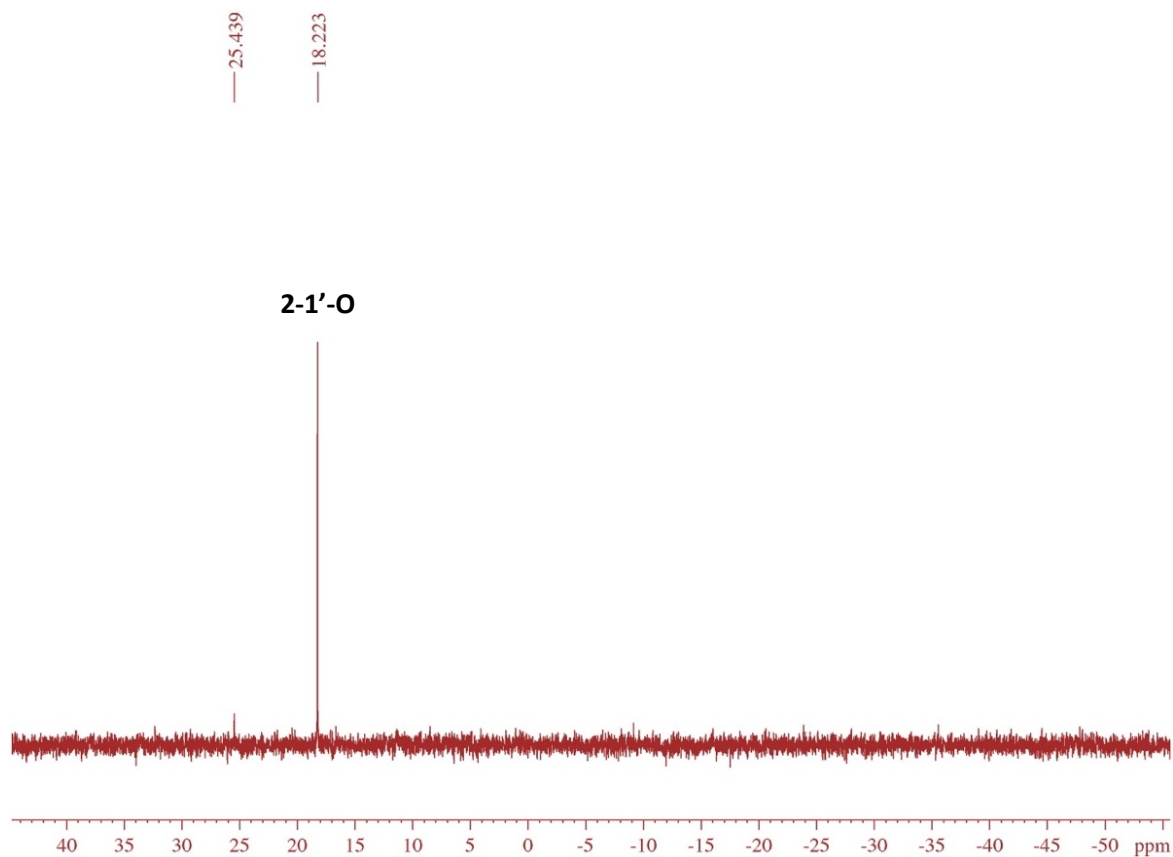


Figure S2.2-7c. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, CDCl_3) for **2-1e** + **2-4** after 2 days showing complete transformation of **[2-1e-P-F]** to **2-1'-O**.

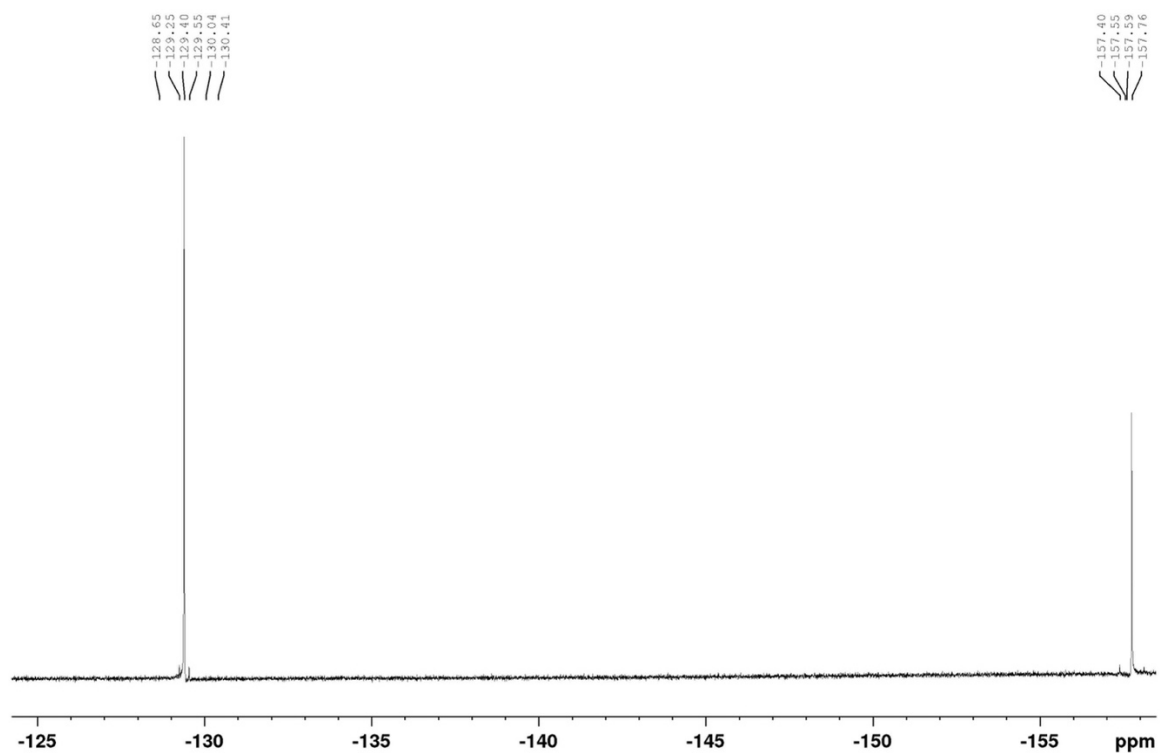


Figure S2.2-7d. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (376.5 MHz, CDCl_3) for **2-1e** + **2-4** after 2 days showing complete transformation of [**2-1e-P-F**] to fluoride by-products.

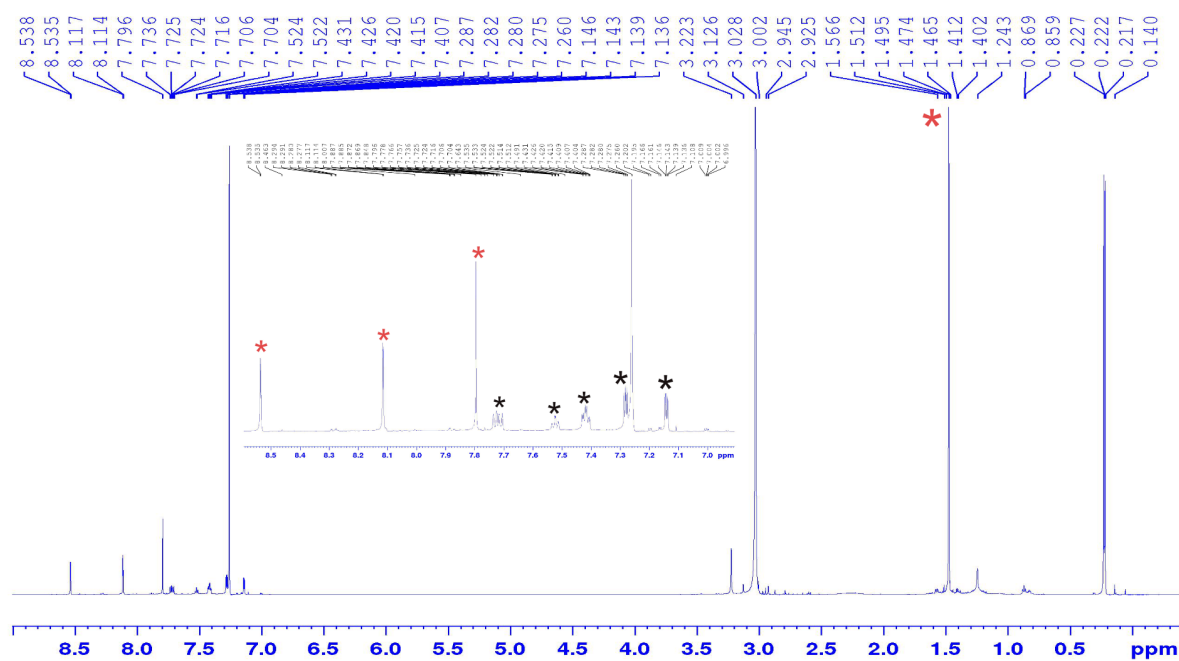


Figure S2.2-7e. ^1H NMR spectrum (700 MHz, CDCl_3) for **2-1e** + **2-4** after 2 days showing formation of **2-1'-O** and **2-5'**. The peaking belonging to **2-1'-O** and **2-5'** represented by * and *.

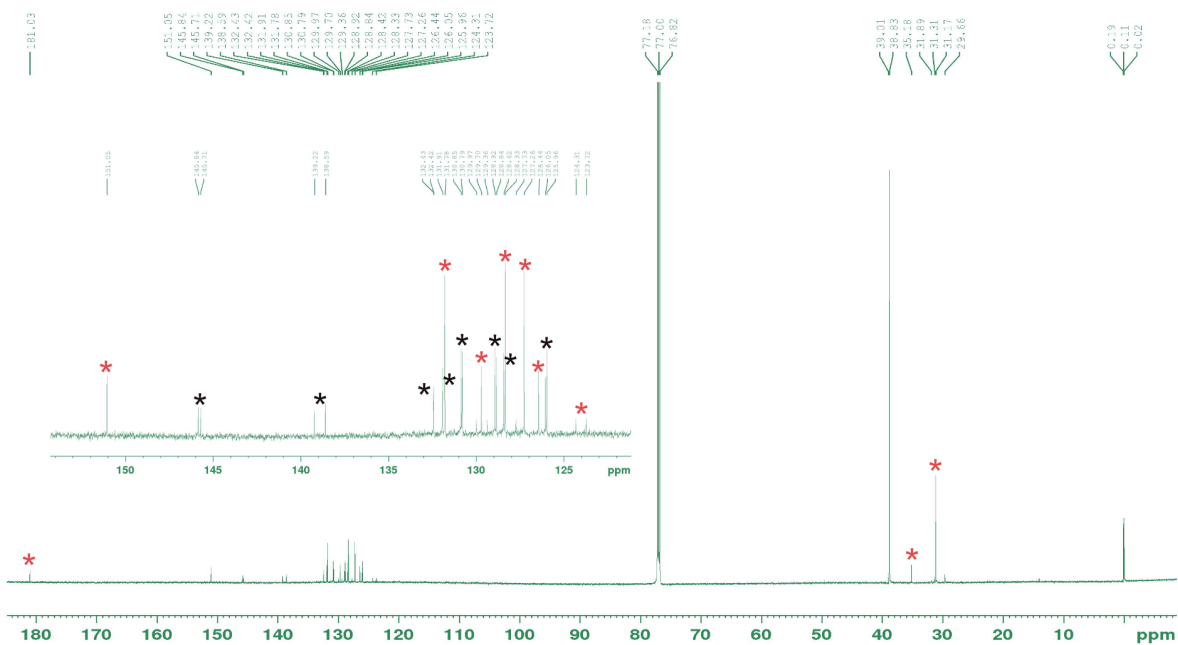


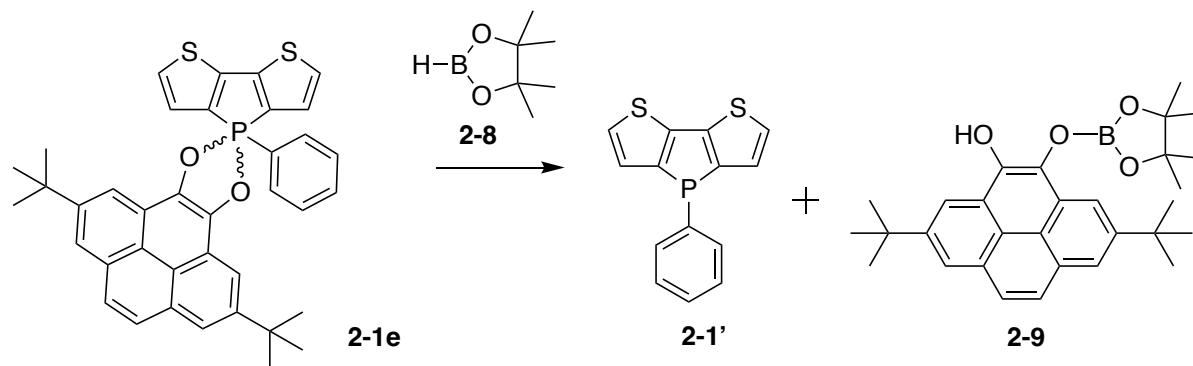
Table S2.2-6. NMR shifts corresponding to formation of $[R_5PF^-]$ as monitored by 400 MHz NMR equipment along with time required for deoxyaryloxylation reaction of hypervalent compounds.

Compounds	^{31}P NMR chemical shifts for $[R_5PF^-]$ species (doublets)	^{19}F NMR chemical shifts for $[R_5PF^-]$ species (doublets)	Time to completely generate 2-1'-O
2-1c	(-138.4, -143.1)	(-28.3, -30.3)	~ 7 days
2-1d	(-135.2, -139.9)	(-23.7, -25.7)	~ 7 days
2-1e	(-136.7, -141.3)	(-23.6, -25.6)	~ 2 days
2-1f	(-133.7, -138.4)	(-23.9, -25.9)	~ 2 days
2-6	(-123.0, -127.9)	(-26.9, -28.9)	~ 5 days
2-7	Not identified	Not identified	immediately
2-10	(-133.5, -138.6)	(-27.7, -28.9)	~ 1 hour

S.2.2.6 Hydride Abstraction

Hydride abstractions were conducted with all derivatives reported. The reaction monitoring of **2-1e** with **2-8** is given here as a representative example here.

i) Reaction of **2-1e** with **2-8**



Scheme 2.2-2. Hydride abstraction reaction.

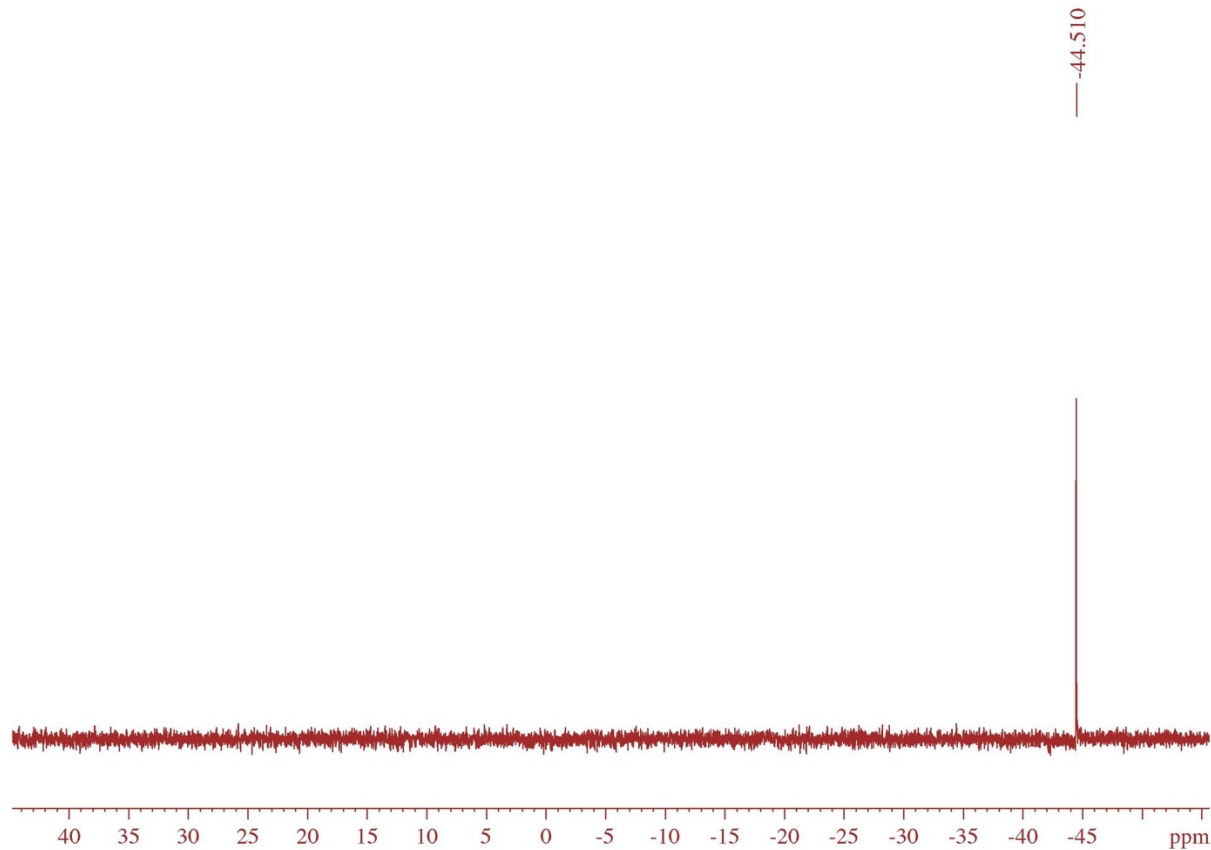


Figure S2.2-8a. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, CDCl_3) for **2-1e** + **2-8** within 1 hour of reaction time, showing no formation of **2-1'**.

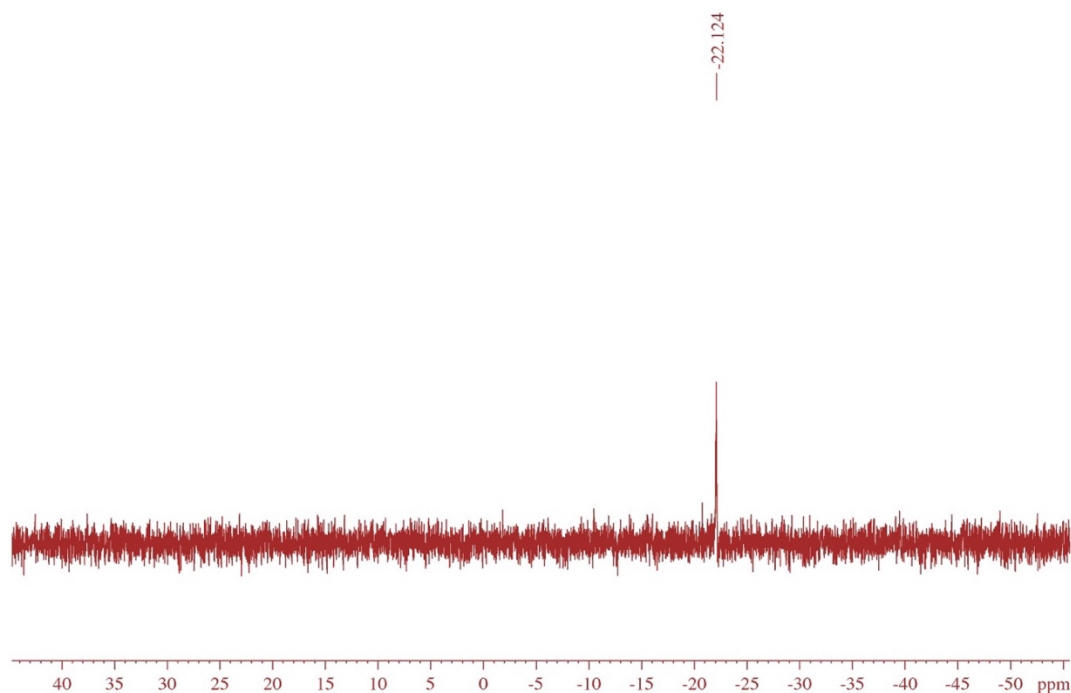


Figure S2.2-8b. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, CDCl_3) for **2-1e** + **2-8**, showing complete formation of **2-1'** within 1 day.

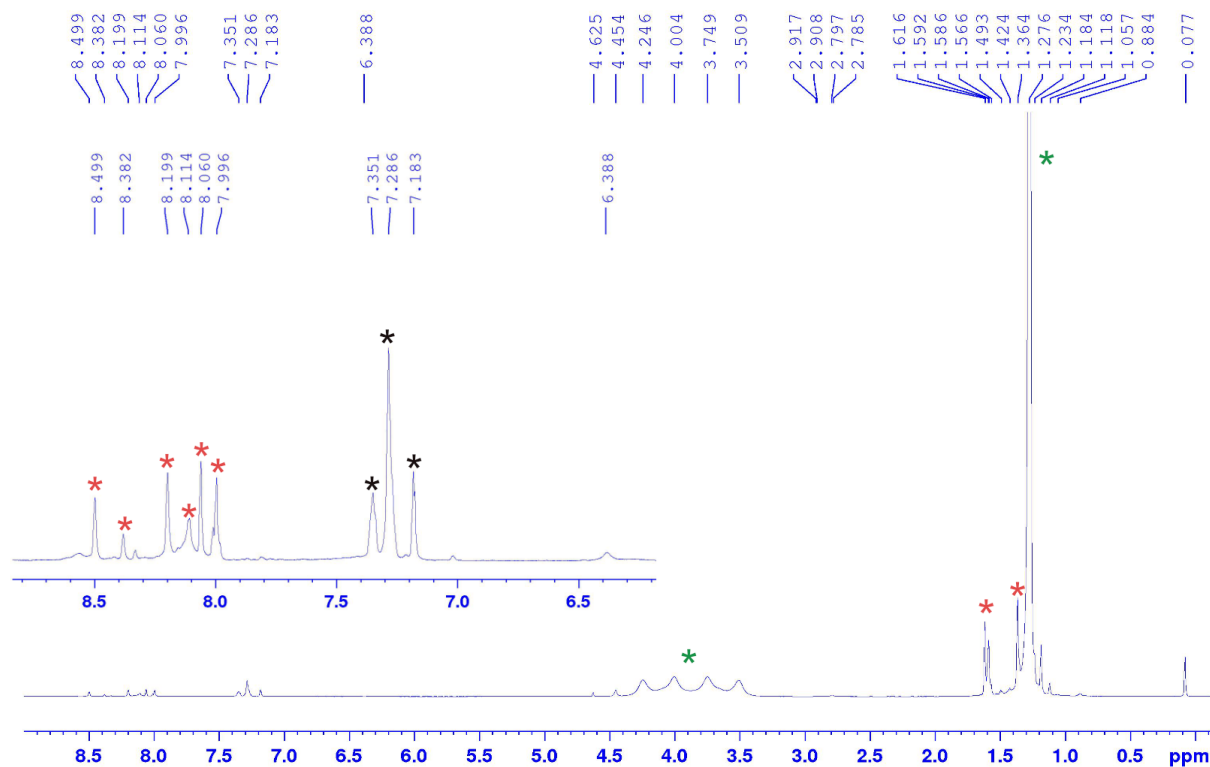


Figure S2.2-8c. ^1H NMR spectrum (700 MHz, CDCl_3) for **2-1e** + **2-8**, showing complete formation of **2-1'** and **2-9** within 1 day. The peaks for **2-1'**, **2-8**, and **2-9** is represented by *, *, and *.

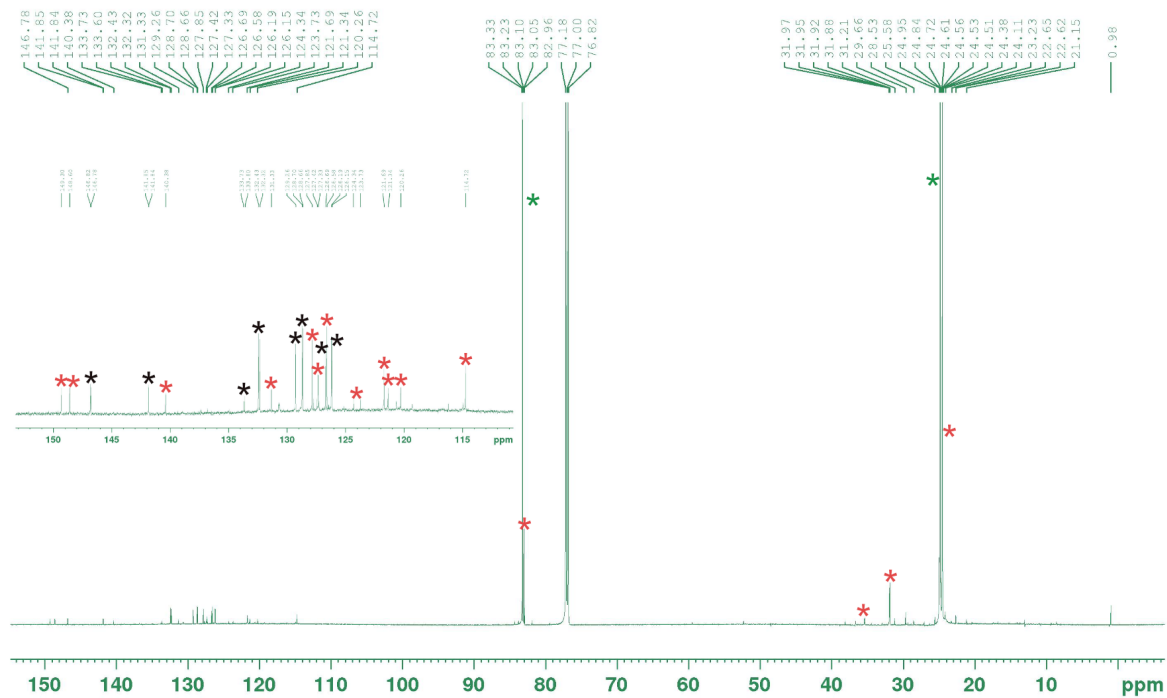


Figure S2.2-8d. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (176 MHz, CDCl_3) for **2-1e** + **2-8** within 1 hour of reaction time, showing complete formation of **2-1'** and **2-9** within 1 day. The peaks for **2-1'**, **2-8**, and **2-9** is represented by *, *, and *.

Table S2.2-7. Reaction time for 1,4-hydroboration for complete conversion of hypervalent compounds to trivalent species, **2-1'**.

Compounds	Time to completely generate 1 on reaction of hypervalent compounds with 2-1'-O
2-1c	~ 1 days
2-1d	~ 5 days
2-1e	~ 1 days
2-1f	~ 4 days
2-6	~ 10 days
2-7	immediately
2-10	~ 1 day

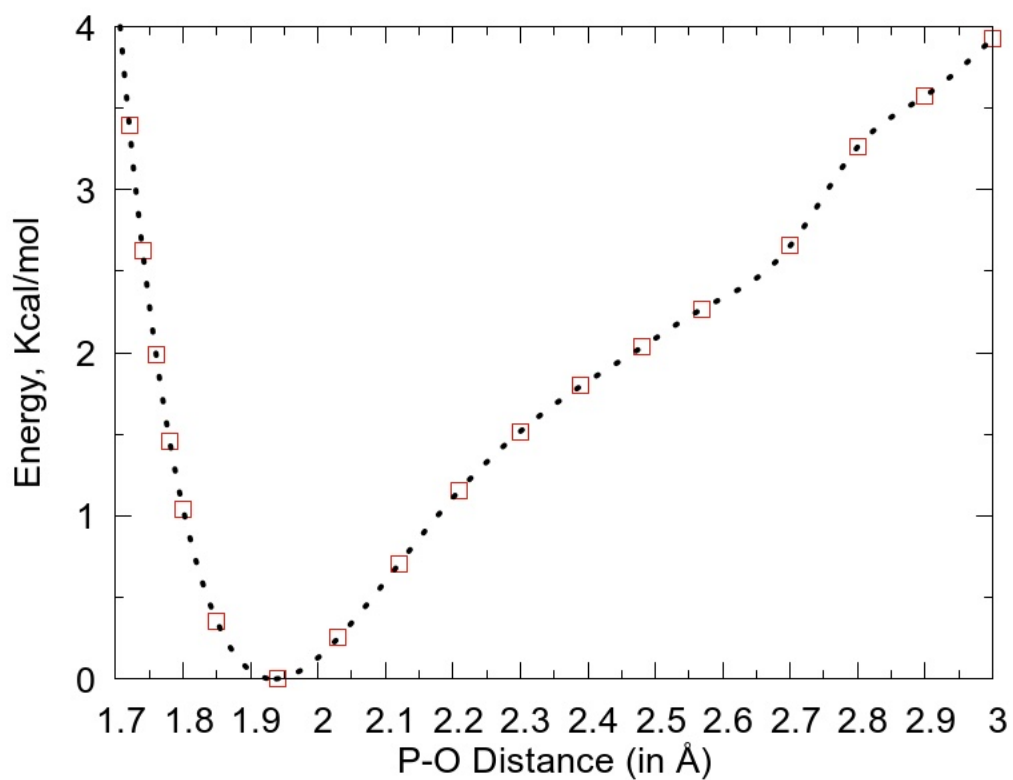
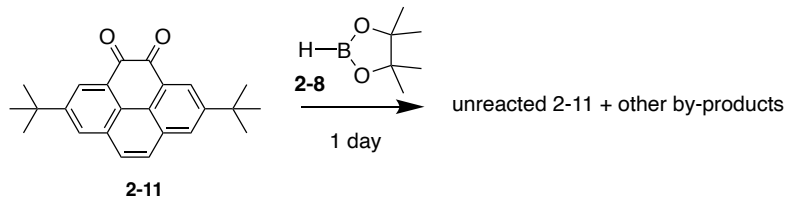


Figure S2.2-9. Scan of P-O bond which keeps increasing as the bond is stretched beyond 2.0 Å in **2-TS7** as depicted in the energy landscape for hydroboration reaction of hypervalent compounds.

ii) Control reaction of o-quinone with 2-8



Scheme 2.2-3. Reaction of o-quinone with **2-8** as control.

A control reaction was conducted with **2-11** and **2-8** in the exact reaction conditions as **2-1e** + **2-8** to show very slow reduction of quinone to give a mixture of by-products.

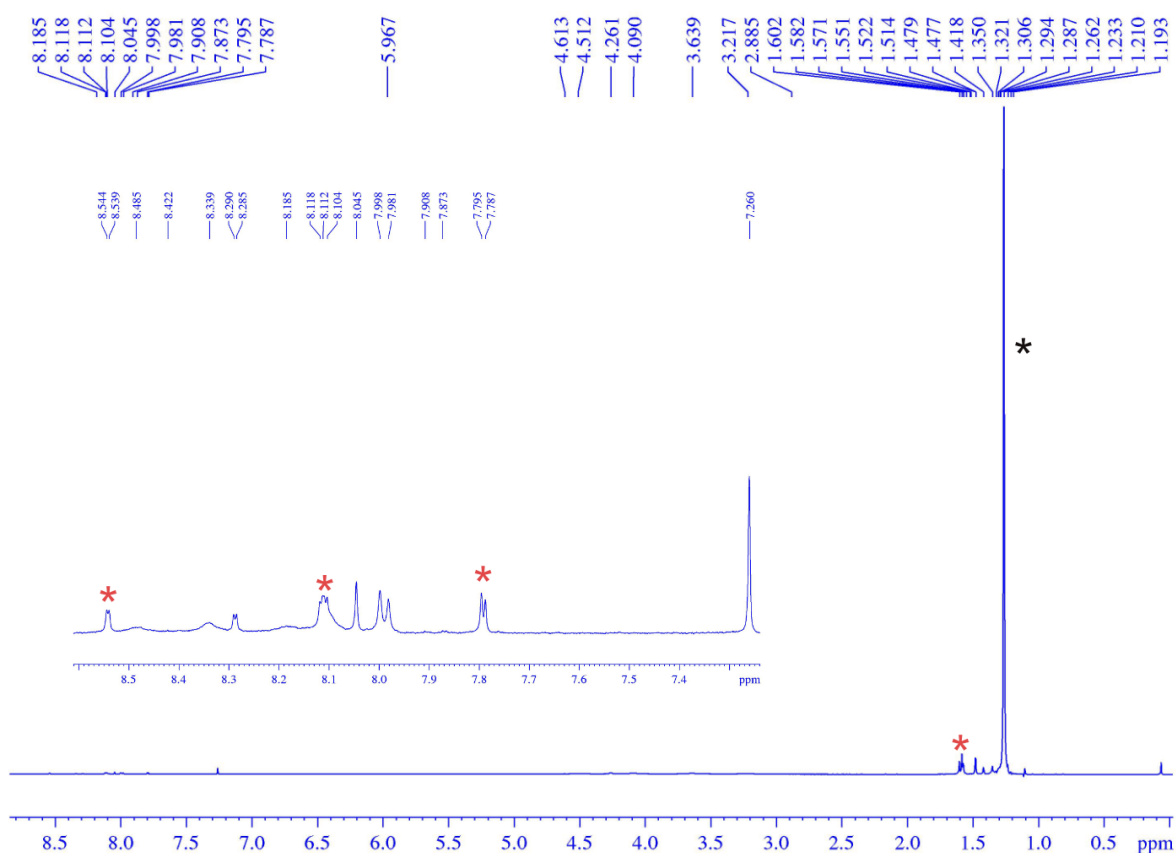
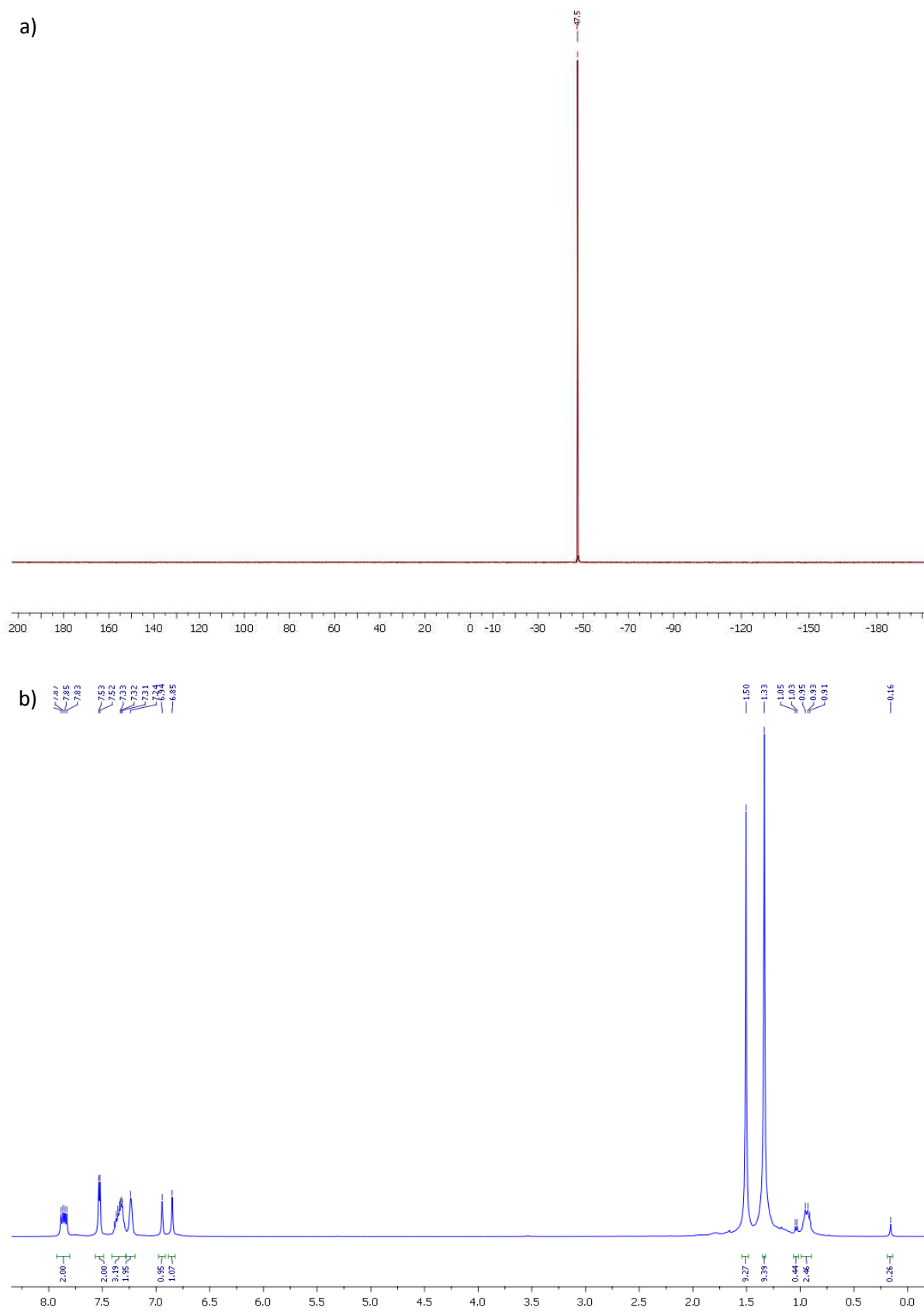


Figure S2.2-10. ^1H NMR spectrum (700 MHz, CDCl_3) for **14** + **11** within 1 day of reaction time, showing only partial reduction of **14** to give mixture of products. The peaks for **2-8**, and **2-11** is represented by * and *.

Figure S2.2-11. a) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, CDCl_3), b) ^1H NMR spectrum (400 MHz, CDCl_3) and c) ^{13}C NMR spectrum (151 MHz, CDCl_3) for compound **2-1c**.



132.33
131.71
131.64
131.52
131.44
130.77
130.71
130.53
130.52
130.22
130.16
128.25
128.10
128.00
125.38
125.29
125.24
125.15
114.63
114.61
114.47
105.89
105.81

77.21
77.00
76.79

34.73
34.66
34.21
31.93
31.68
29.71
29.50
29.44
29.36
22.70
14.13

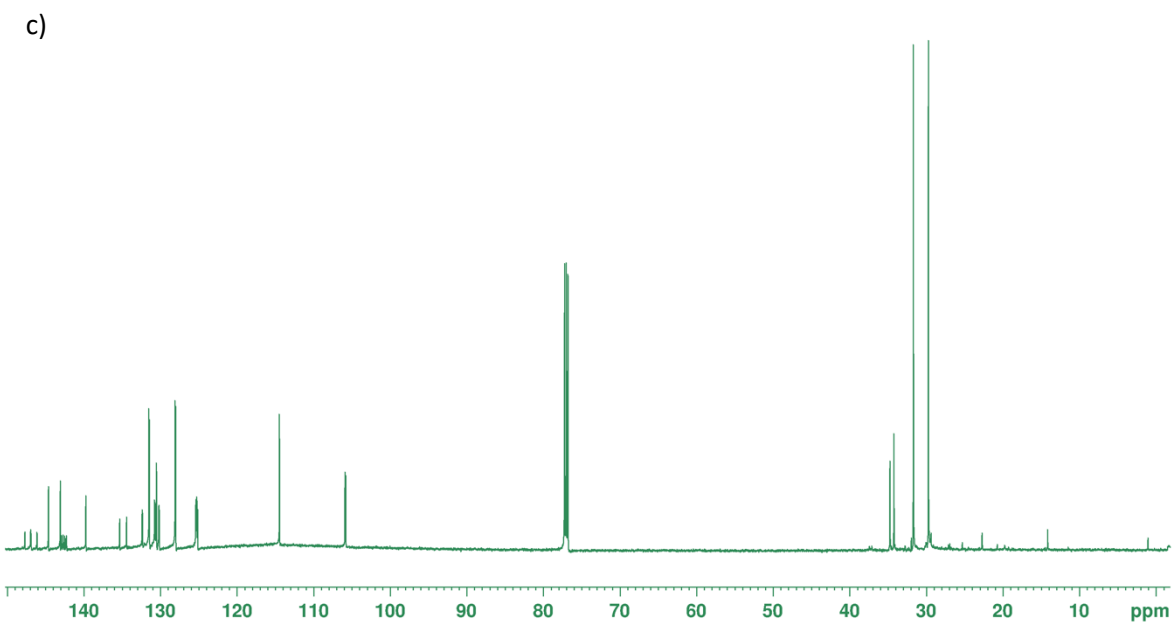
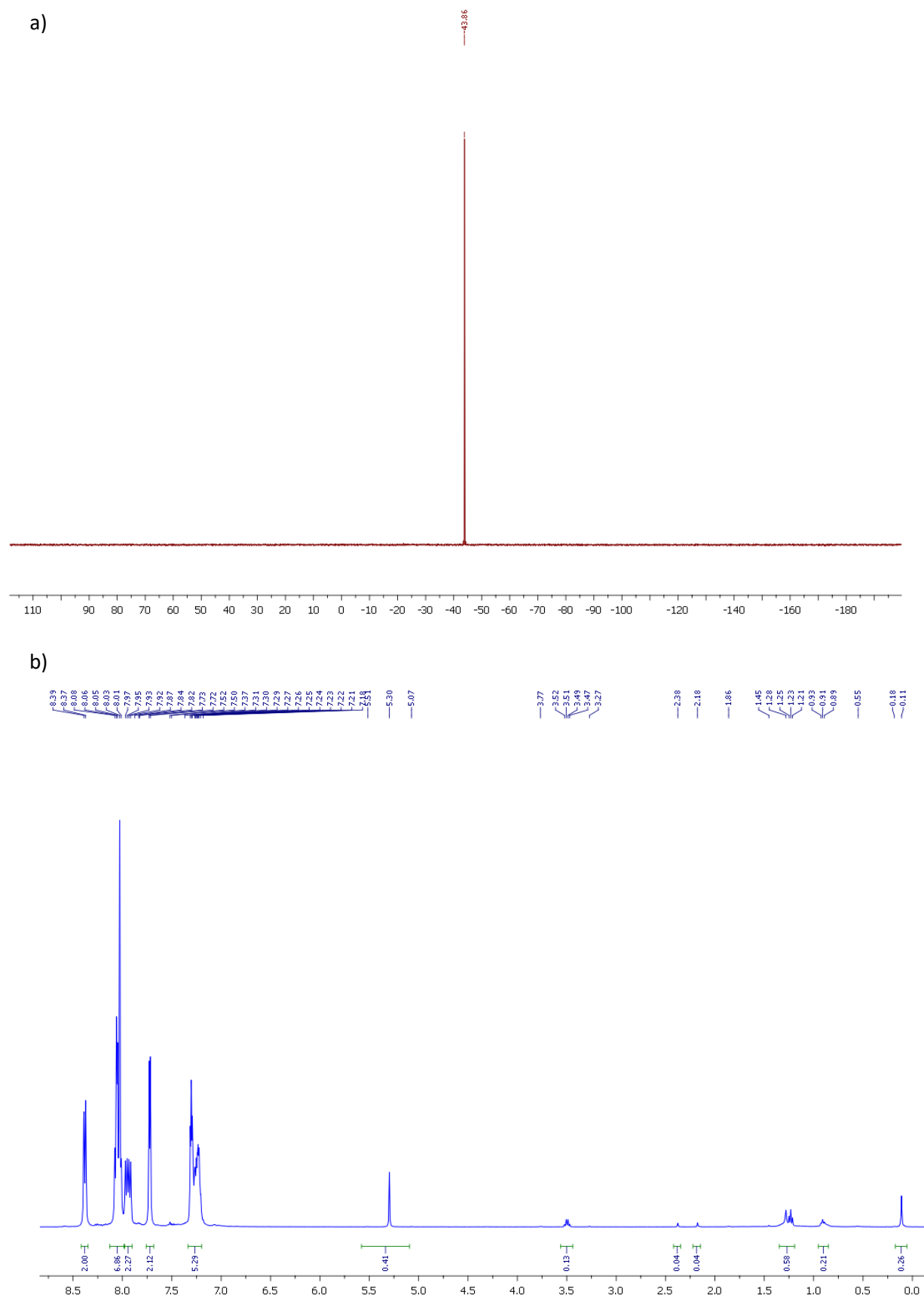


Figure S2.2-12. a) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, CDCl_3), b) ^1H NMR spectrum (400 MHz, CDCl_3), and c) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100 MHz, CDCl_3) for compound **2-1d**.



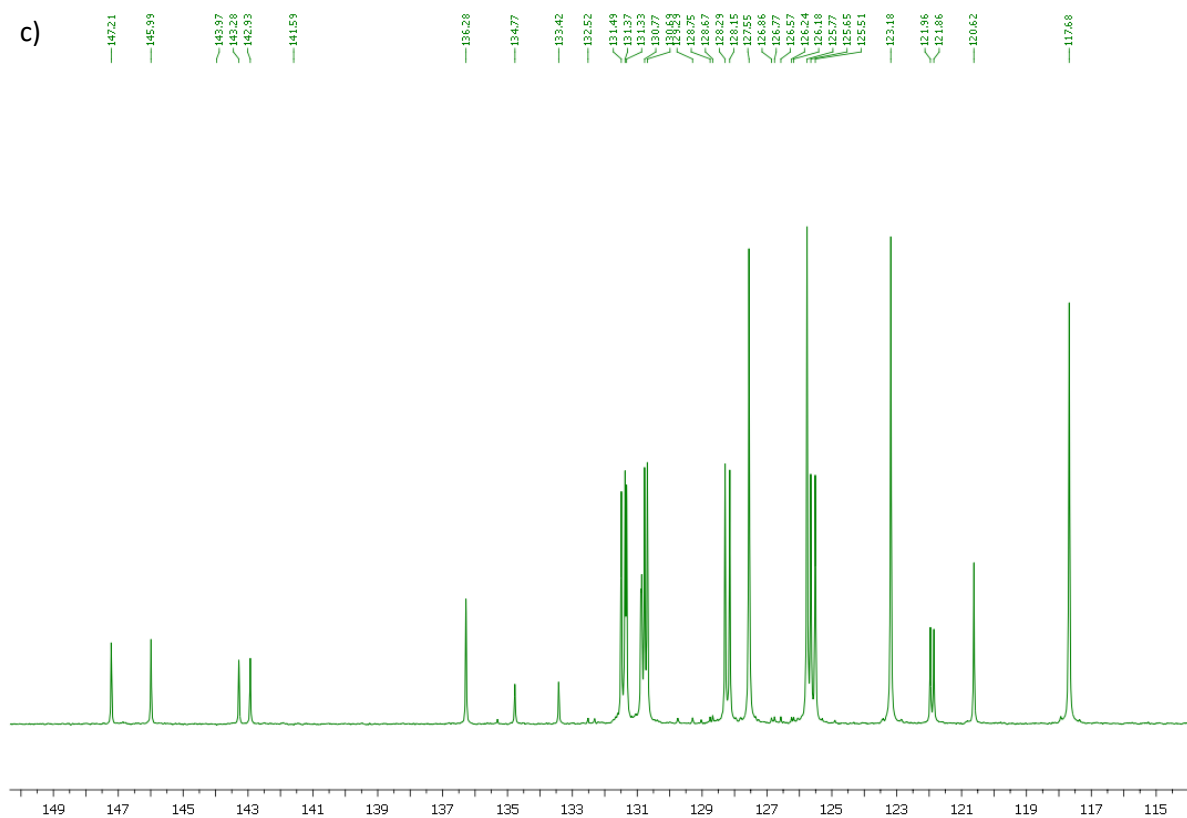
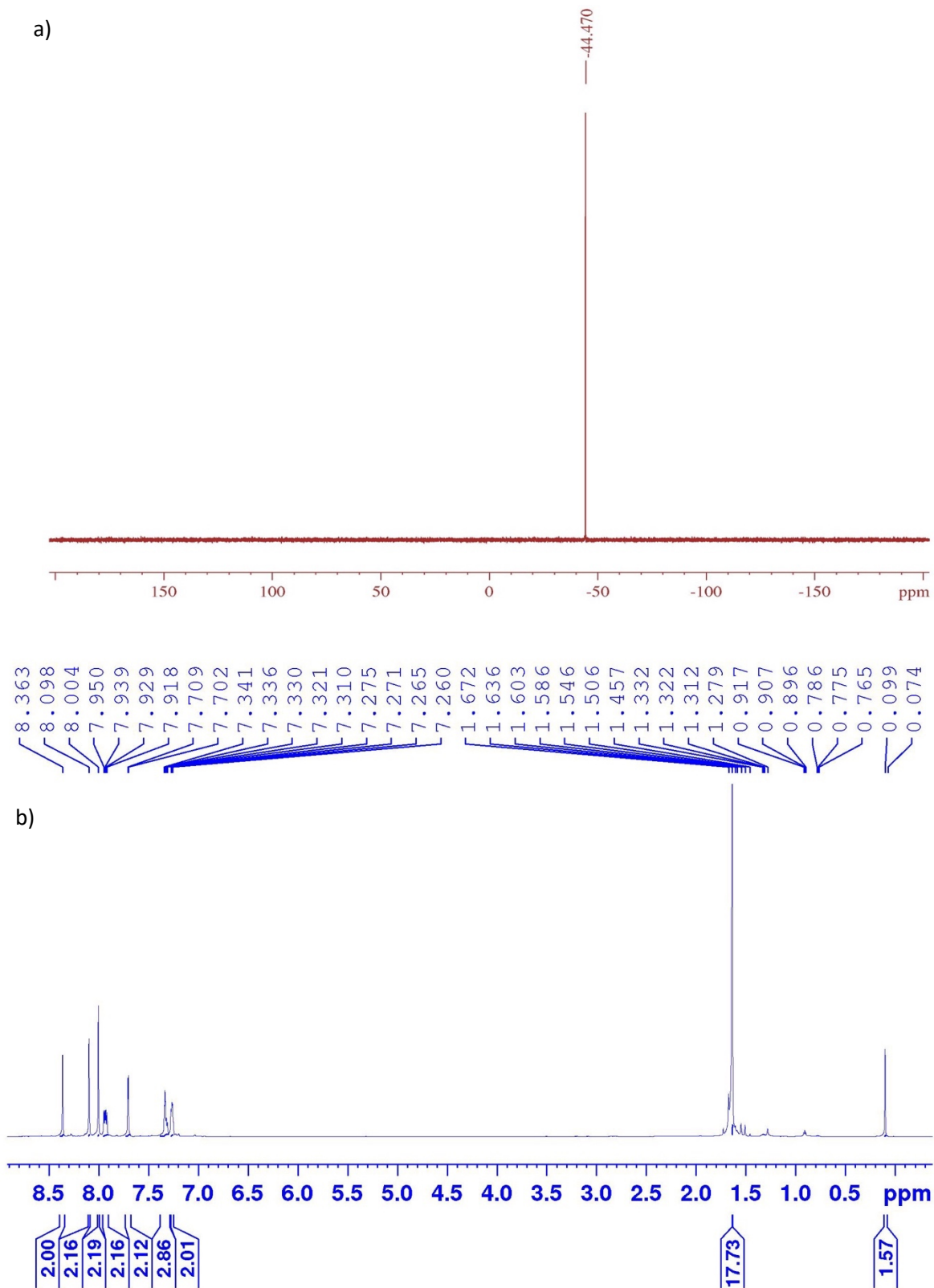


Figure S2.2-13. a) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, CDCl_3), b) ^1H NMR spectrum (700 MHz, CDCl_3), and c) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (176 MHz, CDCl_3) for compound **2-1e**.^{S20}



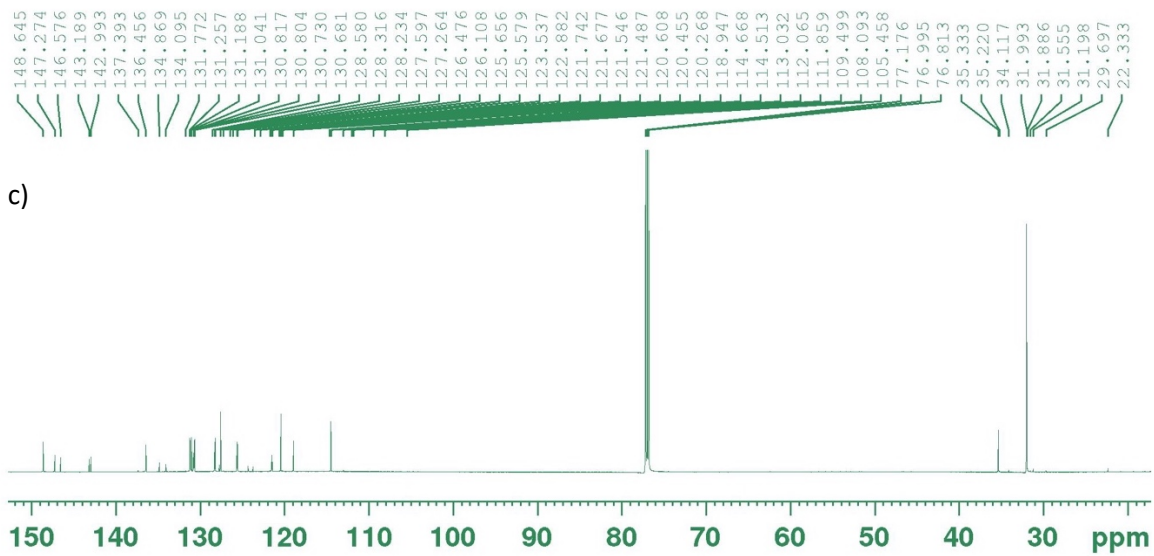
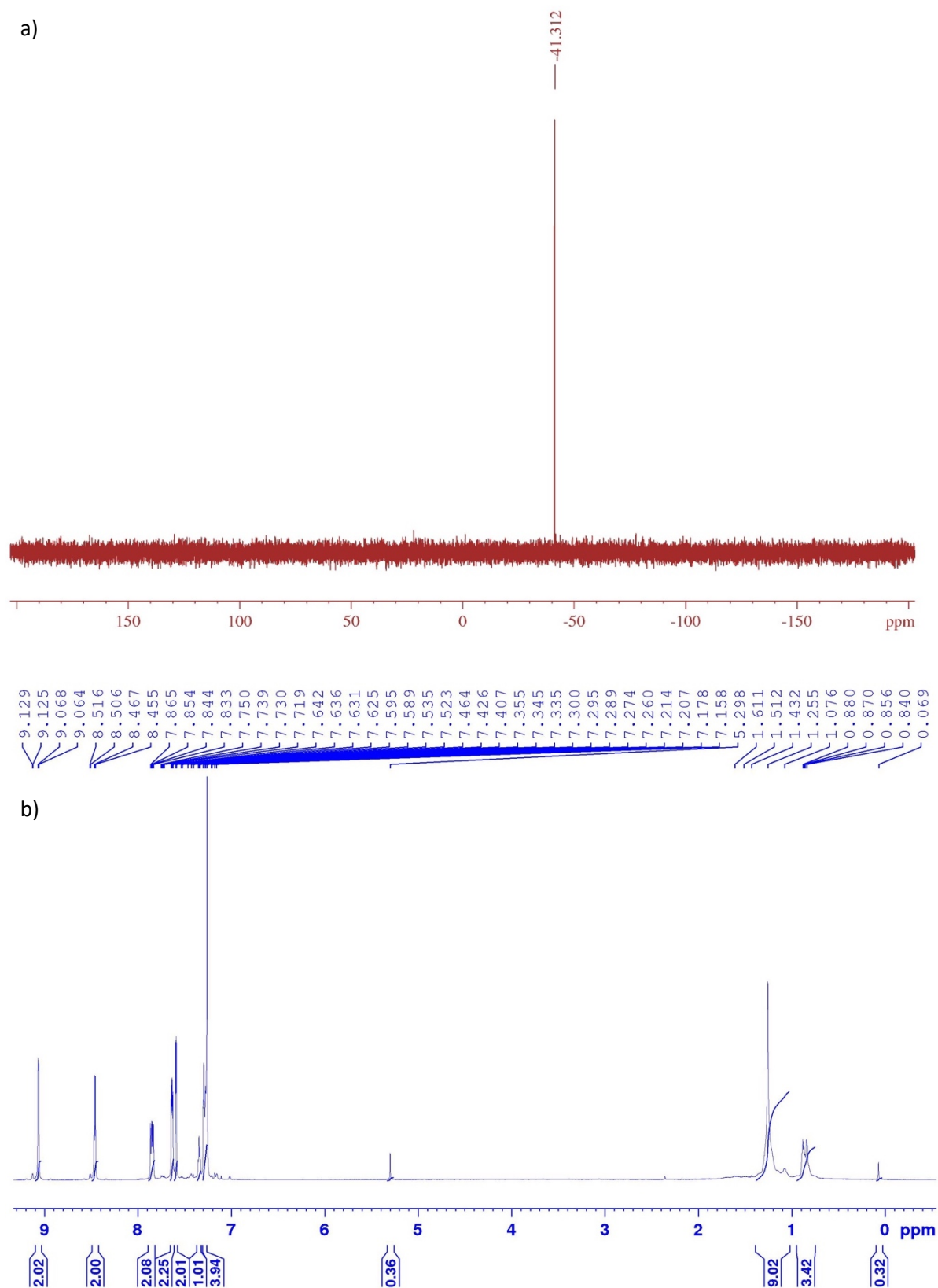


Figure S2.2-14. a) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, CDCl_3), b) ^1H NMR spectrum (700 MHz, CDCl_3), and c) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (176 MHz, CDCl_3) for compound **2-1f**.



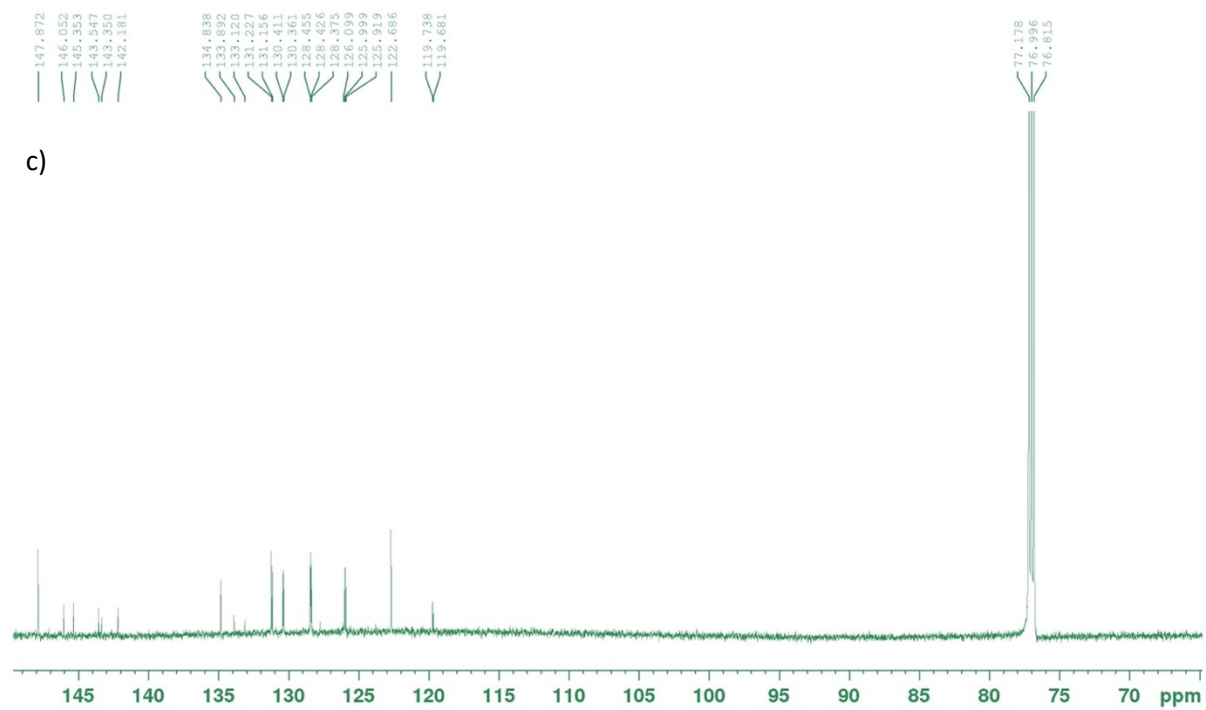
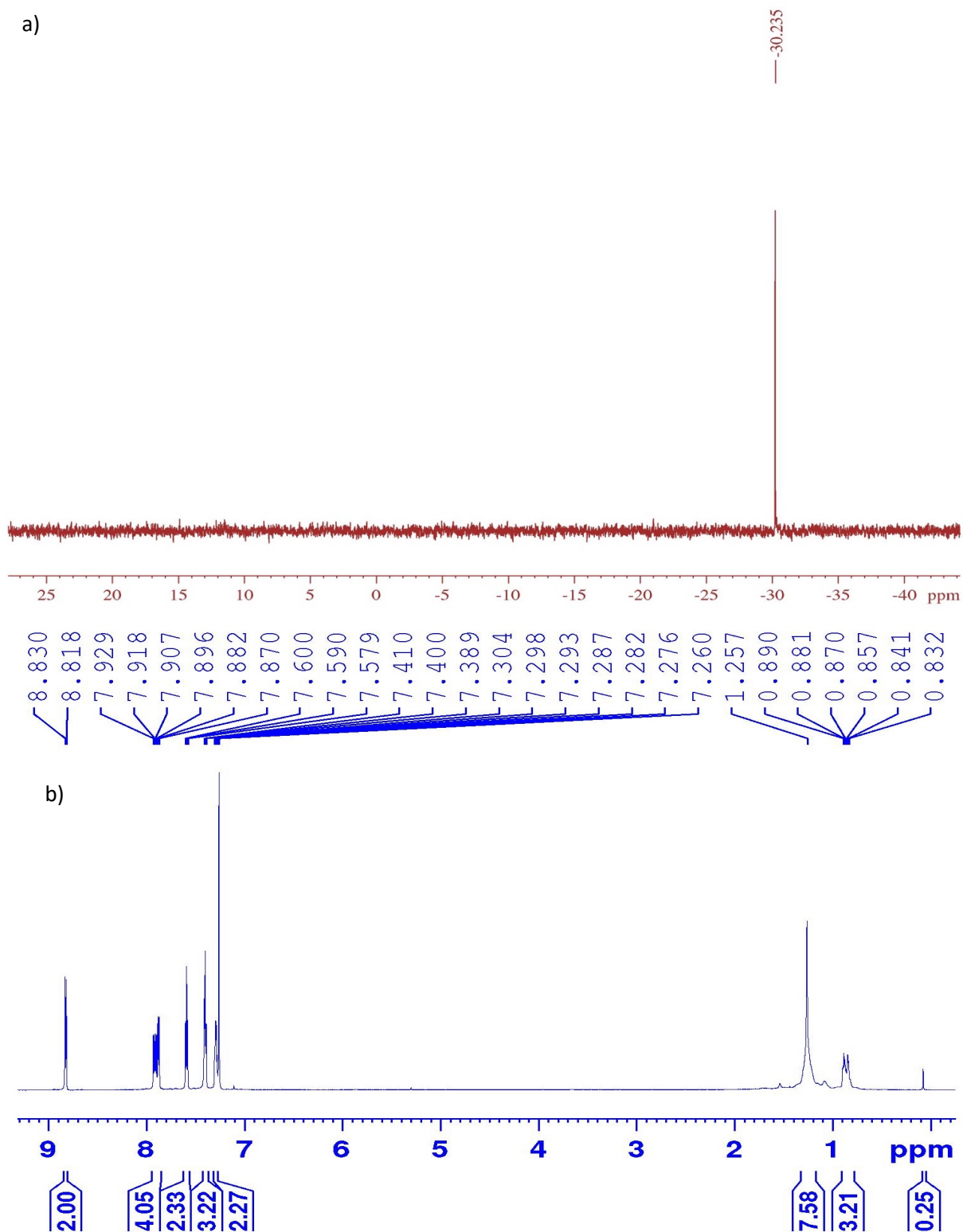


Figure S2.2-15. a) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, CDCl_3), b) ^1H NMR spectrum (700 MHz, CDCl_3), and c) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (176 MHz, CDCl_3) for compound **2-6**.



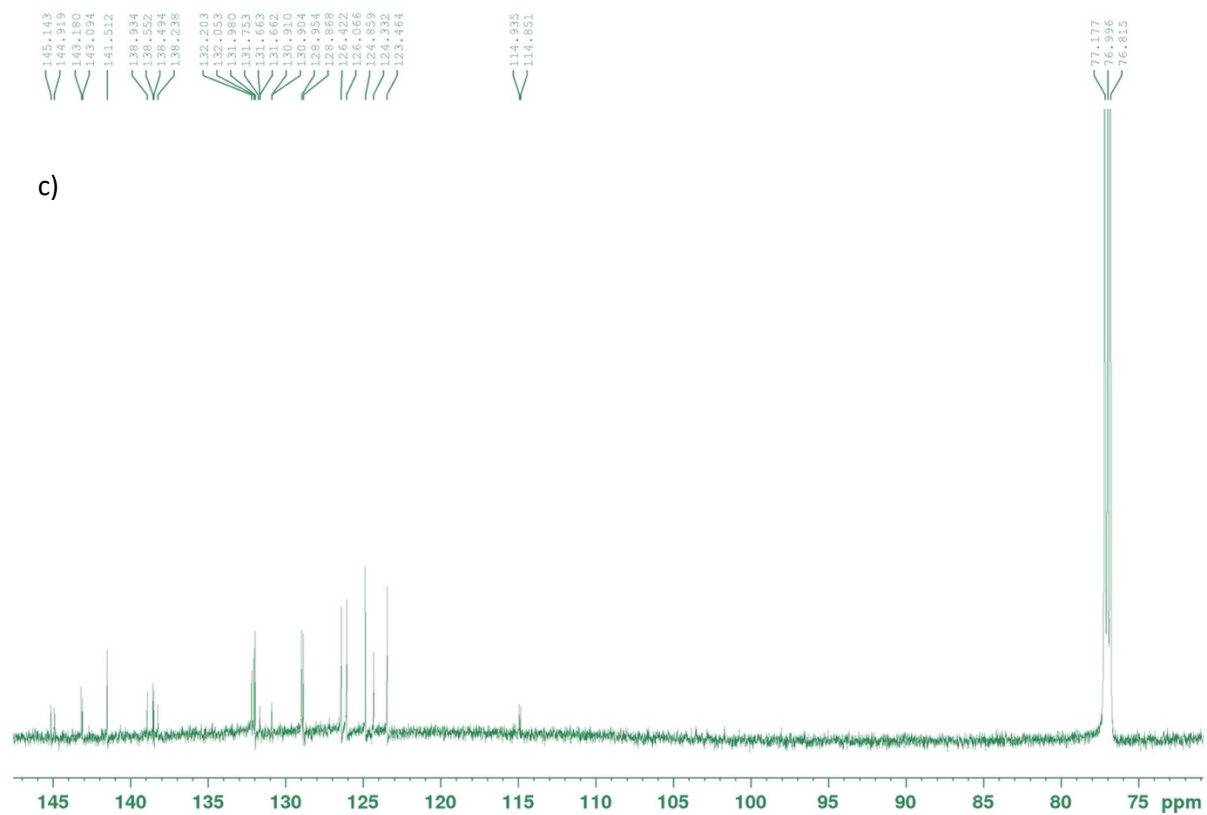
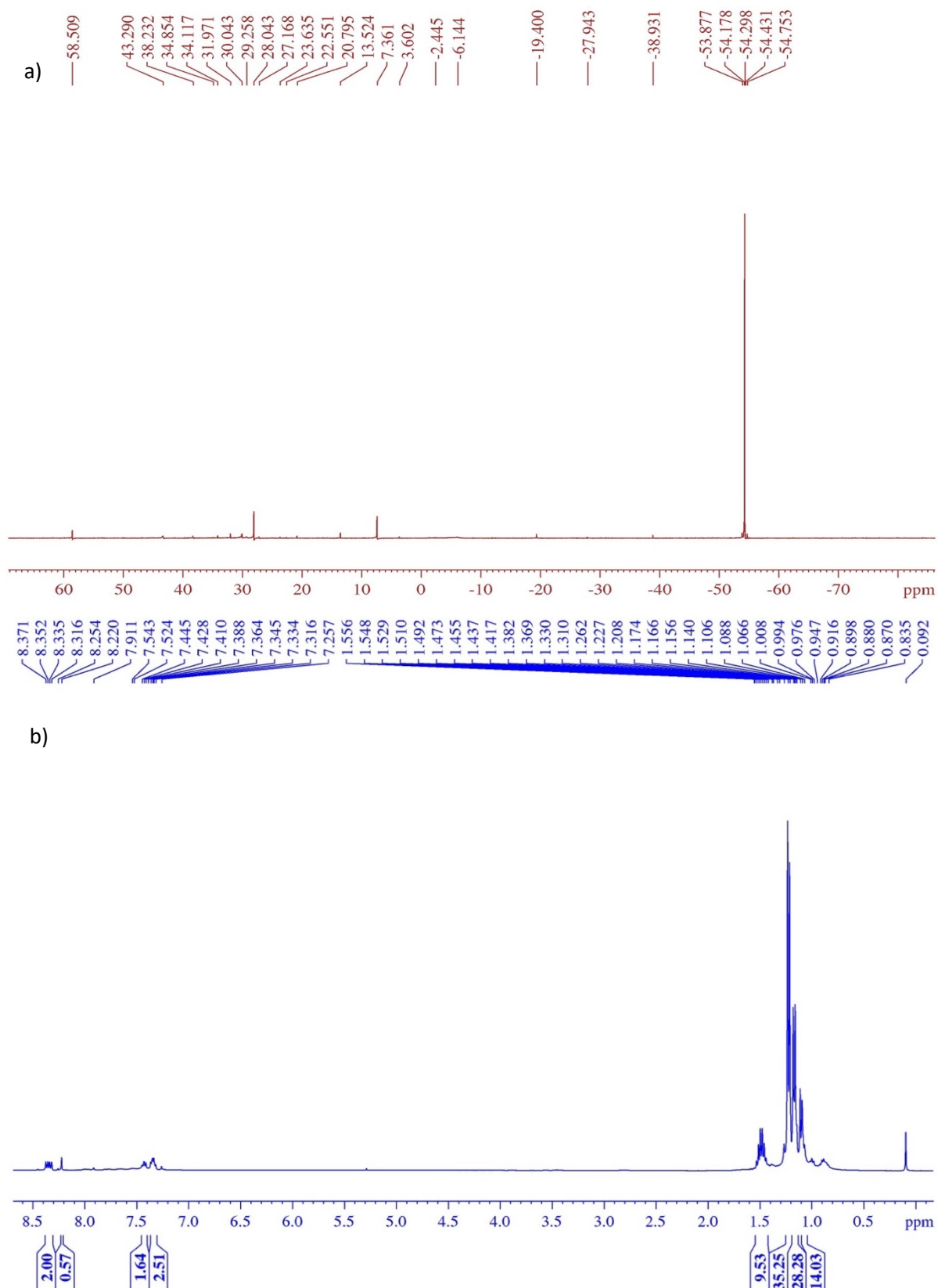


Figure S2.2-16. a) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, CDCl_3), b) ^1H NMR spectrum (400 MHz, CDCl_3), and c) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100 MHz, CDCl_3) for compound **2-7**.



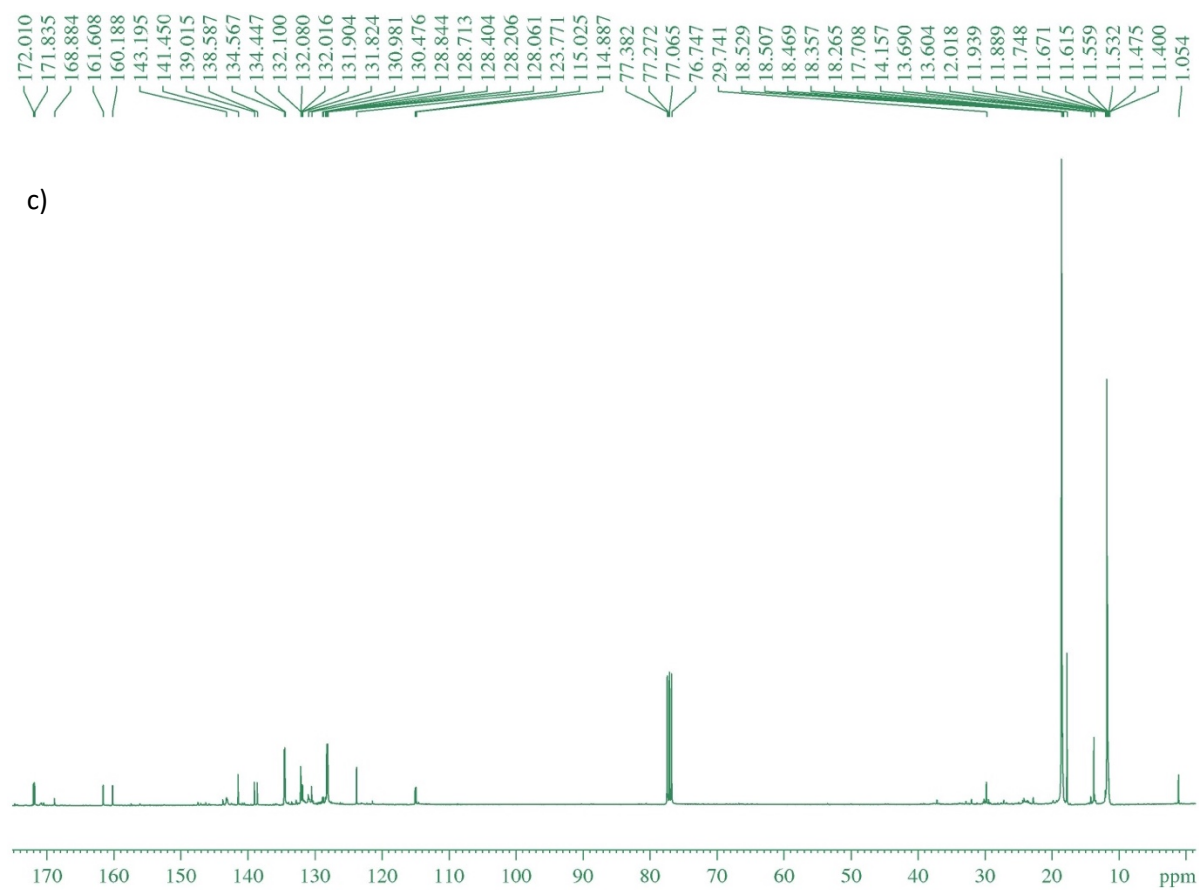
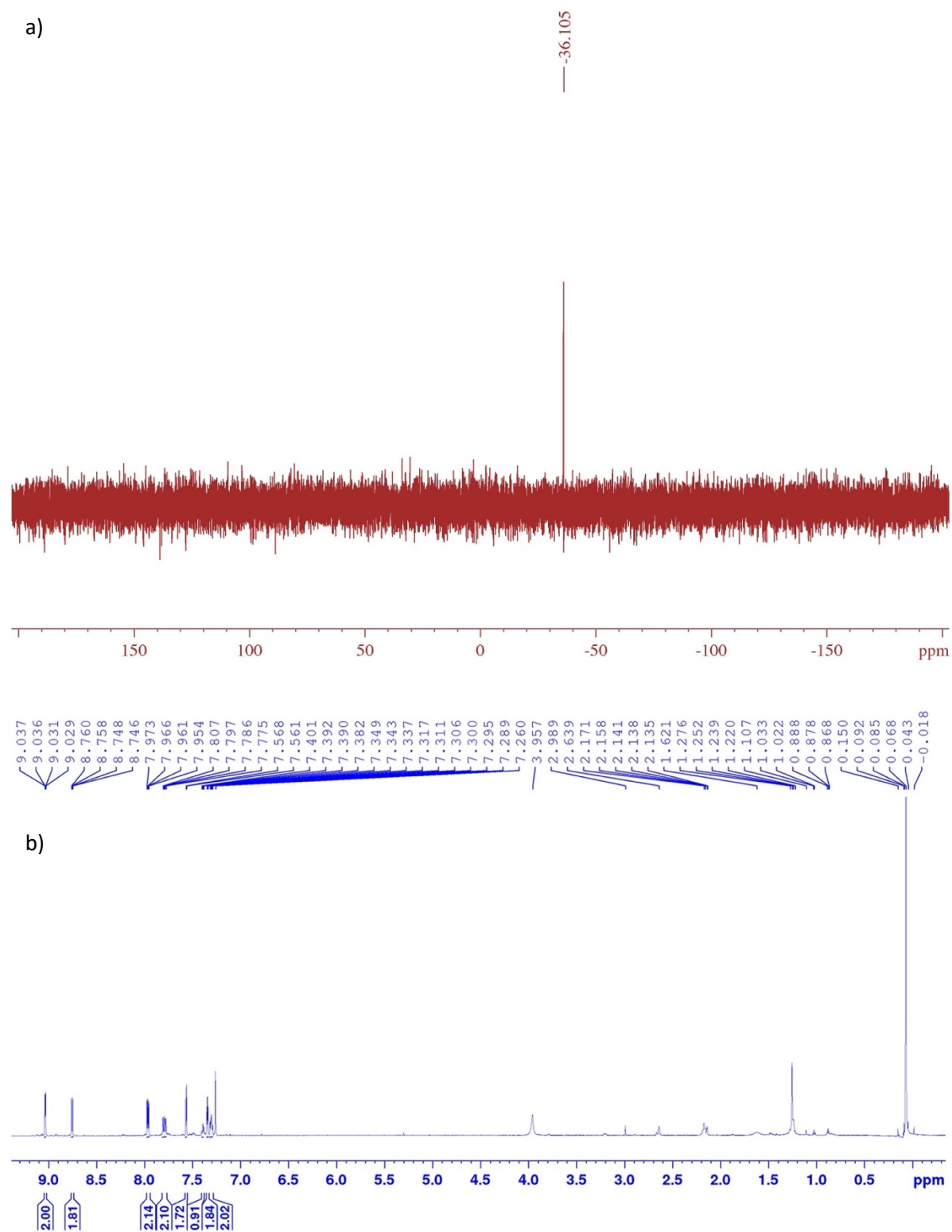
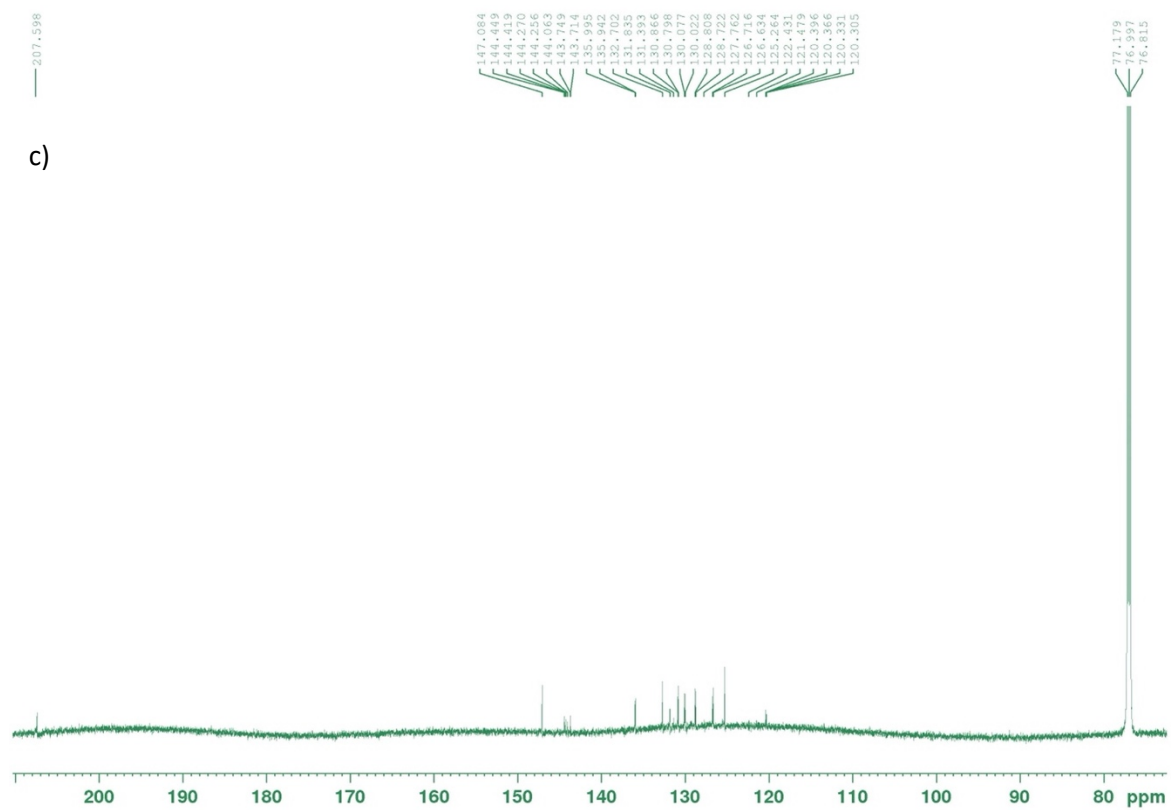


Figure S2.2-17. a) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, CDCl_3), b) ^1H NMR spectrum (400 MHz, CDCl_3), and c) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100 MHz, CDCl_3) for compound **2-10**.

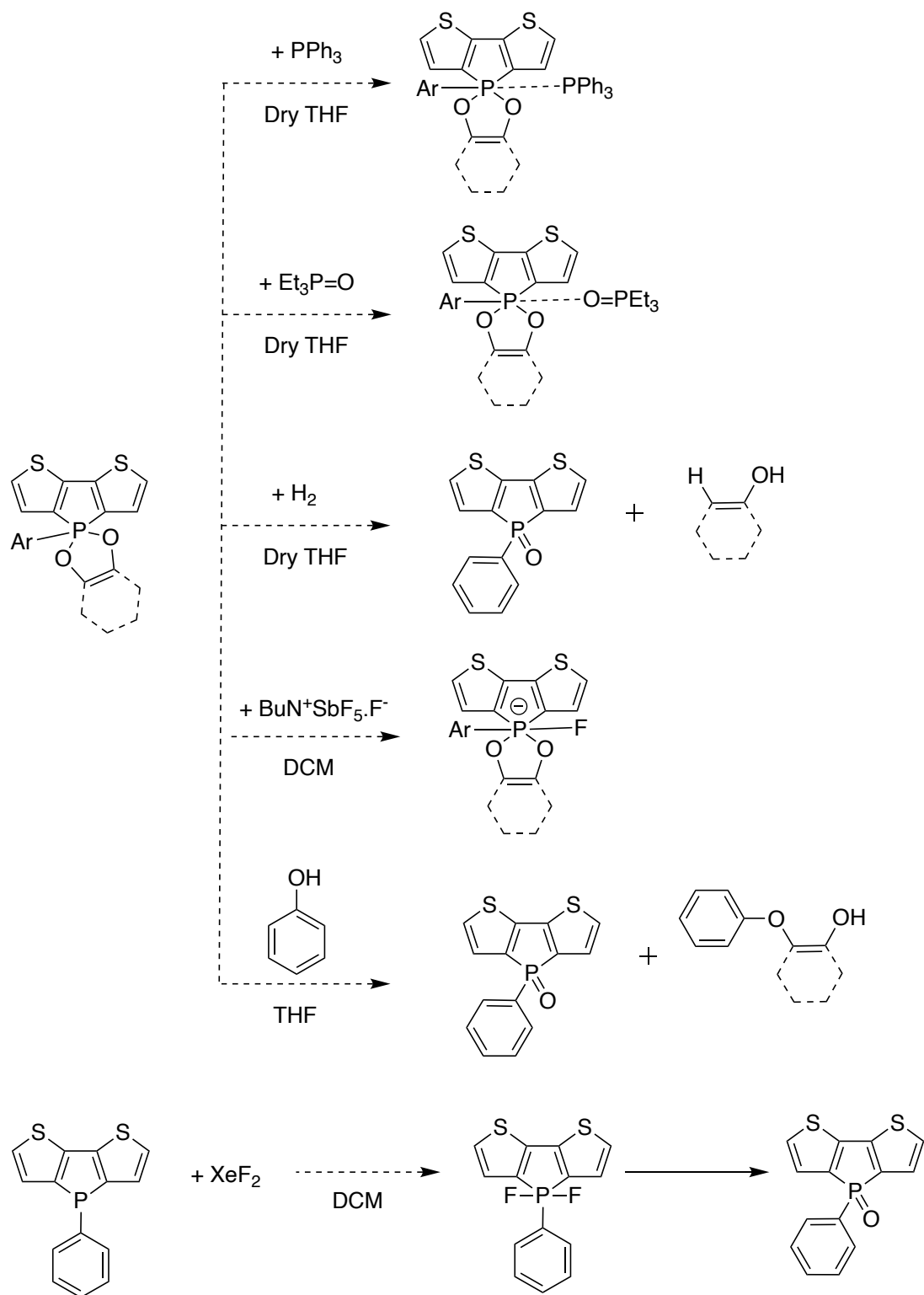


207.598

c)



S.2.2.7 Some unsuccessful reactions showing moderate Lewis acidity of the hypervalent derivatives



CHAPTER THREE: SYNTHESIS, STRUCTURAL INSIGHT, AND OPTOELECTRONIC EXPLORATION OF STEP-CONJUGATED MATERIALS

Chemical and experimental details

Materials and Methods: All reagents were purchased from Sigma Aldrich and Oakwood Chemical. All solvents were purchased from Sigma Aldrich and Fisher chemical. SPS grade solvents (MBraun) from Sigma Aldrich were used for synthesis and characterisations. Compounds 3-2a, 3-4a', and 3-6a' were prepared according to literature procedures.^{S18,S21,S22} The precursors for the synthesis of compounds 3-5 (3-5a') and 3-7 (3-7a') were obtained as synthesized from a previous lab member, Dr. Xiaoming He.

Nuclear Magnetic Resonance (NMR): ^1H , $^{31}\text{P}\{^1\text{H}\}$, $^{19}\text{F}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$ spectra were acquired on Bruker NEO 700, 600, 400 and 300 NMR spectrometers on a 5mm ATM probe using TOPSPIN software version 4.0.8. Chemical shifts are reported in parts per million (ppm). Multiplicities are reported as: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), multiplet (m), quartet (q), and broad (br).

X-Ray Crystallography (XRD): The solid-state structures of the compound were determined using Bruker DQ Quest eco. The structures were solved and refined using OLEX2 software.

UV-Visible Spectroscopy (UV-Vis): All absorption measurements were recorded on an Agilent Technologies Cary 5000 UV-Vis spectrometer at room temperature. All samples for UV-Vis

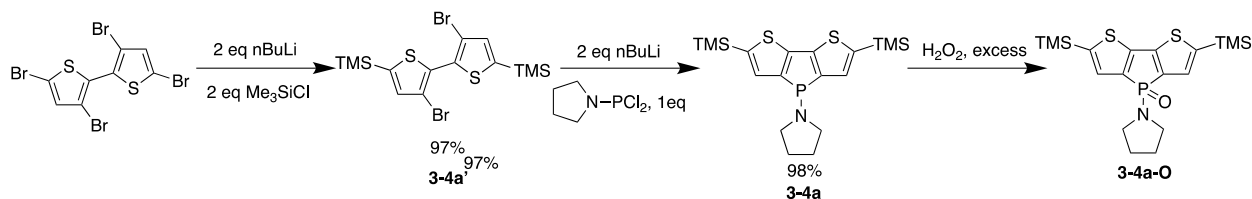
experiments were run in solvents from Sigma Aldrich using 10 mm quartz cuvettes. SPS grade DCM was used as solvent for characterization.

Emission and Photoluminescence (PL) measurements: All emission measurements were recorded using an Edinburgh FS5 spectrofluorometer and processed using Fluoracle software. PLQY measurements were collected using integrating sphere; model SC-30 at room temperature. Lifetime measurements (FS5-TCSPC) were conducted using light source EPL405 with an excitation wavelength of 403 nm. All solutions were prepared using solvents from Sigma Aldrich (SPS grade DCM) and measurements were acquired using 10 mm quartz cuvettes.

Electrochemistry measurements: All electrochemical studies were obtained using Metrohm Autolab potentiostat, with 0.1 M n-Bu₄NPF₆ (Sigma Aldrich, electrochemical grade) that was used after recrystallization from THF as electrolyte. The working, reference and counter electrodes used were glassy carbon, silver/silver chloride (Ag/Ag⁺) and platinum wire, respectively. The electrochemical measurements were carried out at room temperature in dry, degassed THF by bubbling argon through the solution for at least 5 min, and an argon flow was kept over the solution during measurements. The electrochemical cell was recorded using the software NOVA.

S.3.1 Synthesis and NMR Characterization

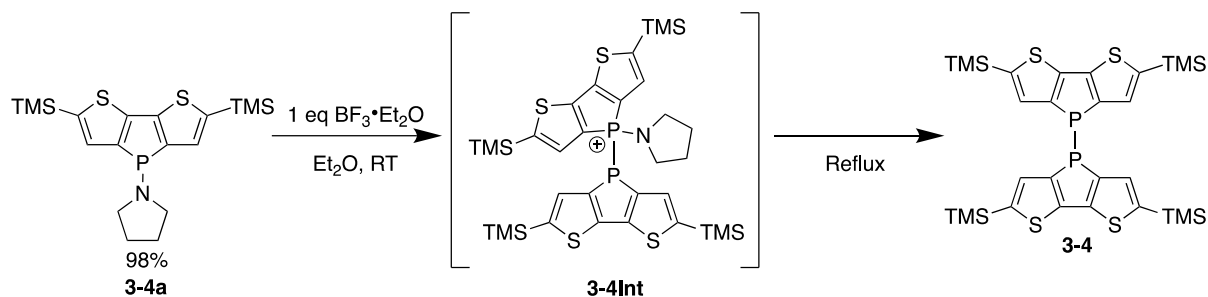
(i) Compound 3-4a



Compound **3-4a'**^{S22} was synthesized by using the protocol according to S.21 at 97% yield (9.50g) and was used for the synthesis of compound **3-4a**. Compound **3-4a'** (2.04g, 5.00 mmol) was dissolved in 100 ml of dry diethyl ether and the solution was chilled to -78°C using liquid nitrogen/acetone bath. n-BuLi (2.05 eq., 0.10 mol, 0.65g) was added to this cold solution with stirring. The solution was stirred for 30 minutes at -78°C and then warmed to room temperature for another 30 minutes. It was cooled again to -78°C and one equivalent of dichloro(pyrrolidiny)phosphane (0.86g, 5.00 mmol) was added with stirring. The cold bath was immediately exchanged for a warm water bath (35°C) and the solution was stirred overnight. The solvent was dried under high vacuum and the brown solid was redissolved in dry pentane and passed through a celite plug. The solution was dried to obtain **3-4a** as a brown oil at 98% yield (2.0g). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.25 (s, 2H), 2.91 (m, 4H), 1.74 (m, 4H), 0.35 (s, 18H). ³¹P{¹H} NMR (162 MHz, CDCl₃, ppm): δ 20.6. ¹³C{¹H} NMR (100.6 MHz, CDCl₃, ppm): δ 148.4 (d, ²J_P=13.8 Hz), 146.7 (d, ²J_P=4.3 Hz), 141.6 (d, ³J_P=3.5 Hz), 133.7 (d, ¹J_P=17.9 Hz), 49.8 (d, ³J_P=4.1 Hz), 26.3 (d, ²J_P=5.1 Hz), 0.2 (s). (Figure S3-6) Some residual impurity peaks are also detected. Compound **3-4a** (2.94g, 7.2 mmol) was stirred overnight with one equivalence of (Me₃SiO)₂ (1.28g, 7.2 mmol) in DCM overnight to observe the formation of the oxide **3-4a-O**. The solvent was dried and redissolved in acetone and the product was obtained as white solid on slow evaporation. Yield was not recorded. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.07 (s, br, 2H),

3.01 (m, 4H), 1.67 (m, 4H), 0.18 (m, 9H). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , ppm): δ 19.1. Solvent impurities are identified along with **3-4a-O**. (Figure S3-7)

(ii) Compound 3-4



By refluxing: One equivalent of etherated BF_3 (0.53g, 3.8 mmol) was added to a solution of **3-4a** (1.54g, 3.76 mmol) in dry ether and a bright yellow precipitate formed within two minutes of stirring. The $^{31}\text{P}\{^1\text{H}\}$ NMR shows that the precipitate is the corresponding phosphonium intermediate **3-4Int** ($^{31}\text{P}\{^1\text{H}\}$; δ (dd) 31.5 ppm, -69.3 ppm, $^1J_{\text{P-P}} \sim 288$ Hz). (Figure S3-1a) After refluxing this mixture for two days, the intermediate evidently converted to the symmetric **3-4** ($^{31}\text{P}\{^1\text{H}\}$ Et_2O : δ (s) -41.3 ppm). The solution was then passed through an alumina plug under argon to yield a yellow oil which is **3-4** (2.55g) at 71% yield. ^1H NMR (700 MHz, CD_2Cl_2 , ppm): δ 8.48 (s, 4H), 2.29 (s, 32H). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , ppm): δ -39.1. $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CD_2Cl_2 , ppm): δ 149.3 (s), 147.5 (s), 143.8 (s), 133.9 (t, $^1J_{\text{P}}=15.8$ Hz), 1.57 (s). (Figure S3-8)

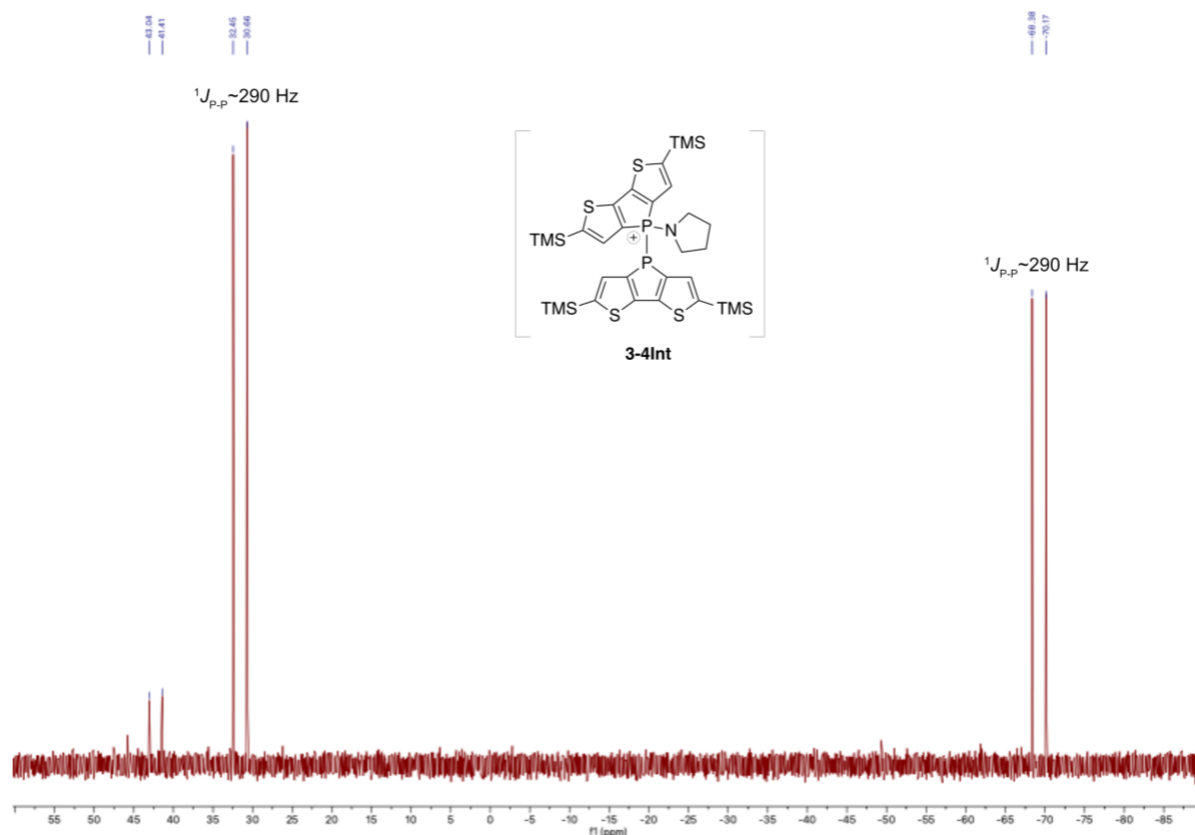
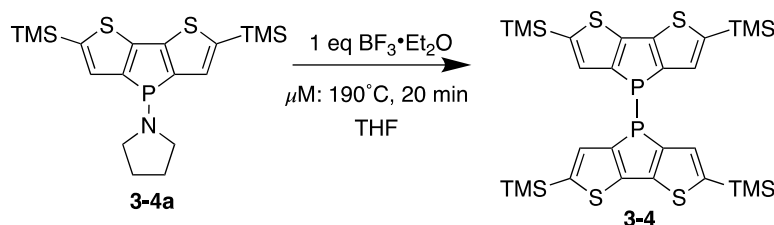
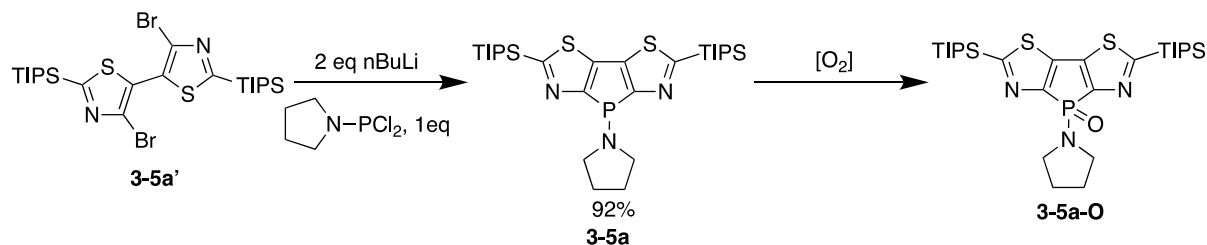


Figure S3-1a. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, Et_2O) showing two pair of doublets corresponding to **3-4Int**.



By microwave reactor: Compound **3-4a** (2.56g, 6.25 mmol) reacted with one equivalence of etherated BF_3 (0.89g, 6.25 mmol) in the microwave reactor for 20 minutes at an elevated temperature of 190°C with one equivalence of BF_3 in dry THF. Compound **3-4** was isolated by passing through a plug of appropriate column material as mentioned early to obtain 50% of **3-4** (4.25g). Attempt to oxidise **3-4** with $(\text{Me}_3\text{SiO})_2$ and Lawesson's reagents are not successful.

(iii) Compound 3-5a



Compound **3-5a**^{S19} (1.52g, 2.38 mmol) was dissolved in 150 ml of dry diethyl ether and was chilled to -78°C using liquid nitrogen/acetone bath. n-BuLi (2.05 eq., 4.90 mmol, 0.31 g) was added to this cold solution with stirring. The solution was stirred for 30 minutes at -78°C and then warmed to room temperature for another 30 minutes. It was cooled again to -78°C and one equivalent of dichloro(pyrrolidinyl)phosphane (0.41g, 2.38 mmol) was added with stirring. The cold bath was immediately switched with a warm water bath (35°C) and the solution was stirred overnight. The solvent was dried under high vacuum and the brown solid was redissolved in dry pentane and passed through a long celite plug. The orange solution was dried to obtain **3-5a** as a yellow solid at 92% yield (1.26g). ¹H NMR (400 MHz, CDCl₃, ppm): δ 2.93 (m, 2H), 1.71 (m, 2H), 1.48 (m, 3H), 1.14 (m, 18 H). ³¹P{¹H} NMR (162 MHz, CDCl₃, ppm): δ 13.9. ¹³C{¹H} NMR (100.6 MHz, CDCl₃, ppm): δ 171.3 (d, ¹J_P=9.8 Hz), 167.0 (d, ²J_P=4.6 Hz), 136.5 (d, ²J_P=9.5 Hz), 50.3 (d, ²J_P=9.1 Hz), 26.4 (d, ³J_P=5.1Hz), 18.6 (s), 11.6 (s). (Figure S3-9) Some residual impurity peaks are also detected. Compound **3-5a** was dissolved in THF and was stirred overnight open to air for oxidation to yield compound **3-5a-O**. The ³¹P{¹H} NMR spectrum was recorded to obtain a signal at -8.2 ppm. (see Figure S3-1b)

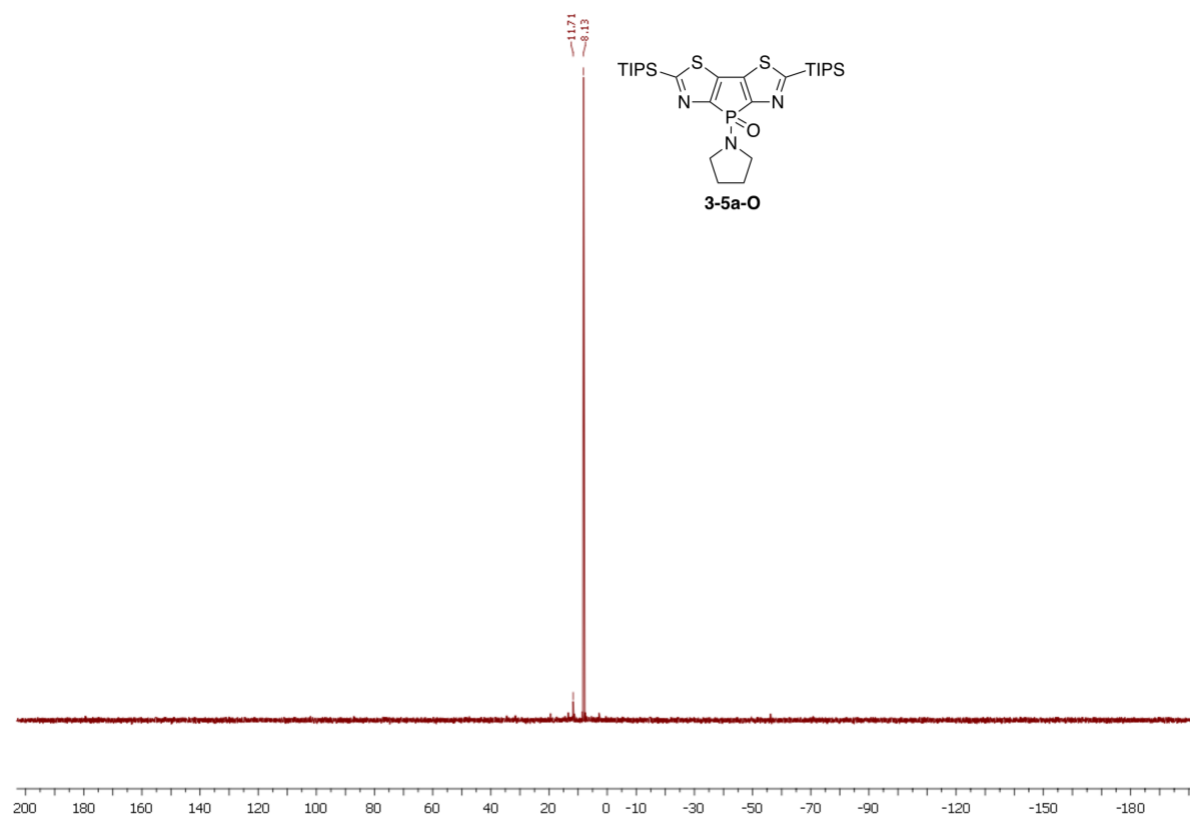
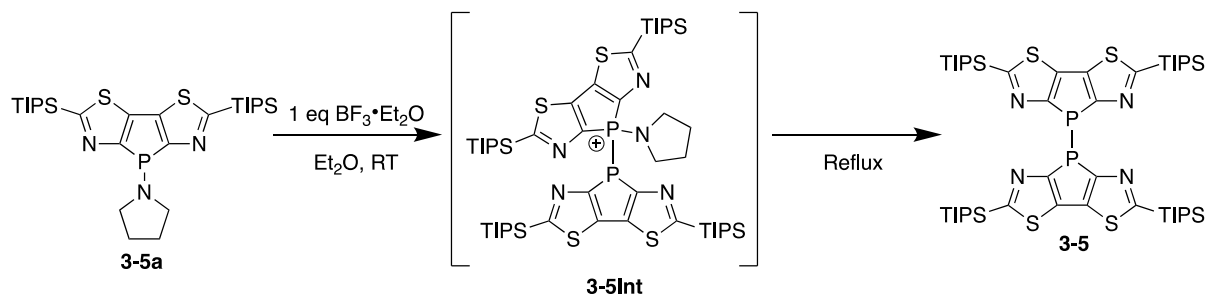


Figure S3-1b. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, THF) showing formation of **3-5a-O**.

(iv) Compound 3-5



By refluxing: The amino derivative **3-5a** (0.27g, 0.5 mmol) dissolved in dry ether was then reacted with BF_3 (1 equiv, 0.1g, 0.5 mmol) to give a pale-yellow cloudy solution, which shows the formation of phosphonium intermediate by NMR spectroscopy (^{31}P ; δ (dd) 32.6 ppm, -67.9 ppm, $^1J_{\text{P-P}} \sim 290$ Hz). (Figure S3-1c) On refluxing the solution overnight, **3-5a** converted to **3-5** and was isolated by using an alumina plug under argon to yield 44% of pure product (0.21g, ^{31}P : δ (s) -53.8 ppm).

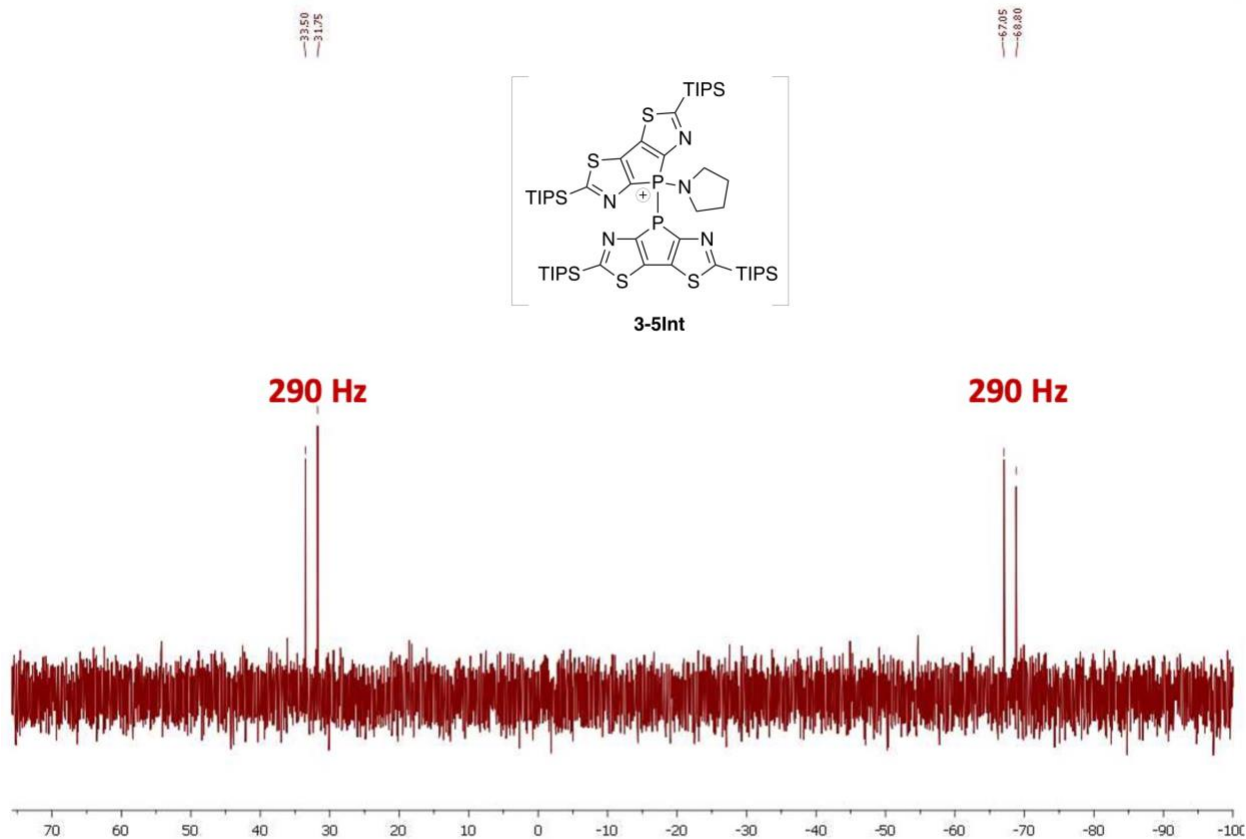
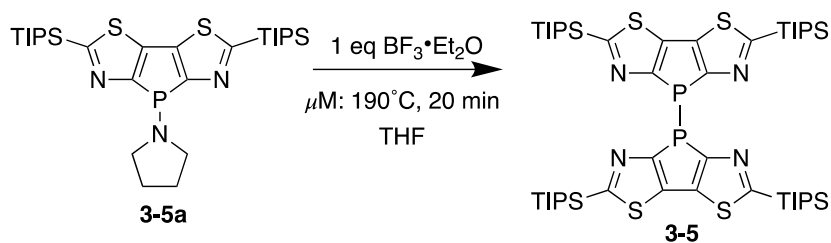


Figure S3-1c. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, Et_2O) showing two pair of doublets corresponding to **3-5Int**.



By microwave reactor: Compound **3-5a** (0.55g, 0.95 mmol) reacted in the microwave reactor for 20 minutes at an elevated temperature of 190°C with one equivalence of BF_3 (0.14g, 0.95 mmol) in dry THF. Compound **3-5** was isolated by passing through a plug of appropriate column material as mentioned early to obtain 50% of **3-5** (0.49g). ^1H NMR (700 MHz, CDCl_3 , ppm): δ 1.38 (septet, 12H, $^3J_{\text{H}}=7$ Hz), 1.11 (d, 72H, $^3J_{\text{H}}=7$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , ppm): δ -52.0.

heating to dissolve towards a saturated solution, the solution colour changed from yellow to orange. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy of the reaction mixture shows a combination of **3-6a** (21.3 ppm) and **3-6** (-38.0 ppm) in 1:1 ratio. (Figure S3-1d)

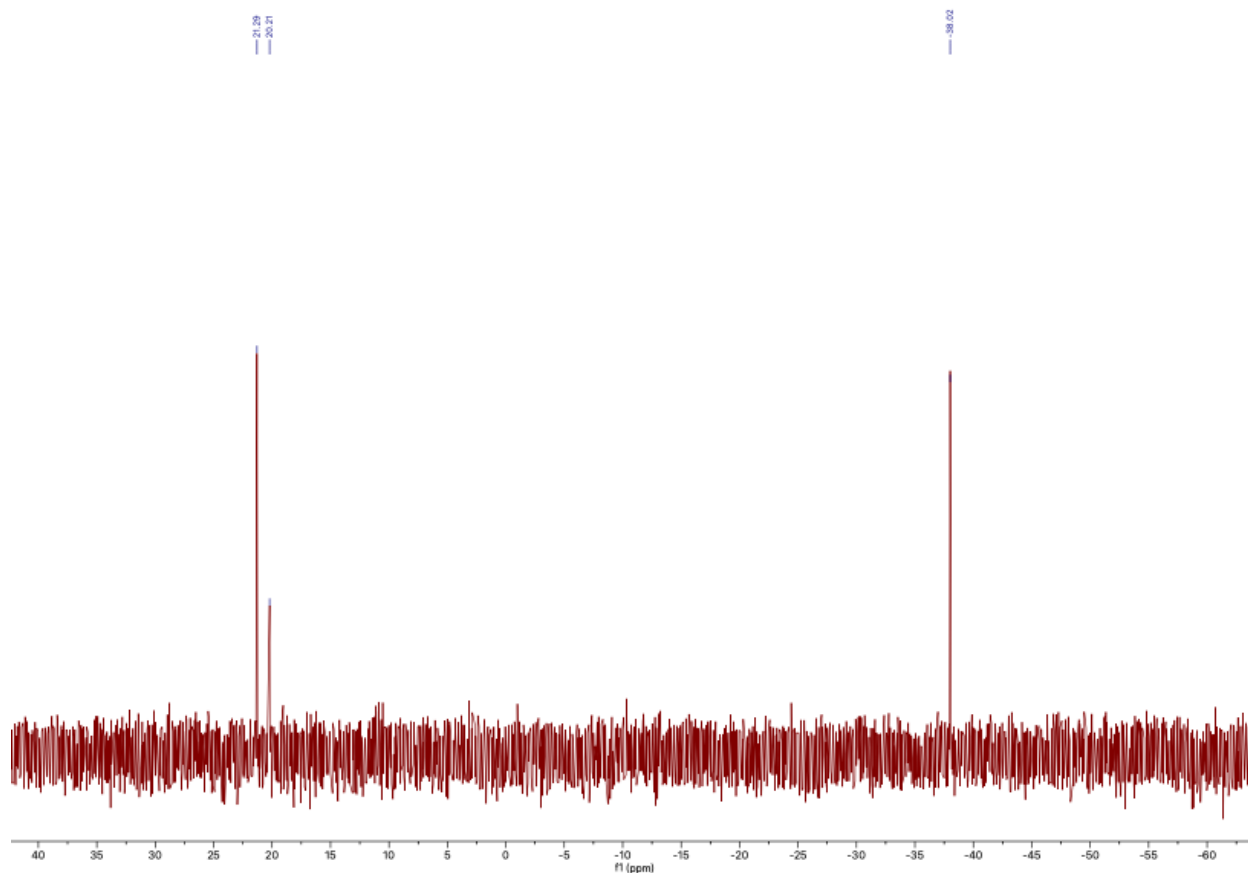


Figure S3-1d. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, THF) showing two peaks corresponding to **3-6a'** and **3-6** on heating **3-6a'** in dry THF.

(vi) Compound 3-6

By microwave reactor: Compound **3-6a** (0.07g, 0.2 mmol) was reacted in a microwave reactor with one equivalence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.03g, 0.2 mmol) at 150°C for 5 min in dry THF to converts to **3-6**. The solution was dried and redissolved in dry DCM. This solution was then passed through a celite plug to purify **3-6**. The solution was dried under vacuum to yield an orange solid at 47% yield. To further explore this enhanced reactivity, **3-6a** dissolved in dry THF was reacted in a

microwave without BF_3 at 190°C for 30 min. The 70% conversion of **3-6a** to **3-6** at this condition (1:1; without any other by-products). (Figure S3-1e) ^1H NMR (400 MHz, CDCl_3 , ppm): δ 7.78 (q, 4H, $^3J_{\text{H}}=8$ Hz, $^4J_{\text{P}}=4$ Hz), 7.28 (m, 8H), 7.09 (d, 4H, $^3J_{\text{H}}=8$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , ppm): δ -38.0. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CD_2Cl_2 , ppm): δ 133.7 (d, $^1J_{\text{P}}=19.5$ Hz), 128.7 (s), 128.5 (d, $^2J_{\text{P}}=7.1$ Hz), 125.1 (s), 124.4 (s), 123.3 (s), 122.1 (s). (Figure S3-12) Residual solvents identified.

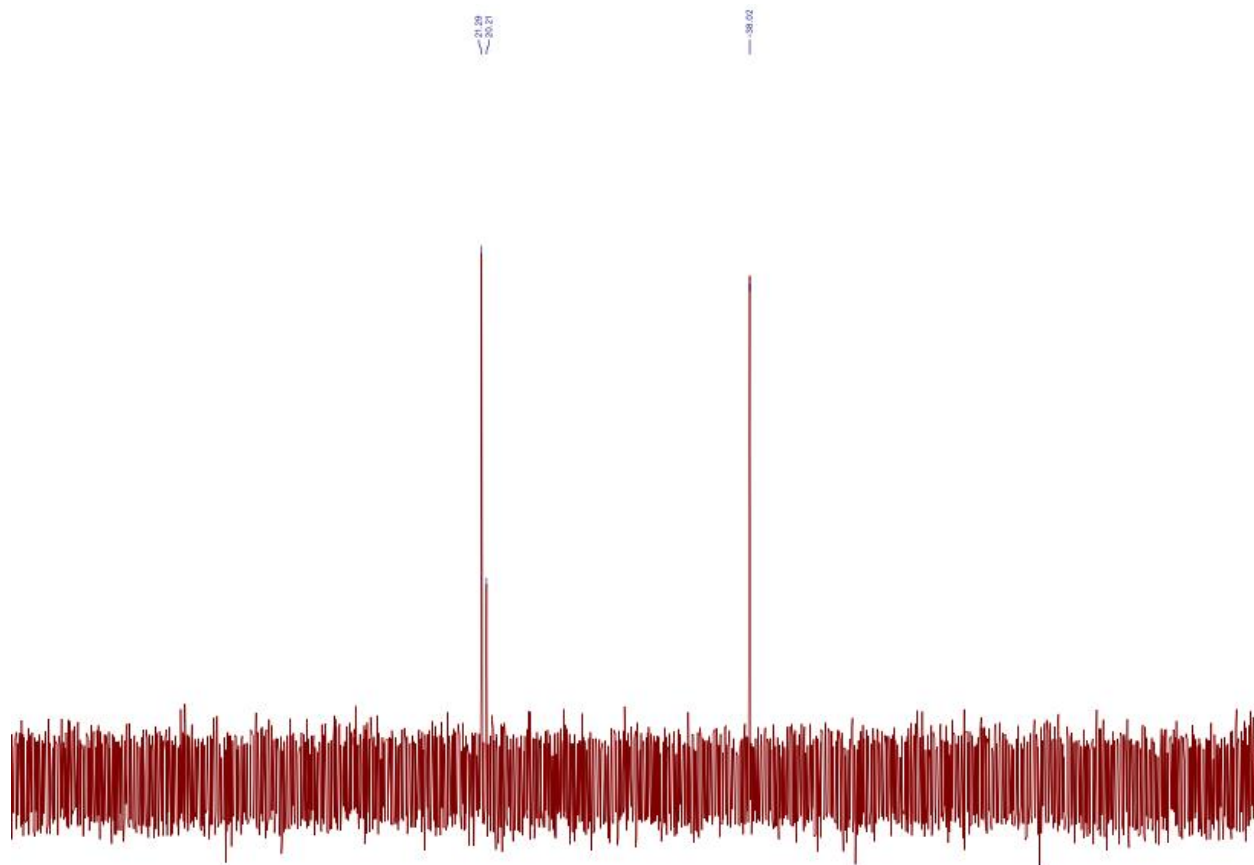
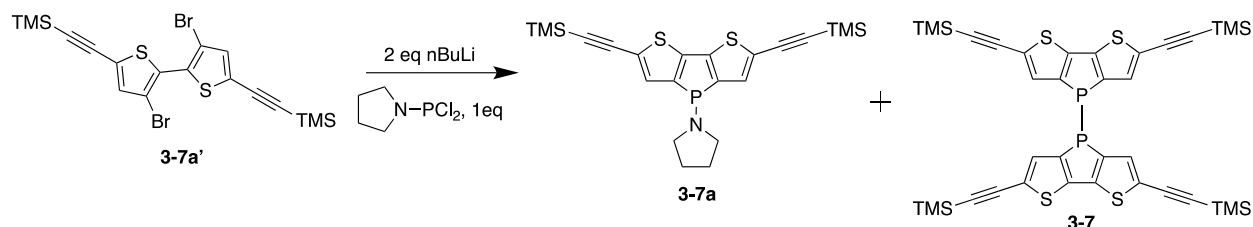


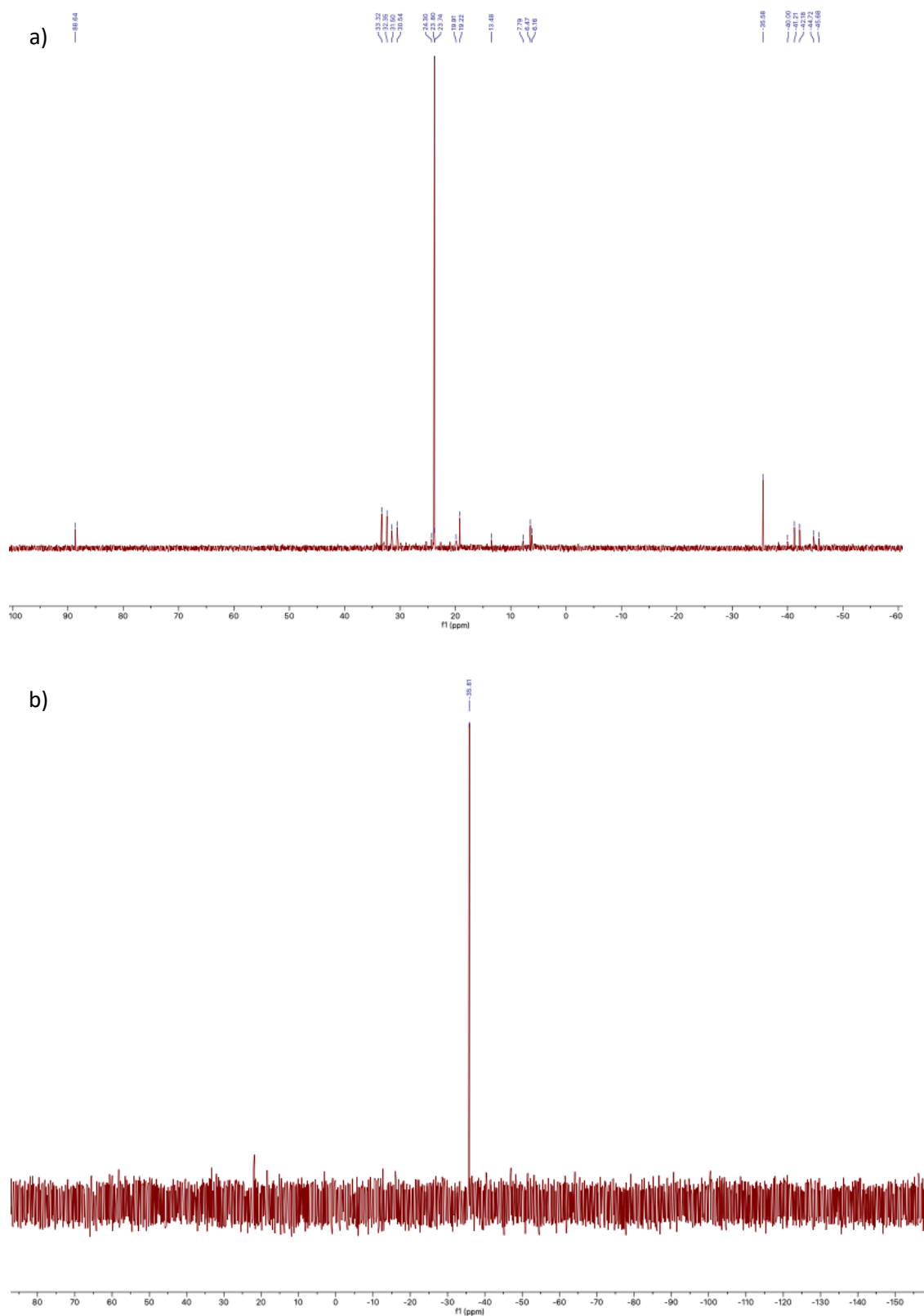
Figure S3-1e. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, THF) showing two peaks corresponding to **3-6a'** and **3-6** on reacting **3-6a'** in a microwave reactor.

(vii) Compound 3-7



Compound **3-7a'**^{S23} (0.68g, 1.31 mmol) was dissolved in 400 ml of dry diethyl ether. The solution was chilled to -78°C using liquid nitrogen/acetone bath and *n*-BuLi (2.05 eq., 2.32 mmol, 0.17 g) was added with stirring. The solution was stirred for 30 minutes at -78°C and then warmed to room temperature for another 30 minutes. It was cooled again to -78°C and one equivalent of dichloro(pyrrolidinyl)phosphane (0.23 g, 1.31 mmol) was added with stirring. The cold bath was immediately switched with a warm water bath (35°C) and the solution was stirred overnight. Surprisingly, during the synthesis of the corresponding aminophosphole **3-7a**, two major peaks (~1:1.5 ratio) were already observed in the ³¹P NMR spectrum of the reaction mixture after stirring for 18 hours at room temperature. (Figure S3-1f) The peak at 23.8 ppm is aligned with those of the other amino-phosphole precursors can be assigned to **3-7a**, while the other significant peak at -35.8 ppm suggested the formation of symmetric biphenyl phosphole **3-7**. The reaction mixture was then filtered and stirred overnight to observe the complete conversion of **3-7a** to **3-7**. (Figure S3-1f)

Figure S3-1f. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, THF) a) showing two peaks corresponding to **3-7a'** and **3-7** and b) showing full conversion of **3-7a'** and **3-7** overnight.



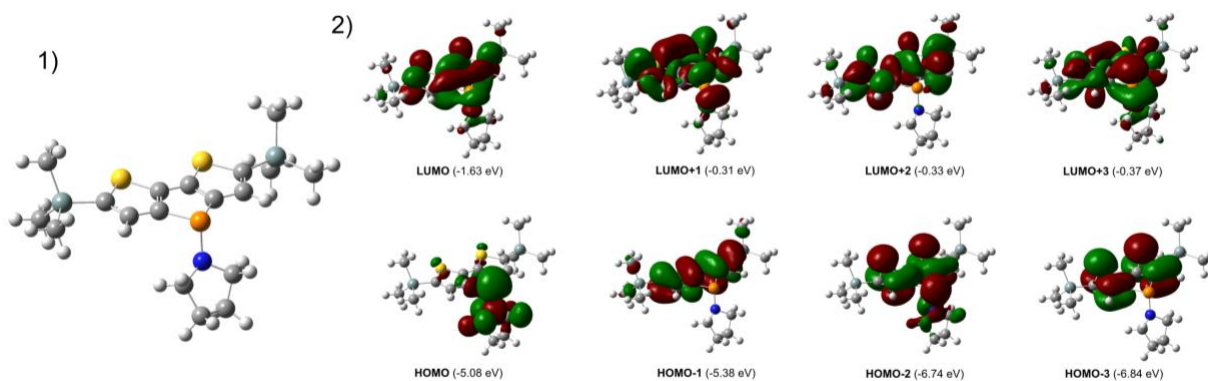
S.3.2 Theoretical Calculations

(i) DFT FMO Calculations

The DFT FMO calculations were conducted at the B3LYP/6-31G+(d) level of theory.^{S3}

a) Compound 3-4a

Figure S3-2a. DFT calculated (B3LYP/6-31G+(d) level of theory) (1) optimized structure and (2) HOMO-3, HOMO-2, HOMO-1, HOMO, LUMO, LUMO+1, LUMO+2 and LUMO+3 levels of 3-4a.



HOMO-LUMO gap: 3.45 eV

Table S3-1a. Cartesian coordinates for the minimized structure of 3-4a.

Center	Atomic	Forces (Hartrees/Bohr)		
Number	Number	X	Y	Z

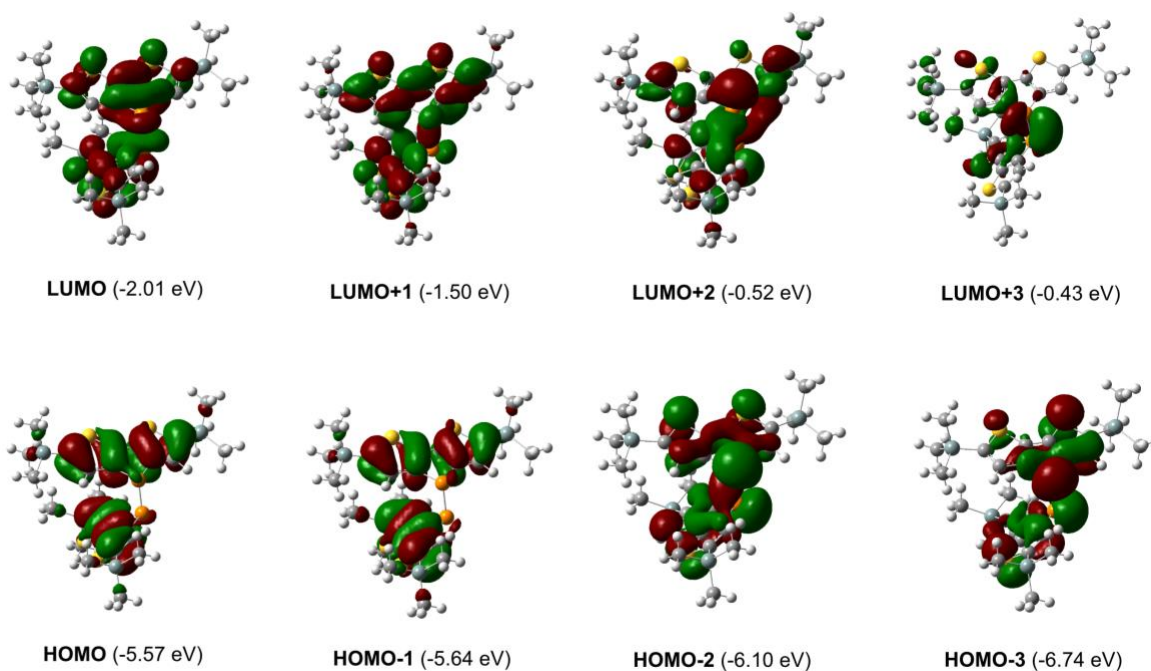
1	6	-0.000000237	0.000003577	-0.000004723
2	6	-0.000003055	-0.000002190	0.000004037
3	6	0.000005815	-0.000001129	-0.000000444
4	6	-0.000005050	0.000007201	0.000003498
5	16	0.000003022	-0.000001826	0.000002104
6	1	-0.000000307	0.000000035	-0.000000215
7	6	0.000002996	-0.000007095	-0.000001072

8	6	-0.000001826	-0.000001586	-0.000001063
9	16	0.000001699	0.000000835	0.000002818
10	6	-0.000000381	0.000002026	0.000003449
11	6	0.000001332	-0.000002625	-0.000006875
12	1	-0.000001086	0.000000393	-0.000000613
13	15	0.000006532	0.000001315	-0.000004227
14	6	-0.000003432	-0.000007576	0.000003940
15	6	0.000001185	0.000002750	0.000005445
16	6	0.000000733	0.000003239	-0.000006567
17	1	-0.000002669	0.000001739	0.000000367
18	1	-0.000001279	0.000001178	0.000000052
19	6	0.000002641	0.000000157	-0.000001538
20	1	-0.000002834	0.000000283	0.000000765
21	1	-0.000000905	0.000000501	0.000000785
22	1	-0.000002083	0.000000031	-0.000000252
23	1	-0.000001128	0.000001109	-0.000000971
24	1	-0.000003052	0.000001098	-0.000001481
25	1	-0.000003447	0.000002206	-0.000000098
26	7	-0.000012861	0.000001113	0.000000018
27	14	-0.000000360	-0.000001493	0.000003072
28	14	0.000000564	0.000000278	0.000003504
29	6	0.000000466	0.000001219	0.000000156
30	1	0.000002344	-0.000000462	-0.000000162
31	1	0.000001126	-0.000000987	0.000000072
32	1	0.000001501	-0.000000247	-0.000000126
33	6	0.000001202	-0.000000025	-0.000001483
34	1	-0.000000089	0.000000915	-0.000002833
35	1	0.000002284	-0.000000296	-0.000001755
36	1	0.000001582	-0.000000309	-0.000001476
37	6	-0.000000142	-0.000002379	0.000000642
38	1	0.000001274	0.000001537	-0.000000055
39	1	-0.000000103	-0.000000454	-0.000001249
40	1	0.000000142	0.000000499	-0.000000083

41	6	0.000000220	-0.000001955	0.000000806
42	1	0.000000728	-0.000000248	0.000001561
43	1	0.000002005	-0.000000925	0.000000874
44	1	0.000001041	-0.000000848	0.000000774
45	6	0.000001334	-0.000000336	-0.000000629
46	1	0.000001492	0.000000027	-0.000000557
47	1	-0.000000428	-0.000000525	-0.000001659
48	1	0.000001223	-0.000000166	-0.000000585
49	6	0.000000411	0.000002218	0.000001834
50	1	-0.000000325	0.000000318	0.000000154
51	1	0.000000438	-0.000001443	0.000000847
52	1	-0.000000254	-0.000000672	0.000001214

b) Compound 3-4

Figure S3-2b. DFT calculated (B3LYP/6-31G+(d) level of theory) HOMO-3, HOMO-2, HOMO-1, HOMO, LUMO, LUMO+1, LUMO+2 and LUMO+3 levels of 3-4.



HOMO-LUMO gap: 3.56 eV

Table S3-1b. Cartesian coordinates for the minimized structure of **3-4**.

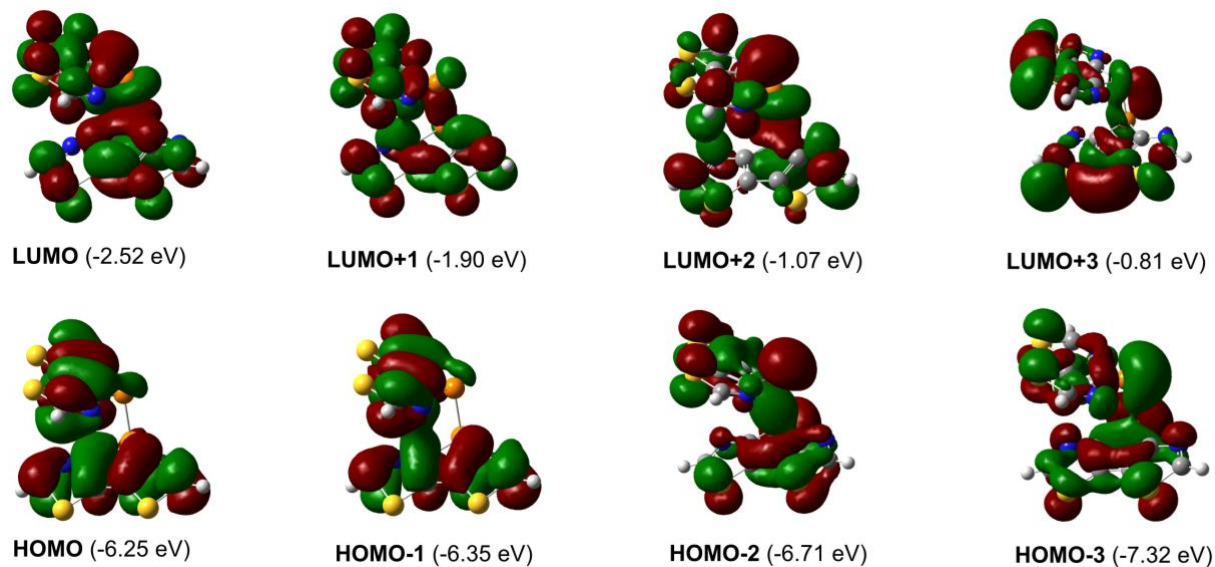
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-4.488444	2.035888	0.416177
2	6	0	-3.228178	2.588801	0.291673
3	6	0	-2.172458	1.737873	0.727937
4	6	0	-2.634166	0.510131	1.191199
5	1	0	-3.070515	3.590894	-0.095666
6	6	0	-0.316048	0.188390	1.617371
7	6	0	0.676207	-0.677478	2.158524
8	6	0	0.181095	-1.876379	2.633979
9	6	0	-1.596752	-0.353104	1.691267
10	1	0	1.733066	-0.431248	2.188314
11	16	0	-1.570561	-1.931292	2.403439
12	16	0	-4.358962	0.396736	1.065729
13	15	0	-0.359983	1.908575	0.996264
14	15	0	0.335330	1.860463	-1.134458
15	6	0	2.149419	1.723571	-0.848529
16	6	0	0.317664	0.106923	-1.659993
17	6	0	3.188650	2.599100	-0.421836
18	6	0	2.631760	0.487206	-1.264296
19	6	0	-0.663481	-0.804355	-2.143979
20	6	0	1.607531	-0.413470	-1.723678
21	6	0	4.455472	2.051932	-0.495861
22	1	0	3.012831	3.605759	-0.054572
23	16	0	4.358886	0.410641	-1.145989
24	6	0	-0.149954	-2.015245	-2.566940
25	1	0	-1.725909	-0.582741	-2.168030
26	16	0	1.608924	-2.009131	-2.395685
27	14	0	-6.155150	2.809126	-0.010764

28	14	0	1.122167	-3.310002	3.418718
29	14	0	-1.069800	-3.504982	-3.268367
30	14	0	6.103199	2.842436	-0.027641
31	6	0	6.977849	1.764054	1.261333
32	1	0	7.034027	0.716053	0.942602
33	1	0	8.003894	2.112827	1.435036
34	1	0	6.447513	1.788363	2.221115
35	6	0	5.736683	4.554104	0.689987
36	1	0	5.225158	5.197179	-0.036495
37	1	0	5.108537	4.491022	1.586635
38	1	0	6.670026	5.056441	0.974279
39	6	0	7.198201	3.001643	-1.563831
40	1	0	8.187995	3.393967	-1.297704
41	1	0	7.346070	2.033704	-2.058405
42	1	0	6.751420	3.682655	-2.298206
43	6	0	-0.450713	-3.854787	-5.024781
44	1	0	0.644229	-3.904508	-5.065739
45	1	0	-0.840435	-4.810360	-5.398547
46	1	0	-0.769356	-3.067184	-5.718538
47	6	0	-2.913040	-3.083644	-3.295139
48	1	0	-3.296778	-2.878245	-2.288790
49	1	0	-3.117477	-2.206143	-3.920394
50	1	0	-3.490327	-3.922388	-3.704321
51	6	0	-0.759719	-5.020743	-2.176049
52	1	0	-1.199862	-5.921544	-2.622607
53	1	0	0.312626	-5.208390	-2.040906
54	1	0	-1.200919	-4.887701	-1.180961
55	6	0	-5.828044	4.538009	-0.705186
56	1	0	-5.310600	5.176087	0.021224
57	1	0	-5.217637	4.499249	-1.615439
58	1	0	-6.774012	5.030549	-0.963115
59	6	0	-7.045758	1.744874	-1.299519
60	1	0	-7.120161	0.698728	-0.978063

61	1	0	-8.065541	2.112055	-1.471833
62	1	0	-6.516474	1.758337	-2.259998
63	6	0	-7.217027	2.921254	1.553708
64	1	0	-8.222889	3.292802	1.319265
65	1	0	-7.329341	1.944012	2.039114
66	1	0	-6.767559	3.603034	2.285766
67	6	0	0.847561	-4.879184	2.393145
68	1	0	1.235330	-5.763708	2.914578
69	1	0	-0.217229	-5.052328	2.194454
70	1	0	1.356823	-4.809974	1.424356
71	6	0	2.956168	-2.850209	3.436170
72	1	0	3.338904	-2.680920	2.422838
73	1	0	3.141399	-1.942324	4.023133
74	1	0	3.548435	-3.658062	3.884376
75	6	0	0.503222	-3.593942	5.186275
76	1	0	-0.583031	-3.744309	5.215126
77	1	0	0.973209	-4.482013	5.627915
78	1	0	0.733731	-2.735811	5.829217

c) Compound **3-5'**

Figure S3-2c. DFT calculated (B3LYP/6-31G+(d) level of theory) HOMO-3, HOMO-2, HOMO-1, HOMO, LUMO, LUMO+1, LUMO+2 and LUMO+3 levels of **3-5'**.



HOMO-LUMO gap: 3.83 eV

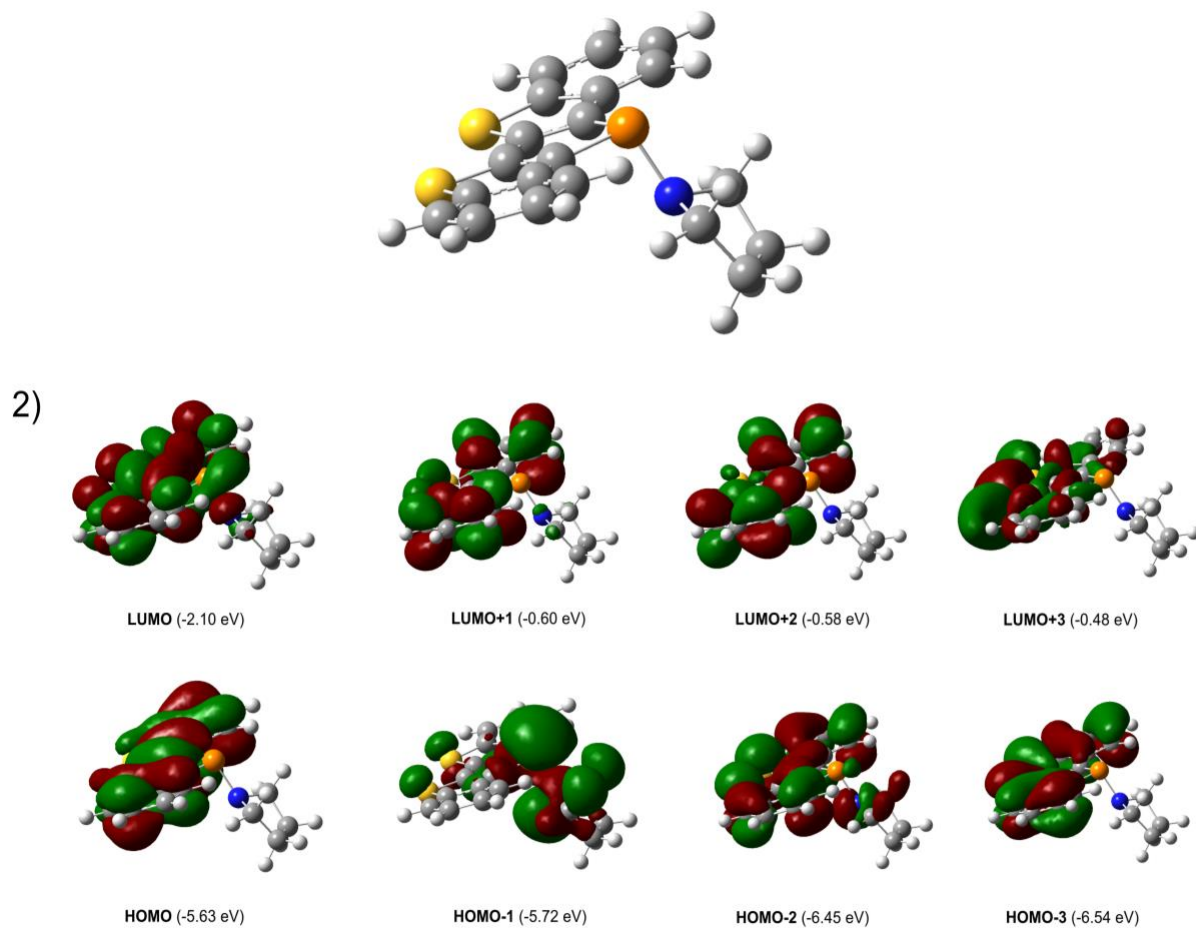
Table S3-1c. Cartesian coordinates for the minimized structure of **3-5'**.

Center Number	Atomic Number	Forces (Hartrees/Bohr)		
		X	Y	Z
1	6	-0.000015949	0.000003240	0.000001373
2	6	0.000037784	-0.000001566	-0.000030749
3	6	-0.000014974	0.000000004	-0.000011270
4	6	-0.000017426	-0.000008219	0.000062579
5	6	-0.000011594	0.000005397	-0.000005574
6	6	-0.000028019	0.000000276	0.000004143
7	16	0.000009150	-0.000000470	-0.000001482
8	16	-0.000002136	-0.000006425	0.000005371

9	15	0.000009376	0.000019524	0.000005191
10	15	-0.000002004	-0.000013667	0.000008323
11	6	-0.000105667	-0.000018891	0.000003747
12	6	0.000060229	0.000007156	-0.000003085
13	6	0.000024149	-0.000003481	-0.000012135
14	6	0.000008371	0.000007129	-0.000006765
15	6	-0.000004869	0.000029411	0.000049885
16	16	0.000016063	-0.000007750	-0.000026523
17	6	-0.000007198	0.000001887	-0.000017021
18	16	0.000005487	-0.000000967	0.000001346
19	7	0.000077507	0.000000665	-0.000024917
20	7	-0.000061081	0.000002245	0.000014582
21	7	0.000035964	0.000006103	-0.000064621
22	7	-0.000011409	-0.000011259	0.000050443
23	1	0.000005228	0.000005982	-0.000001611
24	1	-0.000000549	-0.000012270	-0.000003644
25	1	-0.000003950	-0.000006591	0.000004149
26	1	-0.000002481	0.000002537	-0.000001737

d) Compound **3-6a**

Figure S3-2d. DFT calculated (B3LYP/6-31G+(d) level of theory) 1) optimised structure and 2) HOMO-3, HOMO-2, HOMO-1, HOMO, LUMO, LUMO+1, LUMO+2 and LUMO+3 levels of **3-6a**.



HOMO-LUMO gap: 3.54 eV

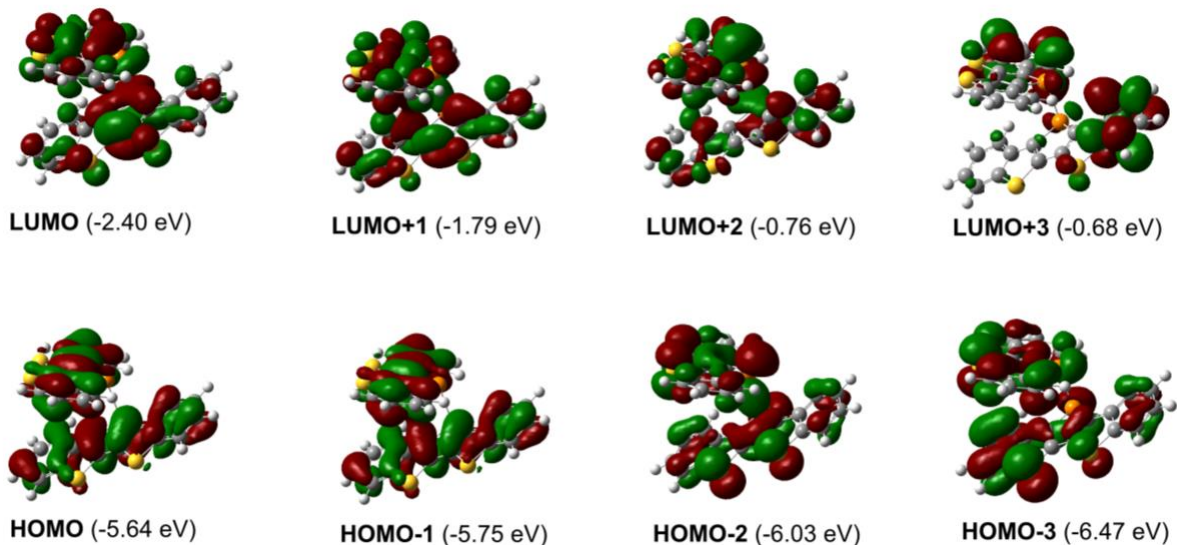
Table S3-1d. Cartesian coordinates for the minimized structure of **3-6a**.

Center Number	Atomic Number	Forces (Hartrees/Bohr)		
		X	Y	Z
1	6	-0.000003612	0.000005715	-0.000002649
2	6	0.000004871	-0.000004097	-0.000002834
3	6	0.000002939	0.000000376	0.000011384
4	6	-0.000002290	-0.000002481	-0.000005861
5	6	0.000004532	-0.000005096	-0.000004647
6	6	-0.000002983	0.000004026	-0.000003169
7	6	0.000002871	0.000001784	0.000003349
8	6	0.000002876	-0.000002037	0.000005479
9	16	0.000004574	0.000001439	0.000000790
10	16	0.000013218	-0.000002290	0.000000484
11	15	0.000015317	-0.000006307	0.000001512
12	6	0.000006275	0.000004625	-0.000001343
13	6	0.000000128	-0.000000083	0.000001322
14	6	0.000003734	0.000002140	0.000002104
15	1	0.000003422	-0.000000727	-0.000000229
16	6	0.000000055	0.000002277	0.000000806
17	1	0.000006982	-0.000000728	-0.000001892
18	1	-0.000000967	0.000001092	-0.000001148
19	1	-0.000003640	0.000000796	0.000000876
20	6	0.000004482	0.000002985	0.000001515
21	6	0.000004334	-0.000003385	-0.000002472
22	6	0.000003582	0.000002905	-0.000000798
23	6	0.000000079	0.000001143	-0.000000062
24	1	-0.000002313	0.000000542	0.000000659
25	1	-0.000000276	0.000001355	0.000000673
26	1	0.000002587	-0.000000010	0.000000149
27	1	0.000005484	-0.000000187	0.000001474

28	6	-0.000010312	0.000004162	-0.000000560
29	6	-0.000009975	-0.000009659	0.000013339
30	6	0.000004669	0.000000829	0.000008170
31	1	-0.000007521	0.000000840	-0.000000610
32	1	-0.000003357	-0.000002196	0.000000293
33	6	-0.000006353	0.000005545	-0.000006495
34	1	-0.000002782	0.000000172	-0.000000958
35	1	-0.000003183	0.000003116	-0.000005616
36	1	-0.000005378	-0.000006298	-0.000001890
37	1	-0.000006573	0.000000900	-0.000002469
38	1	-0.000006234	-0.000007831	0.000000674
39	1	-0.000004736	-0.000002471	0.000006013
40	7	-0.000014525	0.000007118	-0.000015358

e) Compound 3-6

Figure S3-2e. DFT calculated (B3LYP/6-31G+(d) level of theory) HOMO-3, HOMO-2, HOMO-1, HOMO, LUMO, LUMO+1, LUMO+2 and LUMO+3 levels of 3-6.



HOMO-LUMO gap: 3.23 eV

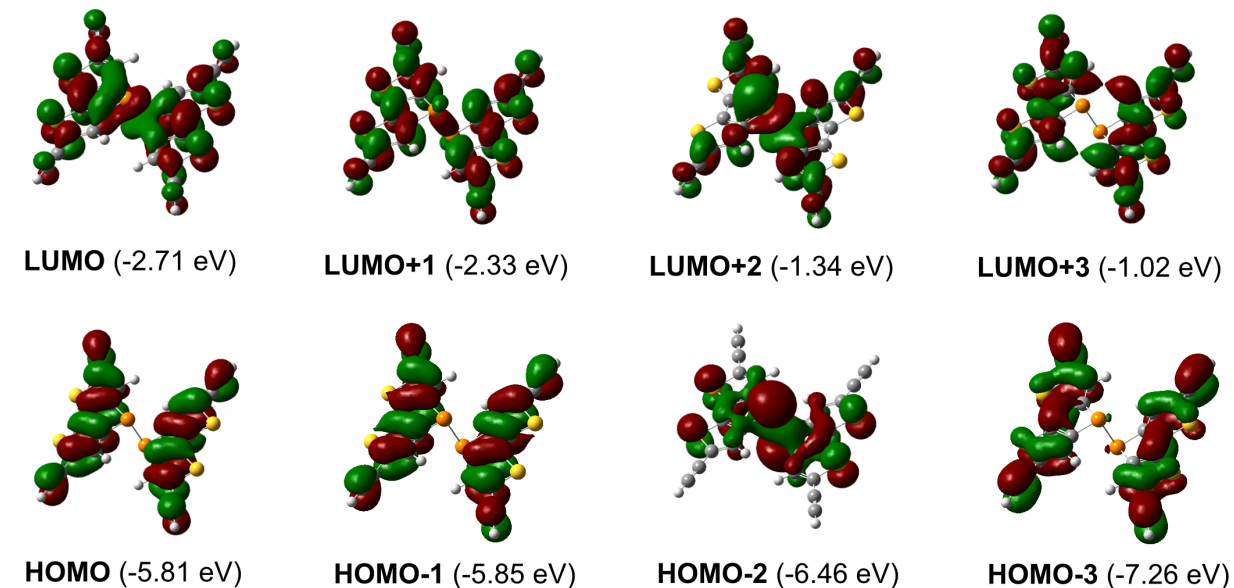
Table S3-1e. Cartesian coordinates for the minimized structure of **3-6**.

Center Number	Atomic Number	Forces (Hartrees/Bohr)		
		X	Y	Z
1	6	-0.000018468	0.000000490	-0.000009794
2	6	0.000016417	0.000014384	0.000011540
3	6	-0.000005873	0.000003778	0.000012748
4	6	0.000028791	-0.000016410	-0.000043689
5	6	0.000034529	-0.000009424	0.000000077
6	6	-0.000006661	0.000008272	0.000020480
7	6	0.000003698	-0.000012019	-0.000018821
8	6	-0.000040020	0.000020287	0.000025388
9	16	0.000005822	0.000003229	-0.000000038
10	16	0.000001439	0.000000752	-0.000002100
11	15	-0.000005205	0.000004554	-0.000016105
12	15	0.000000455	-0.000000192	0.000011567
13	6	0.000010049	0.000006557	0.000000428
14	6	-0.000013891	-0.000009896	-0.000004194
15	6	-0.000002921	-0.000023914	0.000000162
16	6	-0.000001933	0.000001885	0.000004004
17	6	0.000013601	0.000010923	-0.000012862
18	6	0.000007514	-0.000024440	0.000000358
19	6	-0.000032660	-0.000013611	0.000001428
20	16	0.000000731	-0.000000177	0.000004404
21	6	0.000017177	0.000013736	0.000007202
22	16	-0.000000542	0.000010499	-0.000001724
23	6	0.000002682	-0.000005923	-0.000011301
24	6	0.000000201	0.000004267	-0.000008111
25	6	0.000000089	0.000003286	-0.000004822
26	6	-0.000000408	0.000003882	-0.000002291
27	6	-0.000003414	0.000005674	0.000007141

28	6	0.000003893	-0.000006842	0.000006997
29	6	0.000003513	-0.000002819	-0.000000173
30	6	0.000005003	-0.000001976	0.000004336
31	1	0.000004169	-0.000001148	0.000001317
32	1	0.000003226	-0.000002360	0.000003736
33	1	0.000001946	-0.000002225	0.000003143
34	1	0.000002407	-0.000000329	0.000000108
35	1	-0.000000810	0.000000682	-0.000003810
36	1	-0.000000744	0.000002277	-0.000004529
37	1	0.000000469	0.000003332	-0.000005872
38	1	0.000001782	0.000003561	-0.000005310
39	6	0.000008976	0.000020466	0.000004594
40	6	0.000041864	-0.000041095	-0.000001906
41	6	-0.000049677	0.000027441	0.000010832
42	6	0.000031423	0.000015586	0.000009267
43	1	-0.000001322	-0.000003064	0.000005225
44	1	-0.000001832	-0.000003627	0.000005729
45	1	0.000000840	-0.000004123	0.000003807
46	1	0.000001555	-0.000000656	0.000002789
47	6	-0.000025724	-0.000021291	-0.000005918
48	1	-0.000003395	0.000001417	0.000000585
49	6	0.000000053	-0.000006930	-0.000003325
50	1	-0.000002990	0.000002478	-0.000003043
51	6	-0.000003950	0.000016859	0.000001135
52	1	-0.000002015	0.000004012	-0.000005790
53	6	-0.000027537	-0.000000346	0.000005484
54	1	-0.000002322	0.000000270	-0.000000482

f) Compound **3-7'**

Figure S3-2f. DFT calculated (B3LYP/6-31G+(d) level of theory) HOMO-3, HOMO-2, HOMO-1, HOMO, LUMO, LUMO+1, LUMO+2 and LUMO+3 levels of **3-7'**.



HOMO-LUMO gap: 3.10 eV

Table S3-1f. Cartesian coordinates for the minimized structure of **3-7'**.

Center Number	Atomic Number	Forces (Hartrees/Bohr)		
		X	Y	Z
1	6	-0.000004113	-0.000001327	0.000008499
2	6	0.000004064	0.000003390	0.000002620
3	6	0.000001443	-0.000003662	0.000008464
4	16	-0.000004602	-0.000004358	0.000001382
5	1	0.000001479	-0.000000027	-0.000000665
6	6	0.000003443	-0.000002226	0.000003163
7	6	-0.000005401	-0.000000965	0.000009377

8	16	0.000000551	-0.000000305	-0.000001676
9	6	0.000005150	-0.000000261	-0.000009314
10	6	-0.000003165	-0.000004682	0.000015686
11	1	0.000001147	0.000000867	-0.000000427
12	6	0.000000414	-0.000003249	-0.000002624
13	15	-0.000017151	-0.000000081	0.000001300
14	15	0.000011731	0.000002008	-0.000007356
15	6	0.000006295	-0.000001921	0.000001015
16	6	-0.000000779	0.000001292	-0.000005536
17	6	-0.000003689	-0.000000474	-0.000005569
18	1	-0.000000225	0.000000948	-0.000002026
19	6	0.000000358	0.000001083	0.000001471
20	16	0.000000933	0.000002841	-0.000006182
21	6	0.000012872	-0.000001795	0.000000478
22	6	-0.000003371	0.000005177	-0.000004081
23	6	-0.000006773	0.000000882	0.000001705
24	16	-0.000000608	0.000000997	-0.000000541
25	6	0.000004757	0.000001832	-0.000010385
26	1	-0.000001174	-0.000000419	0.000000015
27	6	-0.000003925	-0.000005590	0.000004173
28	6	0.000001183	0.000000184	0.000003568
29	1	-0.000000155	-0.000001492	0.000004928
30	6	-0.000001591	0.000007197	0.000006988
31	6	-0.000000214	-0.000003620	0.000002393
32	1	0.000000114	-0.000002821	0.000004811
33	6	-0.000001409	-0.000001690	-0.000003650
34	6	0.000001580	0.000004035	-0.000006423
35	1	0.000000120	0.000001781	-0.000003544
36	6	0.000000972	0.000006235	-0.000001107
37	6	-0.000000852	-0.000000780	-0.000005462
38	1	0.000000593	0.000000995	-0.000005465

(ii) TD-DFT Calculations

The TD DFT calculations were conducted at the B3LYP/6-31G+(d) level of theory.^{S3}

Table S3-2a. TD-DFT Data for compound **3-2**.

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A' 2.6469 eV 468.41 nm f=0.2851 ($\pi-\pi^*$)
99 ->100 0.70370

Excited State 2: Singlet-A' 3.5181 eV 352.42 nm f=0.0252 ($\pi-\pi^*$)
99 ->101 0.70152

Excited State 3: Singlet-A'' 3.6765 eV 337.24 nm f=0.0025 ($\pi-\pi^*$)
97 ->100 -0.20918
98 ->100 -0.15527
99 ->102 0.64208
99 ->105 -0.10518

Excited State 4: Singlet-A'' 3.7992 eV 326.35 nm f=0.0155 Locally excited (LE)
97 ->100 -0.11003
98 ->100 0.68062
99 ->102 0.12903

Excited State 5: Singlet-A'' 3.8772 eV 319.78 nm f=0.1171 (LE)
97 ->100 0.65892
99 ->102 0.22468

Excited State 6: Singlet-A' 4.1274 eV 300.40 nm f=0.0053 ($\pi-\pi^*$)
99 ->103 0.70250

Excited State 7: Singlet-A' 4.3325 eV 286.17 nm f=0.0063 ($\pi-\pi^*$)
96 ->100 0.68815

Excited State 8: Singlet-A" 4.4659 eV 277.63 nm f=0.0000 (LE)

99 ->104 0.65971

99 ->105 0.22662

Excited State 9: Singlet-A" 4.5011 eV 275.45 nm f=0.0005 (LE)

99 ->104 -0.23082

99 ->105 0.65065

Excited State 10: Singlet-A" 4.5912 eV 270.05 nm f=0.0137 (LE)

94 ->100 0.68539

Excited State 11: Singlet-A" 4.6100 eV 268.95 nm f=0.0004 (LE)

95 ->100 0.66321

98 ->101 0.21114

Excited State 12: Singlet-A" 4.7273 eV 262.27 nm f=0.1937 (LE)

95 ->100 -0.20647

97 ->101 0.10686

98 ->101 0.65468

Excited State 13: Singlet-A' 4.7435 eV 261.38 nm f=0.0414 (LE)

99 ->106 0.68865

Excited State 14: Singlet-A" 4.7779 eV 259.50 nm f=0.1471 (LE)

97 ->101 0.69155

Excited State 15: Singlet-A' 4.8291 eV 256.74 nm f=0.0755 ($\pi-\pi^*$)

93 ->100 0.62782

97 ->102 0.13209

99 ->107 0.22961

Excited State 16: Singlet-A' 4.8948 eV 253.30 nm f=0.0594 ($\pi-\pi^*$)

93 ->100	-0.22139
99 ->107	0.65762

Excited State 17: Singlet-A' 5.0066 eV 247.64 nm f=0.0070 (LE)

98 ->102	0.68466
98 ->105	-0.12653

Excited State 18: Singlet-A' 5.0292 eV 246.53 nm f=0.0036 (LE)

92 ->100	0.30867
93 ->100	-0.13125
96 ->101	0.13816
97 ->102	0.58207

Excited State 19: Singlet-A' 5.1355 eV 241.42 nm f=0.0247 ($\pi-\pi^*$)

92 ->100	0.41120
96 ->101	0.41896
97 ->102	-0.31319
97 ->105	0.12563
98 ->104	0.12747

Excited State 20: Singlet-A' 5.1809 eV 239.31 nm f=0.0417 ($\pi-\pi^*$)

92 ->100	-0.40834
93 ->100	0.10124
96 ->101	0.52471
97 ->102	0.11530

Excited State 21: Singlet-A'' 5.3206 eV 233.02 nm f=0.0792 (LE)

94 ->101	0.17983
95 ->101	-0.14400
97 ->103	0.60819
97 ->107	-0.12658
98 ->103	-0.14313
99 ->108	0.10067

Excited State 22: Singlet-A" 5.3408 eV 232.14 nm f=0.0389 (LE)

95 ->101 0.47844

97 ->103 0.21184

98 ->103 0.37241

99 ->108 -0.21964

Excited State 23: Singlet-A" 5.3990 eV 229.64 nm f=0.0066 ($\pi-\pi^*$)

95 ->101 0.36466

96 ->102 -0.14471

98 ->103 -0.17398

98 ->106 -0.19643

99 ->108 0.50827

Excited State 24: Singlet-A" 5.4461 eV 227.66 nm f=0.1037 (LE)

95 ->101 -0.21232

96 ->102 -0.10552

98 ->103 0.52004

98 ->106 0.16740

99 ->108 0.35134

Table S3-2b. TD-DFT Data for compound **3-4**.

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 2.0674 eV 599.70 nm f=0.0004 ($\pi-\pi^*$)
179 ->180 0.70450

Excited State 2: Singlet-A 2.0709 eV 598.69 nm f=0.0004 ($\pi-\pi^*$)
178 ->180 0.70439

Excited State 3: Singlet-A 2.3595 eV 525.47 nm f=0.0013 ($\pi-\pi^*$)
177 ->180 0.70591

Excited State 4: Singlet-A 2.3664 eV 523.95 nm f=0.0000 ($\pi-\pi^*$)
176 ->180 0.70590

Excited State 5: Singlet-A 3.5189 eV 352.33 nm f=0.0054 ($\pi-\pi^*$)
178 ->181 -0.29770
178 ->182 -0.33434
179 ->181 0.46237
179 ->182 0.27912

Excited State 6: Singlet-A 3.5194 eV 352.29 nm f=0.0033 ($\pi-\pi^*$)
178 ->181 0.41577
178 ->182 -0.26781
179 ->181 0.30903
179 ->182 -0.39004

Excited State 7: Singlet-A 3.5606 eV 348.21 nm f=0.5226 ($\pi-\pi^*$)
178 ->181 0.45421
178 ->182 0.15480
179 ->181 0.12355
179 ->182 0.47256

Excited State 8: Singlet-A 3.5608 eV 348.19 nm f=0.4804 ($\pi-\pi^*$)

174 ->180 0.15614

177 ->182 0.13816

178 ->181 -0.12458

178 ->182 0.48677

179 ->181 0.38729

179 ->182 -0.17107

Excited State 9: Singlet-A 3.5625 eV 348.02 nm f=0.0426 ($\pi-\pi^*$)

174 ->180 -0.25960

176 ->181 0.44073

177 ->182 -0.41845

178 ->182 0.19405

179 ->181 0.11167

Excited State 10: Singlet-A 3.6032 eV 344.09 nm f=0.0068 ($\pi-\pi^*$)

175 ->180 0.54974

176 ->182 0.29053

177 ->181 -0.31705

Excited State 11: Singlet-A 3.6283 eV 341.71 nm f=0.0077 ($\pi-\pi^*$)

174 ->180 0.63101

176 ->181 0.20221

177 ->182 -0.21729

Excited State 12: Singlet-A 3.6293 eV 341.62 nm f=0.0032 ($\pi-\pi^*$)

175 ->180 0.42517

176 ->182 -0.36782

177 ->181 0.41388

Excited State 13: Singlet-A 3.6909 eV 335.92 nm f=0.9022 ($\pi-\pi^*$)

176 ->181	0.49424				
177 ->182	0.49379				
Excited State 14:	Singlet-A	3.7696 eV	328.91 nm	f=0.0010	($\pi-\pi^*$)
176 ->182	0.51877				
177 ->181	0.46552				
Excited State 15:	Singlet-A	3.9119 eV	316.94 nm	f=0.0017	($\pi-\pi^*$)
171 ->180	0.12453				
173 ->180	0.68591				
Excited State 16:	Singlet-A	3.9121 eV	316.92 nm	f=0.0017	($\pi-\pi^*$)
170 ->180	0.12432				
172 ->180	0.68603				
Excited State 17:	Singlet-A	4.3611 eV	284.29 nm	f=0.0187	($\pi-\pi^*$)
160 ->180	-0.10936				
163 ->180	0.10721				
171 ->180	0.66876				
173 ->180	-0.11294				
Excited State 18:	Singlet-A	4.3635 eV	284.14 nm	f=0.0190	($\pi-\pi^*$)
161 ->180	0.11032				
162 ->180	-0.10727				
170 ->180	0.66844				
172 ->180	-0.11274				
Excited State 19:	Singlet-A	4.5213 eV	274.23 nm	f=0.0000	($\pi-\pi^*$)
178 ->184	-0.37638				
179 ->183	0.58673				
Excited State 20:	Singlet-A	4.5227 eV	274.14 nm	f=0.0000	($\pi-\pi^*$)

178 ->183	0.58454
179 ->184	-0.37963

Excited State 21: Singlet-A 4.7461 eV 261.23 nm f=0.0004 Charge transfer (CT)

167 ->180	-0.23405
168 ->180	0.14208
169 ->180	0.64844

Excited State 22: Singlet-A 4.7464 eV 261.22 nm f=0.0004 (CT)

166 ->180	0.26163
168 ->180	0.64630
169 ->180	-0.10210

Excited State 23: Singlet-A 4.7508 eV 260.97 nm f=0.0016 (CT)

166 ->180	0.23500
167 ->180	0.60459
169 ->180	0.26052

Excited State 24: Singlet-A 4.7510 eV 260.96 nm f=0.0016 (CT)

166 ->180	0.60888
167 ->180	-0.27459
168 ->180	-0.22702

Table S3-2c. TD-DFT Data for compound **3-6**.

Excited State 1:	Singlet-A	2.2575 eV	549.22 nm	f=0.1311 (LE)
150 ->152	-0.15717			
151 ->152	0.63872			
151 ->153	-0.23831			
Excited State 2:	Singlet-A	2.4600 eV	504.00 nm	f=0.0344 (LE)
150 ->152	0.59830			
151 ->152	0.24465			
151 ->153	0.26505			
Excited State 3:	Singlet-A	2.5636 eV	483.63 nm	f=0.1091 (LE)
150 ->152	-0.32901			
151 ->152	0.14088			
151 ->153	0.60018			
Excited State 4:	Singlet-A	2.8231 eV	439.17 nm	f=0.1644 (LE)
149 ->152	0.64530			
150 ->153	0.26831			
Excited State 5:	Singlet-A	2.8673 eV	432.41 nm	f=0.1982 (LE)
149 ->152	-0.26885			
150 ->153	0.63722			
Excited State 6:	Singlet-A	3.1205 eV	397.33 nm	f=0.2150 (LE)
149 ->153	0.69493			
Excited State 7:	Singlet-A	3.2659 eV	379.63 nm	f=0.0310 ($\pi-\pi^*$)
148 ->152	0.67825			
Excited State 8:	Singlet-A	3.4749 eV	356.79 nm	f=0.0071 (LE)
145 ->152	-0.10817			

146 ->152	0.14176
147 ->152	0.66297
151 ->154	0.11391

Excited State 9: Singlet-A 3.5401 eV 350.23 nm f=0.0172 ($\pi-\pi^*$)

148 ->153	0.65149
151 ->154	0.21757

Excited State 10: Singlet-A 3.5620 eV 348.07 nm f=0.0468 ($\pi-\pi^*$)

146 ->152	0.22220
147 ->152	-0.14289
148 ->153	-0.23134
151 ->154	0.58991

Excited State 11: Singlet-A 3.6428 eV 340.35 nm f=0.0623 (LE)

146 ->152	0.59430
147 ->153	0.22847
151 ->154	-0.21206
151 ->155	-0.13275

Excited State 12: Singlet-A 3.6949 eV 335.55 nm f=0.0415 (LE)

146 ->152	-0.18642
147 ->153	0.62959
150 ->154	-0.11824
151 ->154	0.11870

Excited State 13: Singlet-A 3.8444 eV 322.51 nm f=0.0079 ($\pi-\pi^*$)

142 ->152	-0.12724
144 ->152	-0.20775
145 ->152	0.58480
146 ->153	0.16605
147 ->152	0.11354

151 ->155 -0.15534

Excited State 14: Singlet-A 3.8865 eV 319.02 nm f=0.1087 (LE)

143 ->152 0.13735

150 ->154 0.61920

151 ->156 0.17447

151 ->157 -0.12962

Excited State 15: Singlet-A 3.9002 eV 317.89 nm f=0.0137 ($\pi-\pi^*$)

142 ->152 -0.10833

143 ->152 0.27138

144 ->152 0.46671

145 ->152 0.16925

150 ->154 -0.21931

151 ->156 0.28959

Excited State 16: Singlet-A 3.9088 eV 317.20 nm f=0.0068 (CT)

142 ->152 0.15973

144 ->152 -0.14079

145 ->152 0.12077

145 ->153 -0.12404

146 ->152 0.10179

151 ->155 0.52554

151 ->156 0.16988

151 ->157 0.18702

151 ->158 0.11354

151 ->162 -0.11276

Excited State 17: Singlet-A 3.9354 eV 315.05 nm f=0.0516 ($\pi-\pi^*$)

142 ->152 -0.20600

143 ->152 -0.20396

144 ->152 0.33709

150 ->154 0.12096

151 ->156	-0.27536
151 ->157	0.33050
151 ->158	0.25876

Excited State 18: Singlet-A 3.9605 eV 313.05 nm f=0.0215 ($\pi-\pi^*$)

143 ->152	-0.10602
145 ->152	-0.19734
145 ->153	-0.22631
146 ->153	0.52164
151 ->155	-0.14669
151 ->156	0.15424
151 ->157	0.17898

Excited State 19: Singlet-A 4.0004 eV 309.93 nm f=0.0592 ($\pi-\pi^*$)

142 ->152	-0.11212
143 ->152	0.40408
144 ->152	-0.14883
145 ->152	-0.12249
146 ->153	0.18446
151 ->156	-0.15325
151 ->158	0.39503
151 ->160	-0.17898

Excited State 20: Singlet-A 4.0250 eV 308.04 nm f=0.0513 ($\pi-\pi^*$)

142 ->152	-0.13096
144 ->152	-0.18369
146 ->153	-0.28513
151 ->155	-0.25747
151 ->156	0.31858
151 ->157	0.35401
151 ->158	0.10365
151 ->160	0.14202

Excited State 21: Singlet-A 4.0610 eV 305.31 nm f=0.0540 ($\pi-\pi^*$)

142 ->152	0.29938
143 ->152	-0.19779
145 ->152	0.11528
145 ->153	0.26539
146 ->153	0.10856
149 ->154	0.10305
151 ->155	-0.15084
151 ->156	0.16017
151 ->157	-0.10916
151 ->158	0.34619
151 ->160	0.13303
151 ->162	-0.10436

Excited State 22: Singlet-A 4.0657 eV 304.95 nm f=0.0300 ($\pi-\pi^*$)

142 ->152	0.48193
143 ->152	0.12423
145 ->153	-0.17382
146 ->153	-0.12221
151 ->155	-0.17319
151 ->156	-0.14170
151 ->157	0.20951
151 ->159	-0.11747
151 ->160	-0.20842

Excited State 23: Singlet-A 4.1321 eV 300.05 nm f=0.0265 (CT)

142 ->152	0.11127
145 ->153	0.14269
149 ->154	-0.13167
151 ->157	0.13310
151 ->159	0.59191
151 ->160	-0.10796

151 ->162 0.13579

Excited State 24: Singlet-A 4.1342 eV 299.90 nm f=0.0046 ($\pi-\pi^*$)

143 ->153 0.11155

144 ->153 -0.26143

145 ->153 0.40710

146 ->153 0.10715

150 ->157 -0.13171

151 ->157 0.20875

151 ->158 -0.21823

151 ->159 -0.16809

151 ->160 -0.23960

S.3.3 Radical based mechanism in the absence of Lewis acid

Figure S3-3a. Reaction coordinates of the proposed radical mechanism in the absence of Lewis acid; the energies are relative to the starting materials. Gibbs free energies and enthalpies (in parentheses) are given in kcal mol⁻¹. (Level of theory: wB97XD/def2TZVP; CPCM(THF))^{S24}

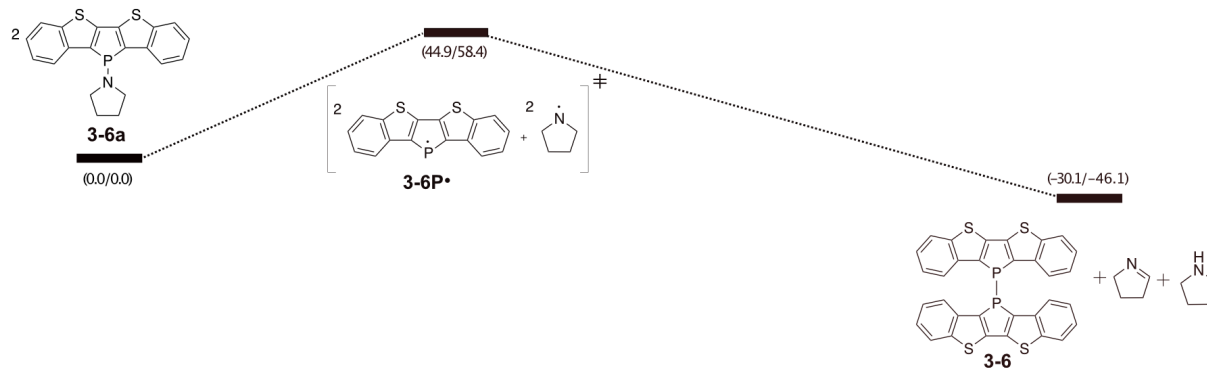
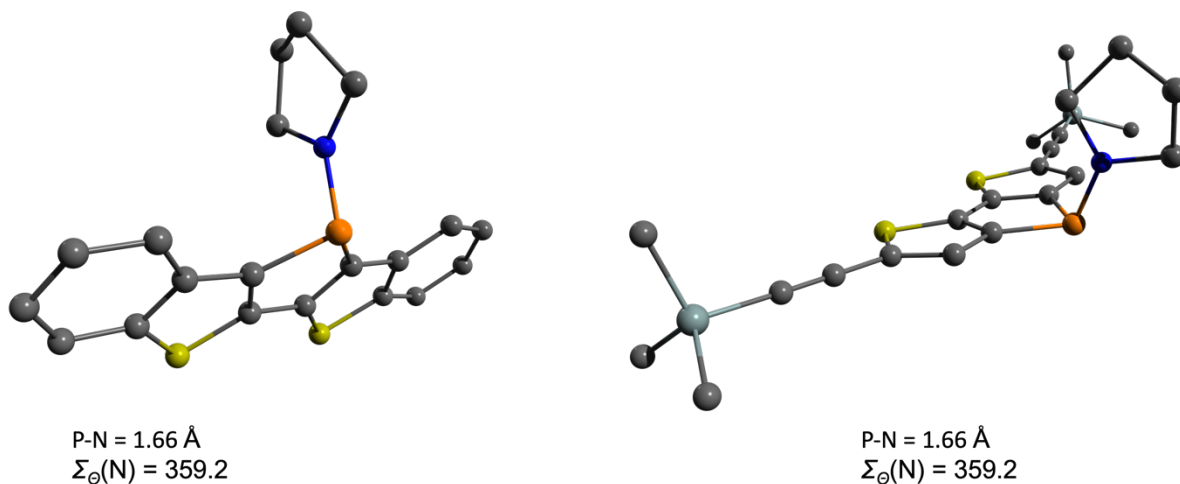


Figure S3-3b. Optimized structure of precursors **3-6a** and **3-7a**. (Level of theory: wB97XD/def2TZVP; CPCM(THF))



No significant difference in the geometry around P-center

S.3.4 Xray Crystallography

The single crystals for compounds **3-4** and **3-5** were obtained from saturated solution of dry THF by multiple cycles of heating and cooling.

Table S3-4. Crystal data for compounds **3-4** and **3-5**.

Parameters	3-4	3-5
Identification code	na_p6_2g_a_a	na_p6_1c_rep_b
Empirical formula	C ₂₈ H ₄₀ P ₂ S ₄ Si ₄	C ₄₈ H ₈₄ N ₄ P ₂ S ₄ Si ₄
Formula weight	683.14	1019.73
Temperature	173 K	173 K
Crystal system	Monoclinic	Monoclinic
Space group	P 1 21/c 1	P 1 21/c 1
a/ Å	7.2412(2)	15.4769(8)
b/ Å	27.3728(7)	27.0016(14)
c/ Å	19.1098(6)	14.8543(7)
α /°	90	90
β /°	95.1010(10)	108.276(2)
γ /°	90	90
Volume/ Å ³	3772.94(19)	5894.5(5)
Z	4	4
$\rho_{\text{calc}}/\text{cm}^3$	1.203	1.149
$\mu(\text{mm}^{-1})$	0.482	0.331

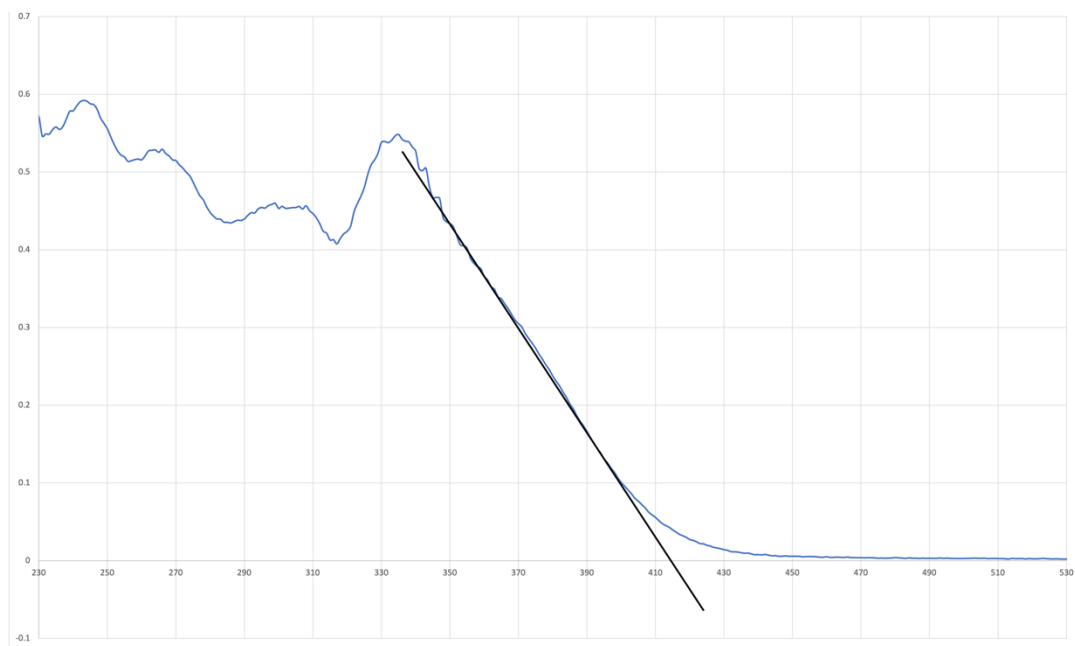
F(000)	1440	2200
Crystal size/ mm ³	0.15*0.15*0.1	0.15*0.15*0.1
Radiation	MoK α ($\lambda = 0.71073$)	MoK α ($\lambda = 0.71073$)
2 Θ range for data collection/°	33.225 to 2.266	27.582 to 2.048
Index ranges	-11 $\leq$ h $\leq$ 11 -42 $\leq$ k $\leq$ 42 -29 $\leq$ l $\leq$ 29	-20 $\leq$ h $\leq$ 20 -35 $\leq$ k $\leq$ 35 -19 $\leq$ l $\leq$ 19
Reflections collected	161056	113261
Independent reflections	14470	13601
Data/restraints/ parameters	11159/0/355	10800/0/583
Goodness-of-fit on F ²	1.076	1.179
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.0885 wR ₂ = 0.1979	R ₁ = 0.1431 wR ₂ = 0.2985
Final R indexes [all data]	R ₁ = 0.0671 wR ₂ = 0.1806	R ₁ = 0.1220 wR ₂ = 0.2884
Largest diff. peak/hole Å ⁻³	3.259/ -0.622	1.830/ -0.654
CCDC number	----	----

S.3.5 Photophysical properties

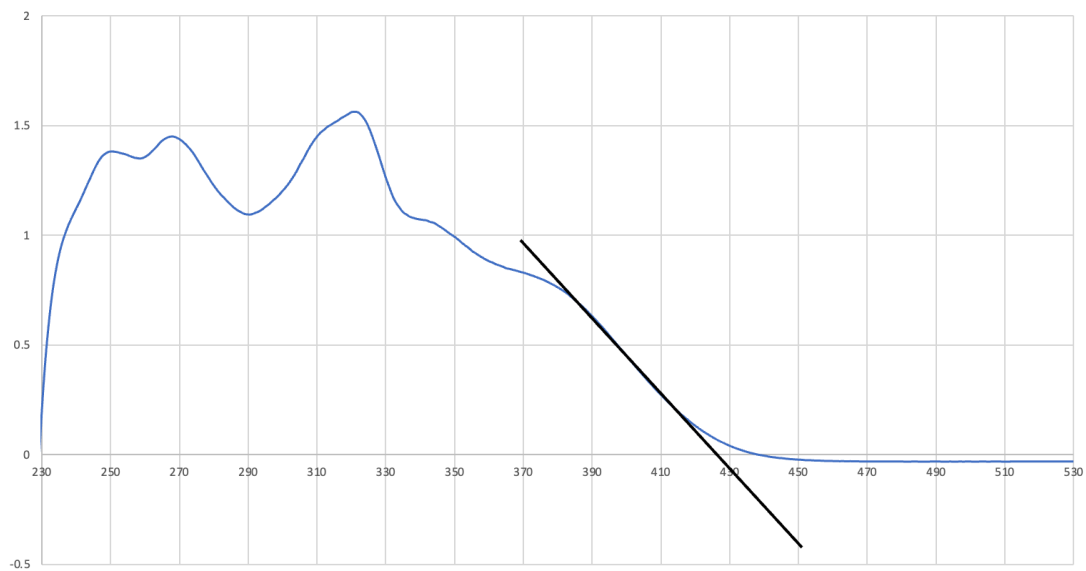
(i) Absorption onset determination

Figure S3-4. Determination of Absorption onset using absorption spectrum.

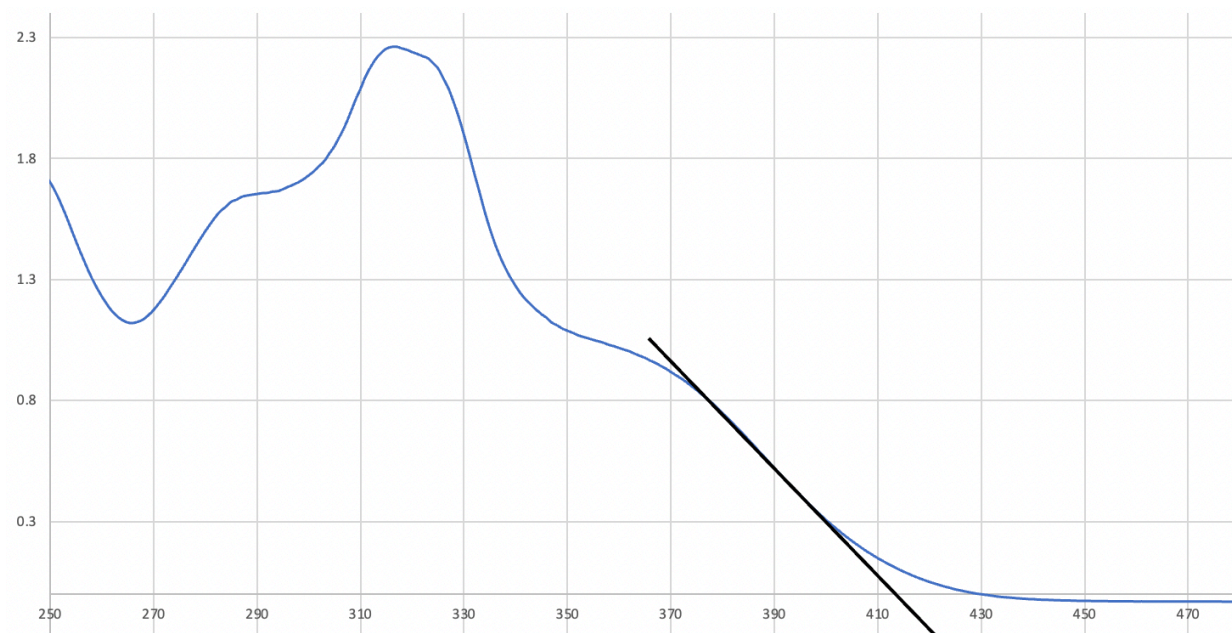
a) Compound **3-2**



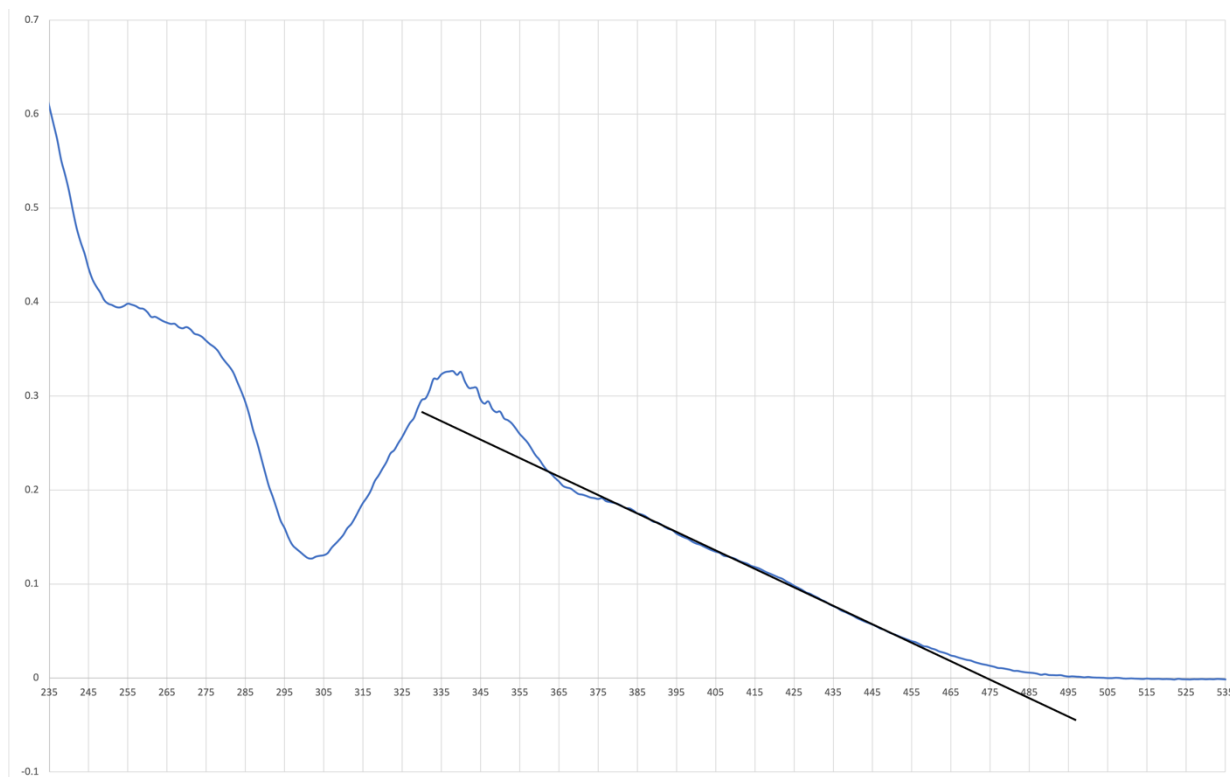
b) Compound **3-4**



c) Compound 3-5



d) Compound 3-6



(ii) Emission and Lifetime

Table S3-5. Excitation and Emission wavelength of bi(dithienophosphole)s in their solutions state. The corresponding quantum yield (QY) and lifetimes are also given.

Compounds	$\lambda_{\text{ex}}^{\text{b}}$ (nm)	λ_{em} (nm)	FWHM (nm)	QY (%)	τ (ns)
3-2	247, 357	470	95	2.4, 4.4	0.5 (10%) 5 (10%) 17 (80%)
3-4	250, 300, 360	453	87	5.3, 16	-----
3-5	264, 356	457	99	4, 3.8	-----
3-6	261, 346, 399	507	114	8.2, 8.4, 30	4.11 (17.6%) 11 (82.4%)

S.3.6 Electrochemical properties

None of these derivatives shows any reversible redox properties, as determined by cyclic voltammetry, but were found to electro-polymerize on the electrode instead. The cyclic voltammetry of compound **3-4** is given below in the figure S3-5.

Figure S3-5. Cyclic voltammetry of **3-4** in THF

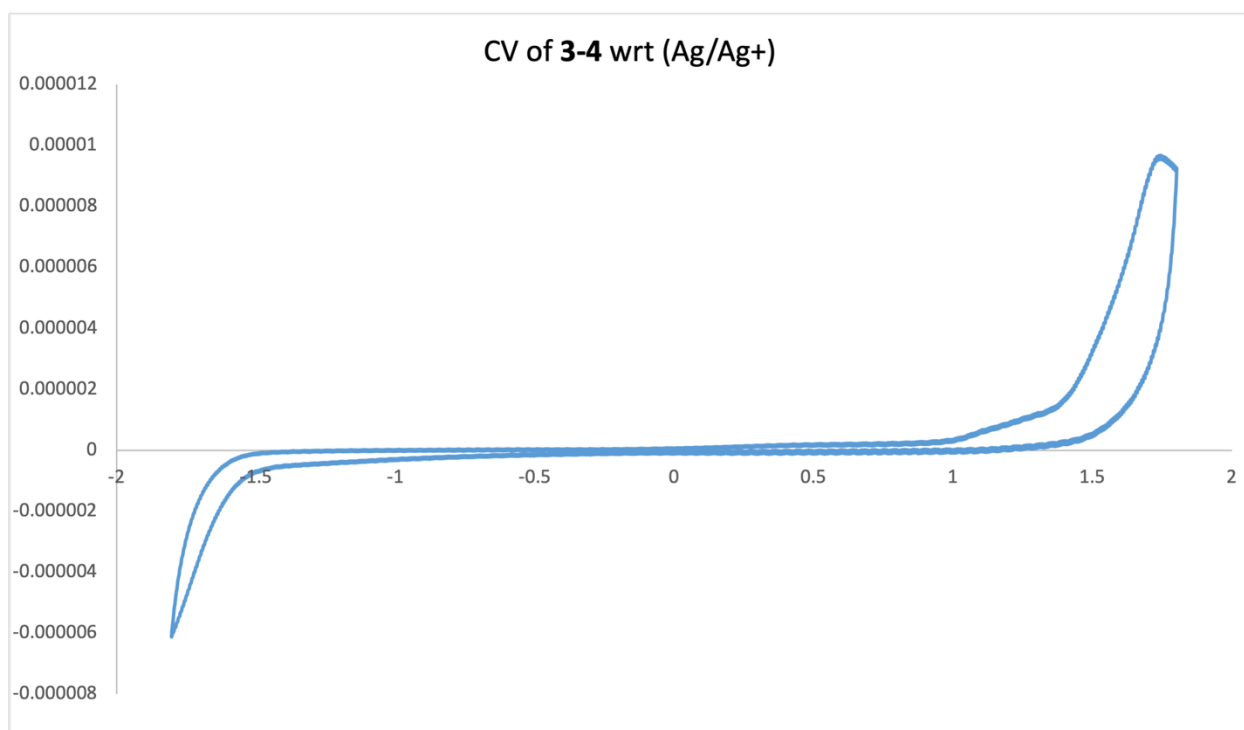
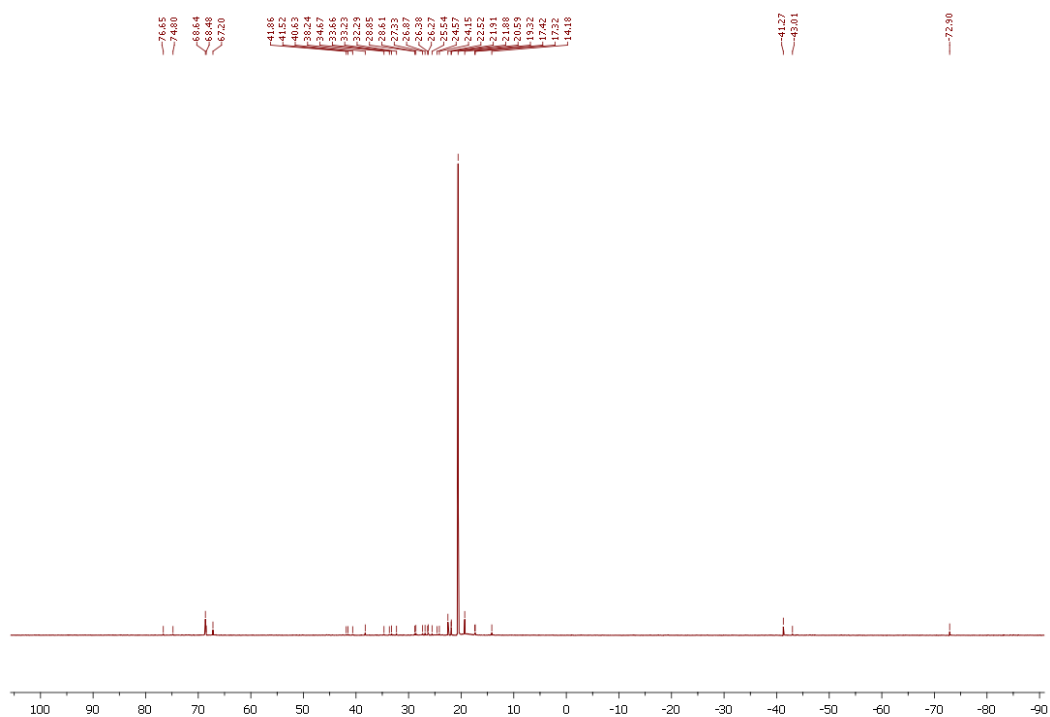
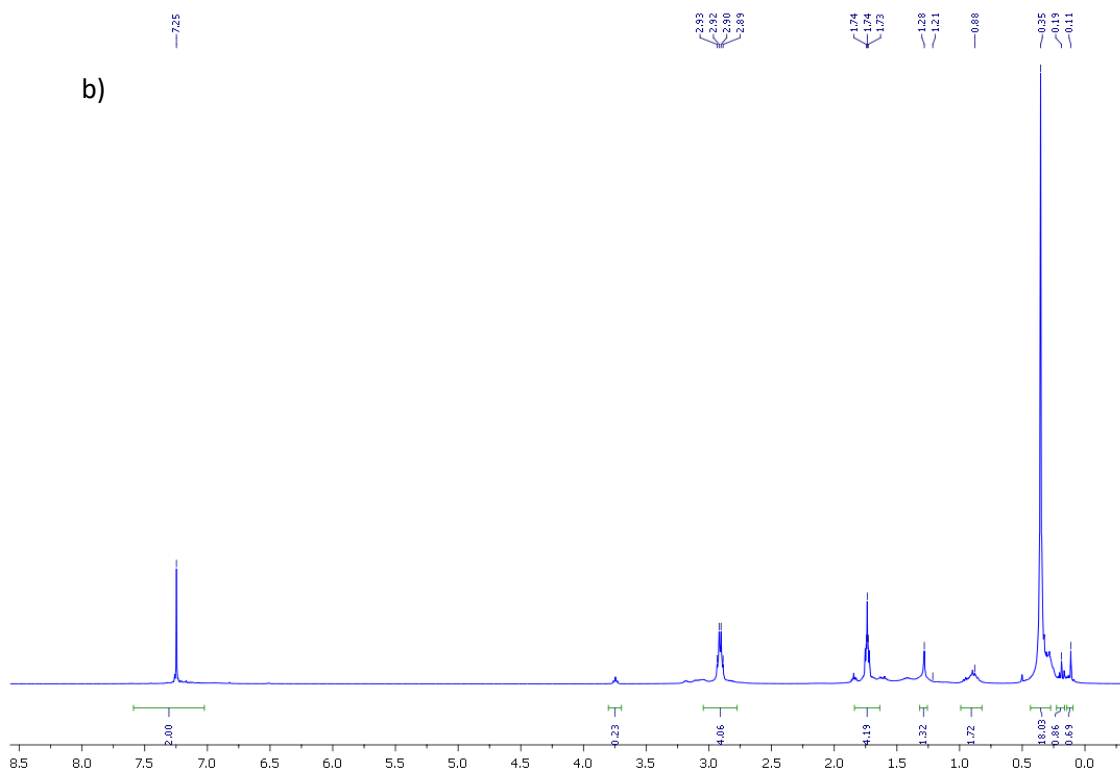


Figure S3-6. a) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, CDCl_3), b) ^1H NMR spectrum (400 MHz, CDCl_3), and c) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100.6 MHz, CDCl_3) for compound **3-4a**.

a)



b)



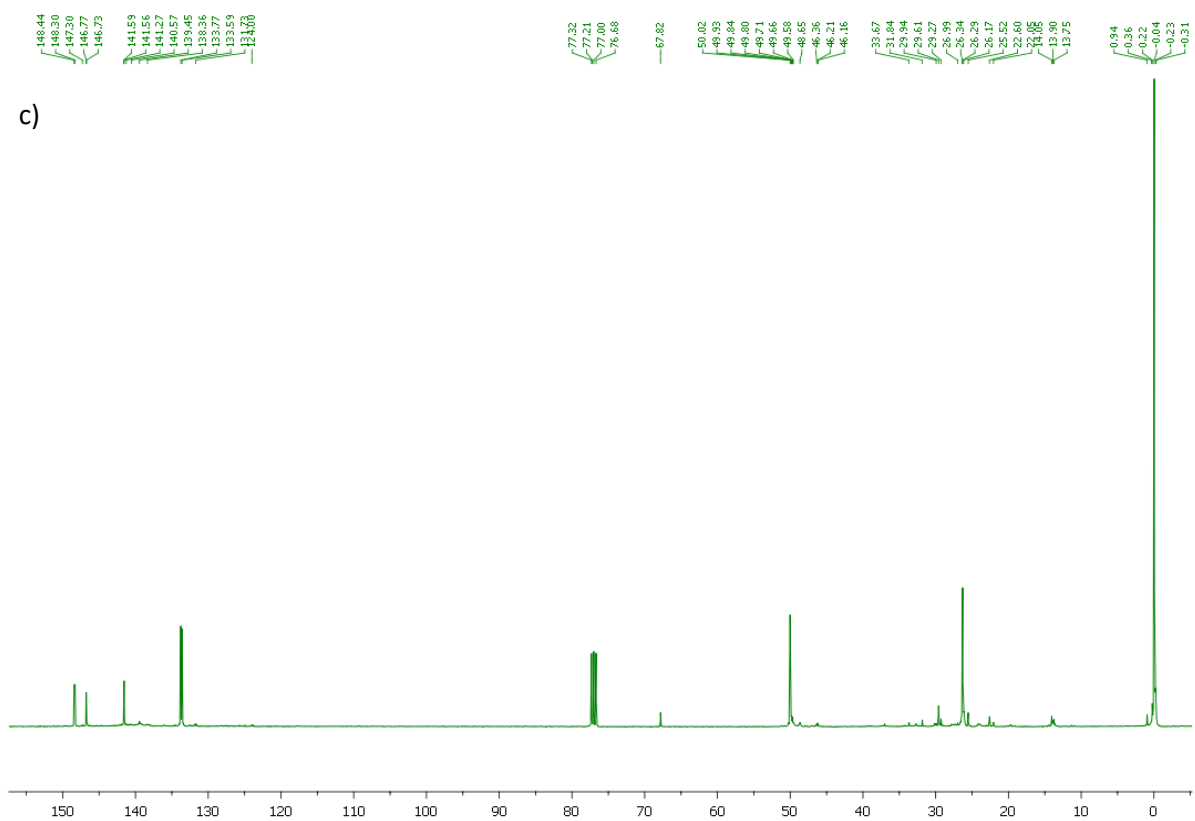
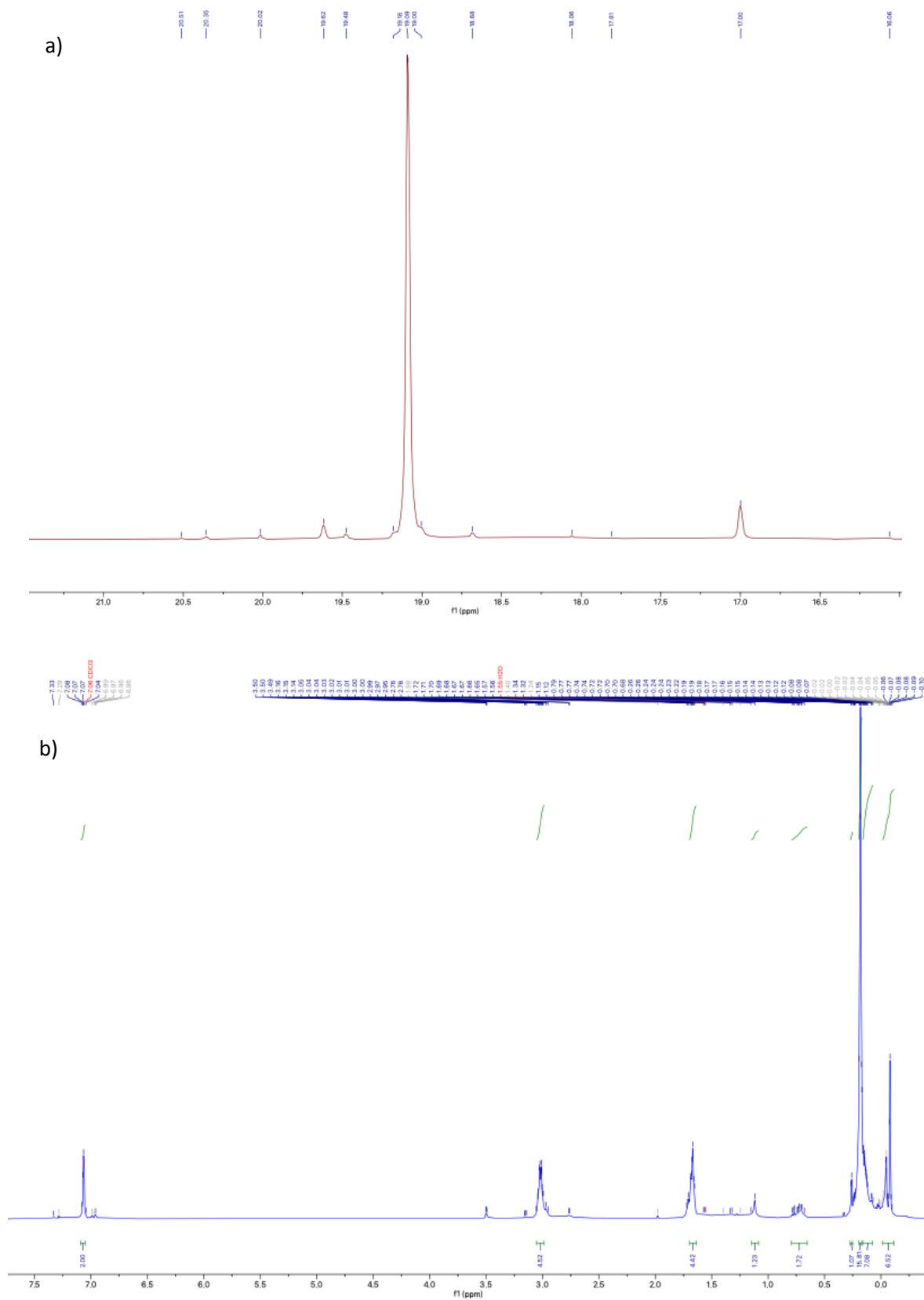


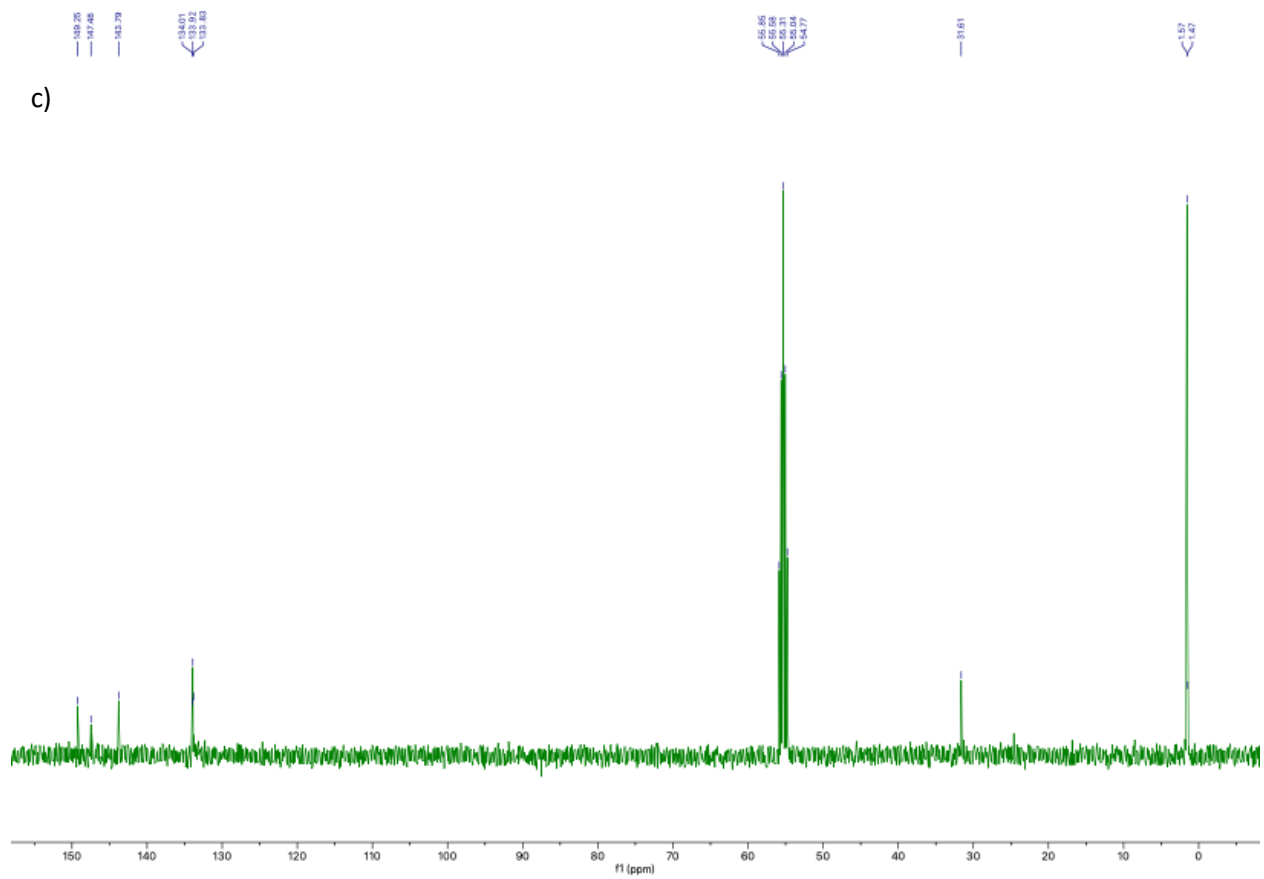
Figure S3-7 a) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, CDCl_3), and b) ^1H NMR spectrum (400 MHz, CDCl_3) for compound **3-4a-O**.



a)

1H NMR spectrum (CDCl₃) showing peaks at approximately 3.4 ppm (triplet, integration 2.00) and 4.0 ppm (quartet, integration 2.00). The x-axis is labeled f1 (ppm) and ranges from 55 to -90. A list of chemical shifts (ppm) is provided at the top: 3.45, 3.40, 3.35, 3.30, 3.25, 3.20, 3.15, 3.10, 3.05, 3.00, 2.95, 2.90, 2.85, 2.80, 2.75, 2.70, 2.65, 2.60, 2.55, 2.50, 2.45, 2.40, 2.35, 2.30, 2.25, 2.20, 2.15, 2.10, 2.05, 2.00, 1.95, 1.90, 1.85, 1.80, 1.75, 1.70, 1.65, 1.60, 1.55, 1.50, 1.45, 1.40, 1.35, 1.30, 1.25, 1.20, 1.15, 1.10, 1.05, 1.00, 0.95, 0.90, 0.85, 0.80, 0.75, 0.70, 0.65, 0.60, 0.55, 0.50, 0.45, 0.40, 0.35, 0.30, 0.25, 0.20, 0.15, 0.10, 0.05, 0.00, -0.05, -0.10, -0.15, -0.20, -0.25, -0.30, -0.35, -0.40, -0.45, -0.50, -0.55, -0.60, -0.65, -0.70, -0.75, -0.80, -0.85, -0.90.





Mass spectrum of compound 10. The x-axis represents the mass-to-charge ratio (m/z) from 0 to 200, and the y-axis represents relative intensity from 0 to 100. The base peak is at m/z 26.17. Other significant peaks are labeled with their m/z values.

m/z	Relative Intensity (%)
61.60	~10
60.22	~10
60.13	~10
59.99	~10
58.92	~10
58.41	~10
26.17	100
26.07	~10
24.83	~10
24.66	~10
20.56	~10
16.48	~10
13.90	~10
7.12	~10
32.95	~10
56.13	~10
56.73	~10
57.48	~10



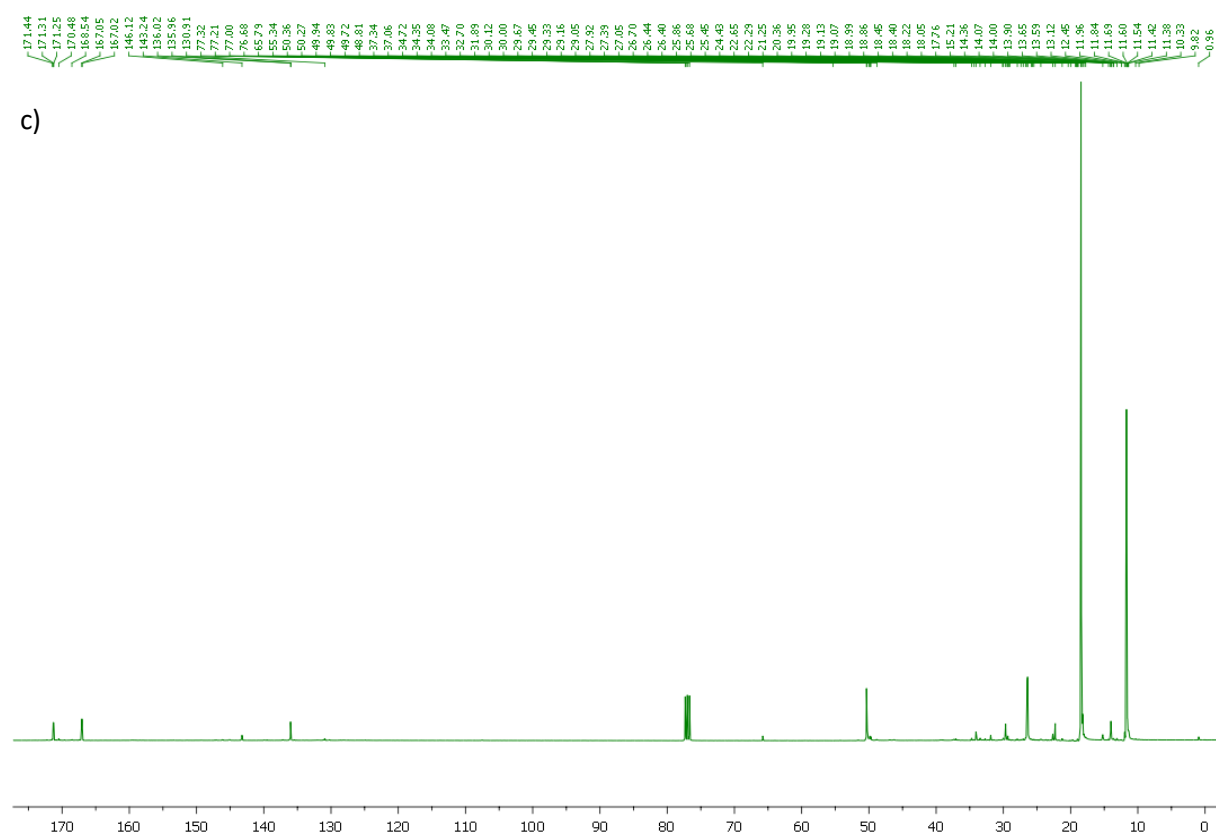


Figure S3-10. a) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, CDCl_3), b) ^1H NMR spectrum (700 MHz, CDCl_3), c) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (175 MHz, CDCl_3) for compound **3-5**.

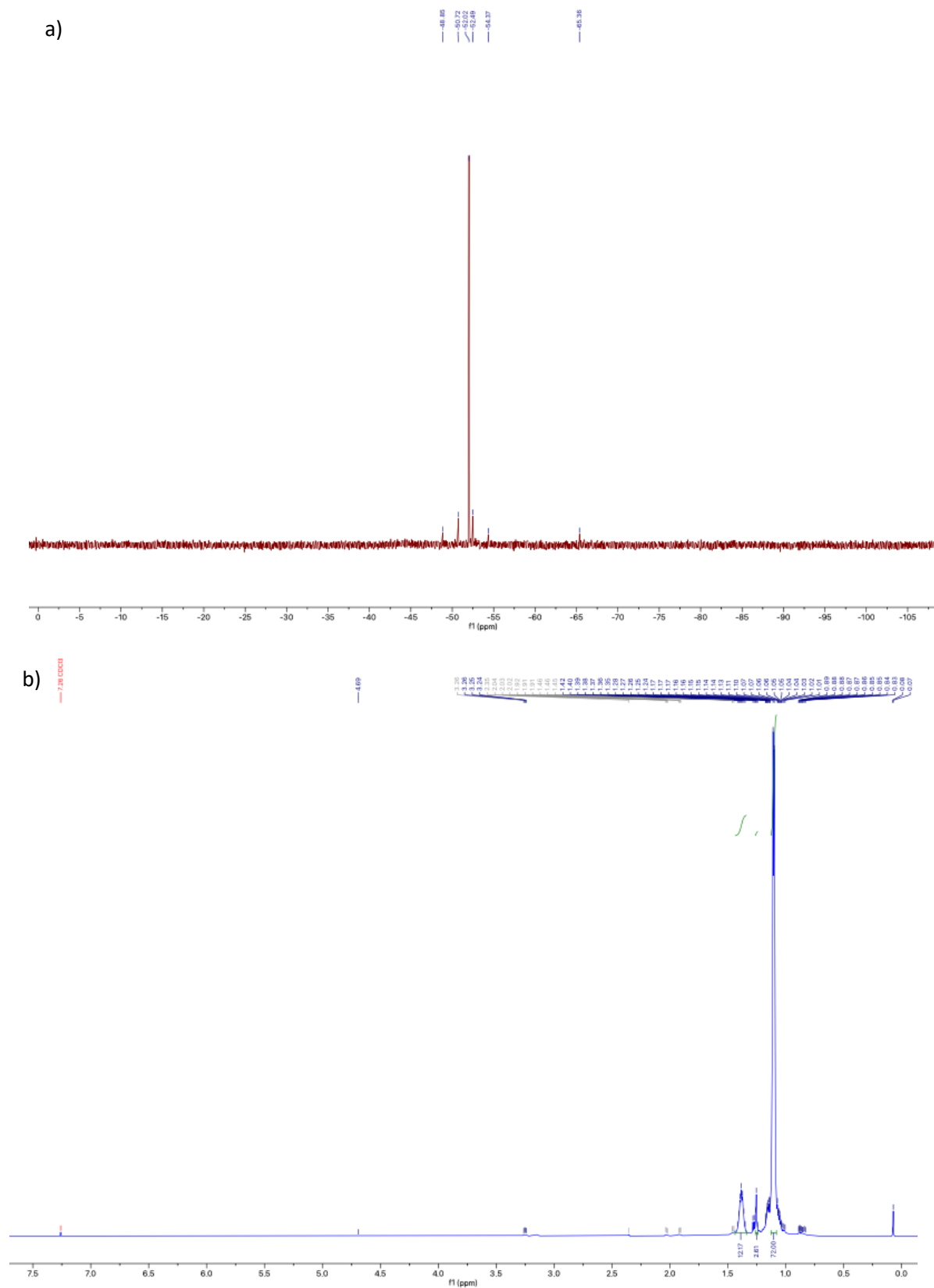
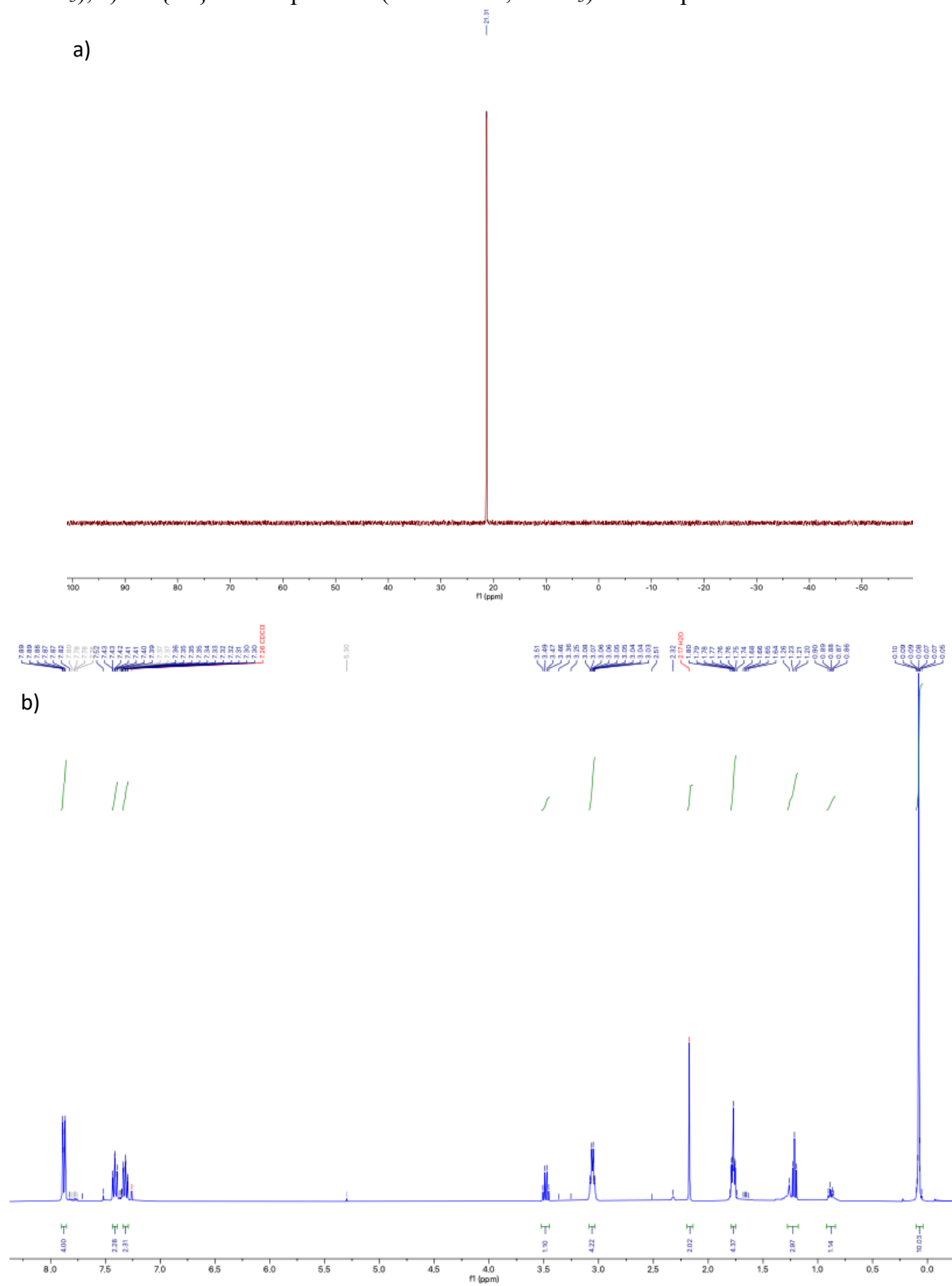


Figure S3-11. a) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, CDCl_3), b) ^1H NMR spectrum (400 MHz, CDCl_3), c) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100.6 MHz, CDCl_3) for compound **3-6a**.



c)

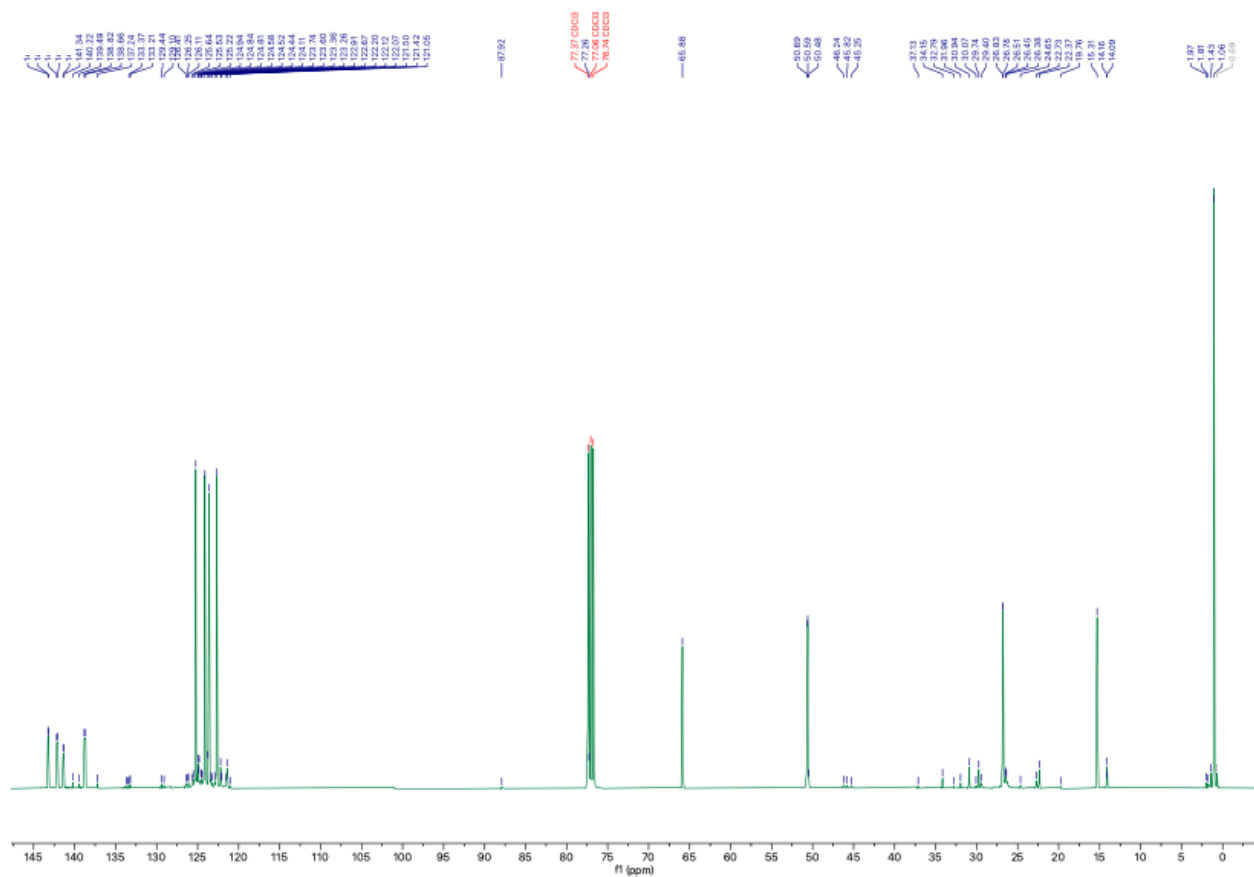
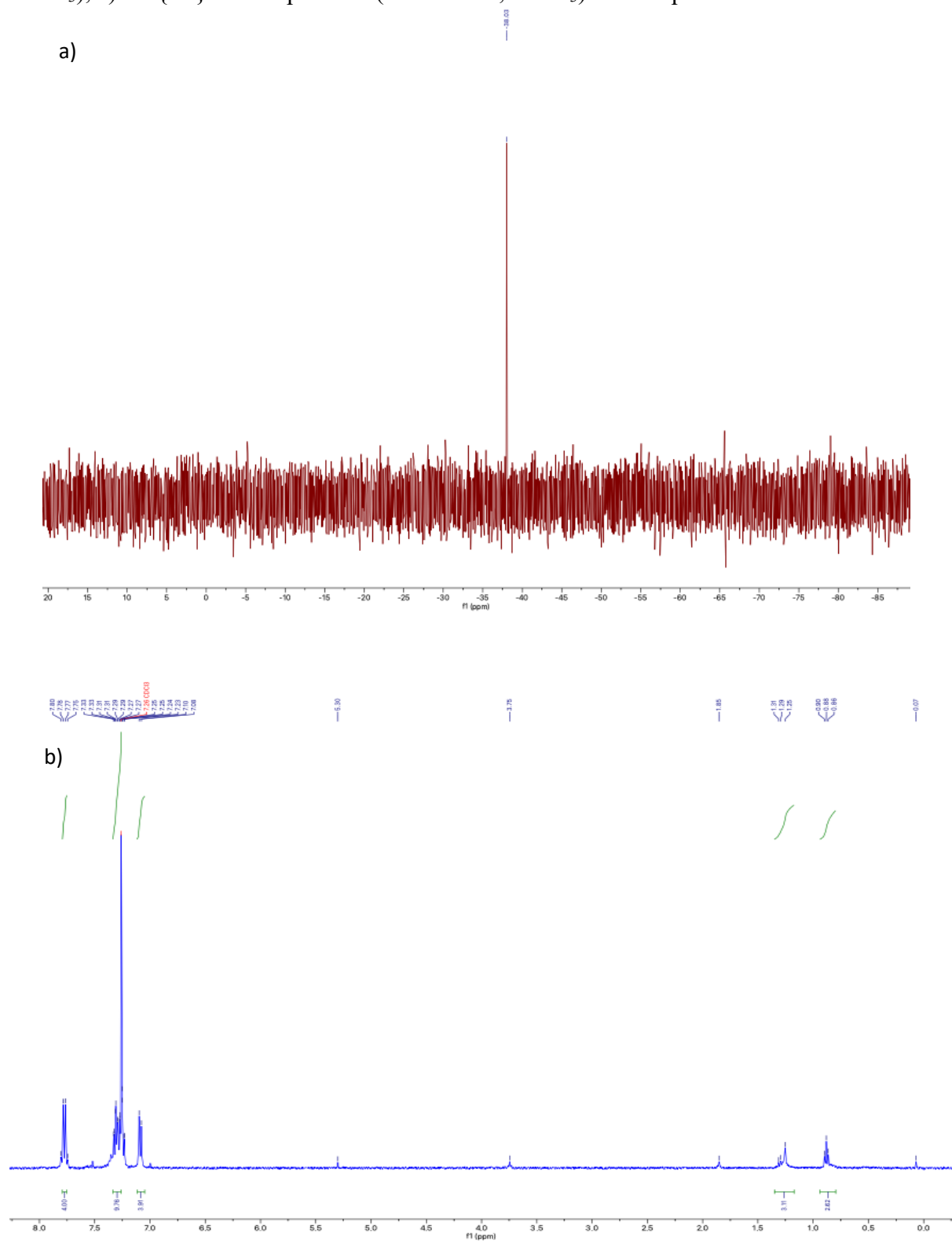
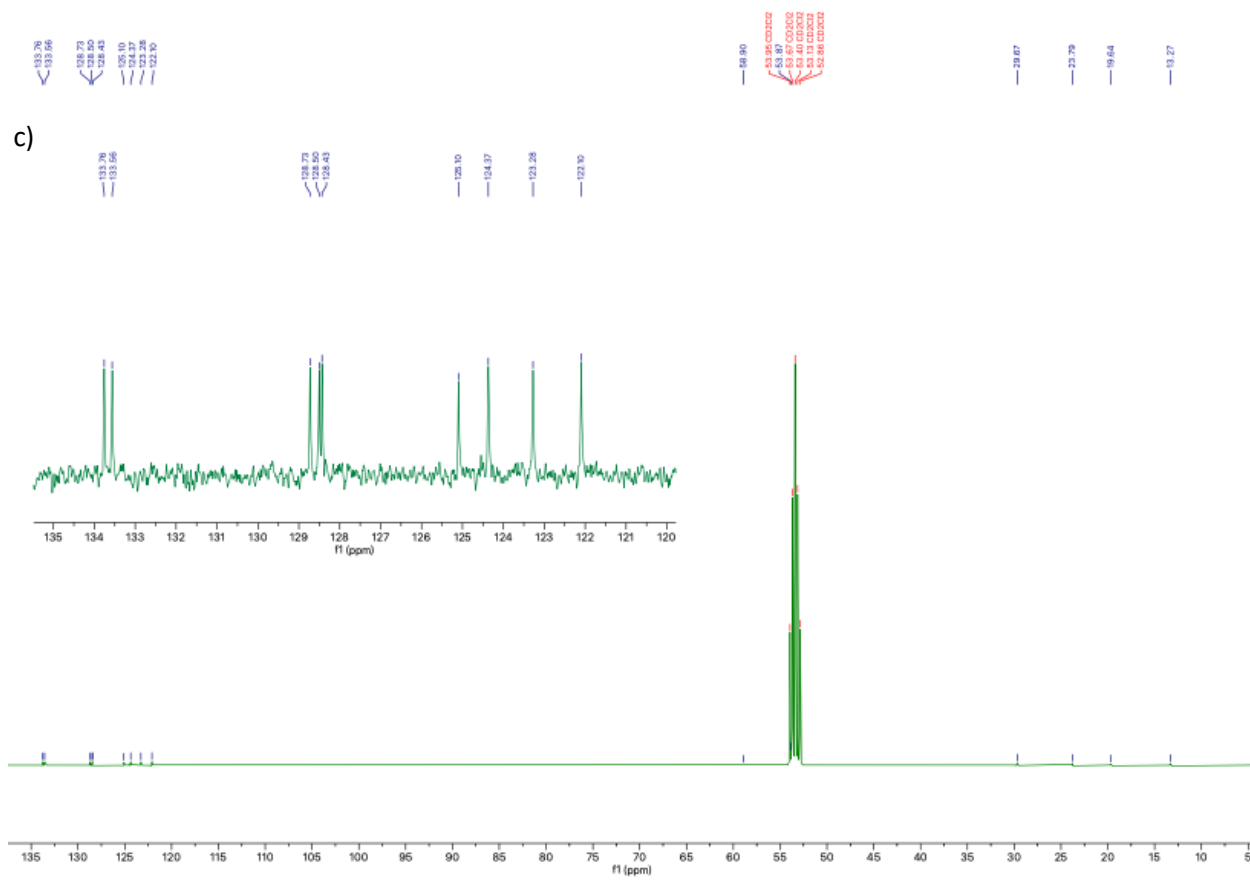


Figure S3-12. a) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, CDCl_3), b) ^1H NMR spectrum (400 MHz, CDCl_3), c) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100.6 MHz, CDCl_3) for compound **3-6**.





CHAPTER FOUR: UNLOCKING VERSATILE TRANSFER AGENTS: SYNTHESIS AND REACTIVITY OF DITHIENO-PHOSPHOLIDE FOR P- C AND P-P BOND FORMATION

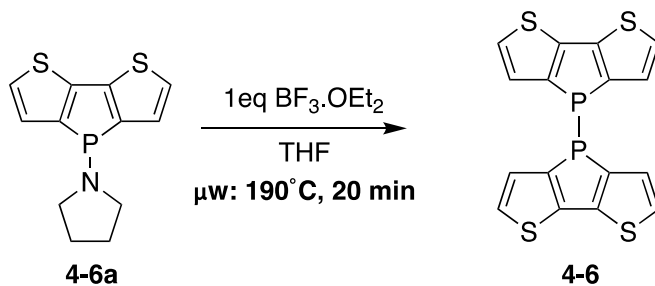
Chemical and experimental details

Materials and Methods: All reagents were purchased from Sigma Aldrich and Oakwood Chemical. All solvents were purchased from Sigma Aldrich and Fisher chemical. SPS grade solvents (MBraun) from Sigma Aldrich were used for synthesis and characterisations.

Nuclear Magnetic Resonance (NMR): ^1H , $^{31}\text{P}\{^1\text{H}\}$, $^{19}\text{F}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$ spectra were acquired on Bruker NEO 700, 600, 400 and 300 NMR spectrometers on a 5mm ATM probe using TOPSPIN software version 4.0.8. Chemical shifts are reported in parts per million (ppm). Multiplicities are reported as: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), multiplet (m), quartet (q), and broad (br).

S4.1 Synthesis and NMR Characterizations

(i) *Bi(dithienophosphole)* 4-6



Compound **4-6a** was synthesized according to the literature. About 3.51g of **4-6a** was dissolved in 10 ml of dry THF. One equivalent of BF_3 was added to the solution and the solution was reacted in a microwave reactor at 190°C for 20 minutes. The solution was passed through a silica plug under argon. The solution was dried to yield a yellow solid at 10% yield (0.5g). The NMR data corresponded to the reported values in ref. S.21.

(i) *Synthesis of dithienophospholide from sodium metal:*

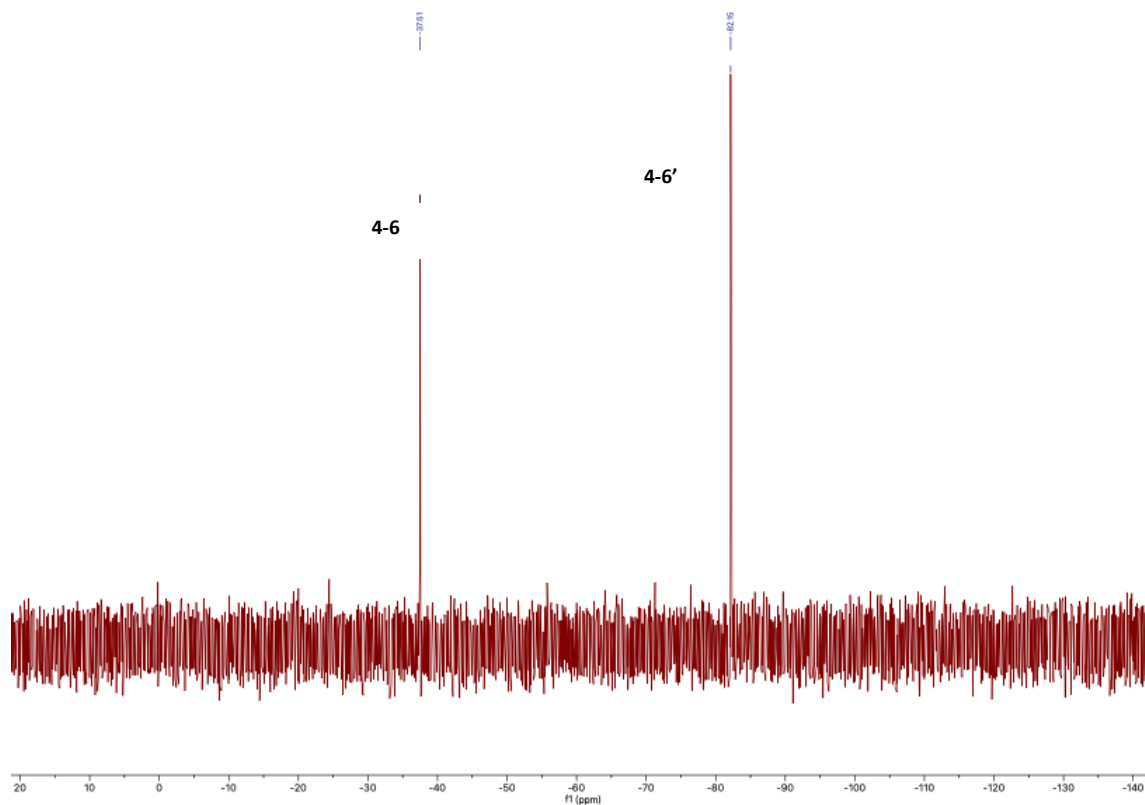


Figure S4-1a. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, Toluene) of the solution in Scheme 4-3b showing the formation of **4-6'**.

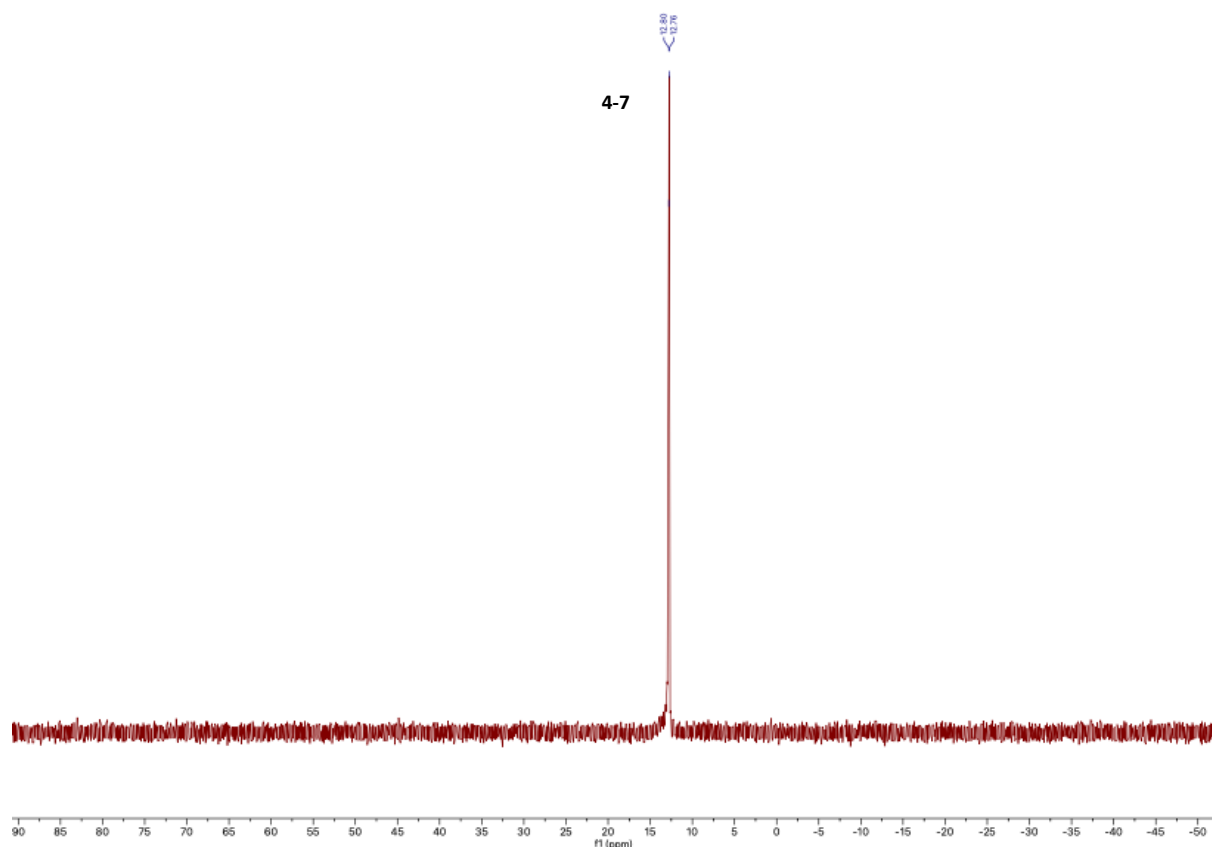


Figure S4-1b. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, THF) of the solution in Scheme 4-3c showing the formation of **4-7**.

By microwave reactor: Compound **4-6** (0.27g, 0.7 mmol) was dissolved in 15 ml of dry THF, and an excess piece of sodium metal was added to the solution. The mixture was reacted in a microwave reactor at 190°C for 30 minutes, resulting in a green colour solution with a black precipitate. The solution was stirred overnight, yielding a brown solution with excess metal. The reaction mixture exhibited complete conversion of starting material to **4-6**. $^{31}\text{P}\{^1\text{H}\}$ (162 MHz, THF): δ 12.3 ppm. Attempts to isolate the product from the suspension of excess fine sodium metal particles using various filtration and chromatographic techniques under argon were unsuccessful, leading to the decomposition of the anion.

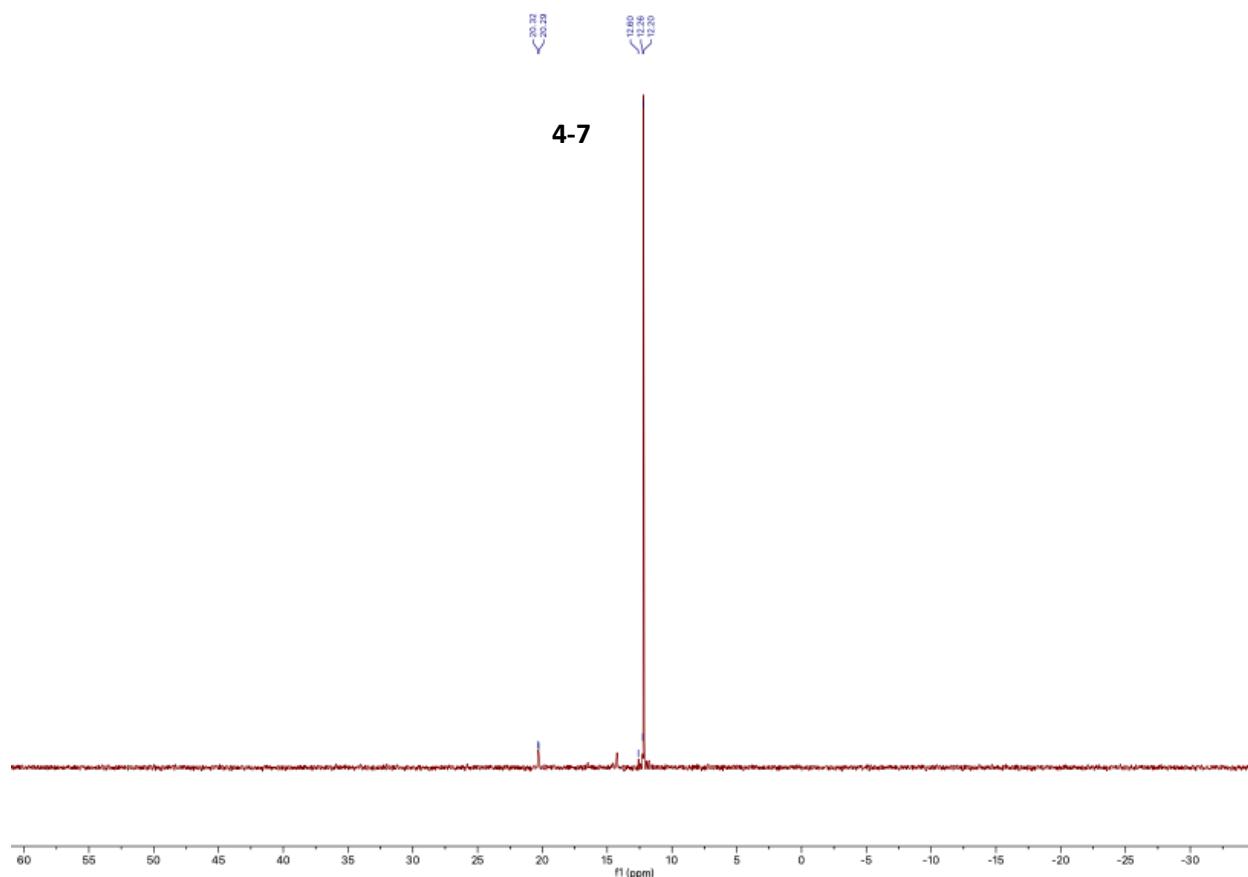


Figure S4-1c. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, THF) of the solution in Scheme 4-4 showing the formation of **4-7**.

(iii) Synthesis of dithienophospholide from sodium naphthalenide:

Naphthalene (0.012g, 1 μmol ; 2 equiv.) was dissolved in 8 ml of dry THF. Following this, a small excess piece of sodium metal was introduced into the solution. The mixture was left to stir under an argon atmosphere, and within ten minutes of introducing the metal, the color of the solution transitioned from colorless to a deep green, confirming the successful formation of sodium naphthalenide [Na^+naph^-]. Stirring of the reaction mixture continued for two hours to ensure the complete reaction of the naphthalene. Subsequently, the sodium metal fragments were carefully

extracted from the solution using tweezers. Continuing the procedure, one equivalents of **4-6** (0.5 μmol , 0.018g) was introduced directly into the solution while stirring. $^{31}\text{P}\{^1\text{H}\}$ (162 MHz, THF): δ 14.8 ppm.

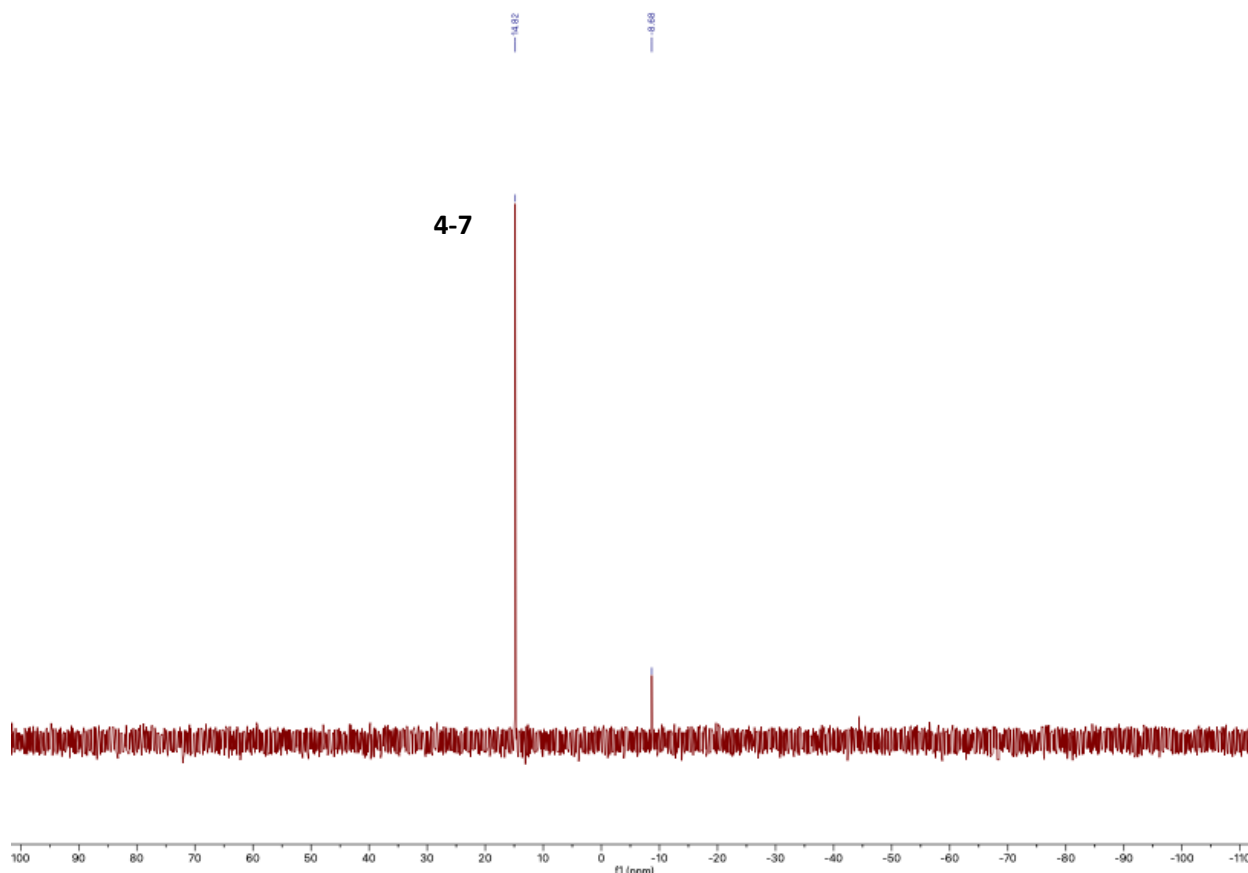


Figure S4-1d. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, THF) of the solution in Scheme 4-5 showing the formation of **4-7**.

(iv) Carbon functionalization of dithienophospholide anion:

Synthesis of 4-8: Naphthalene (0.028g, 0.2 mmol) was dissolved in dry THF (5 ml) and a small piece of sodium metal was added to this solution. The solution was stirred for two hours to yield $[\text{Na}^+\text{naph}^-]$. The excess unreacted sodium was removed with a spatula and 0.1 mmol (0.043g) of **4-6** was directly added to this solution with stirring. The solution colour changed to brown immediately. After stirring for ten minutes, one equivalent (0.2 mmol, 0.037 g) of benzyl bromide

was introduced directly into the reaction mixture under an argon atmosphere with continuous stirring. (Scheme 4-7) Within a mere two minutes of this addition, the solution's brown hue shifted to a pale-yellow translucent appearance. The mixture was stirred for 30 minutes and was meticulously passed through an alumina plug under argon, yielding pure **4-8** at 85% yield (0.051g). $^{31}\text{P}\{^1\text{H}\}$ (162 MHz, THF): δ -19.6 ppm. ^1H NMR (400 MHz, CDCl_3 : δ 7.22 (m, 5H), 7.01 (d, $^3J_{\text{H-H}} \sim 4\text{Hz}$, 4H), 3.15 (s, 2H). residual solvent identified.

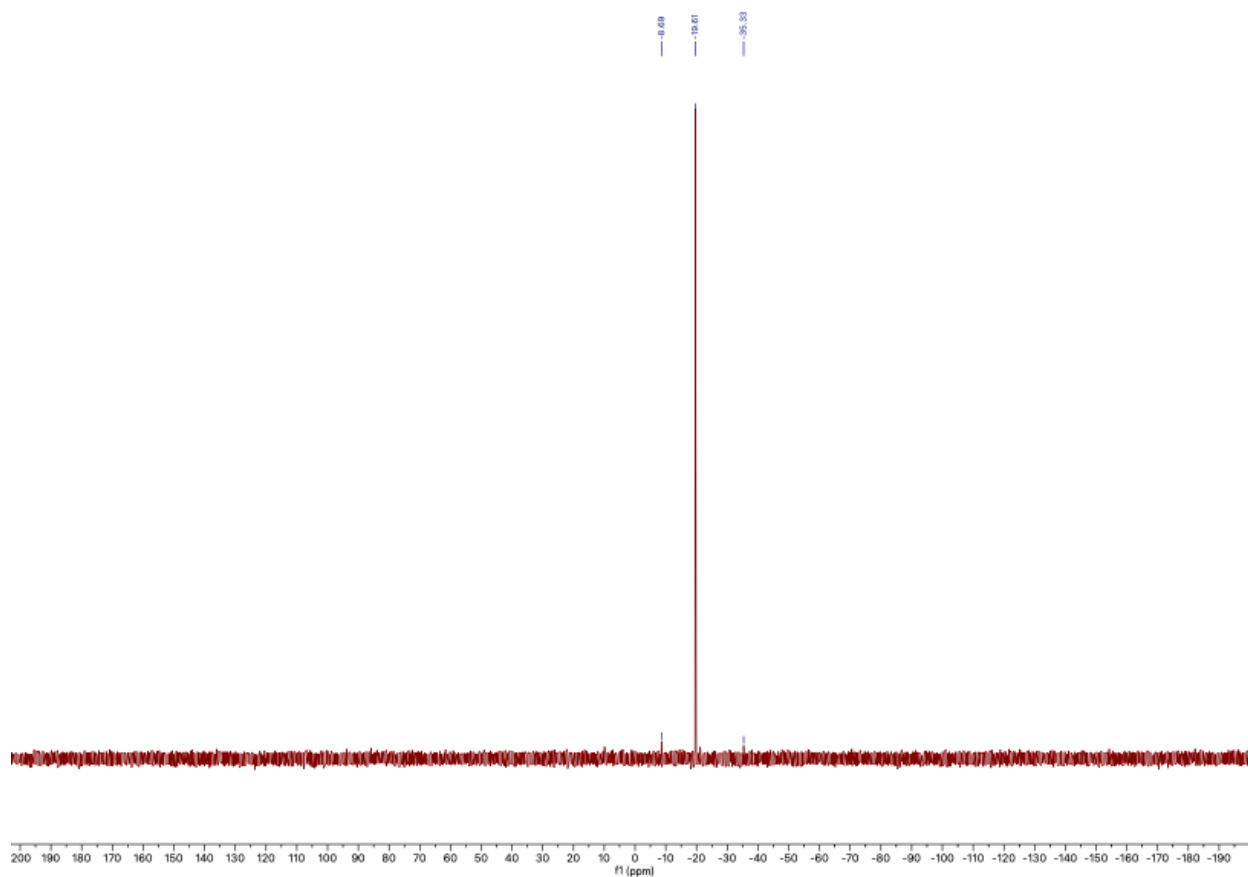


Figure S4-1e. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, THF) of the solution in Scheme 4-6 showing the formation of **4-8**.

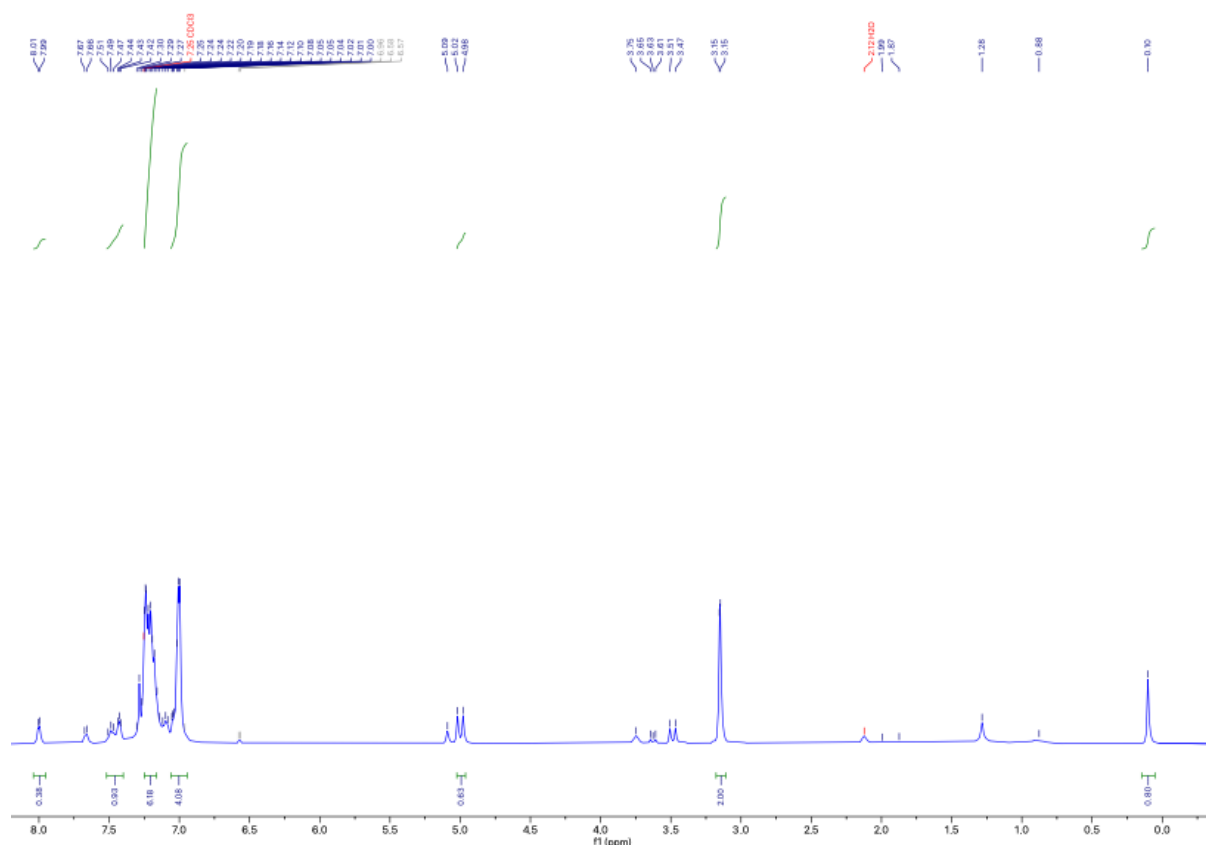


Figure S4-1f. ^1H NMR spectrum (400 MHz, CDCl_3) of **4-8**.

Synthesis of 4-9: Naphthalene (0.026g, 0.2 mmol) was dissolved in dry THF (5 ml) and a small piece of sodium metal was added to this solution. The solution was stirred for two hours to yield $[\text{Na}^+\text{naph}^-]$. The excess unreacted sodium was removed with a spatula and 0.1 mmol (0.039g) of **4-6** was directly added to this solution with stirring. The solution colour changed to brown immediately. After stirring for ten minutes, half an equivalence (0.05 mmol, 0.017 g) of carbon tetrabromide (CBr_4) was introduced directly into the reaction mixture under an argon atmosphere with continuous stirring. (Scheme 4-7) The solution's brown hue intensified with in 3 minutes of addition. The $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectra of the reaction mixture do not show peaks

corresponding to the anticipated product, **4-9**, but rather shows **4-6** as the major product. We anticipate that CBr_4 could react with **4-7** through the following reaction towards formation of **4-6**.

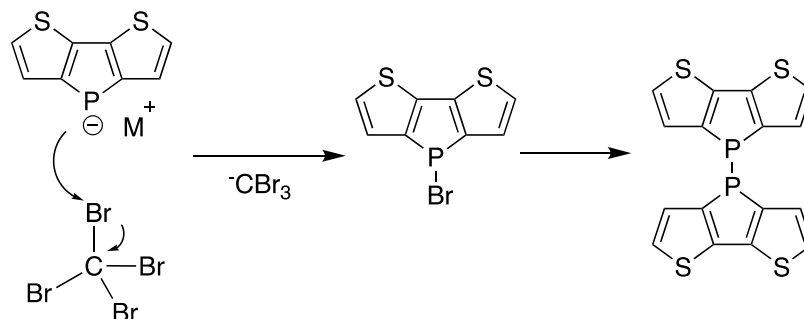


Figure S4-1g. Anticipated reaction of CBr_4 with **4-7**.

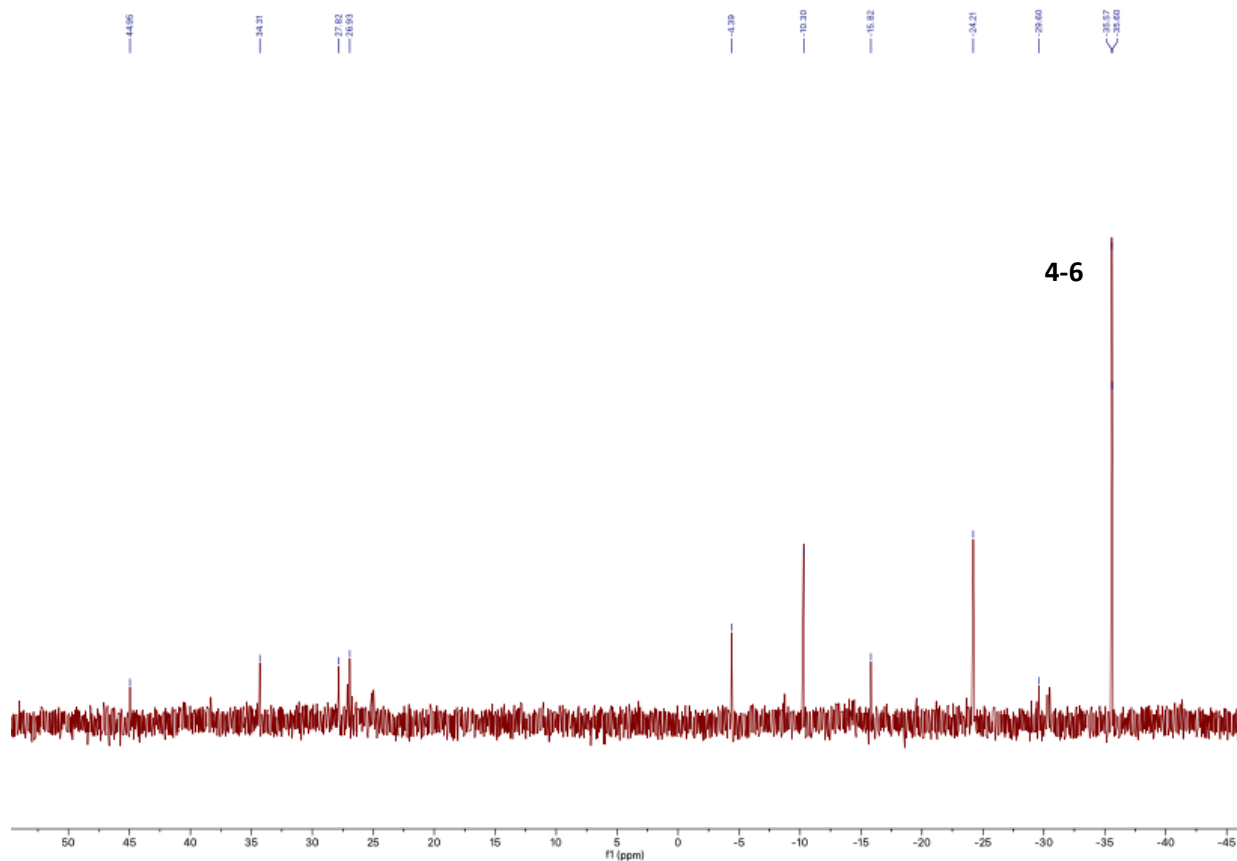


Figure S4-1h. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, THF) spectrum of the solution in scheme 4-7 showing the formation of **4-6** rather than **4-9**.

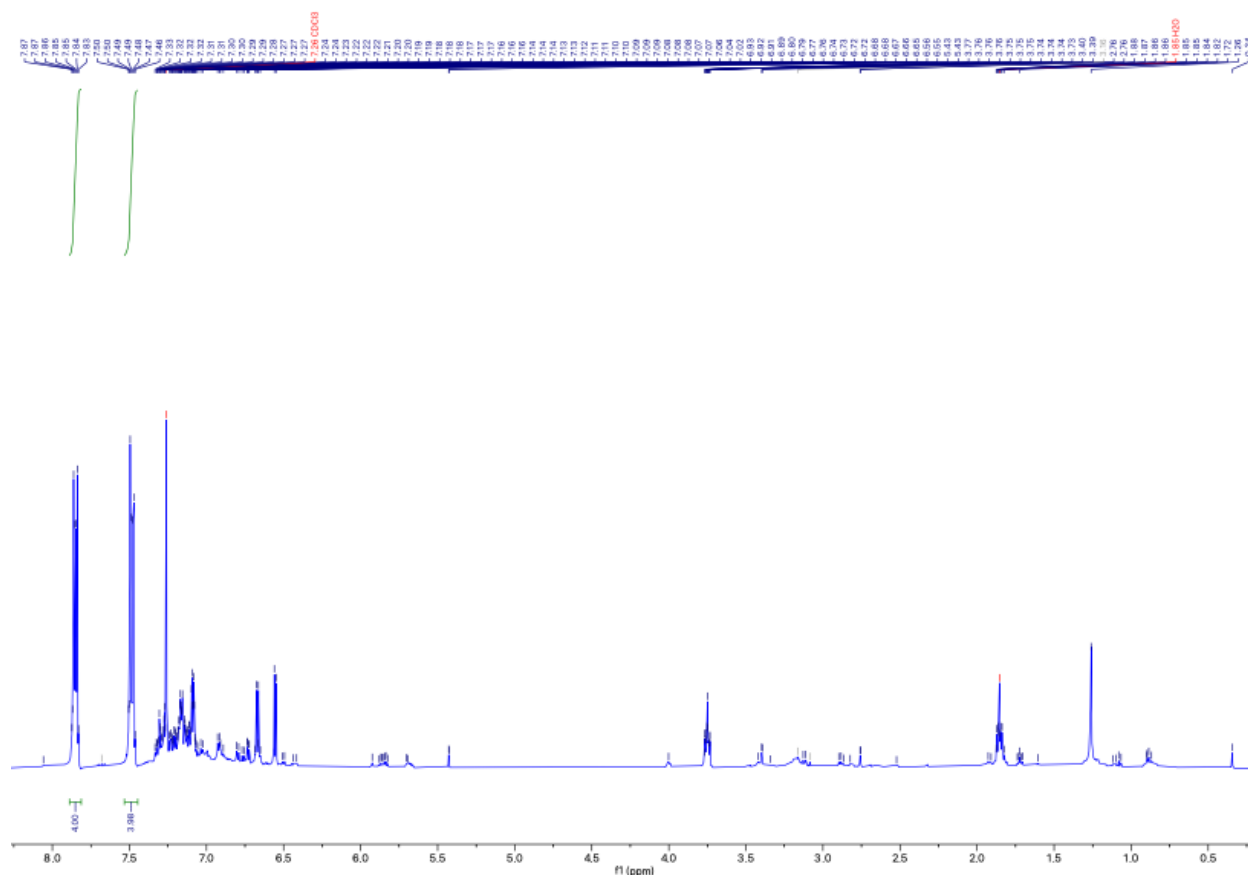


Figure S4-1i. ^1H NMR (400 MHz, THF) spectrum showing the formation of **4-6** rather than **4-9**.

(v) Phosphorus functionalization of dithienophospholide anion:

Synthesis of 4-10:

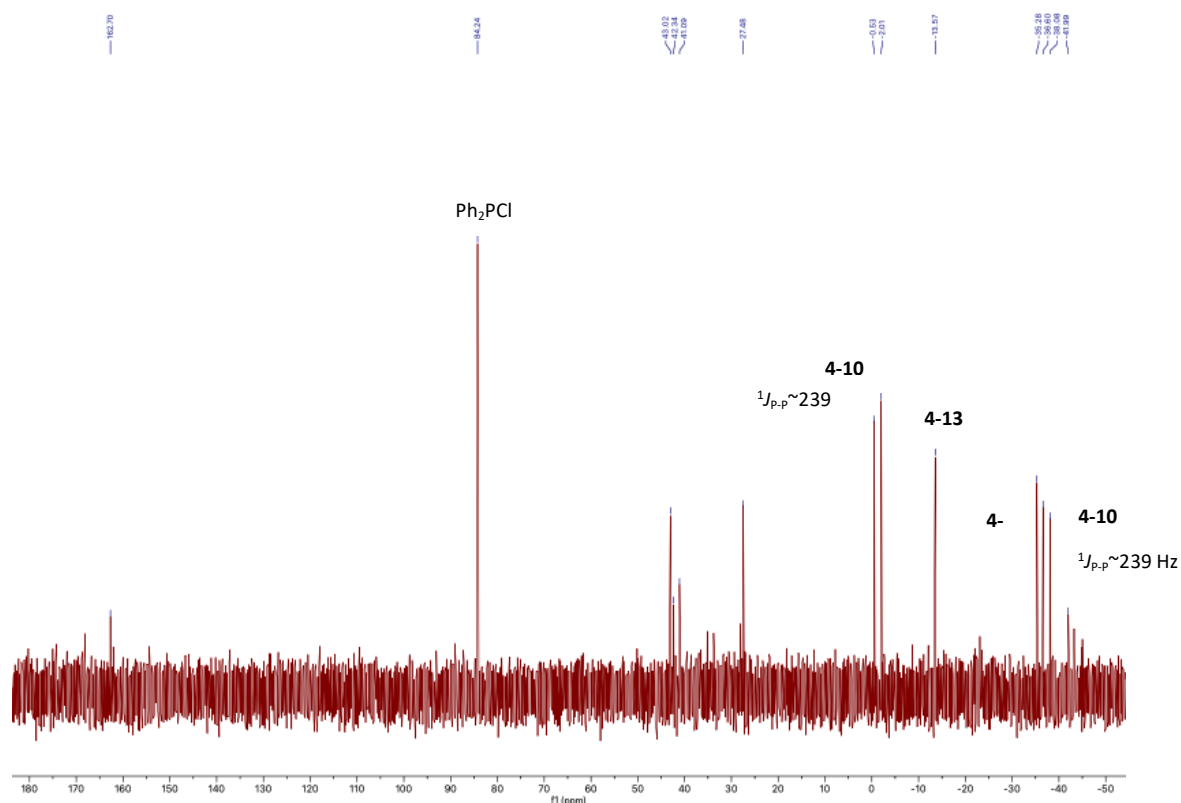
a) By microwave reaction: Compound **4-6** (0.1 g, 0.3 mmol) was dissolved in 6 ml of dry THF, and an excess piece of sodium metal was added to the solution. The mixture was reacted in a microwave reactor at 190°C for 30 minutes and was stirred overnight under argon to yielding a brown solution with excess metal. Two equivalences of Ph_2PCl (0.5 mmol, 0.12g) was added with stirring. The solution colour immediately transformed to pale yellow, displaying a distinct bright

greenish-blue fluorescence. A $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture was obtained within 15 minutes, revealing a mixture of products, with **4-13** being the major product.

b) Using sodium naphthalenide: Naphthalene (0.018g, 0.1 mmol) was dissolved in dry THF (5 ml) and a small piece of sodium metal was added to this solution. The solution was stirred for two hours to yield $[\text{Na}^+\text{naph}^-]$. The excess unreacted sodium was removed with a spatula and 0.07 mmol (0.027g) of **4-6** was directly added to this solution with stirring. The solution colour changed to brown immediately. After stirring for ten minutes, two equivalence (0.1 mmol, 0.031 g) of Ph_2PCl was introduced directly into the reaction mixture under an argon atmosphere with continuous stirring. The solution colour immediately transformed to pale yellow, displaying an albeit less intense greenish-blue fluorescence. A $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture was obtained within 15 minutes, revealing a mixture of products akin to the earlier reaction. However, this mixture shows peaks corresponding to **4-10** at higher intensity, suggesting better selectivity of reaction by this method. On passing the solution through an alumina plug, **4-10** completely transformed to **4-6**. (Figure S4-1j and k)

c) By microwave reaction in the absence of $\text{Na}/[\text{Na}^+\text{naph}^-]$: Compound **4-6** (0.15 mmol, 0.06g) was dissolved in 10 ml of dry THF and two equivalence of Ph_2PCl (0.3 mmol, 0.07g) was added to this solution. The mixture was reacted in a microwave reactor for 190°C for 30 minutes. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture at this stage showed the formation of **4-10**, however along with other by-products. On reacting the mixture for one hour in the microwave reactor at 190°C , the peaks corresponding to **4-10** reverted to **4-6**, suggesting the decomposition of **4-10** at this condition. Since the peak at xx corresponds to **4-14**, the reaction proceeds through a different mechanism involving the heterolytic cleavage of the P-P bond of **4-6** even in the absence

of a reducing metal, facilitated by the elevated temperature and pressure within the microwave reactor. (Figure S4-1l)



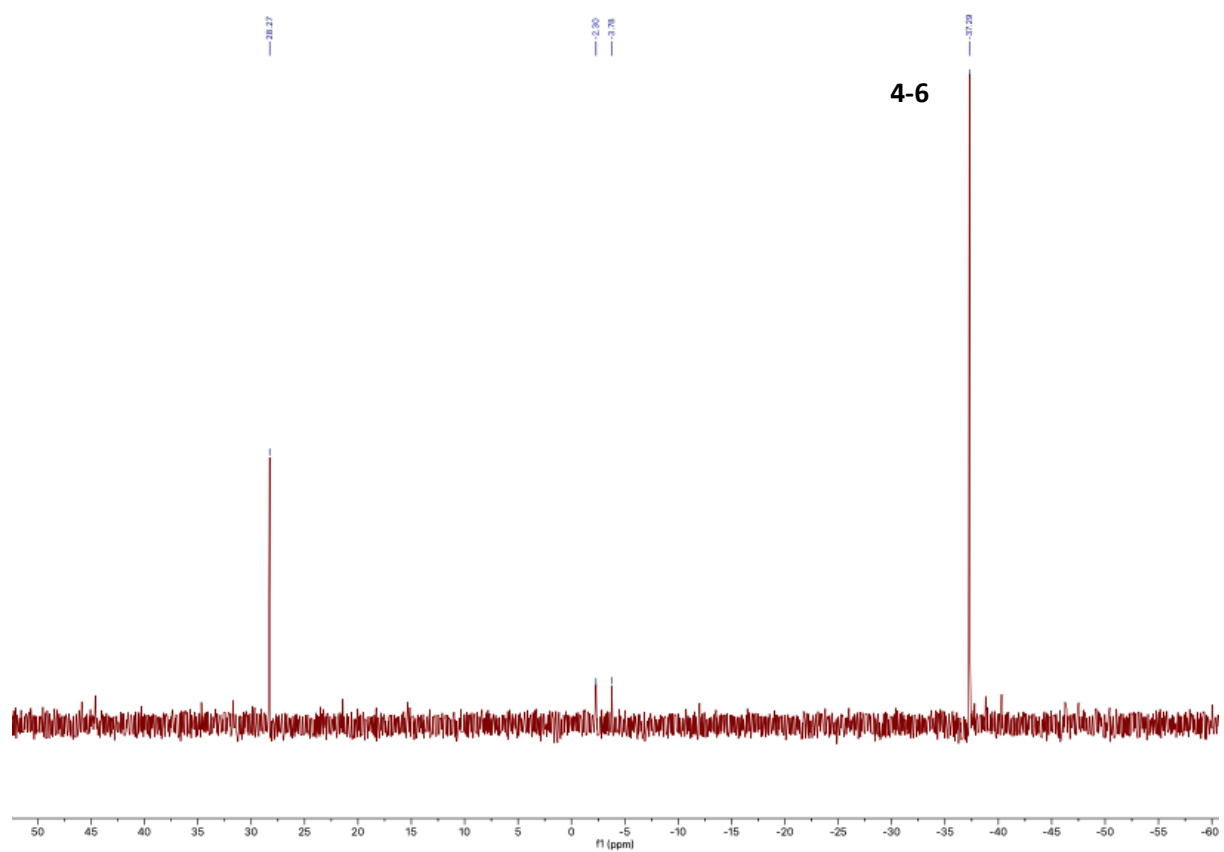


Figure S4-1k. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 Hz, THF) showing decomposition of **4-10** to **4-6**.

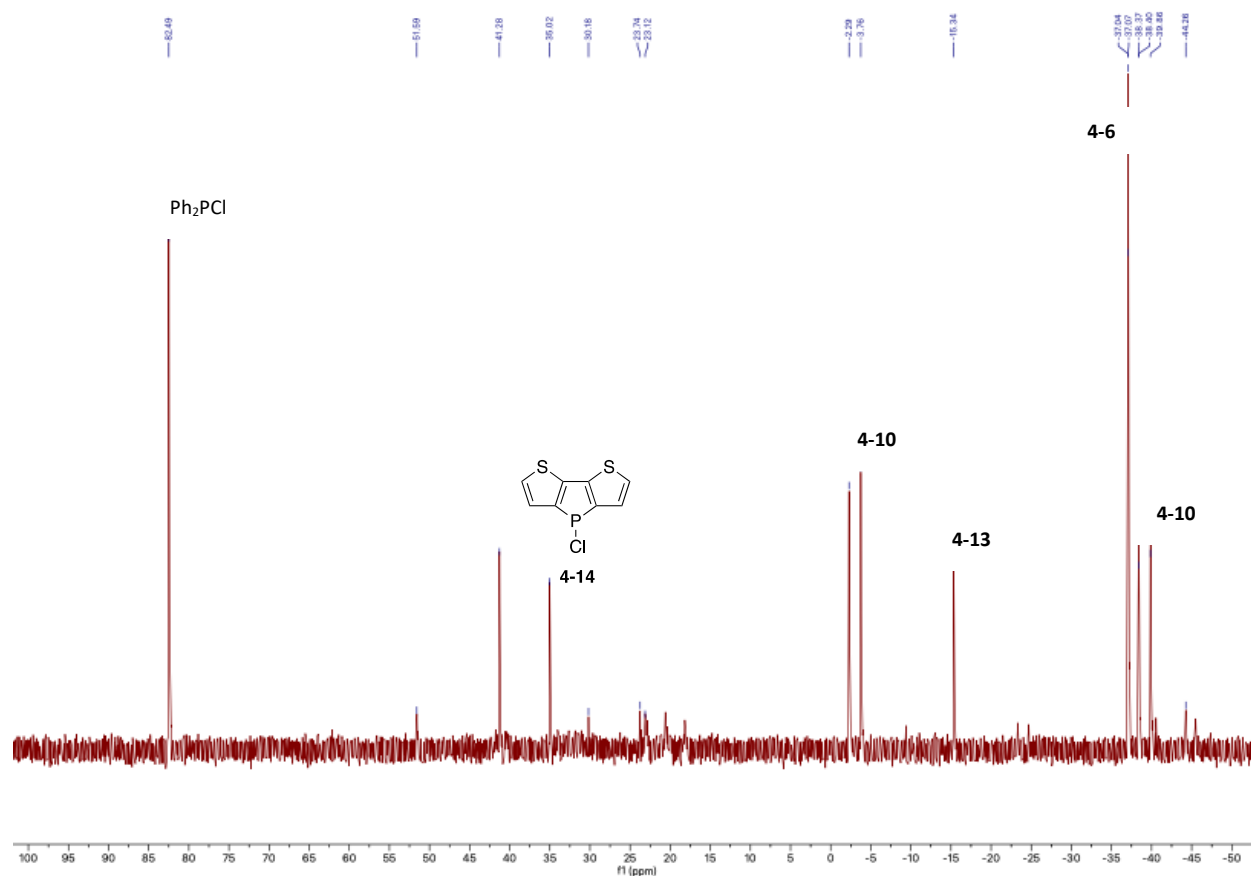


Figure S4-11. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 Hz, THF) of the reaction of **4-6** with Ph_2PCl in the absence of $\text{Na}/[\text{Na}^+\text{naph}^-]$ within 30 minutes of microwave reaction.

Synthesis of 4-11: Naphthalene (0.024g, 0.2 mmol) was dissolved in dry THF (5 ml) and a small piece of sodium metal was added to this solution. The solution was stirred for two hours to yield $[\text{Na}^+\text{naph}^-]$. The excess unreacted sodium was removed with a spatula and 0.09 mmol (0.036g) of **4-6** was directly added to this solution with stirring. The solution colour changed to brown immediately. After stirring for ten minutes, one equivalence (0.09 mmol, 0.017 g) of PhPCl_2 was introduced directly into the reaction mixture under an argon atmosphere with continuous stirring. The solution colour changed to pale brown and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of this mixture was obtained within 15 minutes, revealing a mixture of products with **4-6** being the major product.

S.4.2. Theoretical Calculations

(i) Compound 4-10

The DFT FMO calculations were conducted at the B3LYP/6-31G+(d) level of theory.^{S3}

Table S4-1a. Cartesian coordinates for the minimized structure of **4-10**.

Center	Atomic	Forces (Hartrees/Bohr)		
Number	Number	X	Y	Z

1	6	-0.000001097	0.000003924	0.000004872
2	6	0.000001713	0.000000334	-0.000000902
3	6	-0.000002914	0.000000615	0.000002267
4	6	-0.000004965	0.000001777	0.000002372
5	16	-0.000005133	0.000000777	-0.000000064
6	1	-0.000001831	0.000001236	0.000001583
7	1	-0.000002246	0.000001155	0.000003375
8	6	-0.000005337	-0.000001944	0.000004966
9	6	0.000000040	-0.000000840	-0.000007329
10	16	-0.000004521	0.000002472	-0.000000150
11	6	-0.000002273	0.000000852	0.000002239
12	6	-0.000003140	0.000002437	-0.000000967
13	1	-0.000001553	0.000000495	-0.000000229
14	1	-0.000004692	0.000001664	0.000000574
15	15	0.000003941	0.000001755	0.000012235
16	6	0.000000690	-0.000002182	-0.000000390
17	6	0.000005313	-0.000000617	0.000004633
18	6	0.000000670	-0.000004174	0.000000323
19	6	0.000000407	0.000003396	-0.000002358
20	6	0.000002377	0.000000009	-0.000001053

21	6	0.000000890	-0.000002341	-0.000003923
22	6	0.000001784	0.000001201	-0.000001250
23	1	0.000002789	0.000000178	0.000000083
24	6	-0.000001271	-0.000002968	-0.000000086
25	6	0.000001661	-0.000001642	0.000001249
26	1	0.000001470	-0.000002442	0.000002714
27	6	0.000001725	0.000000379	0.000000746
28	6	0.000003769	-0.000001825	-0.000004537
29	1	0.000003507	-0.000001321	-0.000000470
30	1	0.000000839	0.000000657	-0.000003866
31	6	0.000004871	-0.000001970	-0.000000323
32	1	0.000003687	-0.000001344	0.000002478
33	1	0.000003190	-0.000001622	-0.000001749
34	1	0.000001922	-0.000000563	-0.000002088
35	1	0.000003769	-0.000001612	0.000000387
36	1	0.000000685	-0.000000057	-0.000001765
37	1	-0.000001594	0.000000378	-0.000002824
38	15	-0.000009140	0.000003774	-0.000010773

(ii) Compound 4-11

Table S4-1b. Cartesian coordinates for the minimized structure of **4-11**.

Center	Atomic	Forces (Hartrees/Bohr)		
Number	Number	X	Y	Z

1	6	-0.000004356	0.000000362	-0.000005750
2	6	0.000017589	-0.000000029	0.000015740
3	6	-0.000005313	-0.000000528	-0.000006158
4	6	-0.000000306	0.000000164	0.000006272
5	16	-0.000006288	-0.000000165	0.000000255
6	1	-0.000001145	0.000001706	0.000001350
7	1	0.000002331	0.000001596	-0.000001095
8	6	-0.000012949	-0.000000468	0.000005788
9	6	0.000017271	0.000003669	-0.000003455
10	16	-0.000002135	0.000000940	-0.000000521
11	6	-0.000006379	-0.000001952	0.000003375
12	6	0.000010639	-0.000001080	-0.000005311
13	1	-0.000004270	0.000002863	0.000007418
14	1	0.000000516	-0.000000383	0.000003276
15	15	-0.000007691	-0.000003836	-0.000012654
16	6	0.000014231	-0.000005112	0.000007451
17	6	-0.000011346	-0.000002099	-0.000005556
18	6	-0.000006904	0.000004837	-0.000005143
19	6	0.000004940	0.000002475	-0.000001734
20	1	0.000001399	0.000000016	0.000001042
21	6	-0.000000365	-0.000002050	0.000000788
22	6	0.000001716	-0.000000198	-0.000000002

23	1	0.000001202	0.000001378	0.000000444
24	1	-0.000000517	0.000001405	-0.000002703
25	1	0.000001998	-0.000000414	-0.000000708
26	1	0.000001769	0.000001048	0.000000760
27	15	-0.000001022	0.000015021	0.000023727
28	15	-0.000002945	-0.000012961	-0.000017632
29	6	-0.000006624	-0.000009726	0.000004165
30	6	0.000005797	0.000007750	-0.000007532
31	6	-0.000002094	-0.000000539	-0.000006835
32	16	0.000001118	-0.000002937	0.000000587
33	6	-0.000002634	-0.000001225	0.000003569
34	1	0.000004318	0.000001725	-0.000002350
35	1	-0.000002191	0.000000180	-0.000001211
36	6	-0.000006817	-0.000001015	-0.000005682
37	6	0.000011364	-0.000000476	0.000005826
38	6	0.000000098	0.000001508	-0.000000019
39	16	-0.000005933	0.000001003	-0.000002807
40	6	0.000000822	-0.000000726	-0.000000984
41	1	0.000001518	-0.000000503	0.000001889
42	1	-0.000000412	-0.000001227	0.000002119

(iii) Compound 4-12

Table S4-1c. Cartesian coordinates for the minimized structure of **4-12**.

Center	Atomic	Forces (Hartrees/Bohr)		
Number	Number	X	Y	Z

1	6	0.000004624	0.000001389	0.000005099
2	6	-0.000011120	-0.000012989	-0.000005316
3	6	0.000001550	0.000000426	0.000002927
4	6	0.000003217	0.000003783	-0.000001364
5	16	-0.000000921	-0.000002720	-0.000002620
6	1	-0.000000507	-0.000000852	0.000000974
7	1	-0.000001919	-0.000000330	-0.000000312
8	6	0.000006807	0.000004792	-0.000002563
9	6	-0.000013119	-0.000001032	-0.000006018
10	16	-0.000003068	-0.000001610	-0.000001746
11	6	0.000001476	-0.000002498	0.000002753
12	6	0.000002011	0.000000505	0.000001308
13	1	0.000000680	0.000000451	-0.000000798
14	1	-0.000000561	-0.000000063	-0.000000908
15	15	0.000012714	0.000016485	0.000002751
16	15	-0.000005184	-0.000008987	-0.000006888
17	15	0.000012189	0.000006419	0.000015113
18	6	-0.000013330	-0.000004556	-0.000001116
19	6	0.000006586	0.000000738	0.000003168
20	6	0.000001591	-0.000001583	0.000002717
21	16	-0.000001964	0.000001730	0.000002135
22	6	0.000001447	0.000002414	-0.000000151
23	1	0.000000489	-0.000000668	0.000000919

24	1	-0.000000897	0.000000226	-0.000001120
25	6	-0.000011239	-0.000008898	-0.000010514
26	6	0.000004474	0.000004273	0.000001284
27	6	0.000001439	0.000004126	-0.000002038
28	16	-0.000003298	-0.000001715	-0.000000133
29	6	0.000002976	0.000000926	0.000002848
30	1	-0.000000575	0.000000705	-0.000000826
31	1	-0.000002030	-0.000000547	0.000000320
32	15	0.000004110	0.000001683	0.000001067
33	6	0.000005747	-0.000003085	0.000000579
34	6	-0.000005638	0.000002367	-0.000003156
35	6	-0.000002493	0.000001931	0.000003833
36	16	0.000002861	-0.000002165	-0.000001509
37	6	0.000000561	0.000001836	0.000002749
38	1	0.000001244	-0.000001363	-0.000002174
39	1	-0.000001125	-0.000000934	-0.000001306
40	6	0.000005726	-0.000000334	-0.000002939
41	6	-0.000005729	-0.000002491	0.000003045
42	6	-0.000002649	0.000004838	0.000001185
43	16	0.000002716	-0.000001664	-0.000001271
44	6	0.000000426	0.000002803	0.000001042
45	1	0.000001032	-0.000002330	-0.000000596
46	1	-0.000001330	-0.000001431	-0.000000439

CHAPTER FIVE: CINCLUSION AND OUTLOOK

Chemical and experimental details

Materials and Methods: All reagents were purchased from Sigma Aldrich and Oakwood Chemical. All solvents were purchased from Sigma Aldrich and Fisher chemical. SPS grade solvents (MBraun) from Sigma Aldrich were used for synthesis and characterisations.

Nuclear Magnetic Resonance (NMR): $^{31}\text{P}\{^1\text{H}\}$ spectra were acquired on Bruker NEO 400 NMR spectrometers on a 5mm ATM probe using TOPSPIN software version 4.0.8. Chemical shifts are reported in parts per million (ppm).

Section S5.1. Prospective Hypervalent Dithieno[3,2-b:2',3'-d]phospholes

Corresponding trivalent dithienophosphole was dissolved in dry DCM and equivalent amount of *o*-quinone was added with stirring. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy of the solution was obtained after an appropriate time.

Figure S5-1a. Synthesis attempts of few prospective hypervalent derivatives and their corresponding $^{31}\text{P}\{^1\text{H}\}$ NMR shift.

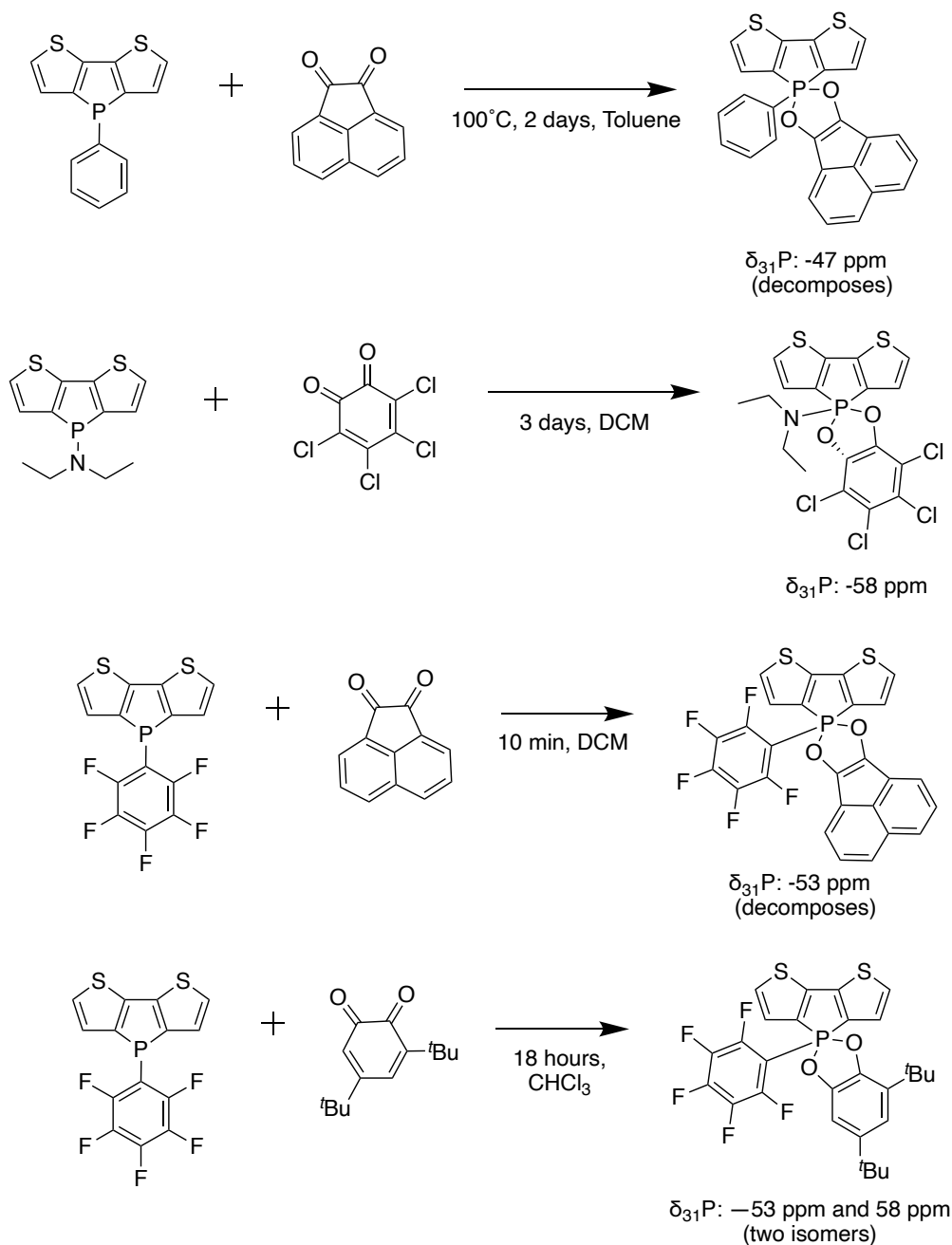
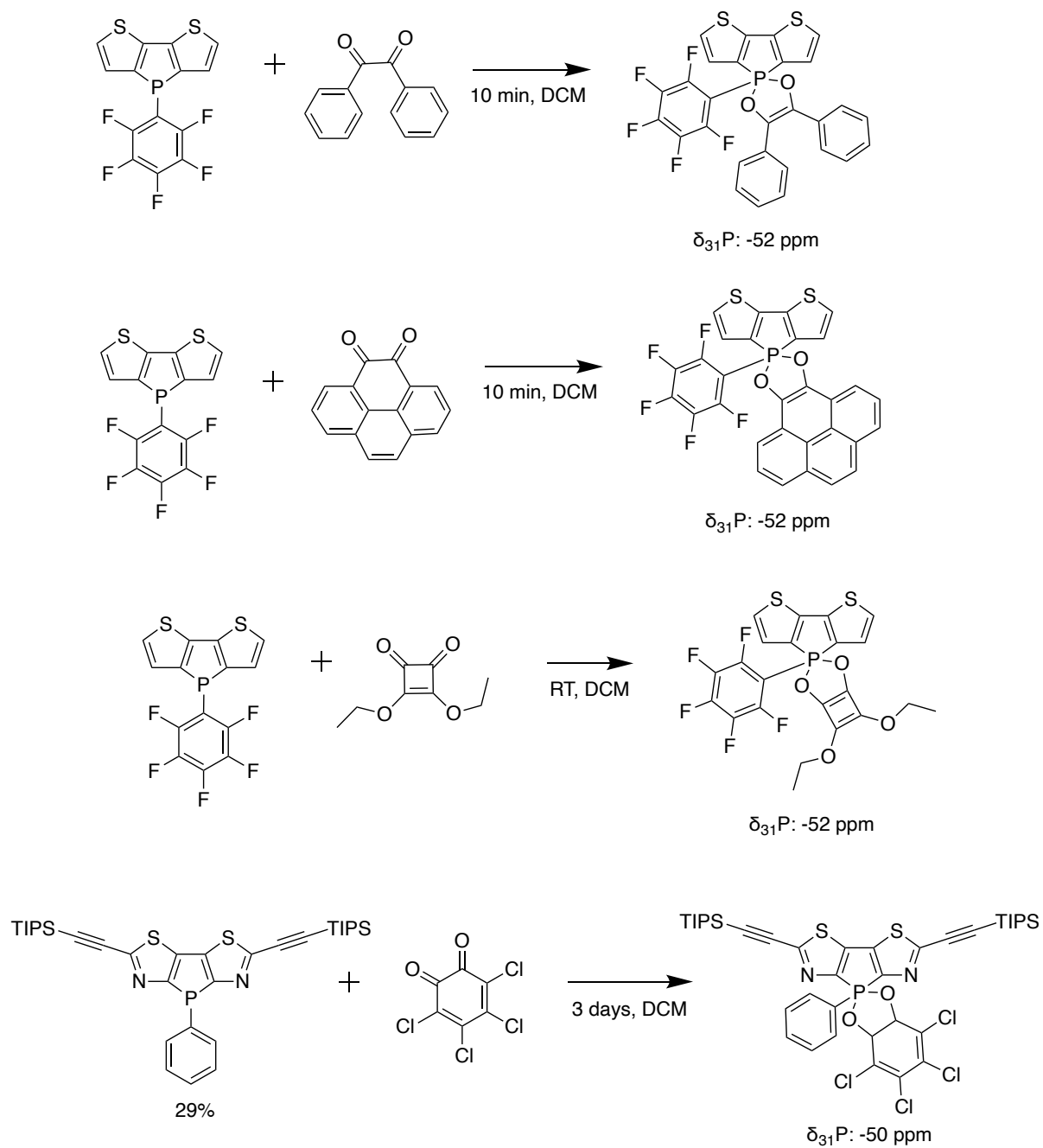
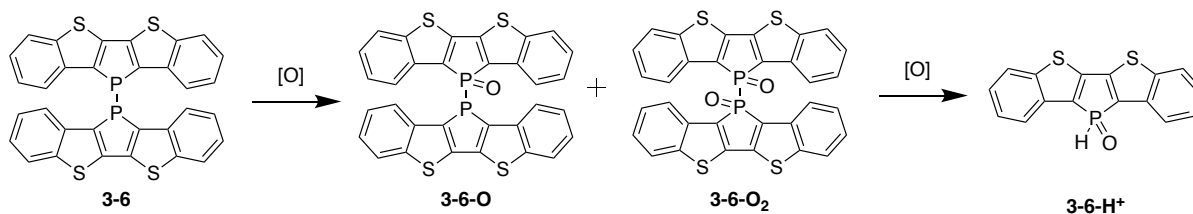


Figure S5-1b. Synthesis attempts of few prospective hypervalent derivatives and their corresponding $^{31}\text{P}\{^1\text{H}\}$ NMR shift.



Section 5.2. Ambient oxidation of **3-6**

The $^{31}\text{P}\{^1\text{H}\}$ NMR solution of **3-6** in CDCl_3 was left on a bench top in a closed NMR tube overnight to observe the formation of a mixture of **3-6-O** and **3-6-O₂** along with **3-6**. (Figure S5-2a) The solution was left undisturbed for another day to observe the complete conversion of **3-6** to **3-6-O₂**. (Figure S5-2b) Further exposure to ambient oxygen converts **3-6-O** and **3-6-O₂**. (Figure S5-2c) However, on attempting to purify the dioxide **3-6-O₂** (alumina plug using dry DCM), the compound decomposes to show a ^{31}P NMR shift at 16.37 ppm that corresponds to the formation of **3-6-H⁺**. (Figure S5-2d,e)



Scheme S5.1. Ambient oxidation of **3-6**.

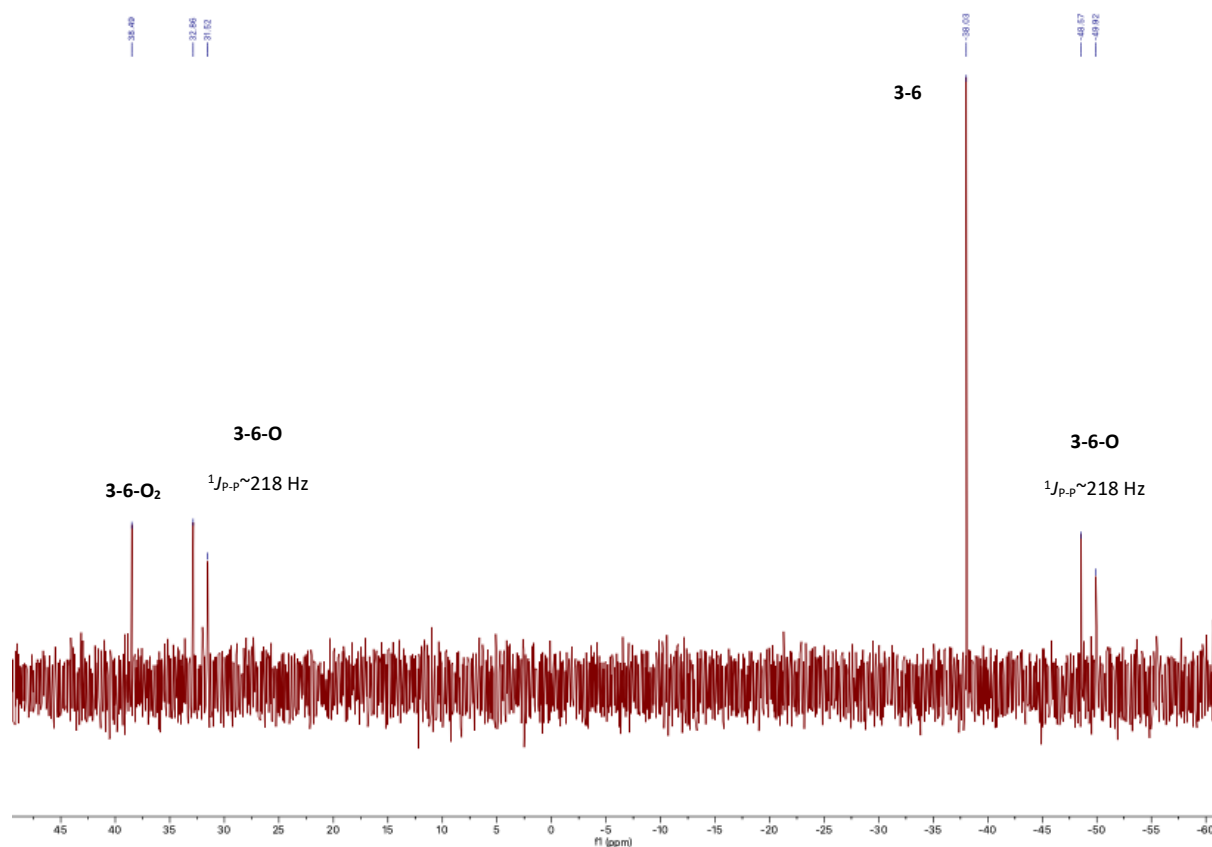


Figure S5-2a. $^{31}\text{P}\{^1\text{H}\}$ (CDCl₃, 162 MHz) NMR spectroscopy of solution of **3-6** after overnight.

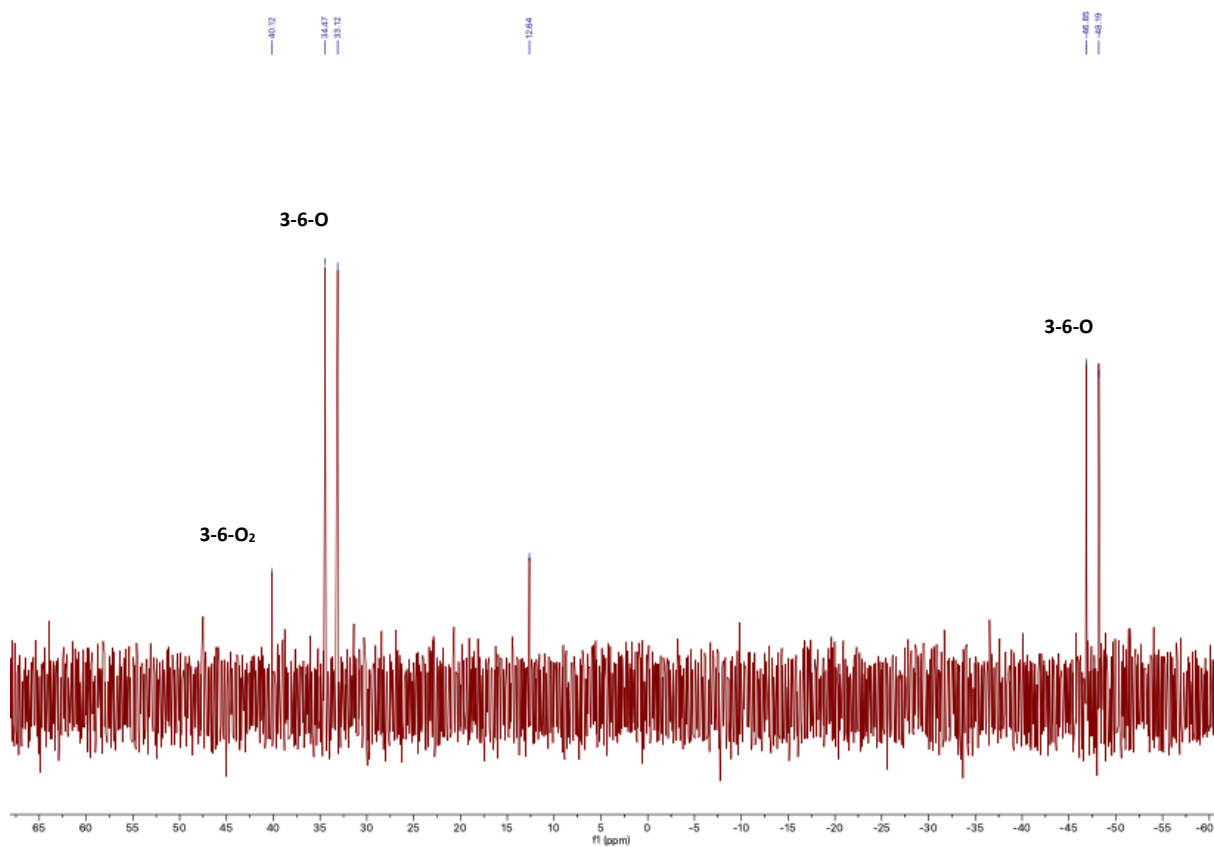


Figure 5-2b. $^{31}\text{P}\{^1\text{H}\}$ (CDCl_3 , 162 MHz) NMR spectroscopy of solution of **3-6** after 1 day.

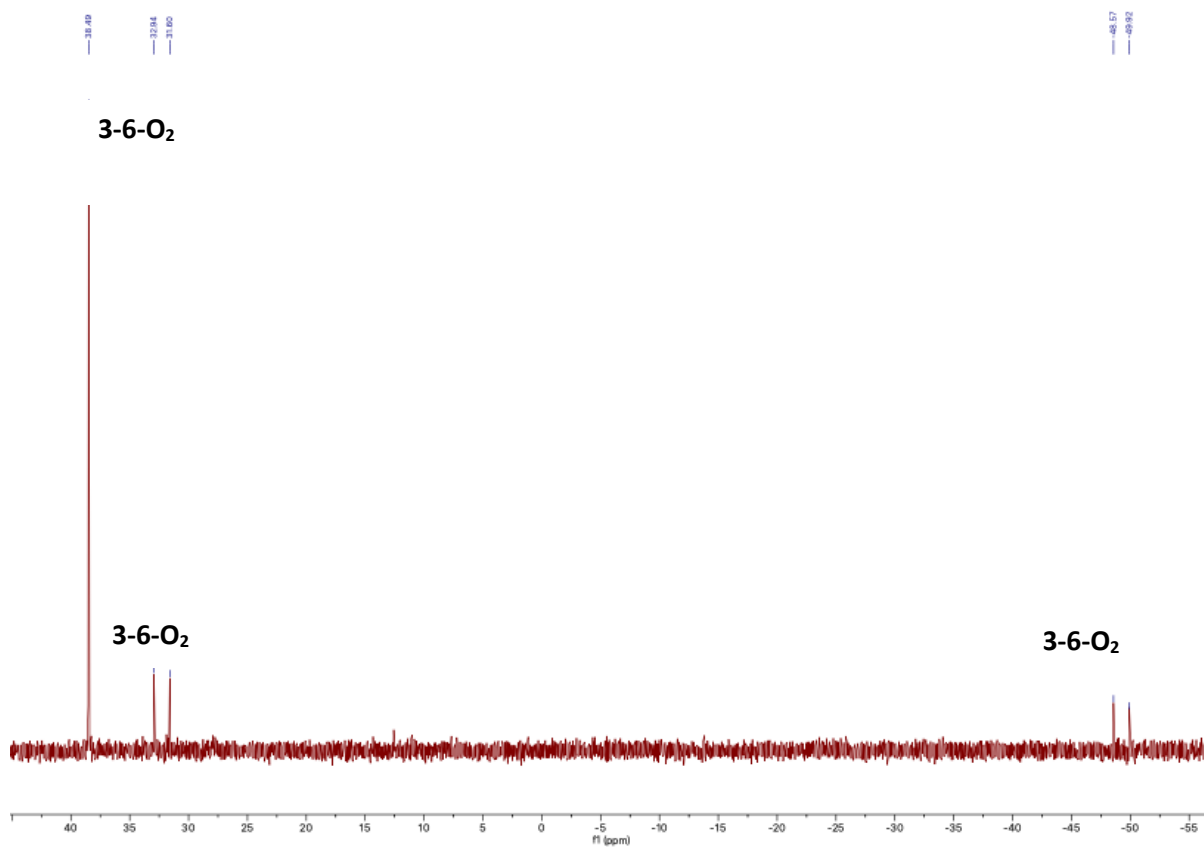


Figure 5-2c. $^{31}\text{P}\{^1\text{H}\}$ (CDCl_3 , 162 MHz) NMR spectroscopy of solution of **3-6** after 2 day.

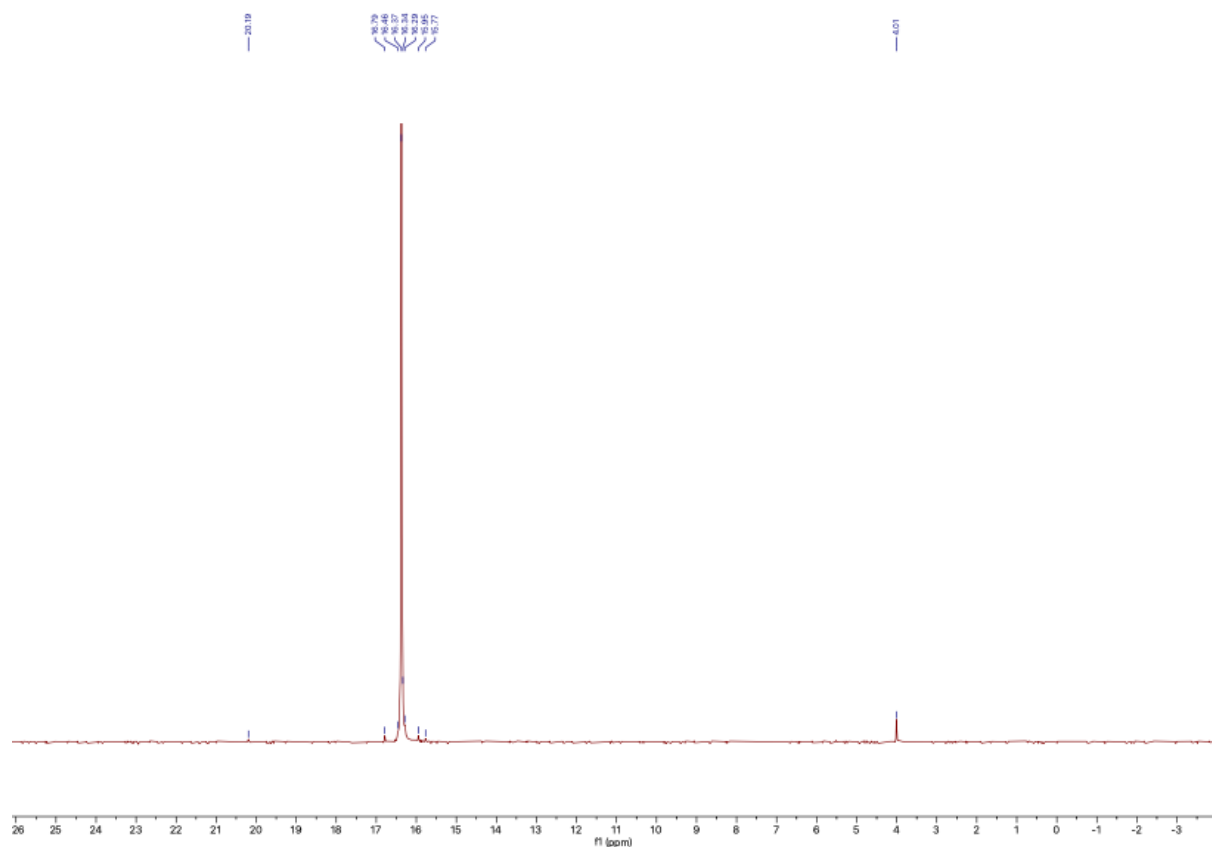


Figure 5-2d. $^{31}\text{P}\{^1\text{H}\}$ (CDCl_3 , 162 MHz) NMR spectroscopy showing decomposition of **3-6- O_2** to **3-6- H^+** .

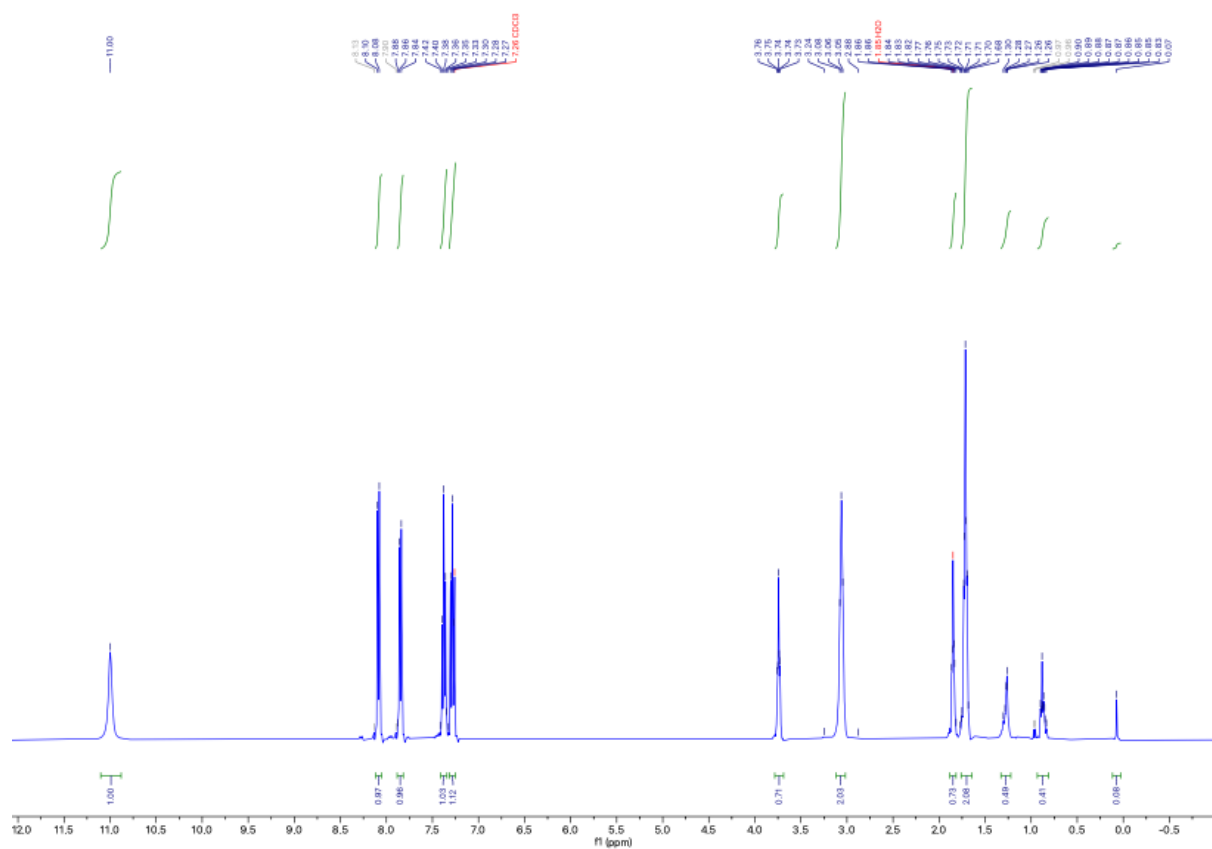


Figure 5-2e. ^1H NMR (CDCl_3 , 400 MHz) spectroscopy of **3-6- H^+** with solvents.

Section 5.3. Theoretical Calculations

The DFT FMO calculations were conducted at the B3LYP/6-31G+(d) level of theory.^{S3}

(i) Compound 5-1a

Table S5-1a. Cartesian coordinates for the minimized structure of **5-1a**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.444739	-1.968298	-0.318563
2	6	0	2.842868	-2.177644	-0.230567
3	6	0	3.191600	-3.468390	0.133277
4	16	0	1.741516	-4.446652	0.393264
5	1	0	3.581520	-1.411794	-0.439149
6	6	0	-0.702709	-2.954347	-0.147174
7	6	0	-1.097182	-1.680515	-0.551877
8	16	0	-2.048866	-4.034806	-0.015052
9	6	0	-2.493354	-1.595768	-0.795813
10	6	0	-3.170048	-2.782120	-0.572523
11	1	0	-2.986220	-0.695010	-1.142934
12	6	0	0.717629	-3.116626	-0.021758
13	15	0	0.348697	-0.591466	-0.878556
14	15	0	0.374471	0.644835	1.063645
15	6	0	-1.071560	1.732204	0.730884
16	6	0	-0.675419	3.000652	0.309264
17	6	0	-2.473802	1.638590	0.927785
18	16	0	-2.024729	4.071359	0.124196
19	6	0	-3.156760	2.802023	0.619149

20	1	0	-2.969342	0.743347	1.283671
21	6	0	1.472936	2.008964	0.484997
22	6	0	0.743994	3.152371	0.172708
23	6	0	2.868737	2.206342	0.355558
24	16	0	1.766649	4.471935	-0.284255
25	6	0	3.213119	3.472866	-0.088663
26	1	0	3.607857	1.444570	0.576359
27	6	0	-4.601590	3.059462	0.676869
28	6	0	-5.171492	4.219962	0.116283
29	6	0	-5.469822	2.143172	1.307855
30	6	0	-6.545033	4.453532	0.180281
31	1	0	-4.539351	4.949256	-0.383219
32	6	0	-6.842042	2.377122	1.368438
33	1	0	-5.070912	1.241671	1.761767
34	6	0	-7.391047	3.534201	0.805721
35	1	0	-6.953161	5.357692	-0.263403
36	1	0	-7.483427	1.651978	1.862007
37	1	0	-8.460761	3.716286	0.855428
38	6	0	4.549970	4.017520	-0.361029
39	6	0	4.730800	5.313882	-0.883397
40	6	0	5.706426	3.252853	-0.098012
41	6	0	6.005455	5.821338	-1.133886
42	1	0	3.867733	5.936740	-1.102095
43	6	0	6.979042	3.761411	-0.348674
44	1	0	5.611837	2.251010	0.308353
45	6	0	7.139538	5.049784	-0.868827
46	1	0	6.109576	6.824507	-1.538475
47	1	0	7.849855	3.147253	-0.135134
48	1	0	8.132234	5.445042	-1.063883
49	6	0	-4.602808	-3.064574	-0.729640

50	6	0	-5.175692	-4.269746	-0.277051
51	6	0	-5.457247	-2.124100	-1.343468
52	6	0	-6.538440	-4.524528	-0.430037
53	1	0	-4.554168	-5.019240	0.205626
54	6	0	-6.818683	-2.379914	-1.493941
55	1	0	-5.056605	-1.185194	-1.711668
56	6	0	-7.370773	-3.581852	-1.038723
57	1	0	-6.948680	-5.464045	-0.069583
58	1	0	-7.449390	-1.635372	-1.972254
59	1	0	-8.432153	-3.780001	-1.157534
60	6	0	4.532296	-4.044787	0.301108
61	6	0	4.719248	-5.389252	0.680602
62	6	0	5.686192	-3.261384	0.085370
63	6	0	5.996975	-5.926214	0.835031
64	1	0	3.858503	-6.028492	0.857507
65	6	0	6.961898	-3.799533	0.239875
66	1	0	5.587142	-2.221608	-0.208992
67	6	0	7.128313	-5.136409	0.616089
68	1	0	6.105741	-6.967030	1.127880
69	1	0	7.830520	-3.170197	0.065217
70	1	0	8.123392	-5.554765	0.736567

(ii) Compound 5-1b

Table S5-1b. Cartesian coordinates for the minimized structure of **5-1b**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.527998	2.849356	0.722806
2	6	0	0.705128	1.497408	1.004445
3	6	0	2.049896	1.175651	1.325521
4	6	0	2.905172	2.261276	1.278032
5	16	0	2.014358	3.733770	0.852922
6	1	0	2.381251	0.172645	1.567683
7	6	0	-0.827657	3.216802	0.420127
8	6	0	-1.724570	2.151055	0.472219
9	16	0	-1.623886	4.708546	0.017159
10	6	0	-3.056374	2.540718	0.180212
11	6	0	-3.187279	3.886166	-0.112802
12	1	0	-3.892560	1.850406	0.144488
13	15	0	-0.899153	0.608458	1.029440
14	15	0	-0.874396	-0.581501	-0.935702
15	6	0	-1.696532	-2.139051	-0.417009
16	6	0	-0.799067	-3.202644	-0.423827
17	6	0	-3.020652	-2.538917	-0.090371
18	16	0	-1.585156	-4.711380	-0.074606
19	6	0	-3.139536	-3.894029	0.154836
20	1	0	-3.860285	-1.857070	0.001194
21	6	0	0.733655	-1.457208	-0.934837
22	6	0	0.556652	-2.819848	-0.709151

23	6	0	2.070400	-1.124934	-1.281583
24	16	0	2.036545	-3.700835	-0.916888
25	6	0	2.921674	-2.213722	-1.304212
26	1	0	2.397332	-0.114427	-1.498625
27	6	0	-4.397411	4.620014	-0.493197
28	6	0	-4.350178	5.813038	-1.234152
29	6	0	-5.674200	4.138581	-0.130757
30	6	0	-5.507688	6.500055	-1.606808
31	1	0	-3.391811	6.211631	-1.557446
32	6	0	-6.831409	4.812280	-0.493375
33	1	0	-5.762465	3.232406	0.461697
34	6	0	-6.763502	6.001155	-1.239839
35	1	0	-5.407118	7.407081	-2.193309
36	1	0	-7.808623	4.434447	-0.207387
37	6	0	-4.340279	-4.649350	0.525915
38	6	0	-4.269523	-5.879057	1.202654
39	6	0	-5.622446	-4.156655	0.203136
40	6	0	-5.418053	-6.595452	1.546443
41	1	0	-3.300492	-6.283317	1.484749
42	6	0	-6.771520	-4.854103	0.553200
43	1	0	-5.715500	-3.228168	-0.353610
44	6	0	-6.680240	-6.078091	1.233542
45	1	0	-5.314208	-7.540739	2.069937
46	1	0	-7.755916	-4.475000	0.294671
47	6	0	4.361478	-2.247496	-1.581537
48	6	0	5.067314	-3.457014	-1.715139
49	6	0	5.099711	-1.053959	-1.728657
50	6	0	6.436055	-3.488269	-1.980900
51	1	0	4.546358	-4.405288	-1.609686
52	6	0	6.461474	-1.073736	-2.002097

53	1	0	4.605442	-0.092588	-1.626759
54	6	0	7.148171	-2.291081	-2.124743
55	1	0	6.933547	-4.449275	-2.064854
56	1	0	7.018819	-0.147821	-2.110397
57	6	0	4.349530	2.303401	1.534128
58	6	0	5.090469	3.496918	1.418955
59	6	0	5.051640	1.138395	1.905938
60	6	0	6.460933	3.532327	1.666559
61	1	0	4.595631	4.417531	1.120045
62	6	0	6.420716	1.167545	2.158225
63	1	0	4.525481	0.193722	2.002275
64	6	0	7.134885	2.364953	2.041847
65	1	0	7.010057	4.463066	1.551837
66	1	0	6.951901	0.262531	2.439150
67	6	0	-7.848242	-8.097280	1.788254
68	1	0	-7.126154	-8.382770	2.563613
69	1	0	-7.628178	-8.639237	0.859293
70	1	0	-8.852591	-8.347646	2.134621
71	6	0	-8.074062	7.947202	-1.844984
72	1	0	-7.247104	8.330063	-2.448930
73	1	0	-8.125000	8.500648	-0.898663
74	1	0	-9.003036	8.085223	-2.403027
75	6	0	8.987250	3.216619	3.279136
76	1	0	8.614335	4.242672	3.165791
77	1	0	10.075079	3.213517	3.183984
78	1	0	8.702293	2.834249	4.268931
79	6	0	9.101040	-3.311083	-3.032366
80	1	0	8.767102	-4.286085	-2.660658
81	1	0	10.175535	-3.220937	-2.859722
82	1	0	8.889998	-3.239944	-4.107873

83	8	0	-7.865530	-6.688802	1.556213
84	8	0	-7.965253	6.548300	-1.586446
85	8	0	8.495430	2.354147	2.248943
86	8	0	8.496529	-2.223032	-2.341109

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S20. A reviewer of this manuscript suggested that the impurities were responsible for the complex emissions seen in the emission spectrum for compound **2-1e**. However, given the low abundance of the impurities seen in the corresponding NMR spectra (~4%, detection limit), as well as that the fact that similar peaks are not seen at different concentrations in the emission of **2-1e**, i.e., the peaks are concentration-dependent, clearly confirms that they are related to the hypervalent phosphole species. It is further highly unlikely that the impurity would be excited at the same (relatively long) wavelength used for excitation of compound **2-1e**.

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