

Design, Synthesis, and Characterization of Novel Phosphorus-
Containing Conjugated Materials based on Vat Orange 3

Reza Dadgaryeganeh

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Abstract

As the global production and diversification of electronic devices—ranging from energy-conversion to energy-storage applications—continues to surge, enhancing their efficiency has become a critical objective. While the well-built metal-based technology of these devices warrants recognition, the associated sustainability and toxicity issues must not be overlooked. This is where π -conjugated organic materials play a pivotal role. Research in the new millennium has provided numerous types of conjugated materials possessing properties that offer clear paths towards integrated electronic devices (e.g., Organic Light-Emitting Devices (OLEDs), Organic Solar Cells (OSCs), Organic Field-Effect Transistors (OFETs), organic batteries) with performances approaching those of their metal-based counterparts. Accordingly, a multitude of developed compounds such as Polycyclic Aromatic Hydrocarbons (PAHs) or strategies that embed main group elements into carbon-based synthons, have all been aimed at this common goal. However, the development of PAHs and incorporation of heavier main group elements such as phosphorus have rarely intersected until recently. This marriage is facilitated by the emergence of vat dyes as cost-effective precursors for organic semiconductors as their scaffolds provide a convenient route to PAH cores, such as anthanthrene and chrysene. Therefore, this thesis is focused on methods of merging phosphacycles with Vat Orange 3, along with investigating the photophysics of these functional materials, their capacity and ease of undergoing redox processes, and the role of phosphorus in modulating the systems' electronics and impact on the overall functional properties. Through bridging heavier main group elements and large conjugated scaffolds, the emerging platform also attempts to overcome long-standing limitations in the literature, such as inefficient low-energy luminescence, restoration of the original keto groups in the vat dye-based frameworks, and doublet emission from phosphorus-containing conjugated materials.

Dedication

To Maryam, and all the brave women in Iran.

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List of Schemes

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List of Symbols and Abbreviations

LED	Light-emitting Device
Pb-A	Lead-acid
UV-vis	Ultraviolet-visible
NIR	Near-infrared
IR	infrared
ε	Molar extinction coefficient ($\text{M}^{-1} \cdot \text{cm}^{-1}$)
μ	Charge Carrier Mobility ($\text{cm}^2/\text{V} \cdot \text{s}$)
Φ	Quantum Yield
OLED	Organic Light-emitting Device
QY	Quantum Yield
OSC	Organic Solar Cell
OFET	Organic Field-effect Transistor
RFID	Radio-frequency Identification
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
FMO	Frontier Molecular Orbitals
NDI	Naphthalendiimide
FC/Fc ⁺	Ferrocene/ferrocenium
eV	electron Volt
SCE	Saturated Calomel Electrode
DE	Dual Emission

PAH	Polycyclic Aromatic Hydrocarbon
TIPS	Triisopropyl silyl
PLQY	Photoluminescence Quantum Yield
VO3	Vat Orange 3
2D	2 Dimensional
GNR	Graphene Nanoribbon
OPV	Organic Photovoltaics
DCM	Dichloromethane
THF	Tetrahydrofuran
MW	Microwave
Å	Angstrom
DFT	Density Functional Theory
TDDFT	Time-dependant Density Functional Theory
NICS	Nucleus-Independent Chemical Shift
PMMA	Poly(methyl methacrylate)
CV	Cyclic Voltammetry
λ_{em}	Emission Maximum Wavelength
λ_{abs}	Absorption Maximum Wavelength
τ	lifetime
R.T.	Room Temperature
BCF	Tris(pentafluorophenyl)borane
δ	Chemical Shift (ppm)
PCBM-C ₆₀	Phenyl-C61-butyric Acid Methyl Ester

DMAD	Dimethyl Acetylenedicarboxylate
HRMS	High-Resolution Mass Spectrometry
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
EPR	Electron Paramagnetic Resonance
DMSO	Dimethyl Sulfoxide
SOMO	Singly Occupied Molecular Orbital
f	Oscillator Strength
TADF	Thermally Activated Delayed Fluorescence
J	Coupling Constant (Hz)
TfO ⁻	Triflate Anion
PCM	Polarized continuum Model
ppm	Parts Per Million

Chapter one: Introduction

1.1. Organic Conjugated Materials – Potential Alternatives for Metals

The late 20th century witnessed a boom in the development and production of electronic devices and computers effecting unprecedented connectivity, information accessibility and of course, significant advances in various fields of science. In the following years and building on that experience, a wide range of devices with energy conversion as their primary function, specifically electricity and light, have been successfully designed and manufactured. Prominent examples in the field of chemistry, material sciences, and biology are light-emitting devices (LED), solar cells, phototransistors, biosensors, and fluorescence-based microscopy techniques.¹⁻³ Moreover, modern societies' progression toward replacing fossil fuels —particularly in transportation— would have been far more laborious, had it not been for the small to large-scale energy storage capabilities of various types of batteries.⁴

The active components in most of these devices to date have mainly been alkali and transition metals. Accordingly, a well-known example is the continued high demand for lead-acid (PbA) batteries, which, despite their long history, remain a robust and low-cost technology.⁵ Nevertheless, the consistent production of such devices has been leading to the steady release of toxic heavy metals into the environment, thereby negating their advantages. Furthermore, the low abundance and high expense of certain metals, coupled with ever-growing environmental mining issues, render their long-term and global use simply unsustainable.⁶

To address these challenges, a few decades of ongoing research have explored organic conjugated materials with carbon-based scaffolds as a suitable replacement to metals. As a result, a new branch of materials science known as organic electronics emerged, with focus on blueprinting electronic

devices that utilize π -organic compounds as their primary constituents.^{7–10} In principle, carbon-based structures are superior in having better processability, lighter weight, and more stability against humidity.¹¹ Furthermore, over the years, different types of organic devices, geared to cover a variety of applications, have been fabricated—some of which displaying outstanding performance.^{12–15} However, the shift toward these new-generation devices on an industrial scale is only feasible, if they can outcompete the efficiency of their metal-based counterparts. This cannot be achieved unless the quality of the functional materials that plays a crucial role in these devices is improved.^{5,16}

To further delve into the details, the required properties for conjugated materials to be applicable in practical applications are: (1) the ability to interact with light, particularly in the UV-vis (ultraviolet-visible), NIR (Near-Infrared Radiation), and occasionally IR (Infrared) regions, (2) the ability of donating or accepting electrons along with the subsequent stability of the oxidized or reduced species, and (3) an acceptable degree of charge conductance (positive or negative) through different layers in the solid state. The interaction of light and matter can be discussed in terms of light absorption gauged by molar absorptivity (or extinction coefficient; ϵ , $\text{M}^{-1} \cdot \text{cm}^{-1}$) and light emission, measured by photoluminescence quantum yield (expressed as decimal or percentage, Φ). There are a number of ways to assess the electrochemistry of a material, with cyclic voltammetry being the commonly most suitable method. The presence of peaks on positive or negative potentials, their resemblance to the ideal “duck shape”, their closeness to the zero potential, and upholding their original peak shape after several runs (Figure 1-1a), all bear pivotal information on whether a material is to be used in a device.^{17,18} Eventually, charge-transport ability of a given material that represents how quickly a charge—electrons or holes (i.e., the lack of an electron)—can move through the layers of a material when an electric field is applied is quantified

with charge carrier mobility (μ , $\text{cm}^2/\text{V}\cdot\text{s}$). As we will investigate in each specific case, at least one of these traits is necessary in a compound for each targeted application.

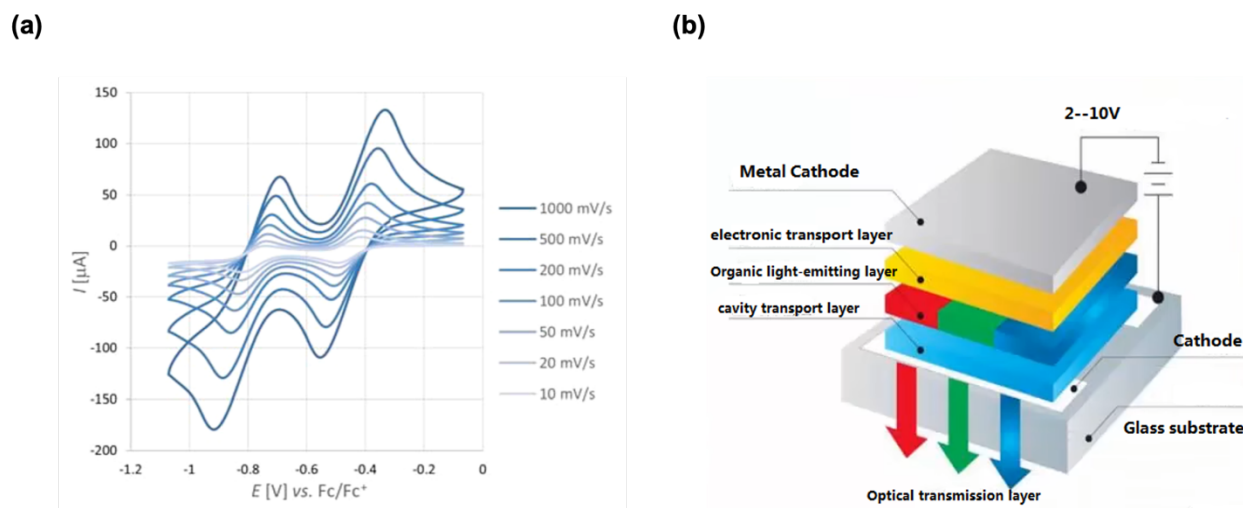


Figure 1-1. (a) Cyclic voltammogram of a conjugated material with reversible reduction peaks, and (b) device structure of an OLED. ((a) is reproduced from Baumgartner et al., *J. Am. Chem. Soc.*, **2015**, 137 (36), 11710-117-17. Copyright© 2015 American Chemical Society. Licenced under CC BY-NC-ND.)

Organic light-emitting devices (OLEDs): the excitation of the conjugated material in the emitting layer occurs through electricity, which subsequently results in light emission. Therefore, the materials' Quantum Yields (QYs), and Frontier Molecular Orbital (FMO) energy gaps that respectively determines the intensity, and the color of the resulting light, are of essence (Figure 1-1b).¹⁹ Also, other semiconducting layers involved in the process use different types of conjugated materials with distinct charge carrier mobilities, ultimately impacting the device efficiency.

Organic solar cells (OSCs): the photoexcitation in the conjugated material takes place by sunlight, and the resulting charges will generate electricity that could be used or stored for further consumption.²⁰ This means that active organic π -system must exhibit high extinction coefficients

in the region where the earth's surface receives maximum solar radiation, which is close to the red-NIR region. Enhancing the performance of OSCs is thus imperative as they offer one of the cleanest methods of generating electricity.

Organic field-effect transistors (OFETs): their main purpose is to act as an electronic switch or amplifier in circuits using organic semiconducting materials. The utilized semiconducting materials are aimed to transport electrons (n-type), holes (p-type), or both (ambipolar), so a high charge transporting mobility is desired. They are key components in flexible, cheap, and typically lightweight electronic devices (e.g., RFID tags).^{21,22}

Organic batteries: The main concept is utilizing redox-active organic π -systems in all organic or hybrid batteries in order to store electricity. Due to the inherently high HOMO (Highest Occupied Molecular Orbital) energy level of organic molecules, oxidation is generally possible; however, the challenge lies in finding π -systems that can undergo reduction without subsequent decomposition. In addition, small metals such as lithium have a high electron-storage capacity as they require small units of mass or volume, so alternative conjugated scaffolds capable of saving multiple electrons are highly sought after.²³

As a result, envisioning and developing functional materials with the mentioned characteristics is a necessary condition to elevate the performance of these devices, but it is not exclusive. The absolute and relative energy of the HOMO and LUMO (Lowest Unoccupied Molecular Orbital) levels in each π -organic compound is also critical; the energy gap(s) between FMO (Frontier Molecular Orbital) orbitals control(s) what wavelength of light is absorbed and emitted by the material. Additionally, electron oxidation occurs at the HOMO, while reduction happens on the LUMO, so raising the HOMO or lowering the LUMO reduces the ease (potential) with which the electron transfer can happen into or out of the system. Consequently, visualizing systems with

adjustable FMO energies is complementary to intense light absorption/emission, or multistage redox abilities in conjugated materials; hence, methods to achieve them will be discussed in the next sections.

Lastly, although properties displayed in solution-phase are important and have certain applications, greater focus is placed on solid-phase characteristics, as most organic devices consists of assembled solid layers. Ordinarily, an isolated unit of a carefully designed π -system features an interesting property (e.g., luminescence), but as intermolecular distances decrease, the powerful interactions between identical units could weaken or even eliminate that property.²⁴ On the other hand, strong π - π interactions between expanded conjugated planes or unsaturated long polymeric chains bring them closer together, facilitating electron transportation between (or within) these units. Therefore, modifying these forces can significantly impact charge-carrier mobility in the semiconductive layers, as both insignificant and dominating π - π interactions can ultimately diminish conductivity in the bulk phase. Consequently, finding ways to adjust 3-dimensional molecular organization without having to fundamentally alter the structure of organic π -systems is vital.^{25,26} This will also be examined in the following chapter.

1.2. Merging Phosphorus with Organic Conjugated Materials

Many conjugated materials with hydrocarbon-based skeletons—occasionally embedded with nitrogen and oxygen atoms—have been the pioneers in materials chemistry with cases showing satisfactory performance in the active layers of organic devices.^{27,28} Similarly, incorporation of main group elements such as boron, silicon, sulfur, selenium, and phosphorus into the framework of organic π -systems is an established method in creating diverse moieties with unique electronic and structural characteristics.^{29,30} Owing to the distinctive properties of phosphorus among other main group elements, our research team is primarily interested in developing π -conjugated

materials embedded with one or multiple P centres. Notably, understanding the photophysical and electrochemical features of P-containing materials hinges on investigating the intrinsic characters of phosphorus, both as an individual element or integrated part of a conjugated heterocycle.³¹

The electron-donating ability of trivalent phosphorus is marked by its lone pair. This is easily reversed by its oxidation to phosphoryl moiety (by O, S, NR, or CR₂) turning it into an electron withdrawing group (Figure 1-2a). This is not merely because of the inductive effect of the oxidizing element, but by π -back donation of its filled p orbital into the antibonding σ^* orbital at phosphorus giving rise to an interaction called negative hyperconjugation (vs. positive hyperconjugation in ethyl carbocation with σ bonds donating to an empty p orbital). Furthermore, phosphorus' limited tendency for hybridization translates into its high inversion barrier energy and pyramidal geometry even as part of a conjugated cycle. This leads to an idiosyncratic situation in which the P-exocyclic σ bond can have partial to strong interaction with the π -system, contributing to its aromaticity (typically positive), whereas additional substituents provide σ^* orbitals that can engage with a π^* orbital (σ^* - π^* interaction) and reduce the energy of the LUMO (Figure 1-2b).³¹

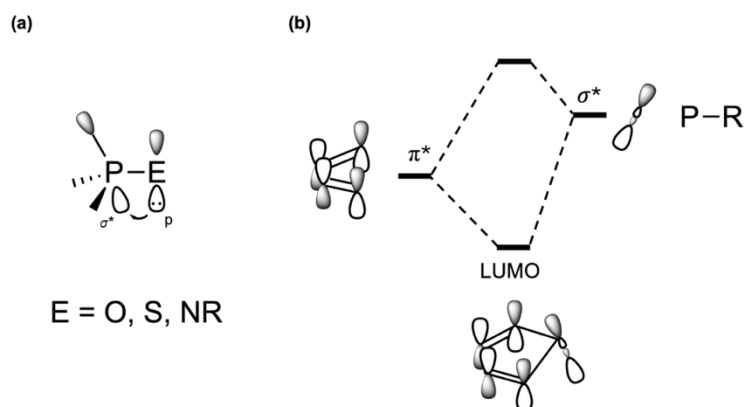


Figure 1-2. (a) Back-donation of a filled p orbital into a σ^* orbital in the phosphoryl group, (b) interaction between P-R and butadiene moieties in a phosphacycle leads to lowered LUMO energy.

This elucidates that 1) the generally low-lying LUMO level of phosphorus-based π -organic structures is the result of negative hyperconjugation in these systems, and 2) varying the degree of these interactions through installation of diverse substituents leads to tunability of the FMO energy levels and the degree of aromaticity in the P-containing ring and commonly, the entire structure.³¹ It should also be mentioned that these effects are well-studied in phosphole, but they are also present to a different extent (depending on the phosphorus or phosphacycle environment) in other phosphacycles such as the 6-membered P-analogue, phosphinine.^{32,33} Moreover, due to the higher s-character of the lone pair on phosphorus and its minimal involvement in conjugation, it is open for post-functionalization reactions. In fact, trivalent phosphorus can attach to a wide variety of substituents including oxidizing (O, S, Se), aryls, alkyls, and amines (Ph, Me, NR₂), main group elements (B, Si, P), and transition metals (Cu, Au, Pd). Every element and type of substituents has a distinctive electronegativity and leads to different interactions with the π -system that greatly influence the FMO energy levels of the compound.³⁴ Thus, P-merged conjugated scaffolds are quintessential examples of compounds with tunable photophysical and electrochemical properties. On that account, various cases of P-based structures along with their behaviours will be reviewed in the following section.

1.2.1. Non-cyclic P-containing Materials

During the 2000s, several organic cores decorated with diphenylphosphine oxide units were prepared by different research teams. Beyond their robust chemical structures, the increased electronegativity of the phosphoryl P=O group and lowered LUMO enabled these materials to display luminescence with activated triplet states and high quantum efficiency up to 20%.^{35–37} The presence of carbazole along with P=O moieties in **1-1** and **1-2**, provides them with ambipolar

character. The compounds in Figure 1-3 are thus suitable in producing blue phosphorescent OLEDs with **1-2** also being used in white OLEDs.

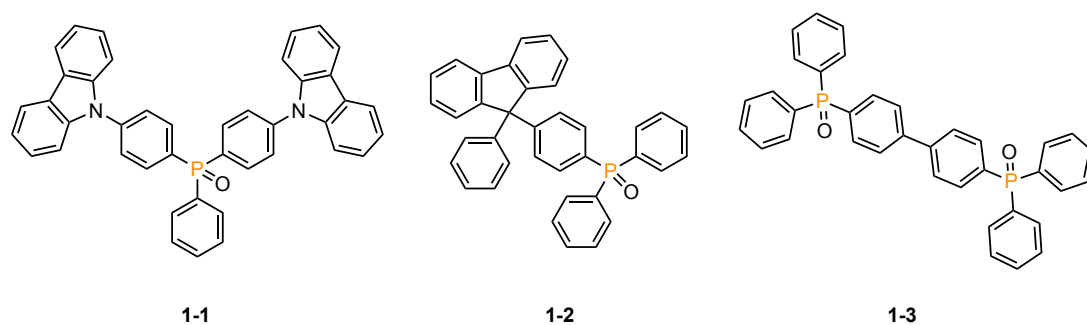


Figure 1-3. Representative diphenylphosphine oxide-containing structures with beneficial luminescence and charge mobility.

After being confirmed as efficient emissive materials, research on non-cyclic P-substituted systems was followed by focusing on their charge transporting abilities. Studies involving P=O-functionalized organic systems revealed their positive impact on enhancing electron mobilities, appropriate HOMO and LUMO energy levels, and outstanding thermal stability. As a result, compounds such as **1-4** to **1-6** were successfully utilized as active n-type semiconductors in the fabrication of green and blue OLEDs (Figure 1-4).³⁸⁻⁴⁰

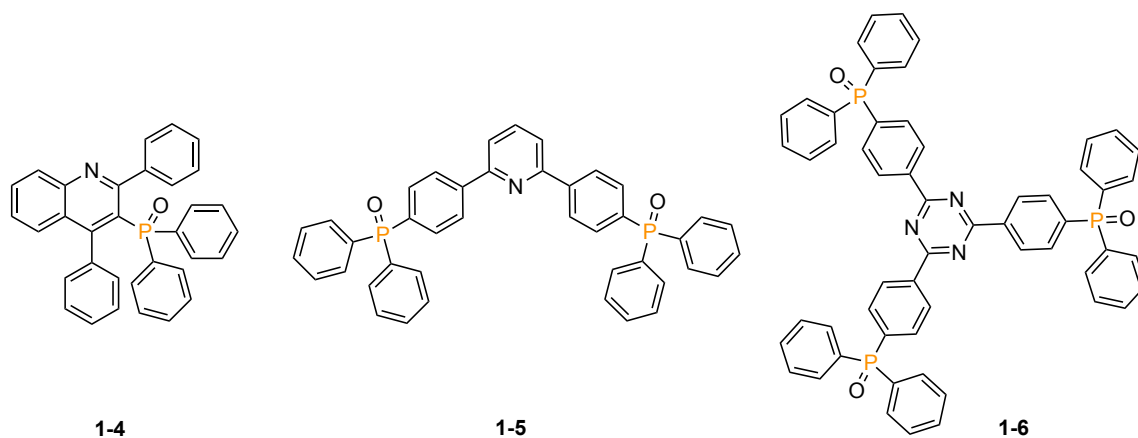


Figure 1-4. Examples of electron-transporting materials in OLEDs.

Furthermore, Mukhopadhyay in 2014 reported the first P-functionalized naphthalenediimide (NDI) using triphenyl phosphonium groups. Compound **1-7** showed two reversible reduction events at impressively low potentials of -0.2* and -0.68 V, corresponding to -4.9 eV for the LUMO energy that categorize the systems among the most electron-accepting materials ever synthesized. The prepared radical anion of **1-7** possesses great stability under ambient conditions as well as silica, which is thanks to the stabilization effect of phosphonium groups on the NDI radical anion core (Figure 1-5).⁴¹ The group later demonstrated diphenylphosphine-oxide extension of NDI **1-8**, to generate a scaffold with reduction potentials close to **1-7** and light absorption in UV-vis-NIR region for **1-8** and its reduced species.⁴² In a recent study, the Bezdek group has demonstrated the transformation of a simple terthiophene scaffold into a system possessing a two-step reduction through installation of diphenyl phosphine oxide functionalities. To add ambipolarity to the structure, addition of SMe groups to the framework was also deemed necessary (Figure 1-5). Notably, cyclic voltammetry and chemical redox reactions proved **1-9** to be endowed with perfectly reversible oxidation and reduction features, along with stable reduced and oxidized states that make the species useful as an electrolyte in redox flow batteries.⁴³

These studies clearly offer the attachment of phosphorus-containing moieties—specifically phosphoryl groups—as a practical means to achieve conjugated materials with enhanced electron-accepting properties and/or attractive photophysics.

*All the potential values in this manuscript are referenced versus Fc/Fc⁺ unless specified.

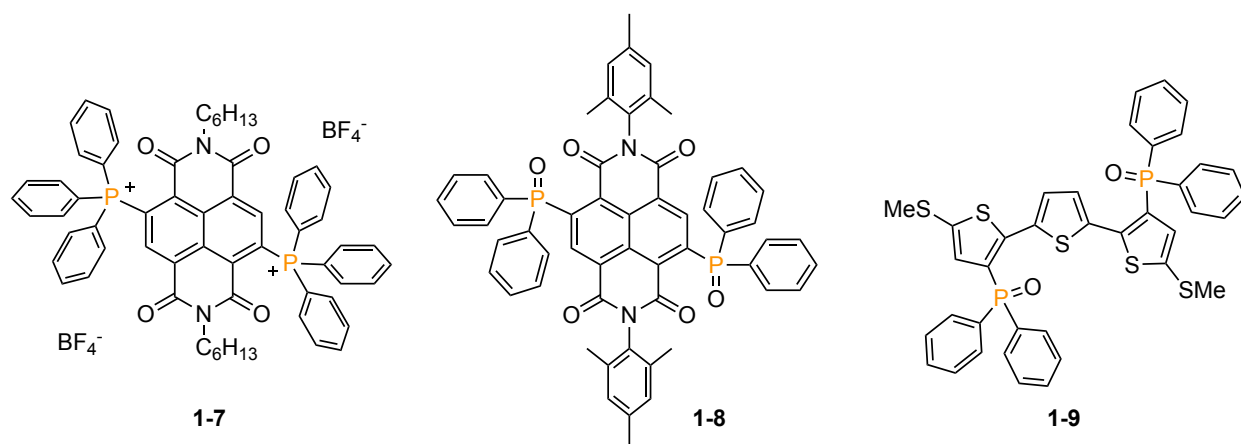


Figure 1-5. Phosphine-modified NDI and terthiophene structures.

1.2.2. Cyclic P-containing Materials: Phosphole

In 2000, one of the first reports of phosphole-based structures **1-10**, focusing on materials applications was highlighted by Réau and coworkers (Figure 1-6). The study indicated the possibility of varying optical properties of phosphole by different substituents on the 2- and 5-positions.⁴⁴ In 2004, our group demonstrated extending the conjugation of phosphole through thiophene fusion that led to the synthesis of dithienophosphole **1-11**. The material's remarkably high luminescence, attributed to its rigid structure and minimal energy loss presented it as a promising platform for development of organic light-emitting compounds. Over the next decade, installation of a diverse array of functionalities on the thiophenes and two exocyclic P-substituents proved the excellent synthetic versatility of the scaffold (**1-12**, Figure 1-6). Indeed, each substituent exerted a distinct influence on the conjugation of the bithiophene backbone and $\sigma^*-\pi^*$ interaction in the phosphole, impacting on the FMO energy levels and enabling the emergence of diverse array of conjugated materials with tunable fluorescence colours.³⁴

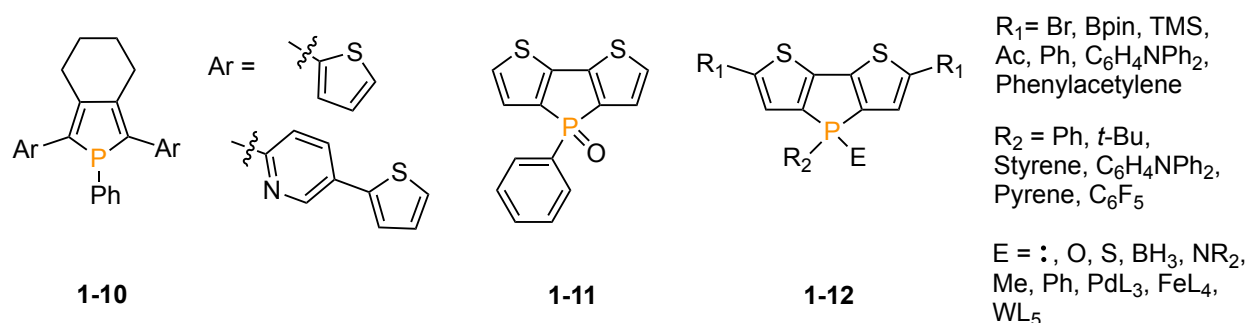


Figure 1-6. Luminescent dithienophosphole structures with chemical modification.

Despite their attractive optical behaviour, stability of dithienophospholes towards accepting extra electrons is not strong. Accordingly, the electron-accepting character can be enhanced by introducing high electron-affinity groups on the phosphorus or thiophene units, yet this is still not accompanied by high stability of the reduced species. Conversely, early studies by Le Floch on dibenzophospholes support the delocalization of electrons in the radical anion species over the whole structure. This is manifested in a reversible reduction peak for the P-methylated dibenzophosphole at -1.5 V (**1-13**, Figure 1-7). In line with that observation, a recent report on unlocking a “green” application of triphenylphosphine oxide-based materials—traditionally considered industrial chemical waste—is particularly noteworthy. The quasi-reversible reduction processes of the mentioned non-cyclic phosphine oxides can be transformed into perfectly reversible reduction peaks for cyclic systems, which are accessible through straightforward high scale synthesis. Dibenzophosphole systems, such as **1-14** and **1-15** with reduction peaks at -2.40 and -1.95 V, exhibit no decomposition in up to 350 charge-discharge cycles in an H-cell, showing great progress with respect to redox flow batteries.⁴⁵ These results clearly classify benzo-fused phospholes as prospective electron-accepting scaffolds despite their rather unremarkable photophysics.

In 2008, Yamaguchi and coworkers reported the synthesis of **1-16**, with two fused phospholes flanked by benzo-rings (Figure 1-7). Interestingly, while the unique structure activates luminescence, incorporation of two phosphole units enhances the electron-accepting property, as reflected in the lowered reduction potentials of -1.63 and -2.14 V.⁴⁶ In 2011, a series of phosphole-based systems with acenaphthene-extended conjugation from different sides were reported by the Matano group.⁴⁷ Compound **1-17** ($E_{\text{red}} = -1.24$ V) and **1-18** ($E_{\text{red}} = -1.00$ V) effectively uphold the observed trend of improved electron-deficiency in the newly synthesized P-based conjugated materials. This, combined with their enhanced electron mobility (up to $\mu_e = 2.4 \times 10^{-3}$), facilitated their application in organic solar cells.

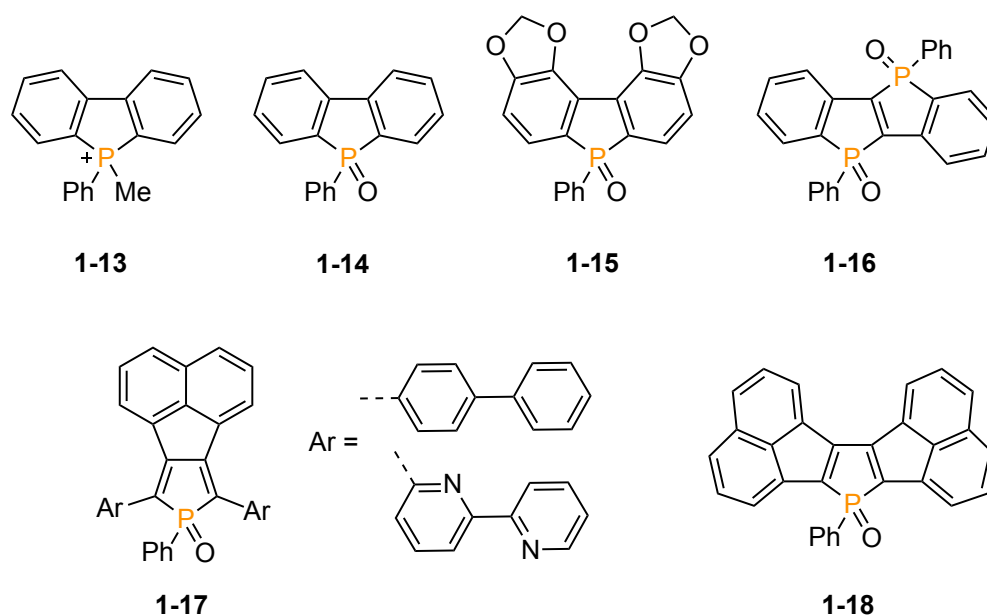


Figure 1-7. Benzofused-phosphole systems with electron accepting property.

Since embedding nitrogen atoms in π -organic systems is a traditional method for lowering LUMO energy levels, our group explored a series of dithiazolophosphole compounds **1-19** (Figure 1-8) with the aim of modifying the electron-accepting property of dithienophospholes. As it turned out,

beyond preserving the favourable optical features, the scaffolds display quasi-reversible reductions at notably lowered potentials between -1.69 to -2.07 V.³⁸ Encouraged by these findings and in order to step up the n-type behaviour of the π -organic materials, our group then pursued a new strategy of merging phosphole units with nitrogen-containing systems possessing advanced electron accepting characters. Accordingly, viologen (**1-20**) with its remarkably simple backbone, is well-known for its two reversible reduction peaks at -1.09 and -1.52 V, and each step marked by distinct colour change. Inspired by this, the phosphole-fused viologen **1-21** was reported to have outstanding electrochemistry comprised of shifting the reduction values of the parent compound to $E_{\text{red1}} = -0.51$ and $E_{\text{red2}} = -1.00$ V, while sustaining peak reversibility at a variety of scan rates ranging from 10-2000 mVs⁻¹.⁴⁸ In later studies, chemical reductions of the arylated viologen analogue **1-22** using zinc, lithium and copper were carried out, leading to the generation of mono- and di-reduced species.⁴⁹ Furthermore, methylation of the phosphorus center in **1-23** not only pushes the reduction processes to exceptionally low values of -0.3 and -0.8 V, but also enables the P-based material to store a third electron within its backbone, which is rare for small conjugated materials (Figure 1-8).⁵⁰ These low reduction potentials are supported by a low LUMO energy (-4.67 eV) and resulted in the isolation of the chemically reduced mono-to tri-reduced species. Moreover, **1-23** was successfully assembled into a Li-ion battery as cathode showcasing decent performance due to its high specific energy density.

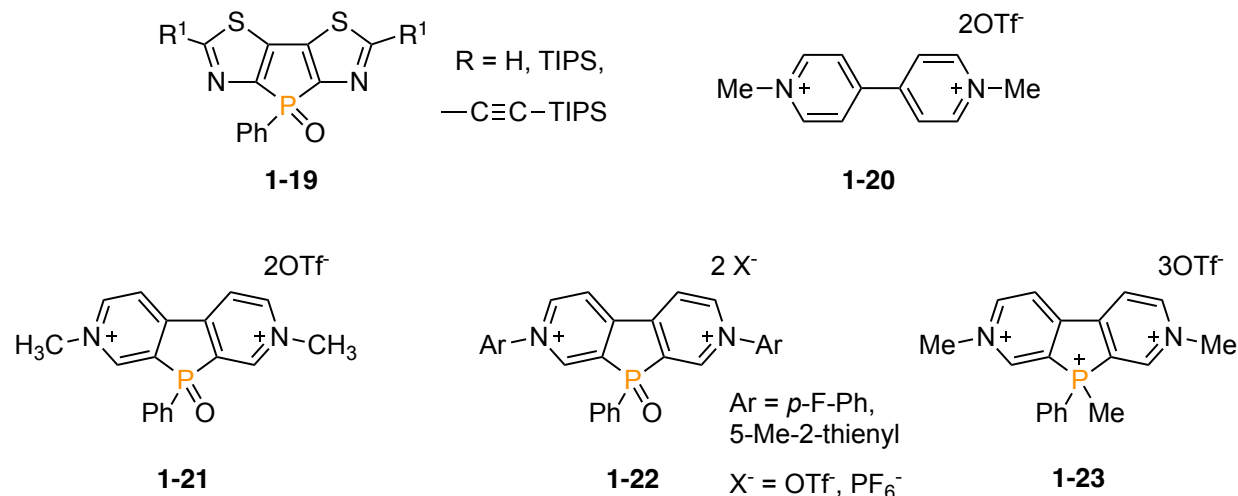


Figure 1-8. N and P-modified conjugated materials with advanced electrochemical features.

1.2.3. Cyclic P-based Materials: Phosphinine

In the context of synthesis, the unsaturated 6-membered P-containing ring, phosphinine, was first reported in the 1960s (**1-24**, Figure 1-9) as an air-sensitive compound with a good degree of stability to acid and base.⁵¹ The effective interaction between the phosphorus p orbital and the π -system endows it with high aromaticity. In addition to its planar structure, the P-localized and coplanar lone pair are key features of this ring. On the other hand, in conjugated materials the 6-membered P-containing ring is typically: 1) fused to other heterocycles and is integrated within the π -system and 2) includes exocyclic P-substituent(s) with the phosphorus in a trivalent, quaternary or oxidized state. This means that in these compounds, the P-heterocycle is essentially not a true phosphinine, but the P-atom rather serves as a bridging moiety. As a result, phosphinine usually lacks aromatic character and, in some cases, even bears antiaromaticity. Furthermore, the interaction of phosphorus orbitals (as well as P-functionalities) with the π -system ultimately results

in low LUMO and high HOMO energy levels, making the 6-membered-phosphacycle incorporated materials have both electron-donating and-accepting properties.⁵¹ These overlaps can be well adjusted by altering the substituents on the phosphorus, introducing conjugated compounds with tunable electronics that is sought after in materials chemistry.

One of the first reports of 6-membered phosphacycle-based compounds—with a nod toward materials application—was by Mathey and coworkers in 2007. They elaborated the synthesis of dithienophosphinine **1-25** and stated the structure has blue fluorescence along with a reduction feature at -1.9 V (vs. SCE).^{52,53} Since introducing electron-withdrawing groups such as carbonyl, nitro, and cyano groups into the backbone of π -organic compounds is a proven method for lowering the energy level of LUMO, our group attempted on synthesis of dithienoketophosphinine **1-26** in 2013 (Figure 1-9).⁵⁴ Fortunately, **1-26** possesses a lowered LUMO at -3 eV, which leads to a reduction peak at -1.5 V. Further alkylation of the P-center in **1-27** shifts the reduction to -1.12 V and unveils a second reduction peak at -1.75 V that is noteworthy for thiophene-based phosphacyclic systems. It should be mentioned that the improvement of the electrochemistry in dithienoketophosphinine comes at the expense of its photophysics, as **1-26** is not luminescent, in contrast to dithienophosphole **1-11**, most likely due to the presence of the keto group. The synthesis of the benzene analogue, dibenzoketophosphinine **1-28**, was reported during the 1970s, however without emphasis on materials applications. This changed when the Kivala group made two main modifications on this structure in 2017: applying phosphorus chemistry to install different groups on the P-centre, and converting the keto group to a dicyanovinylene substituent.⁵⁵ That brought about a series of conjugated materials **1-29** featuring two reversible reduction events ranging from -1.74 to -0.96 V. The P-methylated species, other than being the most electron-accepting, was also

the most stable as the compound showed no sign of degradation after being tested under various scan rates (50-1600 mV).

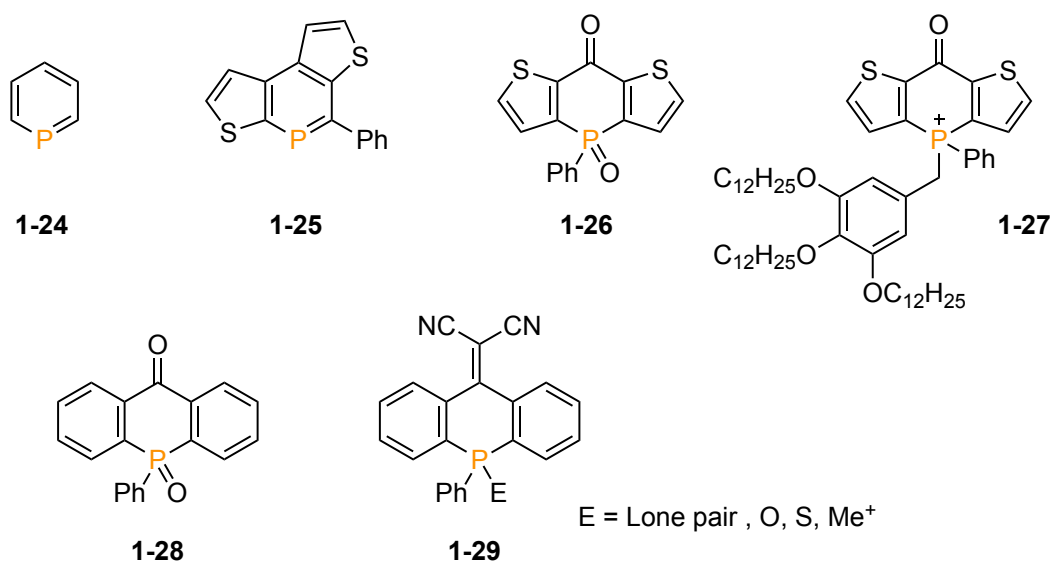


Figure 1-9. Selected organic materials with phosphinine core and insightful electrochemistry.

In 2015, Romero-Nieto et al. reported the synthesis of a set of phosphaphenylene **1-30**, including a naphthalene and a heterocycle fused to a phosphinine (Figure 1-10).⁵⁶ A wide variety of heterocycles, ranging from bulky to electron-rich or -deficient, as well as different P-substituents were applied to the scaffold, each yielding various luminescent emissions spanning from violet to red. As it turned out, merging electron-rich rings to the phosphaphenylene framework raises both the HOMO and LUMO levels, yet since the effect is stronger on the HOMO, it results in smaller energy gap and red-shifted emission. Interestingly, oxidizing the phosphorus center from its trivalent to the pentavalent state has stronger stabilizing impact on the HOMO, causing an increased energy gap and blue-shifted emission. This is intriguing as pentavalent phosphorus typically tends to decrease the energy gap in phospholes and red-shifts the absorption/emission.

Therefore, as it was mentioned, the engagement of the P-substituent with the π -system is present in all the P-containing rings, but the eventual influence on the properties could be vastly different. Other relevant instances of luminescent phosphinine-based conjugated materials are the phosphacycle-extended fluoresceine and rhodamine **1-31** and **1-32**, reported by Yamaguchi and Wang, respectively (Figure 1-10).^{57,58} Both works focus on the development of red to NIR luminescent materials with good quantum yield values and briefly investigate their application in bio-imaging.

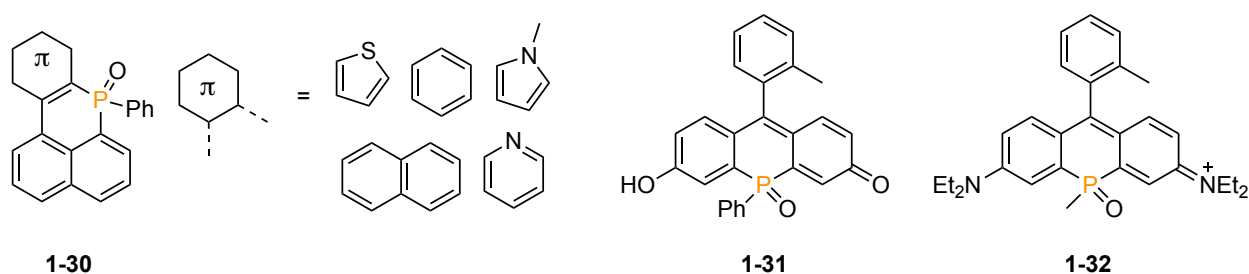


Figure 1-10. Select examples of fluorescent materials with phosphinine core.

1.2.4. Cyclic P-based Materials: Phosphepine

There is a declining trend in the number of literature reports when moving from phosphole- to phosphinine-based conjugated materials. This continues for the 7-membered-ring analogues of all the main group elements such as boron and silicon, and phosphorus.⁵⁹ Accordingly, phosphepine is the phosphorus-containing 7-membered relative, with early reports elaborating on its lability at room temperature and suggesting either protection of the P-center with bulky groups or ring fusion are necessary to address the issue (**1-33**, Figure 1-11).⁶⁰ The unsaturated ring generally adopts a non-planar structure, with phosphorus moiety bending out of the plane. Thus, the degree of interaction of the phosphorus orbitals with the π -system can differ significantly in each case, leading to relatively unexplored reactivity and properties.

In 2013, our group reported the synthesis of a series of dithienodiketophosphepine species **1-34**, with a view to enhance the electron-accepting character through incorporating carbonyl groups to the scaffold. As a consequence, the materials revealed two reduction events as low as $E_{\text{red1}} = -1.15$ and $E_{\text{red2}} = -1.59$ V with a corresponding LUMO at -3.74 eV. Most notably, **1-34** displays excitation-dependant luminescence, including dual emission (DE) in one case, which produced white light that is a rare attribute for a single conjugated material.⁶¹ In the same year, Lammertsma et al. reported the dibenzophosphepine **1-35** with a phosphorus remaining in its trivalent state.⁶² Notably, the compound accepts up to two electrons as indicated by its high-potential reduction events at $E_{\text{red1}} = -2.62$ and $E_{\text{red2}} = -3.03$ V that is not common for species with trivalent phosphorus, as they are electron-donors. Compound **1-35** was also chemically reduced with sodium, which marked the stability of the reduced species. In addition, the dithienophosphepine congeners **1-36** (Figure 1-11) were reported by different groups to have optical properties with moderate quantum yields, and charge mobility leading to their application as p-type semiconducting layer in an OFET device with moderate performance.^{60,63} Dinaphthalenophosphepine **1-37** was reported by Romero-Nieto as chiral scaffold featuring a two-step reduction and blue fluorescence with quantum yields up to 51%.⁶⁴ At last, the unique compound **1-38** containing a phosphepine-fused to a phosphole was merely reported for its synthesis, with no data relevant to materials chemistry.⁶⁵

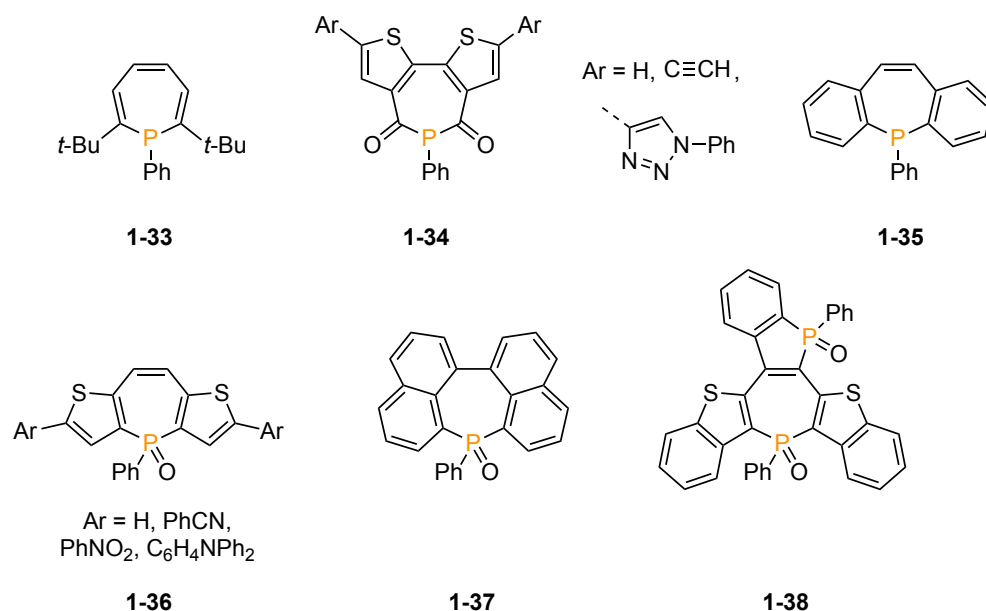


Figure 1-11. A few phosphepine-based systems with various properties.

1.3. Vat Dyes

Vat dyes are a particular class of polyaromatic hydrocarbons (PAHs) marked by their large π -extended hydrocarbon structure containing carbonyl groups in all cases, with some also featuring amines and in a few instances, halogens (Figure 1-12).^{66,67} Their distinctive π -organic systems endow them with intense light absorption in the visible region, leading to their vibrant colours and subsequently, over a century long application in various textile industries (primarily cotton). Moreover, the extended conjugated planes promote the strong π - π interactions and efficient packing in the solid state that is a prerequisite for charge-transporting properties. Consequently, holding these two fundamental characteristics makes them promising candidates for organic π -systems with potential employment in OSCs and OFETs.

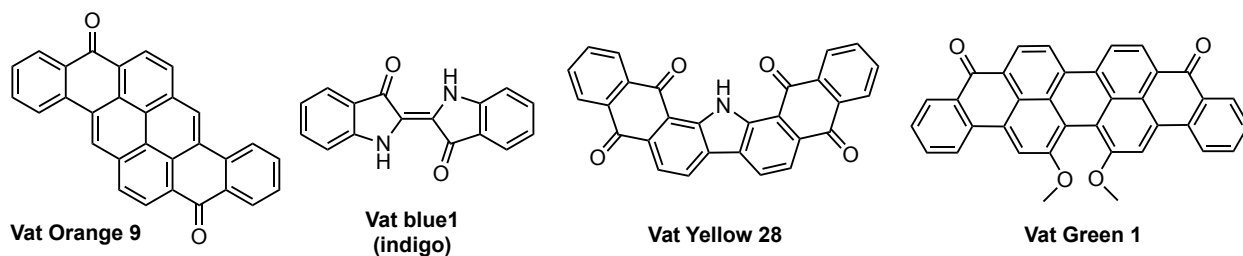


Figure 1-12. Select PAH structures belonging to the family of vat dyes.

The major drawback in using vat dyes is their poor solubility in organic and aqueous environments. A widely adopted traditional method in fabric treatment involves reducing the dyes' keto groups under basic conditions to render them water-soluble (and colourless), thereby enabling effective application. The dyes would then regain their original colour upon exposure to air (molecular oxygen). A similar concept can be implemented to make the dyes soluble in organic solvents, except the reduced keto groups should permanently be attached to a long alkyl chain. Alternatively, the keto groups can be entirely replaced by functionalities such as TIPS-acetylene, which typically changes the electronics in vat dyes and can result in interesting characteristics.⁶⁸ Nevertheless, exploring methods that can avoid compromising the carbonyl moieties may hold substantial novelty and value.

Currently, the annual consumption of vat dyes reaches up to thousands of tons and is a notable fraction of the fabric dye market.⁶⁹ Therefore, their massive production has made them very cheap, especially when purchased in bulk. This, combined with their highly desirable properties, has attracted many materials chemists to utilize the raw or chemically modified dye structures as active components and semiconductors in organic devices.⁷⁰ Thus, selected reports on vat dyes with higher importance along their materials applications will be covered in the following sections.

1.3.1. Exploited Vat Dyes in Organic Electronics

The limited studies on **Vat Blue 4** (indanthrone) primarily focus on the properties of the parent core; yet due to the solubility issues, its alkylated version **1-39**, offers greater potential (Figure 1-13).⁷⁰ Even though **1-39** possesses none of its original carbonyl groups, the phenazine moiety generated during the alkylation, remarkably decreases the energy gap (2.91 to 1.89 eV). As a result, green emission with a PLQY value up 56% is activated in the structure and the fabricated OLED device with **1-39** exhibits moderate luminance efficiency (intensity of light irradiated from a surface in a given area).⁷¹ A study on the same material revealed that shortening the alkyl chains from C₈H₁₇ to C₄H₉ can considerably boost the device performance, which alludes to the significance of controlled π - π interactions.⁷² Different reports on **Vat Yellow 1** (flavanthrone) underscore the n-type charge transport character in the dye. Replacing the keto groups with TIPS acetylene in **1-40** optimizes the π - π stacking between the conjugated units (3.38 Å) and triggers high electron mobility in transistors assembled with **1-40**.⁶⁸ Interestingly, the alkylated version of **Vat Yellow 1** (with OC₆H₁₃) was able to display higher quantum yields compared to its alkylated **Vat Blue 4** analogue (up to 80%) that led to OLED devices with improved performance (**1-40**, Figure 1-13).⁷³

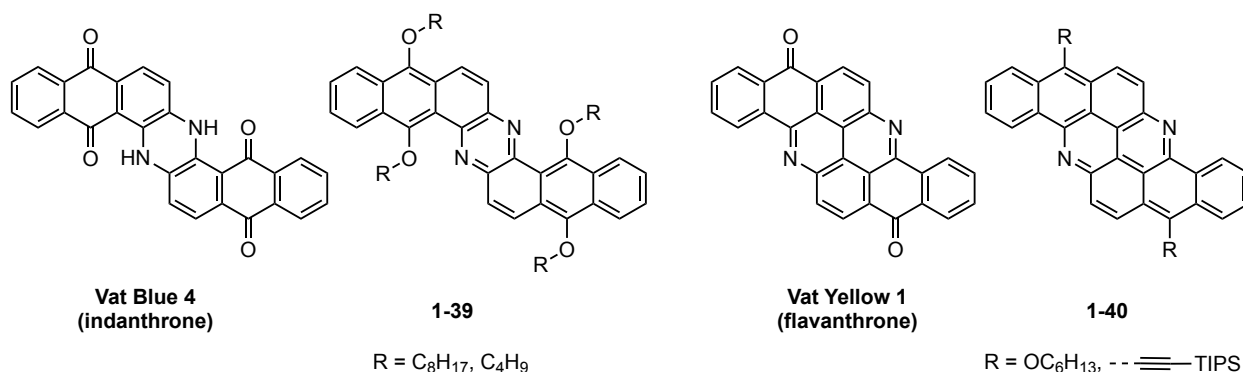


Figure 1-13. Select vat dye-based structures with main application in OLEDs.

A recent study on polymers derived from **Vat Orange 1** proved the materials to exhibit band gaps as low as 1.61 eV and p-type charge transport property (Figure 1-14). Accordingly, organic solar cells prepared with these conjugated materials exhibited up to 1.2% conversion efficiency.⁷⁴ Moreover, individual studies on **Vat Yellow 4** report the utility of the compound as n-type semiconductor in OFET with electron mobilities up to $1.5 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and solar cells with power conversion efficiency of 2.25%.^{75,76} More importantly, the first study also elaborates on the biological impact of some traditional organic semiconductors along with a few vat dyes. In fact, while materials such as fullerene C_{60} or pentacene can initiate DNA damage, no destructive effects were observed from vat dyes such as **Vat Orange 9** (Figure 1-12) or **Vat Blue 20**, which reassures their safe utility in organic devices that are in contacts with human skin.⁷⁵ Eventually, **Vat Brown 45** (Figure 1-14) stands out as a curious case among all vat dyes as it embeds an anti-aromatic pentalene unit within its molecular scaffold. Compound **1-41** with its TIPS-acetylene-modified structure was reported to have an energy gap of 1.41 eV that is incredibly low for any conjugated small-molecule material, which could be further reduced to 1.17 eV for the π -extended system. The materials display absorption features proceeding well into the NIR region, as well as reversible reduction peaks—a rare trait for vat dye-based structures lacking carbonyl groups—likely attributed to the presence of the pentalene unit.^{69,77}

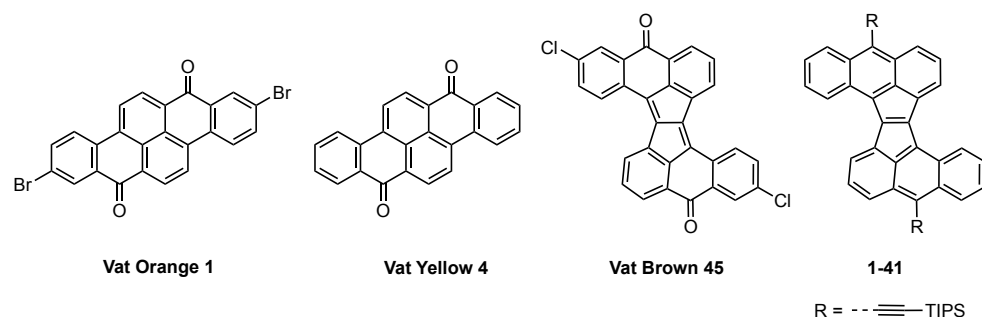


Figure 1-14. Select vat dyes with distinct properties.

1.3.2. Vat Orange 3: Chemistry and Materials Applications

Undoubtedly, among the family of vat dyes (and even PAHs), **Vat Orange 3** distinguishes itself as a prominent case that is highly favoured both in textile industries and materials chemistry (Figure 1-15). The scaffold comprises an anthanthrene core, bearing two keto groups (anthanthrone) and two bromine atoms, offering four possible starting points for chemical functionalization, rendering the materials' electronics readily manipulable. Over the years, various cross-coupling reactions such as Suzuki-Miyaura, Stille, Buchwald-Hartwig, and Sonogashira have been successfully employed to install different aryl groups, amines and substituted alkynes on the 4- and 10-sites of the core, each having notable effects on the framework's FMO energies (Figure 1-15).⁶⁹ Interestingly, the 6- and 12-positions are amenable to chemical alteration with an even broader range of substituents, each imparting distinct inherent characteristics. In addition to replacing the carbonyl groups with aryls, amines and acetylenes—albeit via entirely different methods—other modifications have been attempted, including insertion of dichloroolefins (Ramirez olefination) convertible to diarylolefins, dicyanomethylene (Knoevenagel condensation), and alkoxy groups with different alkyl length.⁶⁹ The varying natures of these substituents (from strongly electron-withdrawing to -donating) has also proven highly effective in generating VO3-based conjugated materials with assorted energy gaps (Figure 1-16).

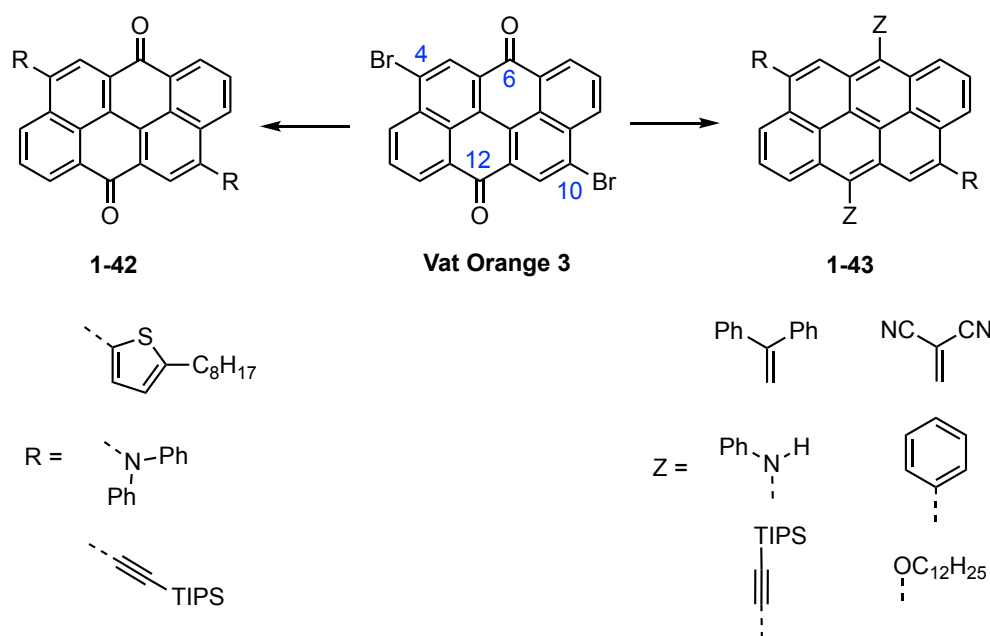


Figure 1-15. Chemical modifications attempted on 4-, 10-, 6-, and 12-positions of Vat Orange 3.

As an example, Neckers et al. investigated the impact of installing different combinations of phenyl groups (numbers and positions) on the emission intensity, which resulted in a set of blue luminescent conjugated materials with moderate to good quantum yields (**1-43** and **1-44**, Figure 1-16).⁷⁸ The fabricated OLED with **1-44** as emitter displayed good brightness (600 cd/m²) and a half-life up to 3500 h.⁷⁹ Moreover, reports on acetylene-substituted anthanthrenes such as **1-45** and **1-46** manifest their potential as p-type semiconductors. Briseno and coworkers mentioned the synthesis of **1-46** and its application in OSCs achieving 1.95% power conversion efficiency.⁸⁰ The Morin group demonstrated that tetraacetylenated anthanthrene derivatives with different terminal aryls, such as **1-45**, can reach hole mobilities up to $7.8 \times 10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ in OFETs, while their implementation in OSC can increase the efficiency up to 2.2% that is promising as these materials show minimal absorption past 600 nm.⁸¹ A series of unsymmetrically substituted VO3 such as **1-47**, were designed as donor-acceptor systems to push the absorption into the red-shifted region.

Thus, the developed OSCs from these materials attained the enhanced power conversion efficiencies of up to 5.3% (Figure 1-16).⁶⁹

The Morin group's research on the influence of different functional groups on the electrochemistry of VO3 offers illuminating insights. Replacement of the bromine atoms (4- and 10-positions) with thiophene, amine, and TIPS acetylene, while retaining the keto groups in **1-42**, reveals two reversible reduction events as low as -0.95 V. Replacing the keto groups with dicyanovinylene leads to a one quasi-reversible reduction event, but reduces the value to -0.58 V.⁸² In a subsequent study, the amine functionalization of two or all four positions in VO3 was explored in **1-48** and **1-49**. While the diamino-substituted **1-48** shows three reversible oxidation peaks, the tetraamino species **1-49** features four oxidation peaks with the lowest one occurring at +0.72 V.⁸³ These studies portray the anthanthrene core as a canvas whose electronics could be drawn towards both the electron-accepting through maintaining the original keto or electron-donating by adding (TIPS)acetylene and in particular, amines.

Ultimately, it is worth mentioning that the Morin group has also reported a number of VO3-based conjugated materials with attached conjugated hydrocarbon rings such as cyclopentane to further extend the fused π -system, such as **1-50**.⁸⁴⁻⁸⁶ These compounds possess a small energy gap (>1.71 eV) as well as reduction potentials as low as -1.38 V.

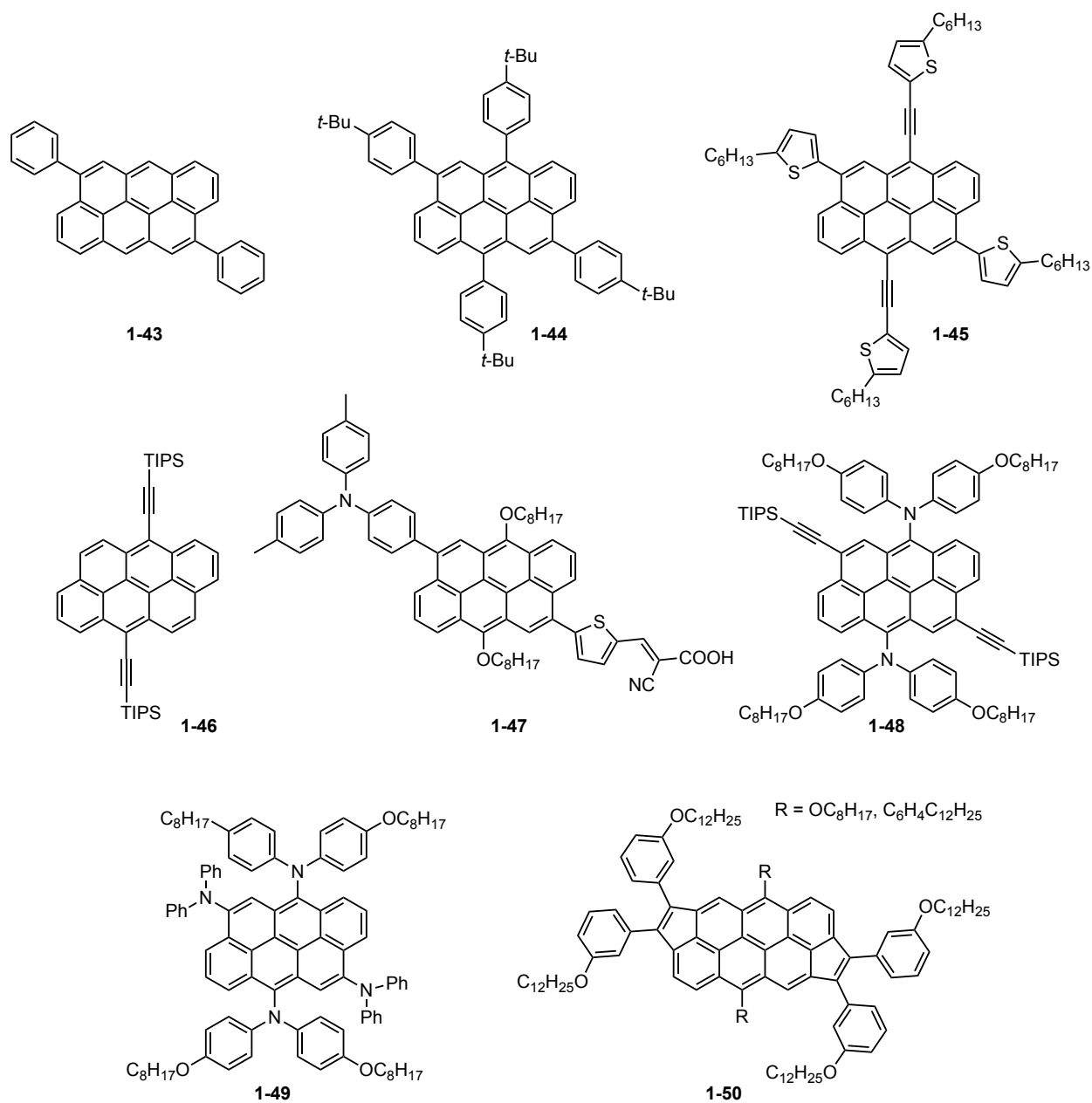


Figure 1-16. Examples of non-cyclic and cyclic scaffolds with anthanthrene core and VO3 as primary precursor.

1.4. Scope of the Dissertation

As demonstrated so far, the literature advocates phosphorus-based organic conjugated materials as strong candidates for intriguing optical and electrochemical properties. This statement remains

valid for vat dyes—specifically Vat Orange 3—as the high utility of their native scaffolds as well as the functionalized structures has been demonstrated in organic electronics. Our exploration of the literature reveals that the number of reports on P-containing conjugated systems with relatively larger π -systems is only limited to a few reports with naphthalene as their core (Figure 1-17).^{25,29,87,88}

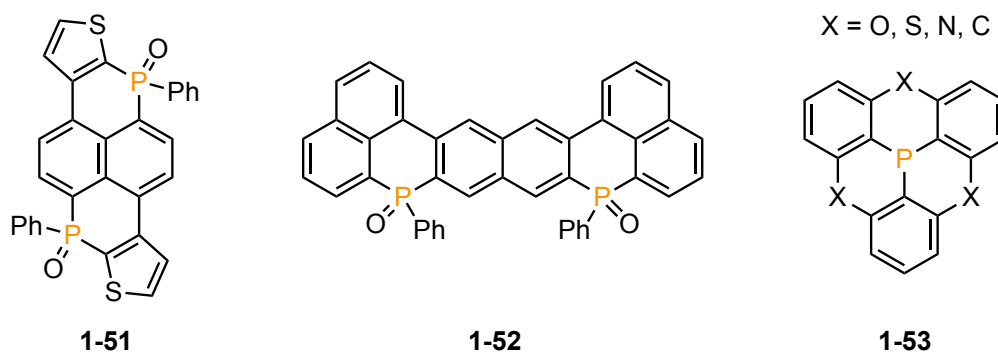


Figure 1-17. Examples of relatively large P-based conjugated materials available in literature.

Additionally, research on the employment of main group elements such as S, P, B, Si as a means of adding structural diversity in vat dyes is limited to such an extent that, to the best of our knowledge, there is no record on π -system extension in vat dyes through heterocycle annulation. Therefore, in order to address these bottlenecks, we are proposing the design of a series of conjugated materials based on Vat Orange 3 with expanded π -system through fusion of phosphorus containing heterocycles.

The primary objectives in each investigation are the exploration of the optimized synthetic methods and analyzing photophysical and electrochemical properties while keeping an eye on their solid-state behaviour along with the molecular packing. Given the limited understanding of the

effect of phosphorus in large π -systems, finding the answers for the following questions is of great importance to this work:

- 1) Considering the fact that the ratio of the phosphorus moieties to the hydrocarbon scaffold is significantly smaller in these systems, can phosphorus still play crucial role in adjusting the electronics of these systems?
- 2) Will phosphorus modification still be able to tune the photophysical and electrochemical properties?
- 3) And could this ability be influenced when the native structure of Vat Orange 3 is used (intact keto groups) vs. when the structure is already altered ($\text{OC}_{12}\text{H}_{25}$ instead of keto)?
- 4) Considering the fact that pentavalent phosphorus (with four substituents) is a stable chiral centre, the presence of two P-centers in these systems leads to isomeric products. Are the structural differences between the resulting diastereomers sufficient to differentially impact their molecular packing and optical property in the solid state?

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Chapter Two: From Flat to Twisted – Multifunctional Phosphacyclic Nanocarbons Based on Vat Orange 3

This chapter, which is the result of a formal collaboration with Carlos Romero-Nieto at UCLM in Spain, has been published and the contents presented here are reproduced from: R. Dadgaryeganeh, J. LeBlanc, E. Pradhan, D. Miao, A. Hussein, H. N. Hunter, T. Zeng, C. Romero-Nieto and T. Baumgartner, *Chem. Sci.*, **2025**, 16, 3680 (DOI: 10.1039/D4SC07106A) with permission from Royal Society of Chemistry (RSC). The supporting information to this Chapter is available online: <https://www.rsc.org/suppdata/d4/sc/d4sc07106a/d4sc07106a1.pdf>. Moreover, I extend sincere thanks to Dr. Ekadashi Pradhan and Dr. Tao Zeng, who were responsible for conducting computational calculations and actively participating in the writing process of this specific section in this Chapter. Jesse LeBlanc has performed the X-ray crystallography, while Dandan Miao and Amaar Hussein have provided synthesis support. I am also appreciative of the support from Dr. Howard Hunter for his help and insights on the NMR spectroscopy for some of the species reported in this Chapter.

Important Note: Number **2** before every number, scheme, and figure in this chapter indicates they belong to **Chapter Two**.

2.1. Introduction

As detailed in Chapter 1, the last two decades have witnessed accelerating development of π -conjugated organic materials with the goal of replacing metals and other limited resources for their negative environmental impact in practical applications.^{1,2} Many π -conjugated molecular systems have led to organic devices with satisfactory performances, however, more research is required to establish this technology widely.³⁻⁵ Key parameters to enhance the value of novel organic materials are, among others, the quality of interaction between the extended π -systems and visible light, ease of gaining or losing electrons, and/or conduction of ionic charges through their bulk phases. The latter requires optimized molecular packing in the solid state.⁶ Thus, to be able exploit the full potential of organic materials in practical devices, novel molecular structures need to be designed that allow: 1) effectively modulating the electronic structure of the systems to attain desirable functional properties and 2) adjusting the solid-state interactions for effectively optimizing the supramolecular organization in the bulk.

In this context, nanocarbons such as nanographenes, graphene nanoribbons (GNRs), and 2-dimensional (2D) polycyclic aromatic hydrocarbons (PAHs) are intriguing cores with desirable photophysical and semiconducting properties for organic electronics.⁷⁻⁹ In addition, recent studies have shown that structural ‘anomalies’ such as non-hexagonal rings, i.e., five-, seven-, or eight-membered carbo- and/or heterocycles¹⁰⁻¹⁶ can unlock intriguing structural diversity (i.e., twisted vs. planar graphenic scaffolds) and enable the exploitation of unique electronic properties not present in smaller systems (e.g., effectively tunable FMOs and energy gaps).¹⁷⁻²⁰

Two fundamental approaches for the preparation of new nanocarbons with improved capabilities include: a) the bottom-up synthesis from thoroughly designed molecular architectures or b) innovative derivatization of industrially produced dyes on large scales. While the former strategy

has indeed led to outstanding molecular architectures, it often suffers from tedious synthetic pathways with the consequent long production times and high costs. The latter approach has the advantage of starting from economically accessible raw materials, which through straightforward synthetic routes, enable cost-effective preparation. However, the disadvantage of this approach is that providing improved capabilities to well-established molecular architectures is often an arduous task.

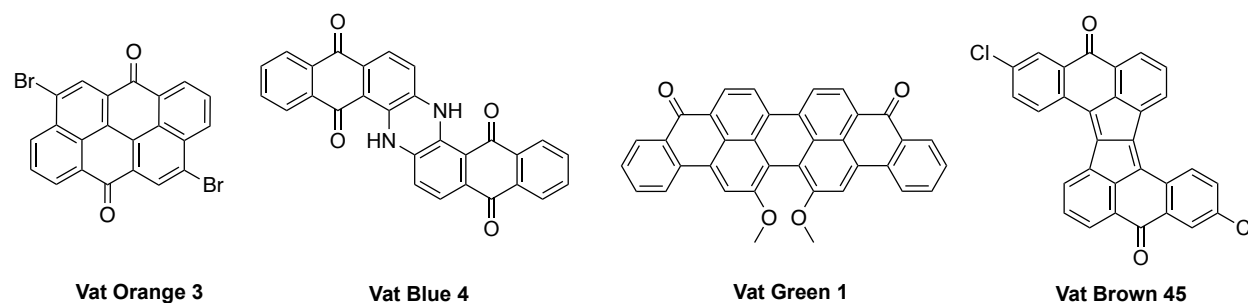


Figure 2-1. Representative vat dyes.

In this context, and as highlighted in the preceding chapter, vat dyes are a particularly interesting family of organic molecules (Figure 2-1).²¹ Their production is estimated to be in the range of 50-100,000 tons per year²² accounting for approximately 5–10% of the total textile dye market.²³ Vat dyes comprise extended π -systems with intense UV-Vis absorption, however, they are inherently insoluble due to strong π - π interactions, in addition to being mostly non-emissive. Nevertheless, owing to their absorption features, vat dyes cover a variety of colours and their massive volumes lower the production cost considerably.^{24,25} Moreover, the presence of nanocarbon units already within the vat dye core (e.g., anthanthrene, rylene) that are otherwise difficult to access due to onerous and expensive synthetic protocols, constitutes a key asset for the effective elaboration of functional materials. In addition, the presence of keto, halogen, and (occasionally) amine groups make them attractive precursor scaffolds.^{26–28} Examples of vat-dye functionalization toward

improved functional properties have been recently reported, revealing potential applicability in organic photovoltaics (OPVs), organic light-emitting devices (OLEDs), and organic field-effect transistors (OFETs).²⁹⁻³⁵ However, there still remains a need for comprehensive research to uncover their full potential. In this context, Vat Orange 3 (VO3, Figure 2-1) is a particularly interesting congener.³⁶⁻⁴⁰ It features an anthanthrene core with strategically placed functional groups - keto and bromo - that can be leveraged for functionalization toward enhanced properties; i.e., solubility, electronic properties, luminescence, etc.

We hypothesized that synergistically embedded heterocycles with inorganic main group elements, such as B, Si, and P, would enable the modulation of the frontier molecular orbital energy levels due to their distinct intrinsic electronics. Simultaneously, the molecular packing in the bulk phase could be also controlled.^{13,41} Among the most suitable main group elements, phosphorus provides several desirable electronic and geometrical characteristics for improved functions through simple chemistry avenues.⁴² For example, several phosphorus-containing conjugated materials with efficient luminescence or pronounced electron-accepting abilities have been reported, as detailed in chapter 1.⁴²⁻⁴⁸ Notably, the tetrahedral geometry of the phosphorus moieties also enables their use as stable chiral centres.⁴⁹ Thus, embedding two phosphorus centers in a π -conjugated scaffold gives rise to two stereoisomers (*cis* and *trans*) that can be leveraged for the modulation of the supramolecular organization in the solid state, while maintaining the photophysics and electronics specific to the π -conjugated core.⁶ Despite the advantages that main group elements, and especially P-containing conjugated systems, provide for the development of improved functional materials,^{13-16,48,50} their influence on the properties of vat dyes remains largely unexplored. Given the well-established benefits of phosphorus in enhancing the electronic properties of smaller carbon-based

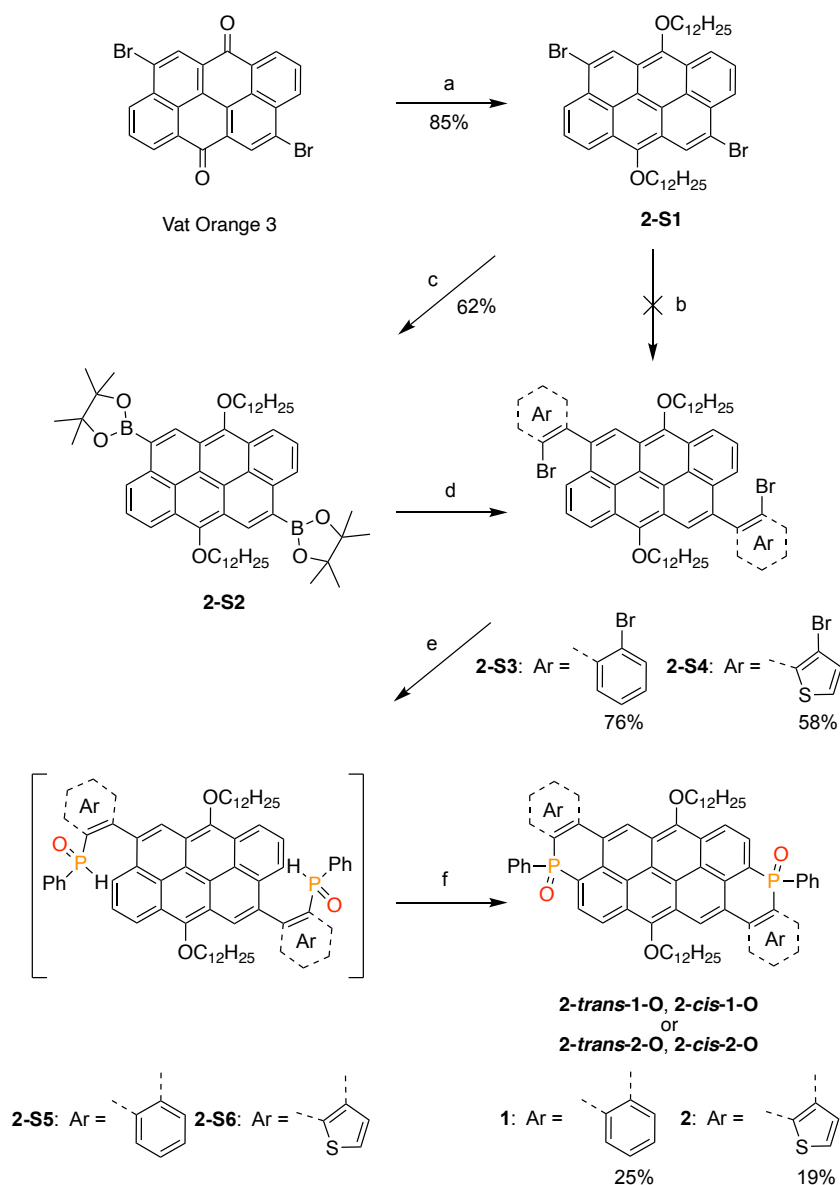
systems, the design and synthesis of novel 2D-expanded π -conjugated frameworks incorporating phosphorus present a promising area for further investigation.

In this chapter, we showcase the design and development of a first-of-its-kind series of highly functional, π -extended VO₃ materials. Through an innovative derivatization strategy, we have fused two six-membered phosphorus heterocycles with the VO₃ core, adding significant value to the overall properties of vat dyes. In particular, our comprehensive structure-property study reveals that the incorporation of the phosphorus-based units to the vat dye core leads to i) an unprecedented class of 2D-extended nanocarbons containing phosphorus heterocycles that are soluble, have highly tunable optical and electronic properties, ii) show intriguing behaviour in films, and iii) the formation of P-based stereoisomers with distinct solid-state packing. Our study thus provides a deeper understanding of the overall impact of phosphorus heterocycles in large, 2D-conjugated nanocarbon scaffolds.

2.2. Results and Discussion

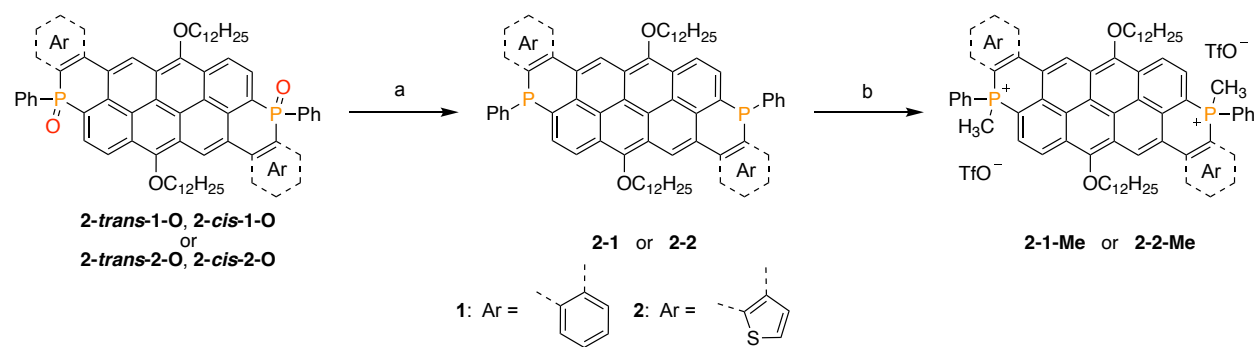
2.2.1. *Synthesis and Characterization*

The synthetic route toward targets **2-1-O** and **2-2-O** is illustrated in Scheme 2-1. To alleviate the well-known poor solubility of vat dyes due to strong π -stacking interactions induced by the planar conjugated units, we first converted VO₃ to **2-S1** in 85% yield. Installing the 2-bromoaryl units on **2-S1** could, in principle, be realized through Suzuki cross-coupling with the corresponding borylated reagent. However, despite several attempts and varied reaction conditions, **2-S4** did not form, which is probably due to the limited nucleophilicity of thiophene on second position. Instead, cross-coupling was accomplished by Miyaura borylation via **2-S2** and the subsequent reaction with the corresponding dibromoaryl derivatives to afford **2-S3** and **2-S4** in 76% and 58% yield, respectively.



Scheme 2-1. Synthetic routes toward **2-1-O**, and **2-2-O** as mixtures of *cis* & *trans* isomers. a) dodecyl bromide, sodium dithionite, 0.1M NaOH, 70 °C, 3 h. b) K₂CO₃, 3-bromo-2-borapinacolatothiophene, Pd(dppf)Cl₂ (7 mol%), 1,4-dioxane, 100 °C, 20 h. c) (Bpin)₂, Pd(dppf)Cl₂, KOAc, dioxane, 100 °C, 20 h. d) 2,3-dibromothiophene (or 1,2-dibromobenzene), Pd(PPh₃)₄ (10 mol%), K₂CO₃, dioxane/H₂O: 3:1, 100 °C, 20 h. e) 1: *n*-BuLi, PhPCl₂, THF, -78 °C, 4 h; 2: H₂O, 1h. f) AgNO₃, CH₃CN/toluene: 1:1, 90 °C, 12 h.

Finally, the phosphoryl groups were incorporated by metal-halogen exchange with *n*-BuLi and subsequent addition of PhPCl₂. Hydrolysis of the remaining P-Cl bond with water then led to the intermediate **2-S5** (or **2-S6**) after Michaelis-Arbuzov rearrangement (see Scheme S2-1). Treatment of the crude mixtures of **2-S5** or **2-S6** with a catalytic amount of AgNO₃⁵¹ led to both **2-1-O** and **2-2-O** as a mixture of *cis*- and *trans*-isomers (referring to P-substituents, Oxygen vs. Phenyl) in 25 and 19% overall yields for reactions *e* and *f* (Scheme 2-1), respectively. The two isomers of **2-1-O** are each characterized by a singlet in their ³¹P-NMR spectra at 9.2 and 8.8 ppm for **2-trans-1-O** and **2-cis-1-O**, whereas the isomers for **2-2-O** feature corresponding singlets at 7.8 and 7.5 ppm for **2-trans-2-O** and **2-cis-2-O**, respectively. Notably, all derivatives are soluble in chloroform and dichloromethane, with accessible concentrations of 1.2x10⁻² M, and 5x10⁻⁴ M, respectively, and present air- and photo-stability for months. Moreover, due to the pronounced polarity difference stemming from the orientation of the P=O groups for both the benzo- and thieno-fused species, the *cis*- and *trans*-isomers were separable via column chromatography (see SI for details). The presence of the phosphorus atoms within the vat dye frameworks provides access to a larger family of differently P-functionalized species. This, however, requires a starting material with trivalent phosphorus atoms (Scheme 2-2). Thus, **2-1-O** and **2-2-O** were treated with trichlorosilane in a microwave reactor at 150 °C, to afford the P-reduced products after 20 minutes. This non-stereoselective reaction⁵² led to isomeric mixtures of **2-1** (δ³¹P: -27.2 ppm, -27.5 ppm) and **2-2** (δ³¹P: -26.6 ppm, -26.8 ppm), even when using pure diastereomers as precursors. The trivalent species are prone to oxidation under ambient conditions, precluding their separation. Consequently, compounds **2-1** and **2-2** were purified under inert atmosphere as isomeric mixtures.



Scheme 2-2. P-modification reactions of **2-1-O** and **2-2-O** toward **2-1** and **2-2** and further modification toward **2-1-Me** and **2-2-Me**, both as mixtures of isomers (inseparable); a) HSiCl_3 , THF, MW, $150\text{ }^\circ\text{C}$, 20 min. b) MeOTf, CH_2Cl_2 , $0\text{ }^\circ\text{C} \rightarrow \text{RT}$, 12 h.

The reaction of **2-1** and **2-2** with an excess amount of methyl triflate in CH_2Cl_2 ($0\text{ }^\circ\text{C} \rightarrow \text{RT}$) led to the dicationic phosphorus derivatives **2-1-Me** ($\delta^{31}\text{P}$: 0.1 ppm, -0.4 ppm) and **2-2-Me** ($\delta^{31}\text{P}$: -1.4 ppm, -1.9 ppm), respectively. The charged **2-1-Me** and **2-2-Me** are stable under ambient conditions but inseparable by chromatographic techniques due to their high polarities. Hence, purification and characterization were performed on the mixture of isomers, similar to the trivalent congeners. The structures of **2-trans-1-O** and **2-cis-1-O** in the solid state, depicted in Figures 2-2, S2-1 and S2-2, were determined by single crystal X-ray diffraction. Notably, **2-cis-1-O** is also chiral and crystallizes as racemic mixture (Figure S2-2a). The noticeably curved π -system of the extended core in both **2-trans-1-O** and **2-cis-1-O** results from steric hindrance of the H atoms in the bay positions, selectively twisting the terminal rings away from the P-phenyl groups leading to overall S- and U-shaped molecular scaffolds for **2-trans-1-O** and **2-cis-1-O**, respectively (torsion angles **2-trans-1-O**: 7.4° ; **2-cis-1-O**: 16.7° and $16.3^\circ/11.8^\circ$ for the two enantiomers; Figures 2-2, S2-1 and S2-2). Moreover, the orientation of the P-centers also has a pronounced influence on the supramolecular packing.

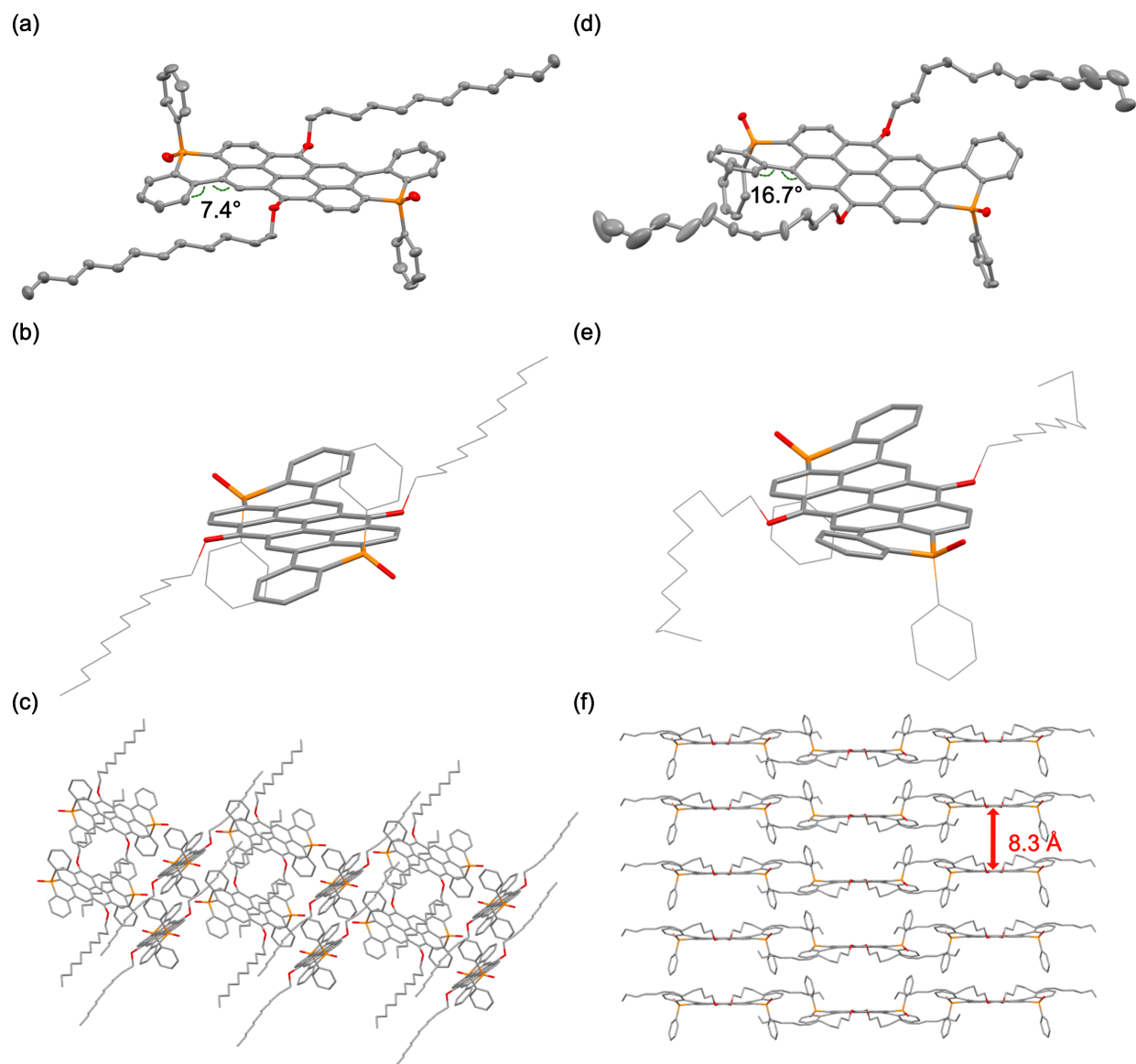


Figure 2-2. Solid-state structures obtained by crystallization from toluene of **2-trans-1-O**: (a) single molecule, (b) molecular curvature, (c) packing; and **2-cis-1-O** (d) single molecule (one enantiomer shown), (e) molecular curvature, (f) packing (a and d: 50% probability level, H-atoms omitted for clarity).

In sharp contrast with the parent VO₃, the P-extended species surprisingly exhibit little to no π -stacking in either case, despite their nanocarbon scaffolds. Compound **2-trans-1-O** exhibits a

slipped stack, herringbone-type arrangement with dodecyl chains separating the neighboring π -systems in an interdigitated fashion (Figure 2-2c). Conversely, the molecular packing of the racemic mixture of **2-*cis*-1-O** exhibits an “H-type” stacking of the conjugated systems, despite the long distance of 8.3 Å with the voids again filled by parts of the dodecyl chains (Figure 2-2f and S2-2). We were also able to crystallize two additional polymorphs of **2-*trans*-1-O** with solvated water and chloroform, respectively (Figure S2-1b,c). While structurally similar overall, in terms of molecular configuration of **2-*trans*-1-O**, each polymorph shows a distinct supramolecular organization due to the co-crystallized solvates. This also results in slightly altered torsion angles of 15.9° and 12.3° (Figure S2-1).

The solid-state structure of the thieno-congener **2-*trans*-2-O** (Figure S2-3) shows a herringbone-type packing pattern and a similarly curved molecular structure as **2-*trans*-1-O**, with a torsion angle of 9.6° (Figure S2-3). These results underscore the strong impact of the stereochemistry of the phosphorus centers that reflects earlier results on smaller linear 1D heteroacenes,⁵³ but also the steric footprint and torsional flexibility of the terminal fused rings on the supramolecular organization in the solid state. Notably, the system’s proclivity for aggregation in different environments is quite evident and suggests an inherently broader scope for fine-tuning the supramolecular organization of these large 2D nanocarbon systems compared to the significantly smaller relatives reported earlier.⁶

To gain some deeper insight into the effect of phosphacycle extension of the VO₃ core and the delocalized π -system of the new nanocarbons, we performed DFT calculations (see SI for technical details). The frontier molecular orbitals (FMOs) are shown in Figures 2-3 and S2-4. Illustratively, the FMOs of **2-*trans*-2-O’** and **2-*trans*-2’** (dodecyl truncated to Me) are spread over most of the scaffold including the phosphorus centres. The energy of the highest occupied molecular orbital

for HOMO and LUMO, respectively (Table 2-1). Nucleus Independent Chemical Shift (NICS) analysis confirms that the anthanthrene core is well preserved in all the synthesized species (Figure 2-3).⁵⁴ The ring current is symmetrically distributed over the extended core. Notably, the formally antiaromatic phosphacycles separate the aromatic currents from the anthanthrene core and the terminal benzo or thienyl rings, respectively.

Table 2-1. Photophysical, electrochemical, DFT data of the **2-1** and **2-2** series of compounds.

Compd	$\lambda_{\text{abs}}/\text{nm}^{[a]}$	$\epsilon / \text{M}^{-1}\text{cm}^{-1[a]}$	$\lambda_{\text{em}}/\text{nm},$ $^{[a]}, \Phi_f^{[b]}$	$\lambda_{\text{em}}/\text{nm}$ 0.2, 1.2% ^[c]	Φ_f 0.2, 1.2% ^[d]	$E_{\text{red1, 2}}/\text{V}^{[e]}$	$E_{\text{LUMO}}/\text{eV}$ (CV) ^[f]	$E_{\text{LUMO}},$ $E_{\text{HOMO}}/\text{eV}^{[g]}$	$E_g/\text{eV}^{[h]}$
2-trans-1-O	356, 509	94,300	528, 0.55	560, 617	0.45, 0.24	-1.70, -2.04	-3.10	-2.85, -5.37	2.52
2-cis-1-O	356, 509	58,600	526, 0.37	559, 632	0.35, 0.19	-1.64, -1.99	-3.16	-2.85, -5.38	2.53
2-1	369, 510	134,200	559, 0.39	562, 587	0.15, 0.08	-1.99	-2.81	-2.42, -4.91 (t) -2.42, -4.91 (c)	2.49 2.49
2-1-Me	363, 533	88,400	573, 0.41	578, 632	0.45, 0.11	-1.24, -1.59	-3.56	-4.08, -6.18 (t) -3.61, -6.09 (c)	2.10 2.48
2-trans-2-O	366, 517	40,500	536, 0.52	575, 657	0.25, 0.13	-1.58, -1.91	-3.22	-2.94, -5.41	2.47
2-cis-2-O	367, 517	61,700	537, 0.22	573, 683	0.13, 0.06	-1.59, -1.96	-3.21	-2.94, -5.40	2.46
2-2	376, 514	67,200	576, 0.31	586, 626	0.09, 0.06	-:-	-:-	-2.45, -4.89 (t) -2.46, -4.90 (c)	2.44 2.44
2-2-Me	373, 540	57,500	585, 0.35	590, 656	0.27, 0.10	-1.13, -1.47	-3.67	-4.12, -6.18 (t) -4.12, -6.19 (c)	2.06 2.07

^[a] Absorption/emission maxima and molar extinction coefficient obtained from CH₂Cl₂ solutions. ^[b] Fluorescence quantum yield determined via integrating sphere. ^[c] Emission maxima from PMMA thin films containing 0.2 and 1.2% P-modified vat dyes. ^[d] Fluorescence quantum yields of PMMA thin films containing 0.2 and 1.2% of P-modified vat dyes determined via integrating sphere. ^[e] Reduction potentials in volts obtained by cyclic voltammetry. ^[f] LUMO energy in eV obtained from the CV measurements. ^[g] Calculated HOMO and LUMO energies by DFT calculations. ^[h] Calculated energy gap.

2.2.2. Photophysical Properties in Solution.

The photophysical characteristics of the new species are summarized in Table 2-1, and representative UV-vis absorption and emission spectra of the benzo-fused series **2-1** are shown in

Figure 2-4 (see Figure S2-9 for spectra of the thieno-fused series **2-2**). Their overall photophysics are more complex, have considerably larger extinction coefficients, and are tunable over a wider range than those of previously reported smaller P-heteroacenes,^{6,53} but largely resemble those of related functionalized anthanthrenes.^{26,55} The observed superior photophysics (compared to smaller P-based scaffolds) can thus be attributed to the distinct molecular geometry of the extended 2D nanocarbon scaffold.

Specifically, all absorption spectra of the **2-1** and **2-2** series of compounds exhibit high- (356-376 nm) and low-energy (509-540 nm) absorption peaks, each with additional vibrational sidebands. Representative TD-DFT calculations for **2-cis-2-O** indicate that the low-energy absorption arises from HOMO→LUMO transition, and the high-energy absorption consists of a combination of HOMO→LUMO+2, HOMO-3→LUMO, and HOMO-1→LUMO+1 transitions (see Figure S2-7). These are symmetry-allowed a_g -to- b_u or b_u -to- a_g excitations. Here, we use the irreducible representations of the C_{2h} symmetry of the core planar structure to label the orbitals. The latter is a typical feature for rigid polyaromatic hydrocarbons including anthanthrenes.²⁶

The overall absorption patterns for the isomers **2-trans-1-O** and **2-cis-1-O** as well as their $\lambda_{\max}$ values are quite similar (356 and 509 nm; Figure 2-4, Table 2-1). The same is true for **2-trans-2-O** and **2-cis-2-O**, albeit somewhat shifted (366 and 517 nm; Figure S2-9a), because of the altered electronics resulting from different terminal rings in **2-1** and **2-2** series. However, the extinction coefficients of **2-trans-1-O** are larger than those of **2-cis-1-O**, while the situation is reversed for **2-trans-2-O** and **2-cis-2-O** (Table 2-1). While TD-DFT calculations show qualitatively identical oscillator strengths within each pair of *cis* and *trans* isomers (Table S2-1), we nonetheless posit that the observed extinction coefficients are due to different absorption cross-sections from geometrically distinct isomers.⁶

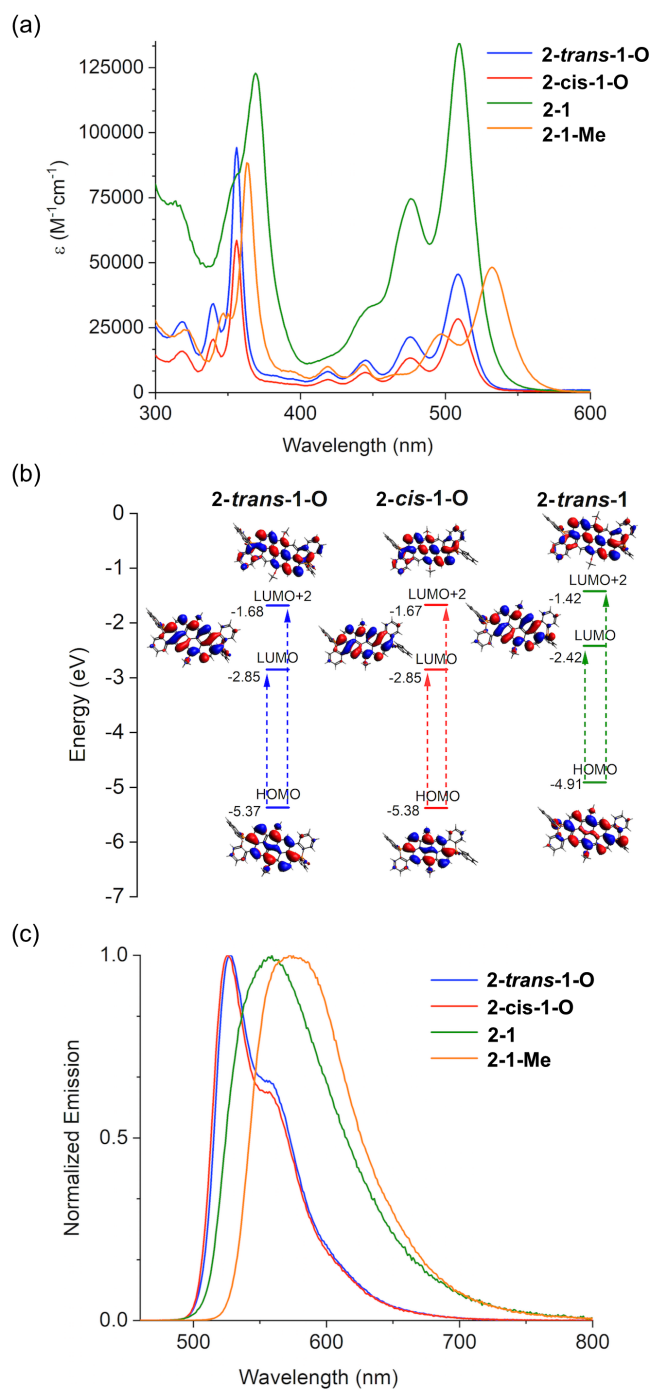


Figure 2-4. Absorption spectra (a), major transitions involved (b), and emission spectra (c) in CH_2Cl_2 of the benzo-fused isomers **2-trans-1-O** and **2-cis-1-O** along with the isomeric mixtures of P-reduced **2-1** and P-methylated **2-1-Me**.

The photophysics of the trivalent species **2-1** and **2-2** experience a small redshift for the high energy bands with $\Delta\lambda_{\text{abs}} = 13$ nm for **2-1** and $\Delta\lambda_{\text{abs}} = 10$ nm for **2-2** (Figures 2-3, 2-4, and S2-9), and their extinction coefficients are the highest in each of their respective series (up to 134,200 $\text{M}^{-1}\text{cm}^{-1}$). Methylation of the P-centers commonly stabilizes the LUMO in similar systems,^{56,57} and this is also manifested in the low energy bands for **2-1-Me** and **2-2-Me** that have the most red-shifted $\Delta\lambda_{\text{abs}}$, with notable values of 24 and 23 nm, in their respective series.

In general, replacing the terminal benzo unit with a thieno ring (i.e., **2-1**→**2-2**) red-shifts the absorption bands, which is also confirmed by DFT calculations (Table S2-2). Moreover, the extinction coefficients are high for all species (40,500 – 134,200 $\text{M}^{-1}\text{cm}^{-1}$), making them attractive materials for a range of applications (e.g., sensors, organic solar cells).

The emission spectra of **2-trans-1-O** and **2-cis-1-O** exhibit a similar shape and emission maxima at $\lambda_{\text{em}} = 527$ nm (Figure 2-4b). This is also the case for **2-trans-2-O** and **2-cis-2-O** (Figures S2-9b), overall exhibiting different shades of green fluorescence. Yet the quantum yields for *trans* isomers are notably much higher than those of the *cis* congeners in both systems, which can also be ascribed to distinct molecular geometries and flexibility of the twisted scaffolds in the excited state (Table 2-1). Reduction of the P-centers significantly red-shifts the emission to yellow ($\Delta\lambda_{\text{em}} = 32$ nm for **2-1**; 40 nm for **2-2**) (Figures 2-3, 2-4b, and S2-9b), an effect also found in other conjugated compounds with six-membered phosphorus heterocycles.^{56,57} Methylation causes a further redshift compared to the oxidized species toward orange luminescence ($\Delta\lambda_{\text{em}} = 46$ nm for **2-1-Me**; 49 nm for **2-2-Me**; (Figures 2-4b and S2-9b). This confirms the considerable impact of the P-centre on the overall electronics and photophysics of the scaffold. The quantum yields of all the new species range from moderate to high (22-55%) and with the benzo-fused series having slightly higher values than the thieno congeners (Table 2-1). The excited-state lifetimes of **2-trans-**

1-O and **2-*cis*-1-O** species range between $\tau = 3\text{-}4$ ns, clearly categorizing the emission as fluorescence (Figure S2-12a).

The two distinctive sets of absorption bands in all the species intrigued us to probe the excited-state photophysics and potential light-harvesting features of the system (Figure 2-5).^{58,59} As representative example, the emission spectra of **2-*trans*-1-O** excited at 356 nm and 509 nm revealed that although the emission maxima and overall patterns are alike, the relative intensities of the emissions depend on the excitation wavelength and also the concentration of the solution. At low concentration (i.e., $c = 10^{-7}$ M), the spectrum excited at 356 nm has a higher emission intensity than the one excited at 509 nm. As the excitation at 356 nm creates more excitons in higher excited states (*vide supra*), it is only logical to assume that at least some return to the LUMO via internal conversion (Kasha's rule) leading to a higher emission intensity than the spectrum excited at 509 nm, where the excited state exclusively involves the LUMO.⁶⁰ However, at higher concentrations ($c > 6 \times 10^{-6}$ M) the emission spectrum excited at 365 nm is less intense; this can be attributed to exciton quenching from non-radiative processes and molecular collisions due to aggregation. This is also reflected by the relative peak intensities in the respective excitation spectra (Figure S2-11), and similar results were obtained for all the new π -conjugated compounds of this series. These results reveal that controlling the aggregation for these systems (although expansive) in solution state is practically achievable.

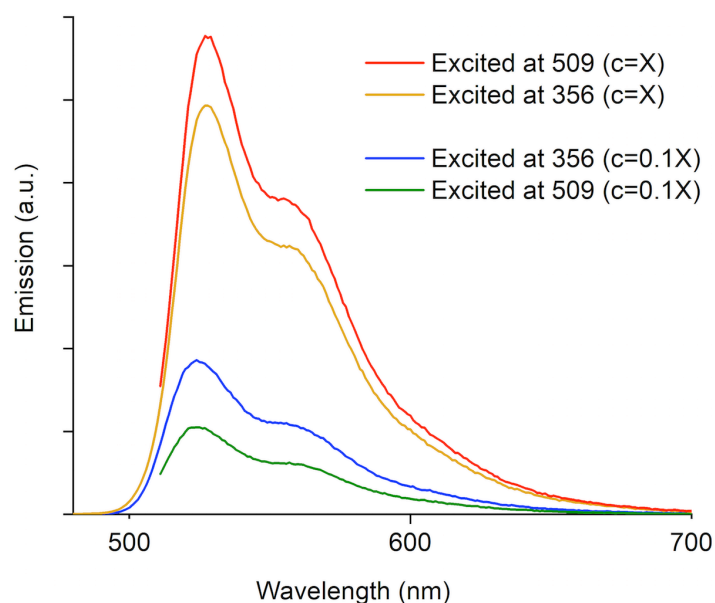


Figure 2-5. Concentration-dependant emission spectra of **2-*trans*-1-O** excited at 356 and 509 nm in CH₂Cl₂ ($X = 6.4 \times 10^{-6}$ M).

2.2.3. Emission Properties in the Solid State

To date, solid-state emission data have not been reported for any of the related systems with 6-membered phosphacycles in the literature.^{6,53} We were thus interested in uncovering the emissive behaviour of the new species in the solid state, as it could provide tangible insight into the potential utility of the materials in practical applications. Not surprisingly, all species were found to display negligible emission in the bulk, as emission quenching is already observed in solution (*vide supra*). This is indicative of strong intermolecular interactions that lead to non-radiative relaxation processes for these expansive π -systems. We thus surmised that separating individual molecules in a rigid matrix could lead to effective emission in solid state. Indeed, when polymethyl methacrylate (PMMA) is used as a matrix to seclude the nanocarbon species, pronounced luminescence emerges for all species. Their emissive behaviour was assessed by preparing 0.2 and

1.2 wt% films of the respective species in PMMA (Figure 2-6). Intriguingly, the emissions of the 0.2 wt% films for all the compounds in series **2-1** and **2-2** are very intense with fluorescence quantum yields up to 45% (Table 2-1). In particular, the 0.2 wt% films of the benzo-fused **2-trans-1-O** and **2-cis-1-O** display quite similar λ_{em} values, whereas a redshift is observed for **2-1** and **2-1-Me**, akin to the trends seen in solution (Figures 2-6a and 2-4b). More importantly, slightly increasing the concentration to 1.2 wt% has a surprisingly strong effect. The λ_{em} values are considerably red-shifted, which is reflected in a switch of the emission colours of the films, i.e., from green to orange for **2-trans-1-O** (Figure 2-6c). In fact, the emission wavelength differences ($\Delta\lambda_{\text{em}}$) between the PMMA films with 0.2 and 1.2 wt% of the benzo-fused series range from 25 nm for **2-1** up to 73 nm for **2-cis-1-O**. In particular, when comparing the emission spectra of the 0.2 and 1.2 wt% films, broader, red-shifted profiles are observed for the films with higher concentration in all cases, suggesting the formation of J-type excimers or aggregates of the dye-based compounds (Figure 2-6a,b).⁶¹⁻⁶³ Intriguingly, the excited-state lifetimes of the 0.2 wt% films of **2-trans-1-O** and **2-trans-2-O** exhibit a 3-4 ns component that is close to the values in solution, but also another component with a longer lifetime of around 10-13 ns that suggests the presence of aggregates already at low concentration. Moreover, the 1.2 wt % films display fluorescence lifetimes of around 30 ns which supports strong aggregation, but a component with a lifetime of about 4-6 ns is still present here as well (Figure S2-12b,c). Thus, even though aggregates may be responsible for the red-shifted emissions, in the PMMA matrix, the latter appear sufficiently isolated from additional deactivation pathways that could lead to a rapid dissipation of the excited state energy.

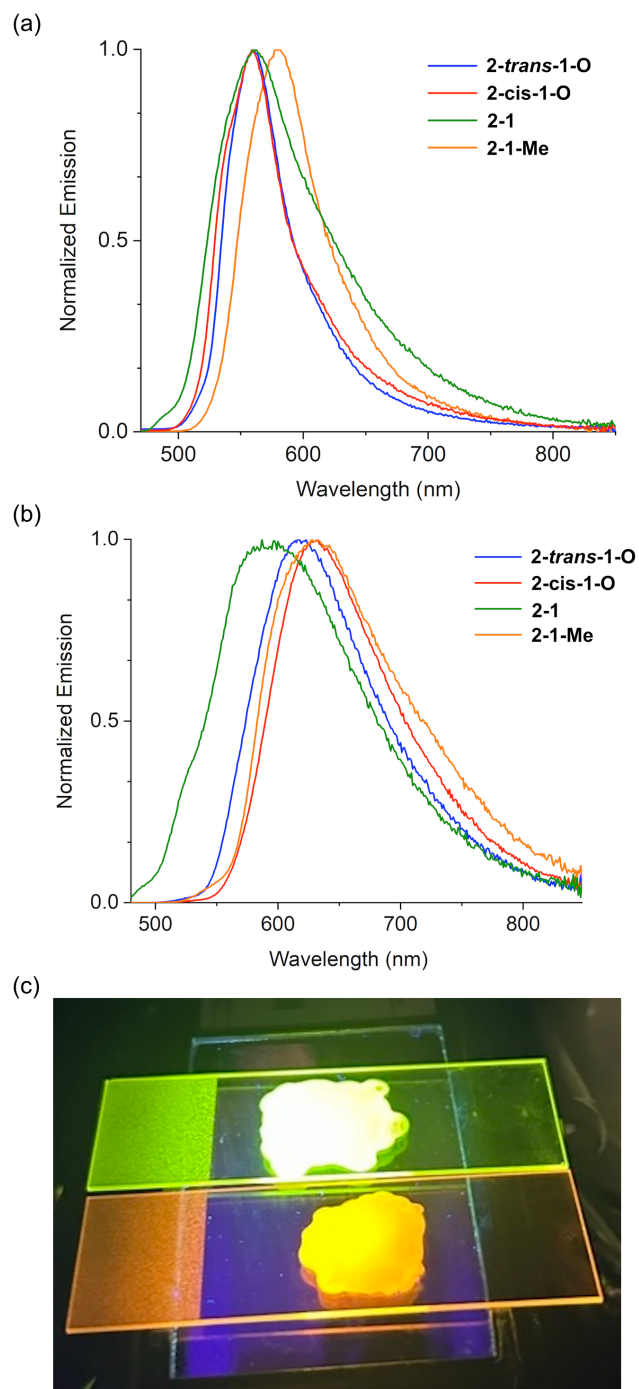


Figure 2-6 Emission spectra of the PMMA films containing (a) 0.2 wt% and (b) 1.2 wt% of the benzo-fused series **2-1**. (c) Emission colour of the PMMA films with 0.2 wt% (top), and 1.2 wt% (bottom) **2-trans-1-O**.

Regardless of the specific underlying processes, such a drastic change in luminescence colour and fluorescence lifetimes of a single, conjugated compound from only a minor change in the concentration is unique. In fact, it is also worth mentioning that films with more than 5 wt% of the phosphacycle-modified vat dyes exhibit aggregation-caused quenching of the emission, similar to the bulk solid.

The measurements on the thieno-fused series **2-2** provided similar emission patterns for the 0.2 wt% films (Table 2-1, Figure S2-10). However, $\Delta\lambda_{\text{em}}$ between the 0.2 and 1.2 wt% films for them is overall more pronounced (40 nm for **2-2** up to 110 nm for **2-cis-2-O**, Figure 2-S10). Moreover, the 1.2 wt% films of the thieno-fused series **2-2** possess considerable emission in the near-IR region. These results convincingly underpin that the delicate balance between molecular and intermolecular interactions of this system has a considerable impact on the overall solid-state photophysics.

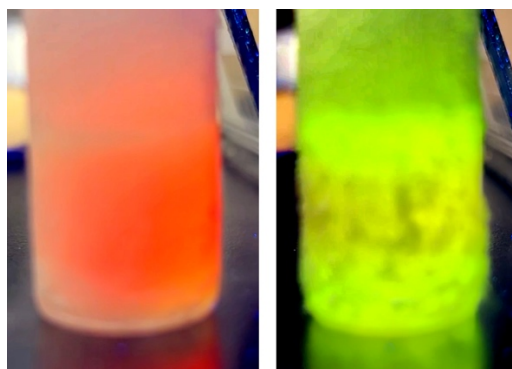


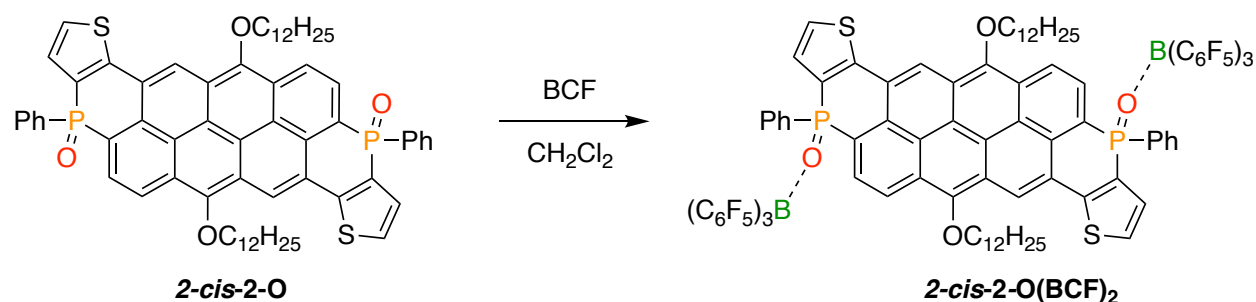
Figure 2-7. Fluorescence of the vials containing CH_2Cl_2 solutions of **2-trans-1-O** at 77K (liquid N_2) (left) and 2 minutes after being taken out of the liquid N_2 (right).

To determine the influence of temperature on the photophysics of these systems and to inherently simulate the rigid environment of the thin films, a qualitative study was undertaken on **2-trans-1-O**. A CH_2Cl_2 solution of **2-trans-1-O** ($c = 10^{-6}$ M) was cooled down to 77 K (liquid N_2)

before warming back up to room temperature, while the luminescence was monitored with a UV lamp at 365 nm (Figure 2-7). Surprisingly, the orange emission of the frozen slurry correlated well with the emission colour for the 1.2 wt% PMMA film. Upon slowly increasing the temperature, the colour gradually changed to green, which is generally observed for solutions at room temperature. Additional experiments revealed that 157 K, sufficient to freeze CH₂Cl₂, is required to simulate the rigid environment of the PMMA films, i.e., to trap the π -extended molecules close to each other and provide the aggregates with red-shifted emission. Notably, similar results were observed for both isomers of **2-1-O** and **2-2-O**, respectively.

2.2.4. Further Functionalization of the P-oxide Species

Since the reduction toward the trivalent species in each series always led to an inseparable mixture of isomers, we were interested in maintaining of the isomeric purity upon P-modification. To this end, we investigated the coordination chemistry of **2-cis-2-O** with the strong Lewis acid B(C₆F₅)₃ (BCF).⁵² We previously established that selective coordination of the P=O bond to a Lewis acid such as BCF red-shifts and often enhances the luminescence because of a stabilized LUMO.^{64,65} To our satisfaction, upon addition of BCF to a solution of **2-cis-2-O**, a prompt emission shift from green to orange was observed, indicating the formation of the adduct **2-cis-2-O(BCF)₂** (Scheme 2-3). This was also supported by a pronounced low-field shift from $\delta = 7$ to 19 ppm in the ³¹P{¹H} NMR spectrum (See SI, ³¹P{¹H} NMR of **2-cis-2-O(BCF)₂**). In order to track the coordination of BCF to the two phosphorus centers, **2-cis-2-O** was titrated with increasing amounts of BCF (0-100 equiv.), and the resulting changes were measured by UV-vis spectroscopy (Figure 2-8a).



Scheme 2-3. Generation of the Lewis adduct **2-cis-2-O(BCF)₂** in CH₂Cl₂ from **2-cis-2-O**.

The clean conversion from **2-cis-2-O** to **2-cis-2-O(BCF)₂** was observed via two isosbestic points at 373 and 531 nm (Figure 2-8a). While the high energy absorption peak is red-shifted by only 11 nm, the low energy band shifts by 38 nm. As revealed by the TD-DFT calculations (*vide supra*), the low-energy absorption arises from the HOMO→LUMO transition. This reveals that the newly added P-terminal rings to the π -system of the vat dyes have a stronger contribution to the lower-energy peaks upon functionalization.

The corresponding emission spectra were measured by exciting the solutions at the two isosbestic points (Figure 2-8b,c). Although exact isoemissive points were not detected (likely due both equilibria occurring at the same time), the presence of three species can be clearly distinguished in the emission spectra that are assigned as follows: uncoordinated **2-cis-2-O**, as well as coordinated **2-cis-2-O(BCF)**, and **2-cis-2-O(BCF)₂**, i.e., with one or two BCF coordinated moieties, respectively. At the outset, **2-cis-2-O** exhibits an emission maximum at $\lambda_{\text{em}} = 537$ nm, while in the presence of 0.25 equiv. of BCF, this peak diminishes and a new peak at 577 nm emerges, which is attributed to the monocoordinated **2-cis-2-O(BCF)**. Upon increasing the amount of BCF beyond 1 equiv. (enough for only one P-centre), the peak at 537 nm disappears, and similarly, a red-shifted peak at 585 nm emerges, suggesting the formation of **2-cis-2-O(BCF)₂** even with less than 2 equiv. of BCF.

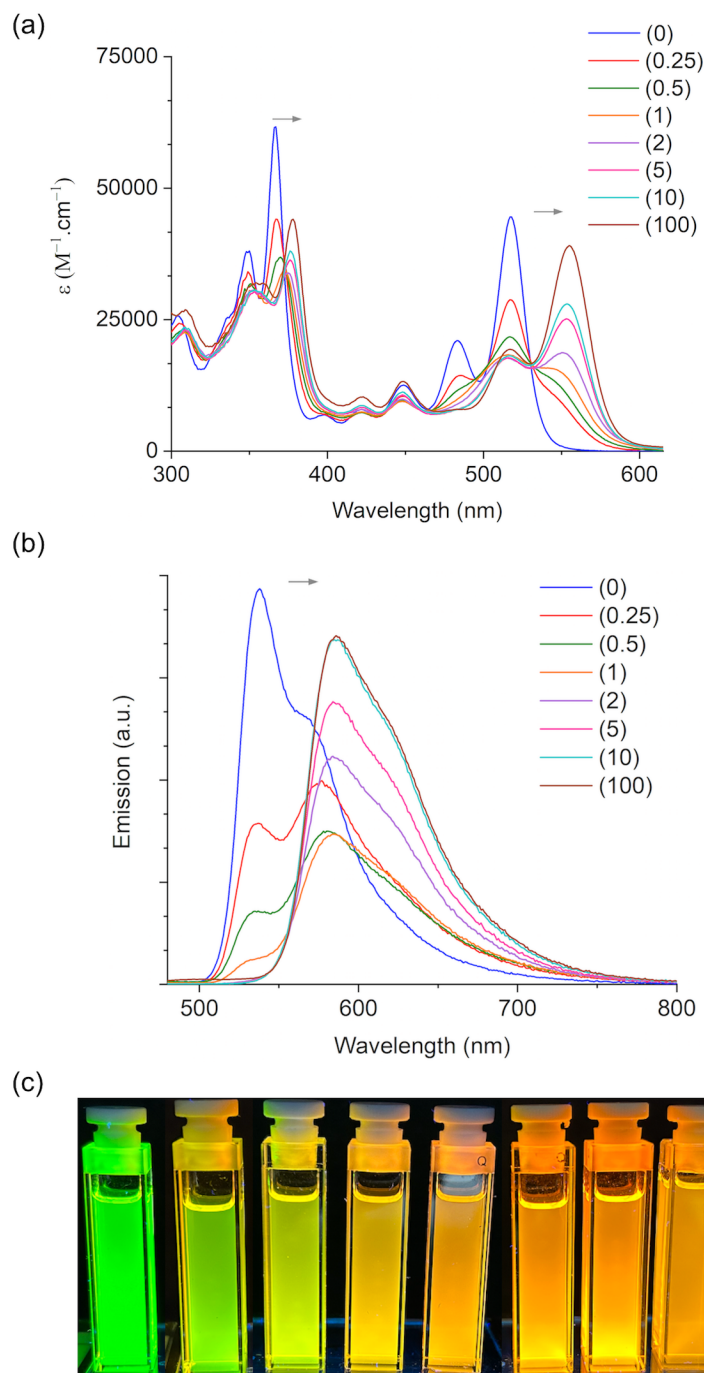


Figure 2-8. Absorption (a) and emission (b) spectra of **2-cis-2-O** upon titration with BCF in CH_2Cl_2 . (c) Solutions with equal concentrations of **2-cis-2-O** with increasing amounts of BCF from 0 (left) to 100 (right) equivalents.

Excess BCF then leads to the complete formation of **2-*cis*-2-O(BCF)₂** with a $\lambda_{\text{em}} = 586$ nm, with an overall redshift of 49 nm for the full conversion of **2-*cis*-2-O** to **2-*cis*-2-O(BCF)₂**, which is more than twice the redshift observed for a related, but smaller 1D systems (20 nm) reported earlier.⁵² This again illustrates the strong influence of phosphorus modification on the overall electronic structure of the nanocarbon system. To further understand the spectral change induced by BCF, we compared the DFT-calculated results for **2-*cis*-2-O** and **2-*cis*-2-O(BCF)₂** (Figure S2-7). BCF coordination lowers the LUMO energy more than the HOMO energy. Consequently, the low-energy absorption that arises from HOMO→LUMO excitation is noticeably red-shifted, which aligns with our previous work on dithienophospholes.⁶⁴

The same coordination study was also performed for **2-*trans*-1-O** (Figure S2-8), however, the best results were obtained for **2-*cis*-2-O**, which is attributed to the overall distinctly twisted scaffolds (*cis* vs. *trans*) and the resulting π -stacking interactions of one of the perfluorophenyl substituents of BCF with the extended nanocarbon main scaffold that is often observed for such systems.^{53,64}

2.2.5. Redox Properties

To measure the influence of the electron-withdrawing phosphorus-containing moieties on the electron-rich anthanthrene core of VO3, cyclic voltammetry was performed on all new species (see Figure 2-9 for series **2-1** and S2-13 for all species). To our satisfaction, **2-*cis*-1-O** and **2-*trans*-2-O** each exhibit two reversible reduction peaks with E_{red1} at -1.64 and -1.58 V, respectively. While **2-*trans*-1-O** and **2-*cis*-2-O** have fully reversible (or quasi-reversible) first reduction peaks (-1.70 and -1.59 V), their second reductions are quasi-reversible. The trivalent isomeric P-species **2-1** have reversible peaks at $E_{\text{red1}} = -1.99$ V and -1.81 V as the result of their higher-lying LUMO. It should be noted that this pronounced degree of (quasi)reversibility is not

observed for the smaller P-containing, or native nanocarbon relatives in the literature that generally show irreversible reduction events.^{6,53,66}

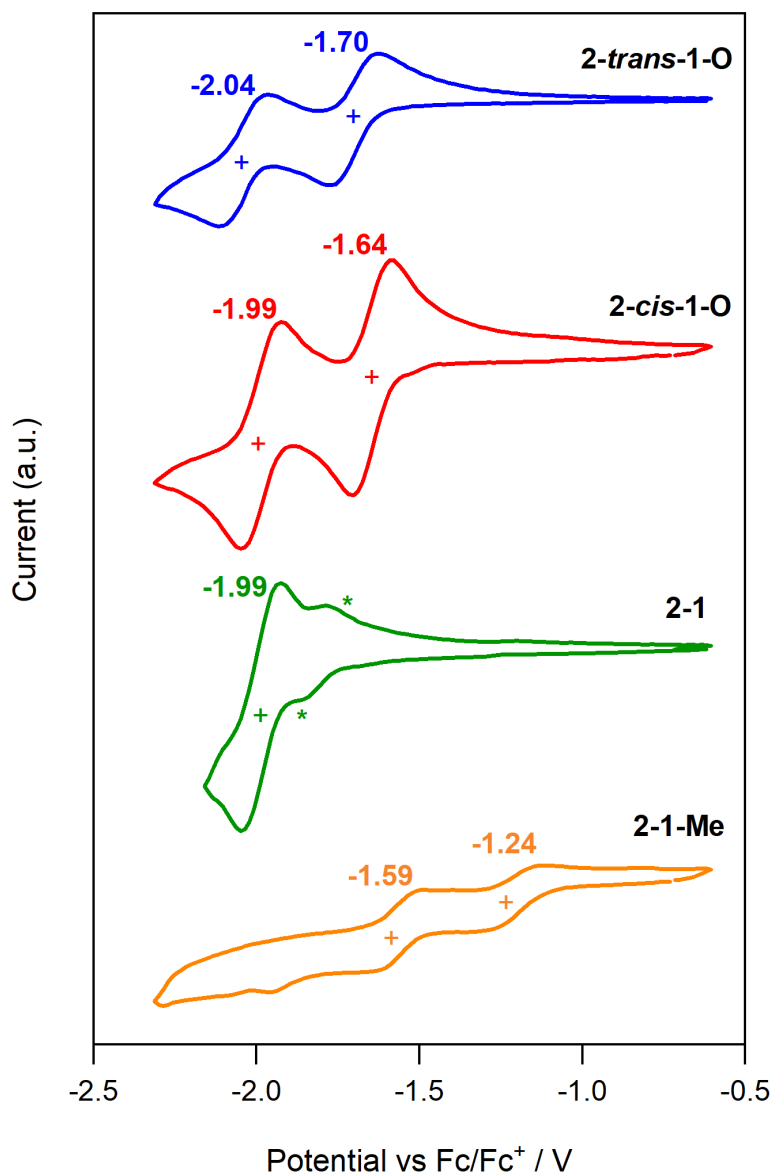


Figure 2-9. Cyclic voltammograms of **2-trans-1-O** (blue), **2-cis-1-O** (red), **2-1** (green; * indicate the anodic and cathodic redox processes for the second isomer), **2-1-Me** (orange), with scan rate 100 mV s⁻¹, in CH₂Cl₂ with 0.1 M NBu₄PF₆, vs. Fc/Fc⁺.

Methylating the P-centers causes a significant decrease in reduction potentials of **2-1-Me** and **2-2-Me**, lowering the E_{red1} to -1.24 and -1.13 V, albeit as quasi-reversible (or irreversible) reductions. Nonetheless, these values correlate well with low-lying LUMO and LUMO+1 energies of -3.56 and -3.67 eV, respectively, akin to those found in PCBM-C₆₀ (-3.7 eV), a strong electron acceptor widely used in electronic devices.⁶⁷ This is remarkable for a such an expansive π system. In addition, most compounds also show one or two oxidation peaks above -0.12 V, but all are irreversible,⁶⁸ which is typical for phosphorus-containing conjugated materials.

2.3. Conclusion

We successfully obtained a new family of π -conjugated 2D-nanocarbons through innovative derivatization of Vat Orange 3 with two phosphorus heterocycles. Our approach provides access to significantly value-added vat dyes, i.e., materials with a longstanding history and multi-ton annual production, thus paving the way for scalable preparation. The new benzo- and thieno-fused species with two chiral, and easily modifiable phosphorus centres present as two diastereomers for each species with distinct packing in solid state, while maintaining similar electronic properties. These materials exhibit not only rich and straightforward chemistry but also intriguing emissive properties in both solution and solid state. They are strong UV-vis absorbers with extinction coefficients of up to 134,200 M⁻¹cm⁻¹ and identical λ_{max} values for the *trans* and *cis* isomers, respectively. Moreover, their photophysical properties can be tailored by P-functionalization, resulting in redshifts in both absorption and emission spectra. Indeed, both the benzo- and thieno-fused vat derivatives can be endowed with intriguing emission properties with moderate to high fluorescence quantum yields. PMMA films of the P-functionalized vat dyes revealed interesting solid-state photophysics. At a very low concentration of fluorophore (0.2 wt%), the films exhibit

strong emission with a slight redshift compared to their solutions. Surprisingly, a minimal increase in concentration of only 1 wt% gives rise to a dramatically red-shifted emission, which we attribute to the formation of aggregates, together with a remarkable increase in fluorescence lifetime. A similar effect was observed for a frozen slurry at 77 K; the solid matrix displayed red-shifted emission, while thawing recovered the original green-yellow emission of the species in solution. Coordination of BCF to the P=O groups of individual diastereomers results in a clean conversion to Lewis adducts with strongly red-shifted photophysics (from green to orange), while maintaining the isomeric purity of the species. Cyclic voltammetry revealed the existence of reversible reduction peaks for **2-1-O** and **2-2-O**, along with very low reduction peaks and LUMO levels at ca. -3.6 eV for **2-1-Me** and **2-2-Me**, rivaling those of widely used fullerene acceptors. Therefore, the integration of phosphorus heterocycles into 2D nanocarbons not only inherently enhances the properties of purely carbon-based systems, but also endows the system with an intriguing degree of tunability that is highly desirable for functional materials chemistry.

All-in-all, this study provides a fundamental cornerstone that underscores the significant potential of main-group chemistry in elevating conjugated materials, particularly by establishing the chemistry of phosphorus-embedded nanocarbons. The first successful integration of the advantageous functional properties of organophosphorus species and the economical availability and abundance of Vat Orange 3, allowed us to synthesize a highly value-added family of materials. Based on the promising results from this initial study, the following chapters will detail our efforts in broadening the scope of organophosphorus-based vat dyes by exploring further molecular scaffolds and architectures.

2.4. References

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- 68 Compound **2** did not show any discernible reduction or oxidation events under the same conditions, despite its relatively high solubility.

Appendix A: Chapter Two

From Flat to Twisted – Multifunctional Phosphacyclic Nanocarbons Based on Vat Orange 3

2.1. General section:

Reactions were carried out in dry glassware and under an inert atmosphere of purified argon using Schlenk techniques. Anhydrous solvents such as CH_2Cl_2 , THF, pentane, were used directly from a solvent purification system (MBraun) or, in case of reactions or column chromatography, were purchased from commercial suppliers and used as received. Standard solvents such as MeCN, chloroform (CHCl_3), CH_2Cl_2 , ethanol (EtOH), *n*-hexane, methanol (MeOH), and toluene were purchased from commercial suppliers and used as received. Deuterated solvents such as chloroform-*d* were purchased from commercial suppliers and used as received. Aluminum oxide, aq. ammonia solution (NH_4OH) (aqueous solution with 25% - 30% NH_3 basis), Celite®, 2,3-dibromothiophene, hydrochloric acid (HCl) (36.5 - 38% aq. solution), magnesium sulfate (MgSO_4), *n*-butyllithium ($n\text{BuLi}$) (2.5 M solution in hexanes), potassium carbonate (K_2CO_3), potassium phosphate tribasic (K_3PO_4), silica gel, sodium carbonate (Na_2CO_3), sodium hydrogen carbonate (NaHCO_3), sodium hydroxide (NaOH), tetrakis(triphenylphosphine)palladium(0) ($\text{Pd}(\text{PPh}_3)_4$), 2-thienylboronic acid, trichlorosilane (HSiCl_3), triethylamine (Et_3N), [1,1'-Bis(diphenylphosphino)-ferrocene]dichloropalladium(II) ($\text{Pd}_2(\text{dppf})\text{Cl}_2$) were purchased from commercial suppliers and used as received.

NMR: ^1H , ^{13}C , and ^{31}P NMR as well as COSY, HSQC and HMBC spectra were recorded on a Bruker NEO 400, 700 spectrometer (400 MHz (^1H), 101 MHz (^{13}C), 162 MHz (^{31}P); 700 MHz (^1H), 176 MHz (^{13}C), respectively). The chemical shift δ values were corrected to CDCl_3 (δ 7.26 ppm for ^1H , δ 77.16 ppm for ^{13}C). Signal descriptions include: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet and br = broad. All coupling constants are absolute values and J values are expressed in Hertz (Hz). All ^{13}C signals are singlets unless stated otherwise.

X-Ray crystallography: X-ray crystal structure analyses were measured at 173 K on a Bruker DQ Quest eco instrument. The structure was solved and refined using OLEX2 and SHELXL. CCDC numbers 2370339 (**2-trans-1-O** without solvent), 2370340 (with H_2O), 2370341 (**2-trans-1-O**, with CHCl_3), 2370342 (**2-cis-1-O**), 2370338 (**2-trans-2-O**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Microwave reactions: Microwave reactions were carried out with an Anton Paar Monowave 200 microwave reactor using suitable reaction vials with Teflon-coated silicone caps.

Theoretical calculations: Molecular optimizations were carried out at the B3LYP/6-311+G(d) level by using the ORCA suite of programs.^{S2-7} Solvent effects (CH_2Cl_2) were considered by using the polarization continuum model (PCM).

Steady-state spectroscopy: Absorption and emission spectra were recorded from CH₂Cl₂ solutions using an Agilent Technologies Cary 5000 UV-Vis spectrometer and Edinburgh FS5 instrument spectrometer with a SC-05 standard cuvette holder, respectively.

Fluorescence quantum yields Φ : Quantum yields were determined using integrating sphere.

Fluorescence lifetimes τ : The fluorescence decays were recorded with an Edinburgh FS5 instrument spectrometer using TCSPC. Fluorescence lifetimes were acquired by an exponential fit according to the least mean square with Fluoracle software.

Electrochemistry: Cyclic voltammograms were recorded using a Metrohm Autolab potentiostat from CH₂Cl₂ solutions using tetrabutylammonium hexafluorophosphate as electrolyte, glassy carbon as working electrode, platinum wire as counter electrode and silver/silver chloride (Ag/Ag⁺) as pseudo-reference electrode. Scan rate is 100 mV s⁻¹. The curves were calibrated using ferrocene as internal standard ($E_{1/2} = 0.60$ V). The voltammogram was recorded using the NOVA software package.

Preparation of the films: Polymethyl methacrylate (PMMA; 0.5 g) was added to 10 mL CH₂Cl₂ solution in a 20 mL vial and stirred overnight. Then, 4 mL of the aforementioned solution (containing 0.2 g PMMA) was added to another 20 mL vial and subsequently charged with 2.4 mg of the compound from series **1** or **2**, and stirred for 1 h. The resulting solution was drop-cast onto a glass slide and the solvent evaporated subsequently. The prepared 1.2 wt% PMMA films were placed in an oven at 80 °C for 30 minutes to fully dry and then directly used in the fluorimeter.

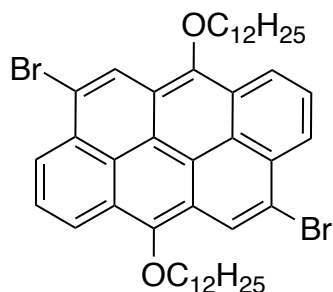
For preparing 0.2 wt % films, 0.4 mg of the respective conjugated compound and 4 ml of CH₂Cl₂ solution of PMMA (containing 0.2 g PMMA) were used in the identical procedure.

A blank slide was used as a reference to establish the absence of additional emission features arising from the glass that could interfere with the film measurements.

2.2. Experimental details

2.2.1. Synthesis

Compound 2-S1

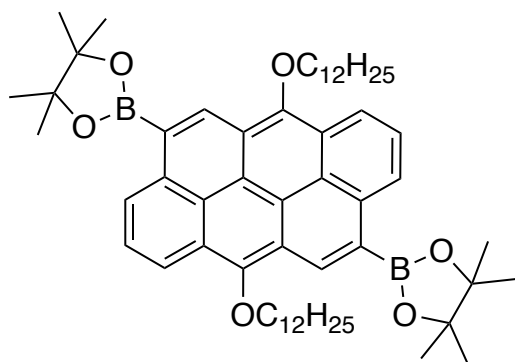


Based on a modified procedure.^{S2-1} To a 250 ml Schlenk flask under argon, vat orange 3 (1.0 g, 2.1 mmol), dodecyl bromide (4.3 g, 17.2 mmol), aliquot 336 (1.2 ml, 2.6 mmol), Na₂S₂O₄ (0.97 g, 5.6 mmol) were added, then dissolved in 100 ml of NaOH solution (0.1M) and the mixture was bubbled with argon for 10 minutes. The reaction was stirred at 70 °C for 3 h. After cooling to room temperature, the water was decanted, and the yellowish-orange solid was filtered and washed with methanol and then acetone. **2-S1** was purified by flash column chromatography using silica (CH₂Cl₂-Hex, 1:1), (85% yield, 1.47g).

^1H NMR (700 MHz, CDCl_3) δ 8.79 (d, J = 8.0 Hz, 2H), 8.77 (s, 2H), 8.63 (d, J = 7.4 Hz, 2H), 8.21 (t, J = 7.7 Hz, 2H), 4.34 (t, J = 6.5 Hz, 4H), 2.16 (t, 4H), 1.77 (t, J = 7.6 Hz, 4H), 1.52 (p, J = 7.6 Hz, 4H), 1.45 (p, J = 7.0 Hz, 4H), 1.41 – 1.35 (m, 4H), 1.35 – 1.20 (m, 22H), 0.89 (t, J = 7.0 Hz, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 149.0, 130.4, 126.4, 126.1, 125.6, 125.0, 124.7, 123.5, 122.1, 121.9, 119.2, 32.0, 30.8, 29.8, 29.7, 29.4, 26.3, 22.7, 14.2.

Compound 2-S2

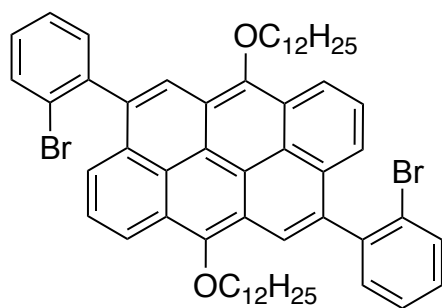


Based on a modified procedure.^{S2-2} Compound **2-S1** (2.1 g, 2.6 mmol), B_2pin_2 (3.0 g, 11.8 mmol), $\text{Pd}(\text{dppf})\text{Cl}_2$ (155 mg, 0.19 mmol) and KOAc (1.5 g, 15.3 mmol) were added to a 250 mL Schlenk flask under argon. After adding 30 ml of dioxane, the mixture was deaerated by bubbling with argon for 10 minutes. The mixture was then refluxed at 100 °C under inert atmosphere for 20 h. Upon completion, 100 mL of methanol were added to the cooled mixture and the generated precipitate was filtered and washed with methanol and acetone. **2-S2** was purified by flash column chromatography using silica (CH_2Cl_2 -Hex, 1:1) obtaining the product as a yellow solid, (62% yield, 1.62 g).

¹H NMR (400 MHz, CDCl₃) δ 9.16 (s, 2H), 9.10 (d, *J* = 7.5 Hz, 2H), 8.79 (d, *J* = 8.1 Hz, 2H), 8.18 (t, *J* = 7.9 Hz, 2H), 4.42 (t, *J* = 6.4 Hz, 4H), 2.96 – 2.88 (m, 2H), 2.23 – 2.12 (m, 5H), 1.88 – 1.76 (m, 8H), 1.50 – 1.38 (m, 12H), 1.38 – 1.24 (m, 55H), 0.93 – 0.86 (m, 12H).

¹³C{¹H} NMR (176 MHz, CDCl₃) δ 150.4, 134.1, 134.0, 126.1, 125.9, 125.6, 125.1, 121.2, 120.9, 120.4, 84.0, 32.1, 31.0, 29.9, 29.9, 29.9, 29.8, 29.5, 26.6, 25.2, 22.8, 14.3.

Compound 2-S3



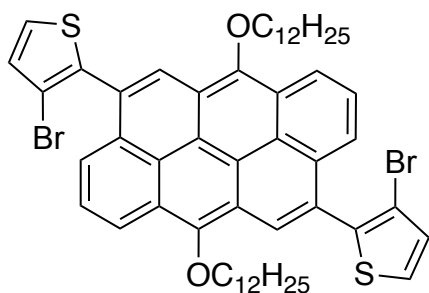
Compound **2-S2** (2.0 g, 2.2 mmol), 1,2-dibromobenzene (2.1 g, 8.9 mmol), Pd(PPh₃)₄ (254 mg, 0.22 mmol), K₂CO₃ (1.2 g, 8.9 mmol) were added to a 250 mL Schlenk flask under argon, then dissolved in dioxane/water (36/9 mL) and the mixture was deaerated by bubbling with argon for 10 minutes. The mixture was then refluxed at 100 °C for 20 h, cooled down to room temperature before 100 mL of water were added to the mixture. The crude product was filtered and washed with methanol and acetone. **2-S3** was purified by flash column chromatography using silica (CH₂Cl₂-Hex, 4:10), obtaining the pure product as a yellow powder (76 % yield, 1.59 g).

¹H NMR (400 MHz, CDCl₃) δ 8.83 (d, *J* = 8.2 Hz, 2H), 8.41 (s, 2H), 8.10 (t, *J* = 7.9 Hz, 2H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.83 (d, *J* = 7.5 Hz, 2H), 7.69 – 7.60 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 2H), 7.48 –

7.39 (m, 2H), 4.46 – 4.37 (m, 4H), 2.20 – 2.08 (m, 4H), 1.75 – 1.62 (m, 4H), 1.51 – 1.40 (m, 4H), 1.39-1.21 (m, 30H), 0.89 (t, $J = 6.6$ Hz, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, CDCl_3) δ 150.1, 141.8, 139.0, 133.2, 132.4, 131.1, 129.5, 127.6, 126.1, 126.0, 124.8, 124.6, 123.5, 123.2, 121.7, 120.9, 120.1, 77.3, 77.2, 77.0, 32.1, 30.9, 29.8, 29.8, 29.8, 29.7, 29.5, 26.4, 22.9, 14.3.

Compound 2-S4

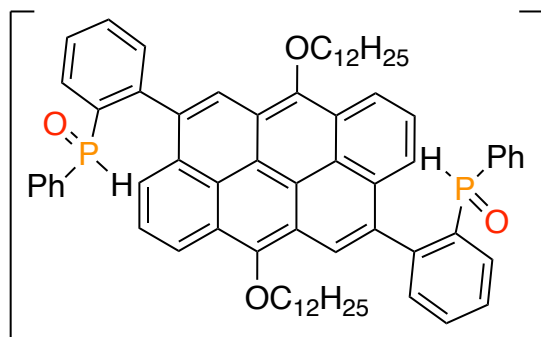


Compound **2-S2** (1.50 g, 1.55 mmol), 2,3-dibromothiophene (1.50 g, 6.20 mmol), $\text{Pd}(\text{PPh}_3)_4$ (179 mg, 0.16 mmol) and K_2CO_3 (0.86 g, 6.2 mmol) were added to a 250 mL Schlenk flask under argon, dissolved in dioxane/water (28/7 ml) and the mixture was deaerated by bubbling with argon for 10 minutes. The mixture was then refluxed at 100 °C for 20 h, cooled down to room temperature before 100 mL of water were added to the mixture. The crude product was filtered and washed with methanol and acetone. Compound **2-S4** was purified with flash column chromatography using silica (CH_2Cl_2 -Hex, 4:10) obtaining the pure product as a yellowish-orange solid, (58% yield, 0.87 g).

^1H NMR (700 MHz, CDCl_3) δ 8.84 (t, 2H), 8.57 (s, 2H), 8.17 (s, 2H), 8.16 (d, $J = 1.4$ Hz, 2H), 7.56 (d, $J = 5.5$ Hz, 2H), 7.28 (d, $J = 5.5$ Hz, 2H), 4.42 (t, $J = 6.6$ Hz, 4H), 2.15 (p, $J = 6.8$ Hz, 4H), 1.72 (p, $J = 7.6$ Hz, 4H), 1.47 (p, $J = 7.3$ Hz, 4H), 1.38 (p, $J = 7.2$ Hz, 4H), 1.35 – 1.21 (m, 27H), 0.89 (t, $J = 7.0$ Hz, 6H).

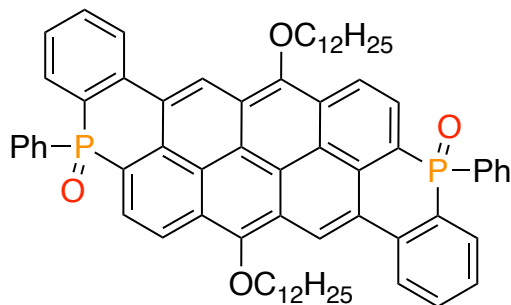
$^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, CDCl_3) δ 150.5, 137.0, 130.9, 130.4, 126.6, 126.4, 126.1, 126.1, 124.9, 123.8, 121.4, 121.2, 120.2, 111.6, 32.1, 30.9, 29.9, 29.8, 29.8, 29.8, 29.8, 29.5, 26.4, 22.9, 14.3.

Compound 2-S5



Compound **2-S3** (1.0 g, 1.05 mmol) was added to a 250 mL Schlenk flask with 150 mL of degassed THF under argon and the temperature was reduced to -78 °C. $n\text{-BuLi}$ (0.92 mL, 2.30 mmol, 2.50 M) was slowly added to the mixture and stirred for 1 h at low temperature. Next, PhPCl_2 (0.30 mL, 2.20 mmol) was added to the mixture and stirred for 3 h. Then, 7 mL of H_2O were added to the mixture, and it was stirred for 1 h. The solvent was evaporated under reduced pressure, the crude was re-dissolved in CH_2Cl_2 , and the organic phase washed with water. The organic phase was dried using MgSO_4 , the solvent was evaporated under vacuum. The product **2-S5** was obtained as a reddish crude, which was used for the next step without further purification.

Compounds **2-*trans*-1-O** and **2-*cis*-1-O**



The crude containing **2-S5** from the previous step was dissolved in a 100 mL round-bottom flask under air with a mixture of toluene/acetonitrile (1:1, 20 mL) and wrapped with aluminum foil. Then, the reaction flask was charged with silver nitrate (0.04 g, 0.24 mmol), capped and stirred at 90 °C for 12 h. The reaction was allowed to reach room temperature and the solvent was evaporated under reduced pressure. Compounds **2-*trans*-1-O** and **2-*cis*-1-O** were purified by flash column chromatography using silica (CHCl₃-Acetone, 10:1, *trans*-isomer elutes first) and then recrystallized in a mixture of CH₂Cl₂ and hexane at -10 °C, obtaining the pure compounds as orange solids. The calculated reaction yields are for the overall transformations from **2-S3** and to **2-*trans*-1-O** or **2-*cis*-1-O** (e and f steps of Scheme 2-1, main text).

Note: The *trans*- and *cis*-isomers are formed in an uneven ratio (confirmed by ³¹P NMR{¹H} of the crude mixture). Also, due to the lower solubility of the *trans*-isomer, it precipitates preferentially during the recrystallization process.

Trans-isomer **2-*trans*-1-O**: (14.5%, 0.16 g)

¹H NMR (700 MHz, CDCl₃) δ 9.61 (s, 2H), 8.97 (d, *J* = 8.3 Hz, 2H), 8.74 – 8.65 (m, 4H), 8.17 (dd, *J* = 12.2, 6.8 Hz, 2H), 7.83 (t, 2H), 7.73 – 7.67 (m, 4H), 7.63 (t, *J* = 7.2 Hz, 2H), 7.42 (td, *J* = 7.3, 1.4 Hz, 2H), 7.37 (td, *J* = 7.6, 3.0 Hz, 4H), 4.50 – 4.42 (m, 4H), 2.25 – 2.16 (m, 4H), 1.85 –

1.80 (m, 4H), 1.53 (p, $J = 7.4$ Hz, 4H), 1.49 – 1.41 (m, 4H), 1.40 – 1.34 (m, 5H), 1.34 – 1.21 (m, 24H), 0.88 (t, $J = 7.1$ Hz, 6H).

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ 9.2.

$^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, CDCl_3) δ 152.4, 138.1 (d, $J = 7.0$ Hz), 135.2 (d, $J = 110.9$ Hz), 132.6, 132.5 (d, $J = 7.0$ Hz), 131.7 (d, $J = 3.5$ Hz), 131.3 (d, $J = 10.6$ Hz), 131.0 (d, $J = 5.3$ Hz), 129.0 (d, $J = 10.6$ Hz), 128.9 (d, $J = 10.6$ Hz), 128.7 (d, $J = 12.3$ Hz), 128.6 (d, $J = 102.1$ Hz), 128.4 (d, $J = 7.0$ Hz), 127.9, 125.5 (d, $J = 8.8$ Hz), 124.4 (d, $J = 10.6$ Hz), 123.9 (d, $J = 102.1$ Hz), 122.5, 122.4, 122.3, 119.4, 78.3, 32.1, 31.0, 30.0, 29.9, 29.8, 29.8, 29.8, 29.5, 26.8, 22.8, 14.3.

$^{13}\text{C}\{^1\text{H}\}$ DEPT 135 NMR (176 MHz, CDCl_3) δ 132.5, 132.4 (d, $J = 7.0$ Hz), 131.6, 131.2 (d, $J = 10.6$ Hz), 128.9 (d, $J = 10.6$ Hz), 128.6 (d, $J = 14.1$ Hz), 128.2 (d, $J = 7.0$ Hz), 125.4 (d, $J = 8.8$ Hz), 122.3, 122.2, 78.2, 31.9, 30.9, 29.8, 29.7, 29.7, 29.7, 29.7, 29.4, 26.7, 22.7, 14.1.

E.A. (%) calcd for $\text{C}_{70}\text{H}_{74}\text{O}_4\text{P}_2$ (1041.31): C 80.74, H 7.16. Found: C 80.21, H 7.29.

Cis-isomer **2-*cis*-1-O**: (11.0%, 0.12 g)

^1H NMR (400 MHz, CDCl_3) δ 9.52 (s, 2H), 8.94 (d, $J = 8.5$ Hz, 2H), 8.74 (dd, $J = 11.9$, 8.4 Hz, 2H), 8.63 (dd, $J = 8.4$, 5.3 Hz, 2H), 8.18 (dd, $J = 13.0$, 7.6 Hz, 2H), 7.83 (t, $J = 7.8$ Hz, 2H), 7.66 – 7.55 (m, 6H), 7.43 – 7.33 (m, 2H), 7.32 – 7.27 (m, 4H), 4.44 (t, $J = 6.4$ Hz, 4H), 2.27 – 2.15 (m, 4H), 1.84 (p, $J = 6.9$ Hz, 4H), 1.61 – 1.51 (m, 4H), 1.50 – 1.42 (m, 4H), 1.41 – 1.17 (m, 24H), 0.88 (t, $J = 6.9$ Hz, 6H).

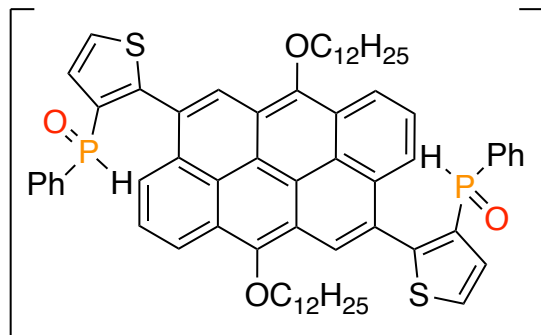
$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ 8.8.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 152.3, 137.9 (d, $J = 6.1$ Hz), 135.7 (d, $J = 110.1$ Hz), 132.7, 132.2 (d, $J = 6.1$ Hz), 131.5 (d, $J = 2.0$ Hz), 131.0 (d, $J = 10.1$ Hz), 130.8 (d, $J = 7.1$ Hz), 129.0, 128.9 (d, $J = 5.1$ Hz), 128.6 (d, $J = 12.1$ Hz), 128.4 (d, $J = 86.9$ Hz), 128.1 (d, $J = 6.1$ Hz), 127.7

(d, $J = 2.0$ Hz), 125.6 (d, $J = 10.1$ Hz), 124.2 (d, $J = 6.1$ Hz), 123.7 (d, $J = 99.0$ Hz), 122.3, 122.2, 122.2, 119.1, 78.2, 32.1, 31.0, 30.0, 29.9, 29.8, 29.5, 26.8, 22.8, 14.3.

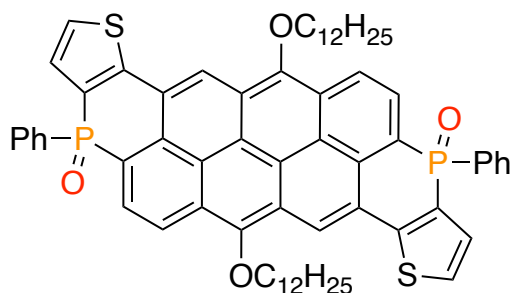
E.A. (%) calcd for $C_{70}H_{74}O_4P_2$ (1041.31): C 80.74, H 7.16. Found: C 79.79, H 7.12.

Compound 2-S6



Compound **2-S4** (1.0 g, 1.03 mmol) was added to a 250 mL Schlenk flask with 150 mL degassed THF under argon and the temperature was reduced to -78 °C. *n*-BuLi (0.91 mL, 2.27 mmol, 2.50 M) was slowly added to the mixture and stirred for 1 h at low temperature. Next, $PhPCl_2$ (0.29 mL, 2.17 mmol) was added to the mixture and stirred for 3 h. Then, 7 mL of H_2O were added to the mixture and stirred for 45 minutes. The solvent was evaporated under reduced pressure, the crude was re-dissolved in CH_2Cl_2 , and the organic phase was washed with water. The organic phase was then dried using $MgSO_4$ and the solvent was evaporated, obtaining **2-S6** as a reddish crude, which was used for the next step without further purification.

Compounds 2-*trans*-2-O and 2-*cis*-2-O



The crude containing **2-S6** from the previous step was dissolved in a 100 ml round-bottom flask under air with a mixture of toluene/acetonitrile (1:1, 20 ml) and wrapped with aluminum foil under air. Then, the mixture was charged with silver nitrate (0.04 g, 0.24 mmol), capped and stirred at 90 °C for 12h. The reaction was allowed to reach room temperature and the solvent was evaporated under reduced pressure. Compounds **2-trans-2-O** and **2-cis-2-O** were purified by flash column chromatography using silica (CHCl₃-acetone, 10:1, *trans*-isomer comes off first) and then recrystallized in a mixture of CH₂Cl₂ and hexane at -10 °C, obtaining the pure products as orange solid. The calculated reaction yields are from overall transformations from **2-S4** and to **2-trans-2-O** or **2-cis-2-O** (e and f steps of Scheme 2-1, Chapter 2).

Note: The *trans*- and *cis*-isomers are formed in an uneven ratio (proven by ^{31}P NMR $\{^1\text{H}\}$ of the crude mixture). Due to the lower solubility of *trans*-isomer, it precipitates more during the recrystallization process.

Trans-isomer **2-trans-2-O**: (13%, 0.14 g)

¹H NMR (400 MHz, CDCl₃) δ ppm 9.26 (s, 2H), 8.92 (d, *J* = 8.4 Hz, 2H), 8.62 (dd, *J* = 12.2, 8.5 Hz, 2H), 7.77 (dd, *J* = 13.0, 7.2 Hz, 4H), 7.61 – 7.52 (m, 4H), 7.51 – 7.46 (m, 2H), 7.46 – 7.38 (m, 4H), 4.43 (t, *J* = 5.6 Hz, 4H), 2.27 – 2.12 (m, 4H), 1.94 – 1.77 (m, 4H), 1.60 – 1.50 (m, 4H), 1.50 – 1.42 (m, 4H), 1.41 – 1.16 (m, 25H), 0.88 (t, *J* = 6.7 Hz, 6H).

³¹P{¹H} NMR (162 MHz, CDCl₃) δ 7.8.

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 152.5, 149.7 (d, *J* = 10.1 Hz), 134.9 (d, *J* = 113.1 Hz), 132.0 (d, *J* = 3.0 Hz), 131.5 (d, *J* = 11.1 Hz), 130.2, 129.9 (d, *J* = 11.1 Hz), 129.5 (d, *J* = 6.1 Hz), 129.1 (d, *J* = 3.0 Hz), 128.8 (d, *J* = 12.1 Hz), 128.4 (d, *J* = 133.3 Hz), 127.1 (d, *J* = 16.2 Hz), 126.7 (d, *J* = 10.1 Hz), 125.4 (d, *J* = 104.0 Hz), 124.1 (d, *J* = 10.1 Hz), 122.7 (d, *J* = 12.1 Hz), 122.5, 122.3, 119.4, 78.5, 32.1, 30.9, 29.9, 29.8, 29.5, 26.7, 22.8, 14.3.

¹³C{¹H} DEPT 135 NMR (101 MHz, CDCl₃) δ 131.8, 131.3 (d, *J* = 10.1 Hz), 129.7 (d, *J* = 12.1 Hz), 128.9 (d, *J* = 7.1 Hz), 128.6 (d, *J* = 12.1 Hz), 126.9 (d, *J* = 17.2 Hz), 122.5 (d, *J* = 13.1 Hz), 122.3, 78.3, 31.9, 30.8, 29.7, 29.7, 29.6, 29.3, 26.5, 22.6, 14.1.

E.A. (%) calcd for C₆₆H₇₀O₄P₂S₂ (1053.35): C 75.26, H 6.70. Found: C 71.15, H 6.56.^{S3,S4}

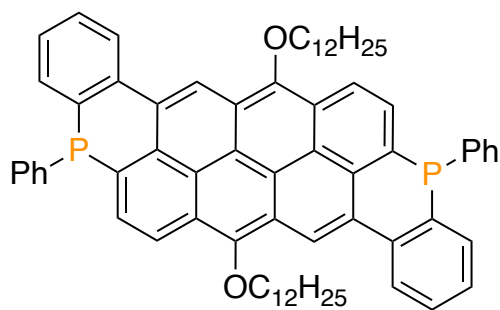
Cis-isomer **2-cis-2-O**: (6.5%, 0.07 g)

¹H NMR (400 MHz, CDCl₃) δ 9.20 (s, 2H), 8.89 (d, *J* = 8.5 Hz, 2H), 8.62 (dd, *J* = 12.2, 8.5 Hz, 2H), 7.75 (dd, *J* = 12.7, 7.0 Hz, 4H), 7.60 – 7.51 (m, 4H), 7.50 – 7.44 (m, 2H), 7.43 – 7.36 (m, 4H), 4.47 – 4.33 (m, 4H), 2.26 – 2.10 (m, 4H), 1.89 – 1.76 (m, 4H), 1.61 – 1.50 (m, 4H), 1.49 – 1.41 (m, 4H), 1.40 – 1.11 (m, 26H), 0.88 (t, 6H).

³¹P{¹H} NMR (162 MHz, CDCl₃) δ 7.5.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 152.2, 149.7 (d, $J = 10.1$ Hz), 134.8 (d, $J = 113.1$ Hz), 131.7 (d, $J = 2.0$ Hz), 131.4 (d, $J = 11.1$ Hz), 130.1, 129.8 (d, $J = 11.1$ Hz), 129.0, 129.0, 128.7 (d, $J = 13.1$ Hz), 128.1 (d, $J = 170.7$ Hz), 127.0 (d, $J = 16.2$ Hz), 126.1 (d, $J = 10.1$ Hz), 125.1 (d, $J = 104.0$ Hz), 123.6 (d, $J = 10.1$ Hz), 122.7 (d, $J = 12.1$ Hz), 122.3, 121.8, 118.8, 78.3, 32.0, 30.8, 29.9, 29.9, 29.8, 29.5, 26.7, 22.8, 14.2. E.A. (%) calcd for $\text{C}_{66}\text{H}_{70}\text{O}_4\text{P}_2\text{S}_2$ (1053.35): C 75.26, H 6.70. Found: C 74.77, H 6.74.

Compound 2-1



A mixture of **2-trans-1-O** and **2-cis-1-O** (1:1, 30 mg) was dissolved in 20 ml of THF in a microwave vial under inert atmosphere and reacted with HSiCl_3 (100 eq, 2.97 mmol, 0.30 ml) under microwave irradiation at 150 °C for 20 minutes. The mixture was allowed to cool to room temperature, then transferred into a Schlenk flask and the solvent was evaporated under reduced pressure. The crude mixture containing **2-1** was recrystallized with DCM/pentane at -30 °C, obtaining a mixture of isomers. (77% yield, 22 mg).

Note: Due to the inability of separating the isomers **2-trans-1** and **2-cis-1**, the ^1H , $^{31}\text{P}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the mixture containing both isomers have been reported in here. In case of the ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR data, precise peak assignments for the respective isomers are improbable as the chemical shifts appear too close to each other.

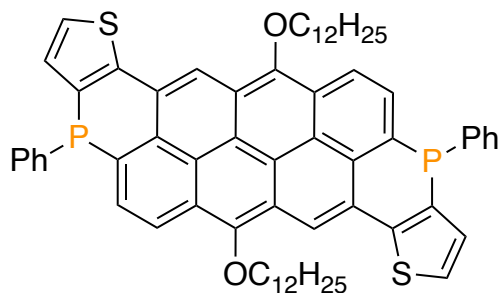
¹H NMR (400 MHz, CDCl₃) δ 9.25 (s, 2H), 8.69 (d, *J* = 8.5 Hz, 2H), 8.52 (d, *J* = 8.2 Hz, 2H), 8.13 (dd, *J* = 10.6, 8.3 Hz, 2H), 7.65 – 7.55 (m, 4H), 7.55 – 7.44 (m, 4H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.32 – 7.26 (m, 4H), 4.39 (t, *J* = 6.4 Hz, 4H), 2.24 – 2.12 (m, 4H), 1.83 (p, *J* = 7.1 Hz, 4H), 1.60 – 1.48 (m, 4H), 1.48 – 1.40 (m, 4H), 1.40 – 1.16 (m, 32H), 0.87 (t, 8H).

³¹P{¹H} NMR (162 MHz, CDCl₃) δ -27.2 (*trans*), -27.5 (*cis*).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 150.1, 141.1 (d, *J* = 24.2 Hz), 136.5, 134.6, 134.4 (d, *J* = 21.2 Hz), 134.3, 134.3 (d, *J* = 20.2 Hz), 133.8 (d, *J* = 4.0 Hz), 131.6, 130.9 (d, *J* = 32.3 Hz), 130.1, 129.5 (d, *J* = 10.1 Hz), 128.8 (d, *J* = 8.1 Hz), 127.9 (d, *J* = 11.1 Hz), 126.2, 125.7, 125.0, 122.5, 120.6 (d, *J* = 11.1 Hz), 120.3, 118.7, 77.4, 32.1, 31.1, 30.0, 29.9, 29.9, 29.9, 29.8, 29.5, 26.9, 22.9, 14.3.

E.A. (%) calcd for C₇₀H₇₄O₂P₂ (1009.31): C 83.30, H 7.39. Found: C 79.58, H 7.30.^{S2-3, S2-4}

Compound 2-2



A mixture of **2-*trans*-2-O** and **2-*cis*-2-O** (1:1, 40 mg) was dissolved in 15 ml THF in a microwave vial under inert atmosphere and reacted with HSiCl₃ (100 eq, 3.92 mmol, 0.40 ml) under microwave irradiation at 150 °C for 20 minutes. The mixture was allowed to cool down, transferred into a Schlenk flask and the solvent was evaporated under reduced pressure. The crude mixture

was recrystallized with DCM/pentane in -30 °C, obtaining a mixture of isomers with uneven ratio. (71% yield, 28 mg).

Note: Due to the inability of separating the isomers **2-trans-2** and **2-cis-2**, the ^1H , $^{31}\text{P}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the mixture containing both isomers have been reported in here. In case of the ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR data, precise peak assignments for the respective isomers are improbable as the chemical shifts appear too close to each other.

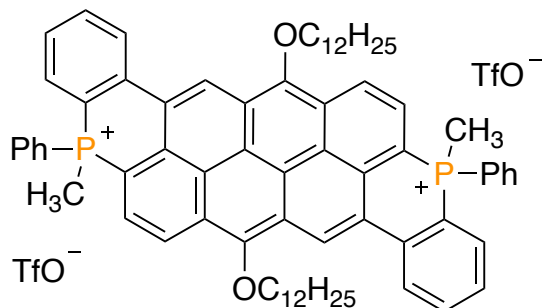
^1H NMR (400 MHz, CDCl_3) δ 8.80 (s, 2H), 8.66 (d, $J = 8.7$ Hz, 2H), 8.15 (dd, $J = 11.4, 8.5$ Hz, 2H), 7.58 – 7.49 (m, 4H), 7.44 (dd, $J = 5.2, 2.6$ Hz, 2H), 7.33 – 7.26 (m, 6H), 7.13 (dd, $J = 5.2, 2.8$ Hz, 2H), 4.36 (t, $J = 6.5$ Hz, 4H), 2.22 – 2.12 (m, 4H), 1.84 (p, $J = 7.1$ Hz, 4H), 1.54 (p, $J = 6.9$ Hz, 4H), 1.45 (p, $J = 7.1$ Hz, 5H), 1.41 – 1.17 (m, 30H), 0.88 (t, $J = 6.9$ Hz, 7H).

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ -26.6 (*trans*), -26.8 (*cis*).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 149.7, 142.7, 139.9 (d, $J = 27.3$ Hz), 134.0 (d, $J = 21.2$ Hz), 132.9, 131.7 (d, $J = 29.3$ Hz), 131.6 (d, $J = 35.3$ Hz), 129.7, 128.9 (d, $J = 8.1$ Hz), 128.5, 126.3, 125.9 (d, $J = 9.1$ Hz), 124.6, 122.5, 120.8, 120.7, 117.7, 77.4, 32.1, 31.0, 29.9, 29.9, 29.6, 26.8, 22.9, 14.3.

E.A. (%) calcd for $\text{C}_{66}\text{H}_{70}\text{O}_2\text{P}_2\text{S}_2$ (1021.35): C 77.62, H 6.91 Found: C 60.86, H 5.32.^{S2-3,S2-4}

Compound 2-1-Me



Compound **2-1** (30 mg) was dissolved in 10 ml of dry CH₂Cl₂ in a 25 mL Schlenk flask under argon and the temperature was cooled to 0 °C. MeOTf (100 eq, 2.97 mmol, 0.33 mL) was slowly added to the reaction mixture and it was stirred overnight at room temperature. Then, the solvent was evaporated under reduced pressure and the mixture **2-1-Me** was purified by recrystallization from a small amount of ethanol at -10 °C, obtaining a mixture of isomers (86 % yield, 34 mg).

Note: Due to the inability of separating the isomers **2-trans-1-Me** and **2-cis-1-Me**, the ¹H, ³¹P{¹H} and ¹³C{¹H} NMR spectra of the mixture containing both isomers have been reported in here. In case of the ¹H NMR and ¹³C{¹H} NMR data, precise peak assignments for the respective isomers are improbable as the chemical shifts appear too close to each other.

¹H NMR (400 MHz, CDCl₃) δ 9.46 (s, 2H), 9.27 (s, 2H), 8.94 – 8.69 (m, 10H), 8.50 (d, *J* = 8.4 Hz, 2H), 8.38 – 8.30 (m, 2H), 8.29 – 8.24 (m, 2H), 8.23 – 8.14 (m, 5H), 8.11 – 8.00 (m, 9H), 7.99 – 7.91 (m, 4H), 7.84 (dd, *J* = 14.0, 7.8 Hz, 4H), 7.76 (dd, *J* = 7.2, 1.9 Hz, 2H), 7.74 – 7.67 (m, 4H), 7.63 (dd, *J* = 7.3, 1.9 Hz, 2H), 7.60 – 7.51 (m, 4H), 4.37 – 4.19 (m, 4H), 4.10 (q, *J* = 6.6 Hz, 2H), 4.02 (q, *J* = 7.8 Hz, 2H), 3.52 (d, *J* = 13.6 Hz, 6H), 3.20 (d, *J* = 13.6 Hz, 6H), 2.09 – 1.98 (m, 4H), 1.93 – 1.75 (m, 4H), 1.67 – 1.57 (m, 5H), 1.50 – 1.15 (m, 80H), 0.84 (t, 14H).

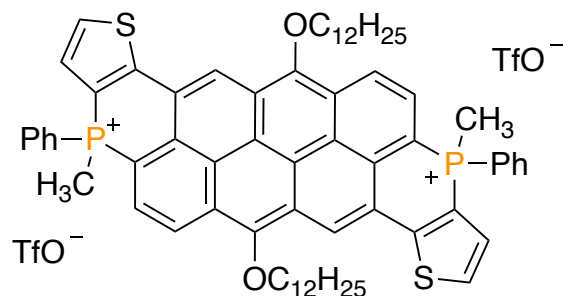
³¹P{¹H} NMR (162 MHz, CDCl₃) δ -0.1 (*trans*), -0.4 (*cis*).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 153.5, 152.8, 138.6, 138.6, 138.5, 136.2, 136.0, 135.3, 135.1, 133.8, 133.7, 133.02 (d, *J* = 11.1 Hz), 132.6 (d, *J* = 11.1 Hz), 131.7, 131.7, 131.5, 131.3, 131.2, 131.1, 131.1, 130.8 (d, *J* = 14.1 Hz), 130.6 (d, *J* = 13.1 Hz), 129.5, 129.1 (d, *J* = 10.1 Hz), 128.7, 128.0, 127.0 (d, *J* = 12.1 Hz), 126.8 (d, *J* = 13.1 Hz), 124.3, 123.9, 123.8, 123.3, 123.2 (d, *J* = 11.1 Hz), 122.7, 122.6, 122.4, 122.4, 120.5 (q, *J* = 321.2 Hz), 118.5, 117.8, 114.0, 113.9, 113.2, 113.0,

109.7, 109.6, 108.8, 108.8, 79.5, 79.4, 32.0, 30.8, 30.6, 29.9, 29.9, 29.8, 29.8, 29.7, 29.6, 29.5, 26.5, 26.3, 22.8, 14.2, 12.3 (d, $J = 59.6$ Hz), 12.0 (d, $J = 59.6$ Hz).

E.A. (%) calcd for $C_{74}H_{80}O_8P_2S_2F_6$ (1337.5): C 66.45, H 6.04 Found: C 63.56, H 5.96.^{S2-3, S2-4}

Compound 2-2-Me



Compound **2-2** (25 mg) was dissolved in 10 ml of CH_2Cl_2 in a 25 ml Schlenk flask under argon and the temperature was cooled down to 0 °C. MeOTf (100 eq, 2.45mmol ,0.27 ml) was slowly added to the reaction mixture and it was stirred overnight at room temperature. Then, the solvent was evaporated under reduced pressure and the mixture **2-2-Me** purified by recrystallization from a small amount of ethanol at -10 °C, obtaining a mixture of isomers (82 % yield, 27 mg).

Note: Due to the inability of separating the isomers **2-trans-2-Me** and **2-cis-2-Me**, the 1H , $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra of the mixture containing both isomers have been reported in here. In case of the 1H NMR and $^{13}C\{^1H\}$ NMR data, precise peak assignments for the respective isomers are improbable as the chemical shifts appear too close to each other.

1H NMR (400 MHz, $CDCl_3$) δ 9.05 (dd, $J = 14.2, 8.6$ Hz, 2H), 8.84 (s, 2H), 8.55 (s, 2H), 8.26 – 8.06 (m, 2H), 7.97 (dd, $J = 14.3, 7.7$ Hz, 4H), 7.83 – 7.67 (m, 5H), 7.66 – 7.56 (m, 3H), 4.53 – 4.15 (m, 1H), 3.92 (q, $J = 7.7$ Hz, 2H), 3.83 (q, $J = 8.7$ Hz, 2H), 3.61 (d, $J = 14.0$ Hz, 5H), 3.23 (d,

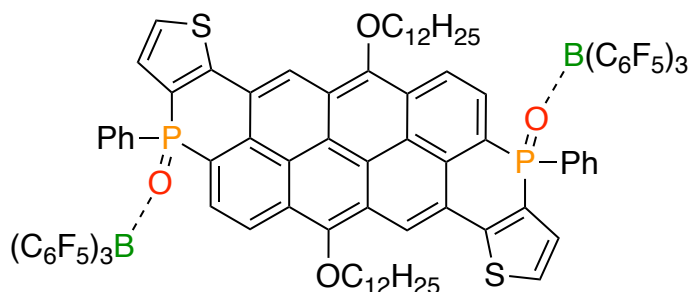
$J = 13.8$ Hz, 1H), 2.11 – 1.94 (m, 1H), 1.85 – 1.68 (m, 3H), 1.50 – 1.05 (m, 40H), 0.85 (t, $J = 6.6$ Hz, 7H).

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ -1.4 (*trans*), -1.9 (*cis*).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 153.4 (d, $J = 8.1$ Hz), 152.2, 135.4, 133.6 (d, $J = 12.1$ Hz), 132.8 (d, $J = 13.1$ Hz), 132.4 (d, $J = 12.1$ Hz), 130.9, 130.7, 128.9 (d, $J = 5.0$ Hz), 128.5, 127.2, 124.9 (d, $J = 10.1$ Hz), 123.7, 122.7, 122.3 (d, $J = 10.1$ Hz), 121.8, 119.6, 119.4 (q, $J = 348.4$ Hz), 112.1, 111.4, 111.2, 110.5, 79.8, 32.0, 30.5, 29.8, 29.7, 29.7, 29.6, 29.5, 29.5, 25.9, 22.8, 14.2, 12.9 (d, $J = 58.6$ Hz).

E.A. (%) calcd for $\text{C}_{70}\text{H}_{76}\text{O}_8\text{P}_2\text{S}_4\text{F}_6$ (1349.54): C 62.30, H 5.69 Found: C 53.64, H 5.75.^{S2-3, S2-4}

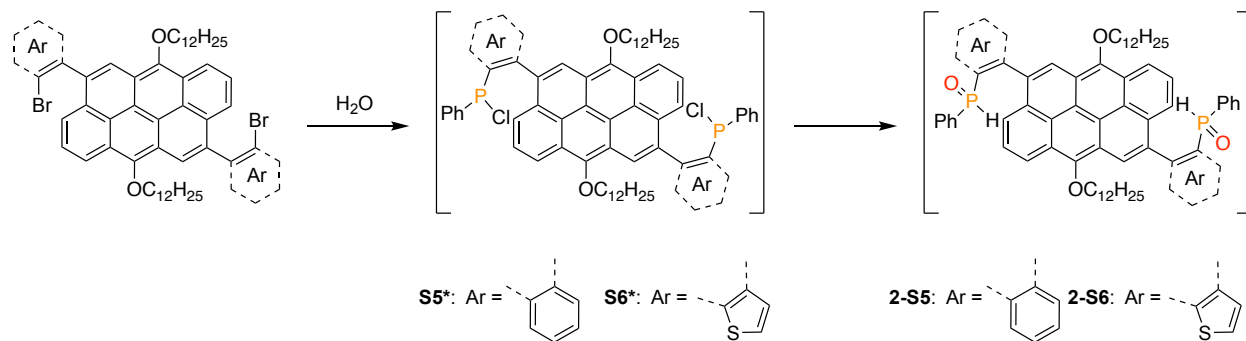
Compound 2-*cis*-2-O(BCF)₂



Compound **2-*cis*-2-O** (5 mg) was dissolved in a small volume of deuterated chloroform containing BCF (2 eq, 0.01 mmol, 4.9 mg) at room temperature. Quantitative transformation was monitored and verified by NMR.

^1H NMR (400 MHz, CDCl_3) δ 9.38 (s, 2H), 9.01 (dd, $J = 8.6, 1.8$ Hz, 2H), 8.45 (dd, $J = 13.3, 8.6$ Hz, 2H), 7.96 (dd, $J = 15.1, 7.2$ Hz, 4H), 7.77 – 7.69 (m, 2H), 7.67 – 7.57 (m, 6H), 7.45 (t, $J = 4.9$ Hz, 2H), 4.70 – 4.60 (m, 2H), 4.59 – 4.48 (m, 2H), 3.75 (s, 2H), 2.35 – 2.19 (m, 4H), 2.00 – 1.79 (m, 6H), 1.59 (p, 4H), 1.49 (p, $J = 6.6$ Hz, 4H), 1.43 – 1.22 (m, 24H), 0.87 (t, 6H).

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ ppm 19.2.



Scheme S2-1. Details of the reaction mechanism toward the formation of the **2-S5** and **2-S6**.

2.3. X-ray diffraction data

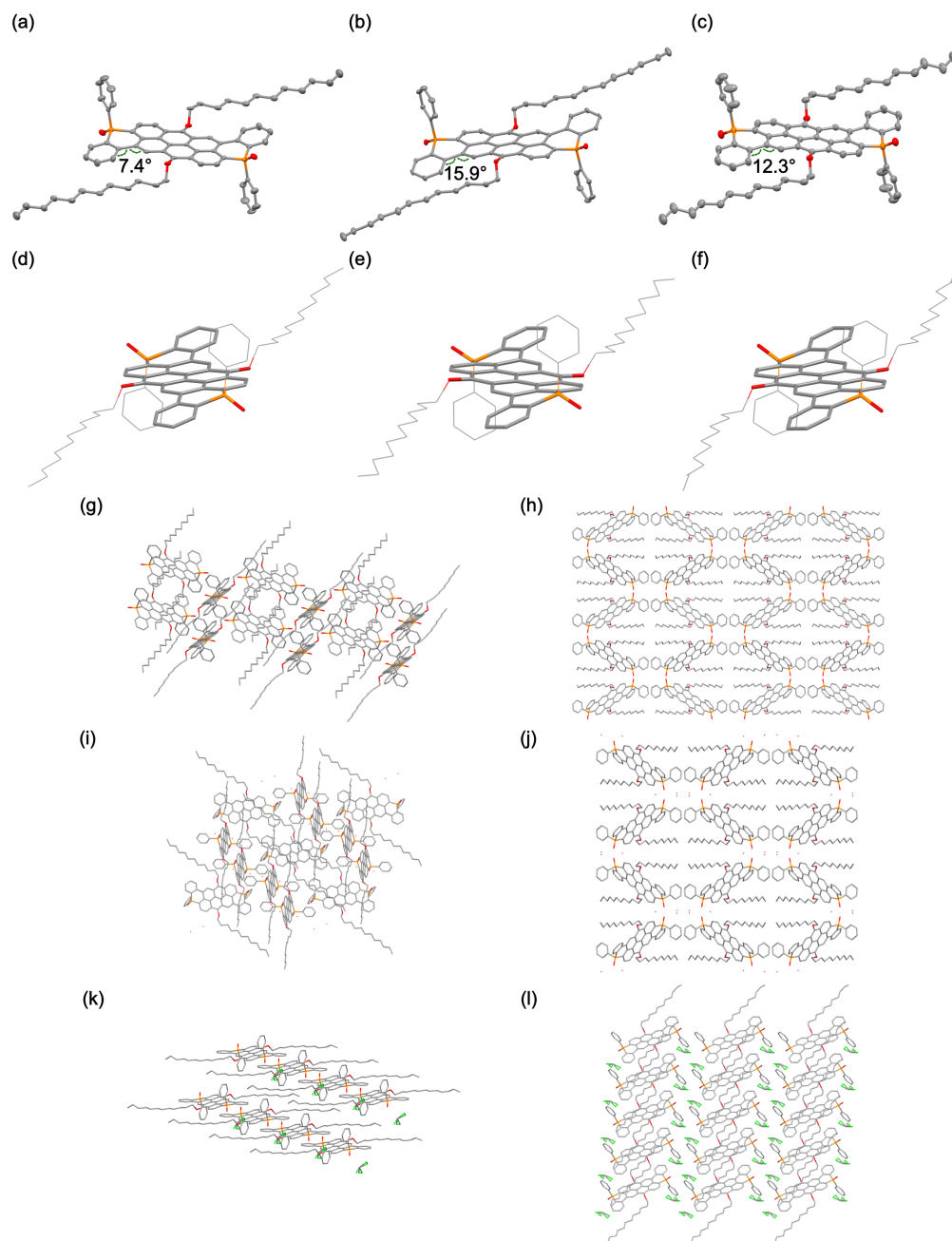


Figure S2-1. Structures of **2-trans-1-O** in the solid state without crystallized solvate (a), with water (b), and with chloroform (c) along with their respective twist (d, e, f). Packing of **2-trans-1-O** (g, h: with no crystallized solvate), (i, j: with water), (k, l: with chloroform).

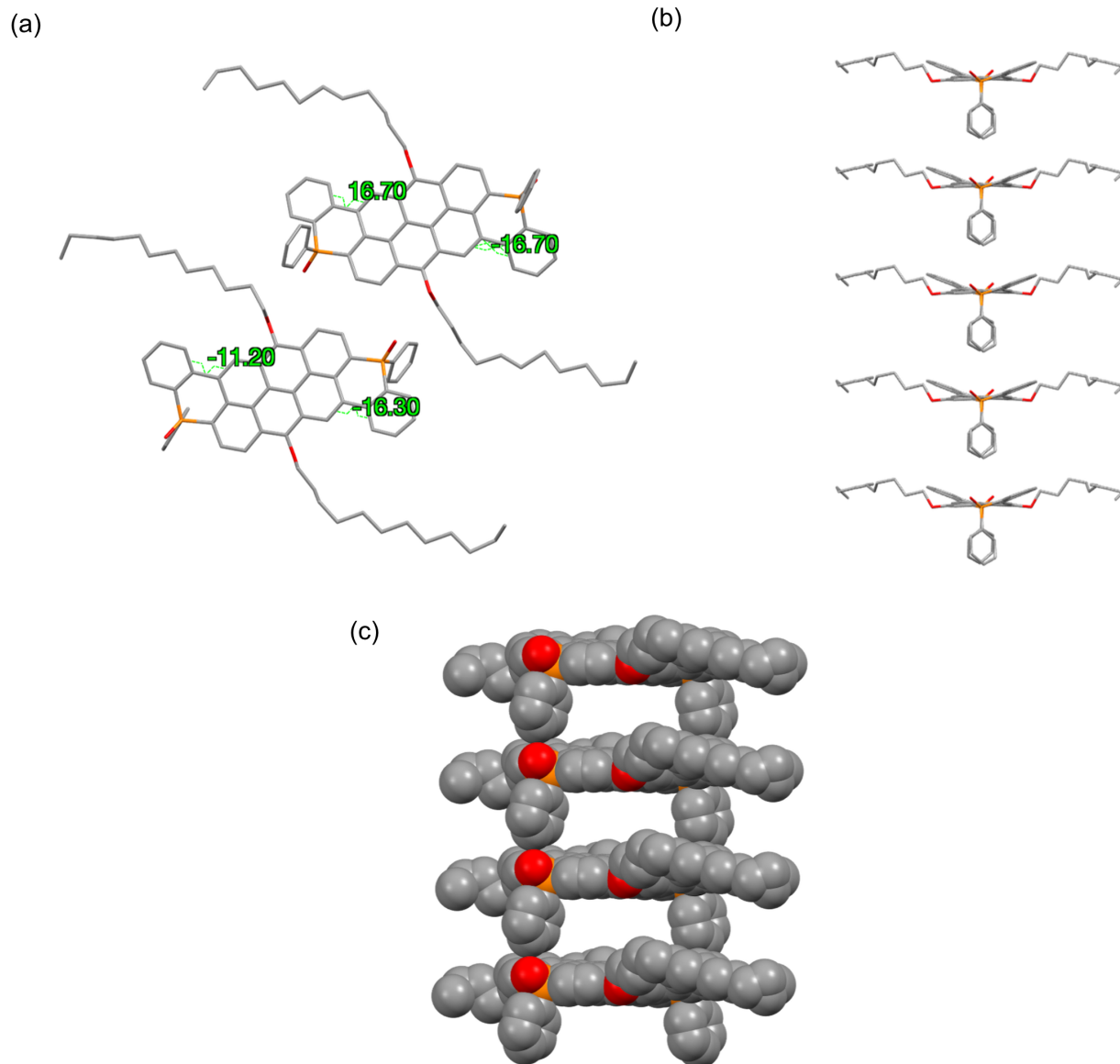


Figure S2-2. Unit cell of 2-*cis*-1-O showing both enantiomers with their torsion angles (a). Packing of 2-*cis*-1-O (b), and space filling view (c). H-atoms omitted for clarity.

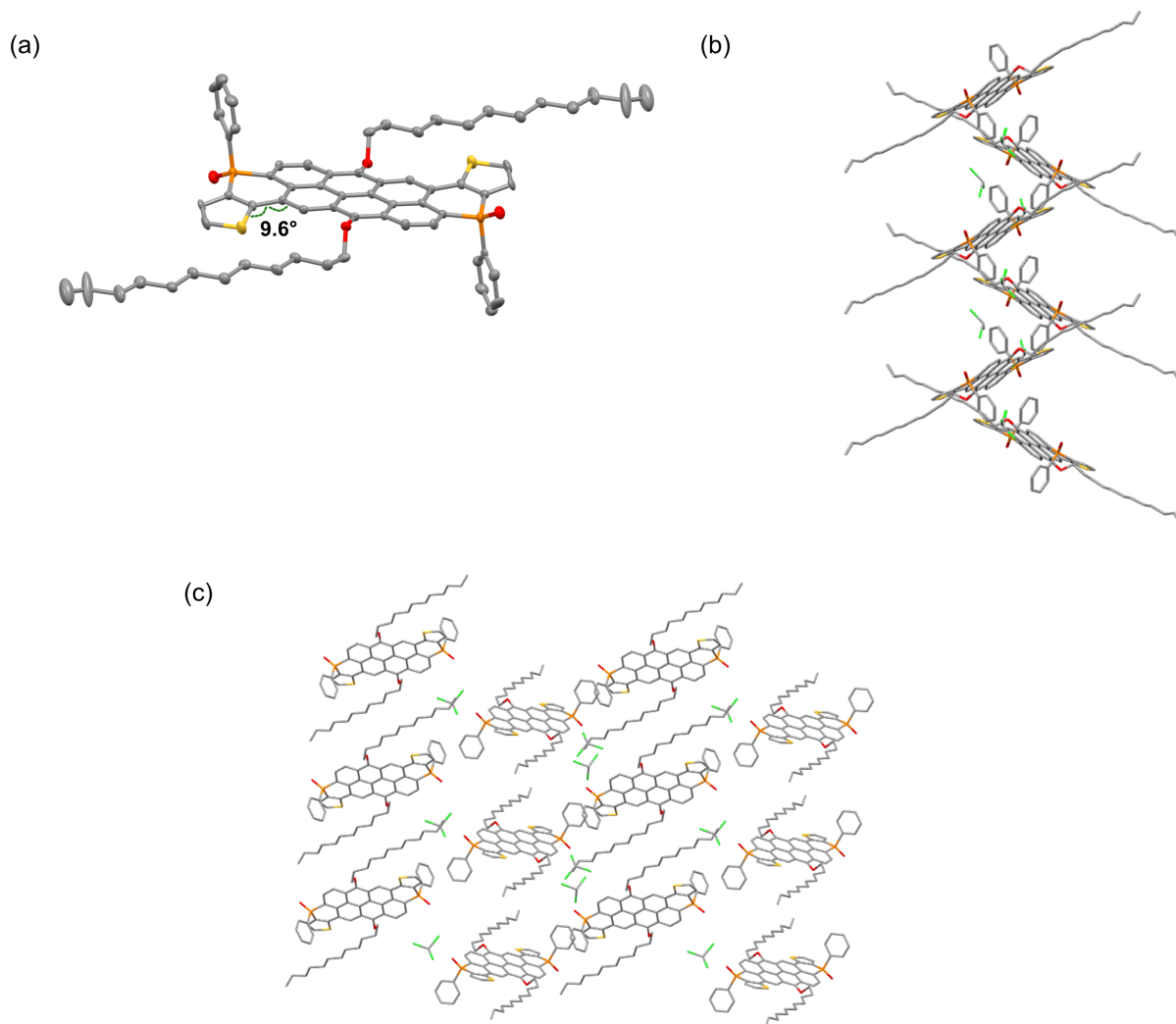


Figure S2-3. Molecular structure (a), and packing of **2-trans-2-O** side and front view (b,c). H-atoms omitted for clarity.

2.4. Theoretical calculations

2.4.1. Computational Details

The computational methodology adopted in this study involved a series of steps to comprehensively analyze the electronic and aromatic properties of the new compounds. All calculations were performed at the B3LYP^{S2-5}/def2-TZVP^{S2-6}/CPCM(CH₂Cl₂)^{S2-7} level of theory, unless further specified. All 12 compounds were subjected to structural optimizations, followed by Hessian calculations to confirm the optimized structures are minima on their ground-state potential energy surfaces. TD-DFT calculations were then performed at the optimized structures to calculate vertical excited states and vertical excitation energies. The calculated excitation energies and oscillator strengths enable the assignment of peaks in experimental absorption spectra and explanation of the absorption intensities. Nucleus-Independent Chemical Shifts^{S2-8} were calculated at 1.0 Å above (i.e., NICS(1)_{zz}) rings of interest of the optimized structures to estimate their aromaticities or antiaromaticities, at the ω B97X^{S2-9}/cc-pVTZ level. The key calculated results are summarized in Table S2-2.

2.4.2. Summary of Calculated Results

Table S2-2. Experimental and calculated absorption maxima obtained by TD-DFT calculations and NICS values obtained for all derivatives from series **2-1** and **2-2**.

Compd	$\lambda_{\text{abs}}^{[\text{a}]}$ (calc)	$\lambda_{\text{abs}}^{[\text{b}]}$ (expt)	$f_{\text{osc}}^{[\text{c}]}$ (calc)	$\epsilon^{[\text{d}]}$ (expt)	NICS(1) _{zz} in ppm ^[e]				
					R ₁	R ₂	R ₃	R ₄	R ₅
2-trans-1-O	361, 496	356, 509	0.33, 0.17	94K	-23.7	12.6	-31.2	-26.2	-5.0
2-cis-1-O	360, 496	356, 509	0.33, 0.17	59K	-23.9	11.3	-30.7	-26.1	-4.7
2-trans-1	376, 507	369, 510	0.30, 0.23	134K	-22.9	12.1	-31.1	-26.2	-4.1
2-cis-1	377, 506	369, 510	0.23, 0.20	134K	-22.7	13.5	-30.1	-26.0	-3.8
2-trans-1-Me	337, 558	363, 533	0.35, 0.23	88K	-22.7	11.4	-26.6	-23.3	-5.5
2-cis-1-Me	366, 506	363, 533	0.33, 0.19	88K	-23.2	11.5	-29.9	-25.5	-3.8
2-trans-2-O	350, 507	366, 517	0.22, 0.16	40K	-19.2	11.7	-31.5	-26.0	-4.6
2-cis-2-O	349, 509	367, 517	0.22, 0.15	62K	-19.3	10.0	-31.4	-25.9	-4.5
2-trans-2	386, 516	376, 514	0.23, 0.20	67K	-19.2	10.7	-31.1	-25.9	-3.5
2-cis-2	386, 516	376, 514	0.20, 0.18	67K	-19.1	12.0	-30.7	-25.6	-3.4
2-trans-2-Me	363, 572	373, 540	0.50, 0.18	57K	-18.6	11.3	-29.5	-26.0	-6.8
2-cis-2-Me	364, 572	373, 540	0.51, 0.20	57K	-18.8	11.1	-29.6	-25.9	-6.7

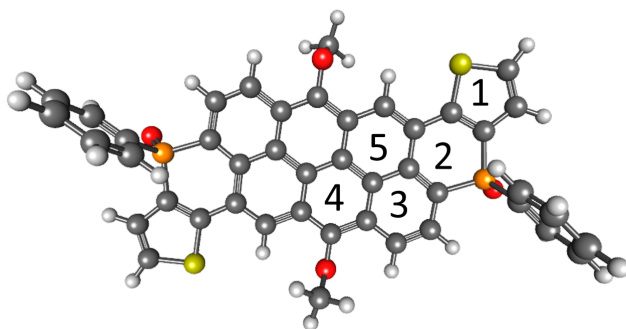
^[a] Calculated absorption maxima. ^[b] Experimental absorption maxima. ^[c] Oscillator strength. ^[d] Experimental molar extinction coefficient. ^[e] Calculated NICS(1) values in ppm. See assignments below.

Results of TD-DFT Calculations and the Simulated Absorption Spectra

The two main absorption peaks of the TD-DFT-calculated and experimental absorption spectra of the 12 new compounds are compared in Table S2-1, in terms of their absorption wavelengths and intensities (calculated oscillator strengths vs. experimental extinction coefficients). The calculated absorption wavelengths (λ_{abs}) are all in close agreement with the experimental values. Notably, the calculated excitation energies and oscillator strengths are again insensitive to the *cis* or *trans* configurations of each isomer, respectively. The TD-DFT calculations allow us to assign excitation schemes for the observed peaks; see Figure S2-6 for **2-*cis*-2-O** as an example. The assignment also applies to the other 11 investigated compounds since the photophysics of all the compounds are similarly dominated by the anthanthrene core.

2.4.3. NICS Results and Aromaticities of the series 2-1 and 2-2.

For each compound of the series **2-1** and **2-2**, NICS(1)_{zz} calculations were performed for the 5 rings exemplified in the figure below, which are unique in the context of the inherent C_{2h} symmetry of the core planar structure. They are labeled as Rings 1 to 5, and abbreviated as R1 to R5 in the discussion below. All 60 calculated NICS(1)_{zz} values are summarized in Table S2-2.



Labeling of rings in compound **2-*cis*-2-O**

The NICS(1)_{zz} results are almost insensitive to the *cis* vs. *trans* configurations. R1 is aromatic in all compounds and the aromaticity is reduced in the replacement of the terminal benzo group by a

thieno unit, as anticipated. R2 is antiaromatic in all compounds, likely due to the tetrahedral geometry of the P atom, and the antiaromaticity remains largely unchanged in all compounds. The P-containing rings also disconnect the electronic ring current between the central anthanthrene core, comprising R3-5 and their C_2 symmetry images, and the terminal rings R1 and its C_2 image. Notably, the NICS(1)_{zz} values of R3-5 are consistent and follow the order of the values, -34, -29, and -12 ppm, of the corresponding rings of the free standing anthanthrene.^{S2-10} Evidently, the aromaticity of the anthanthrene core is preserved in all the 12 compounds, despite the various modifications introduced to the system via π -expansion and additional phosphorus chemistry.

2.4.4. Frontier Molecular Orbitals

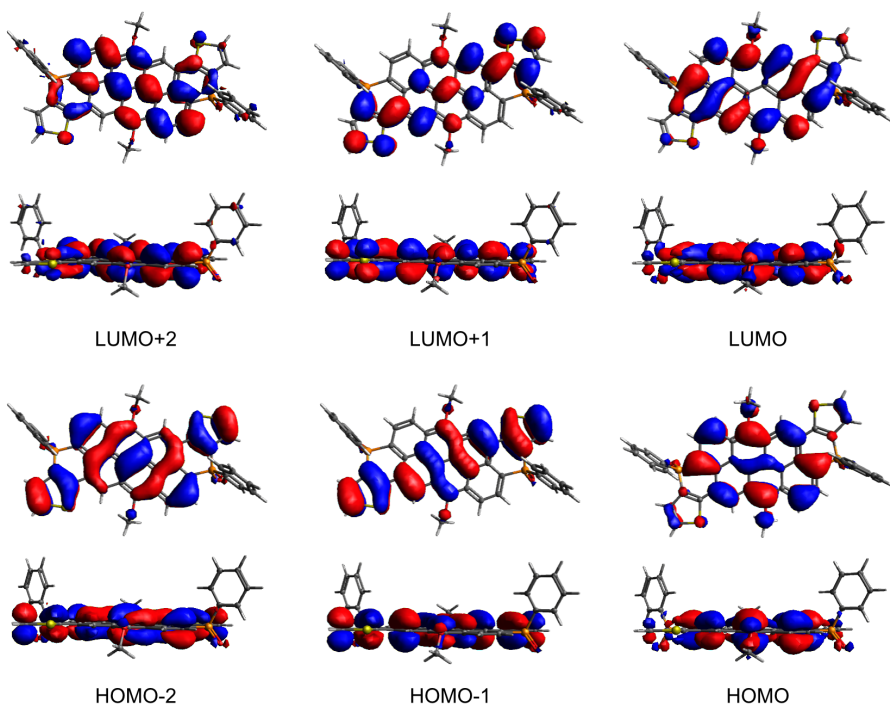
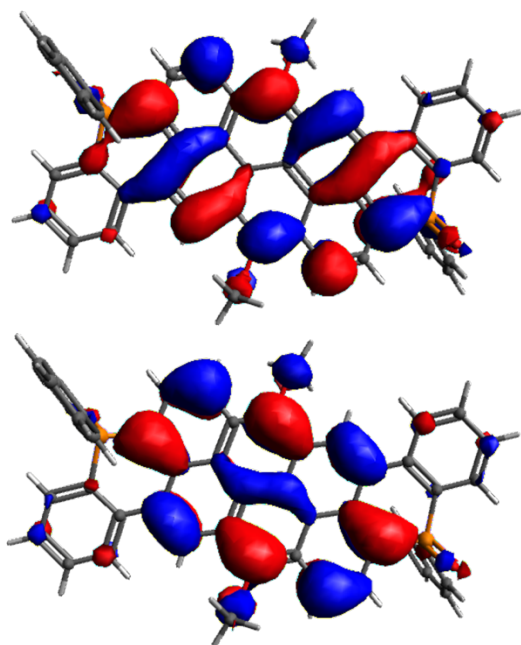


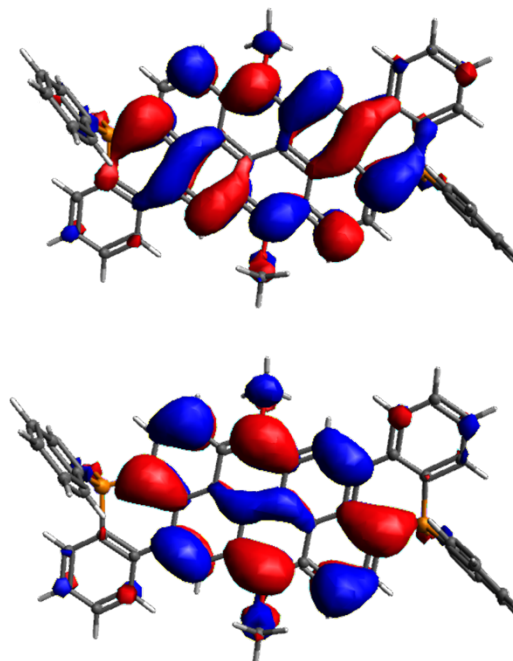
Figure S2-4. Frontier molecular orbitals of **2-*cis*-2-O** from HOMO-2 to LUMO+2. Both top and side views are presented for each orbital. They resemble frontier molecular orbitals of the other investigated species, which are hence not plotted.

Frontier molecular orbitals of the synthesized species; LUMO (top) and HOMO (bottom).

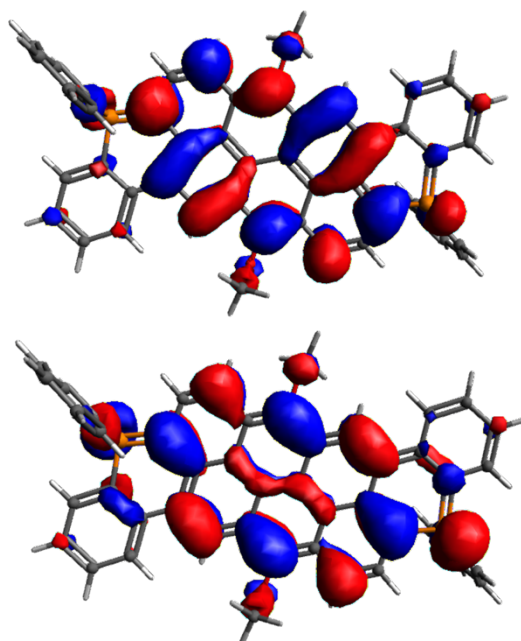
2-trans-1-O



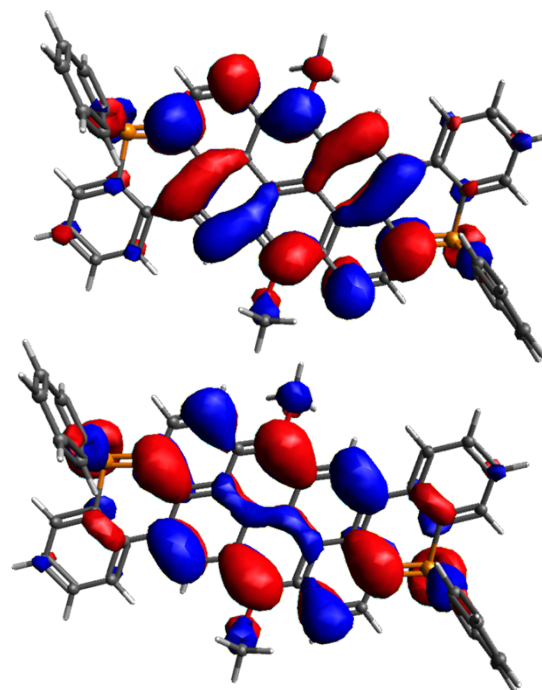
2-cis-1-O



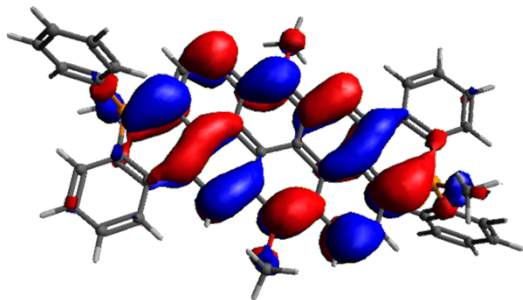
2-trans-1



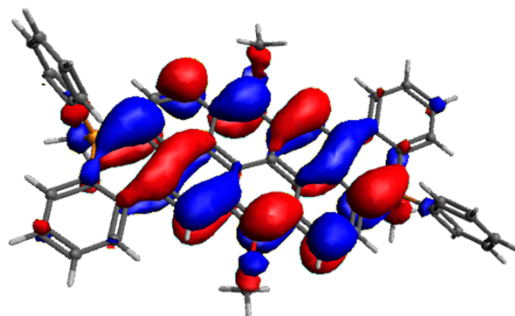
2-cis-1



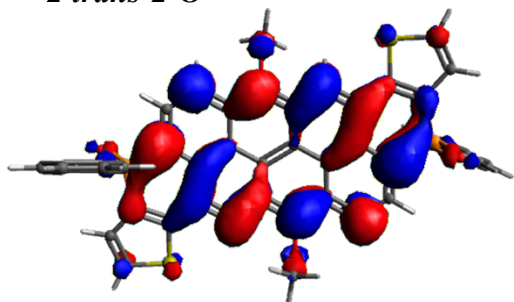
2-trans-1-Me



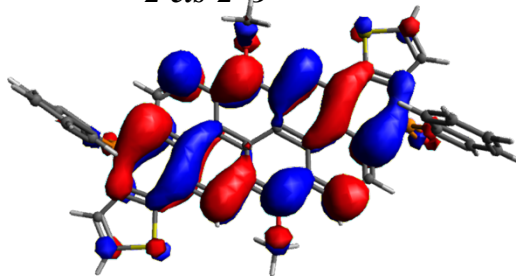
2-cis-1-Me



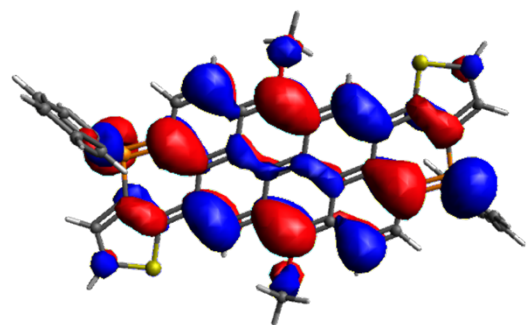
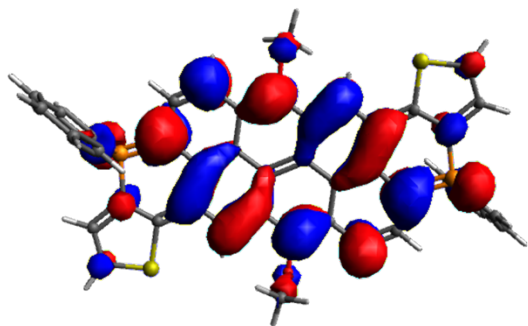
2-trans-2-O



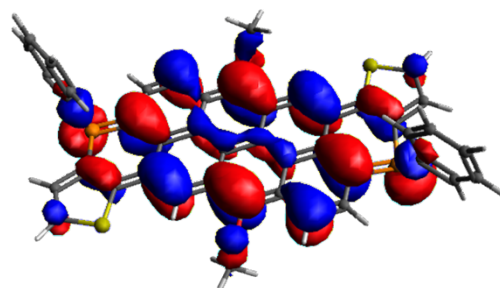
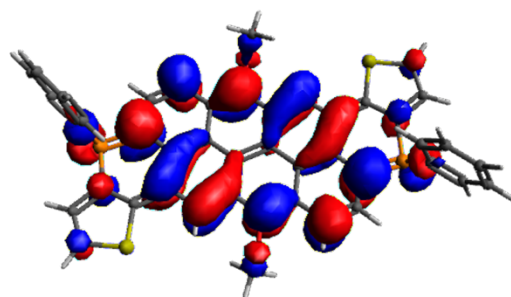
2-cis-2-O



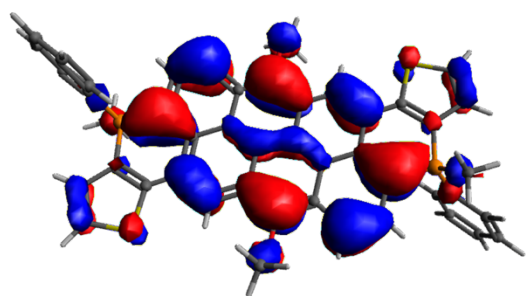
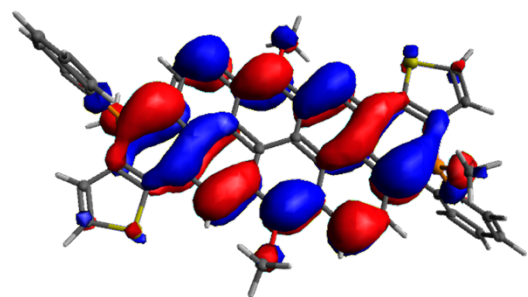
2-trans-2



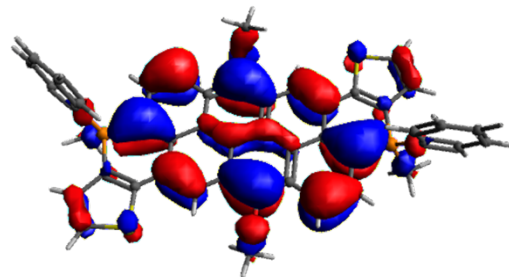
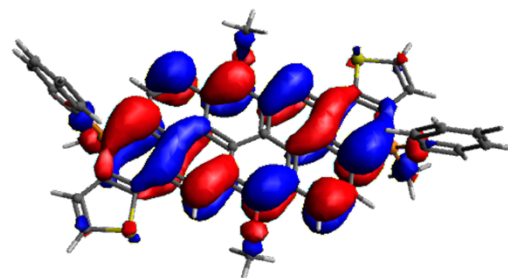
2-cis-2



2-trans-2-Me

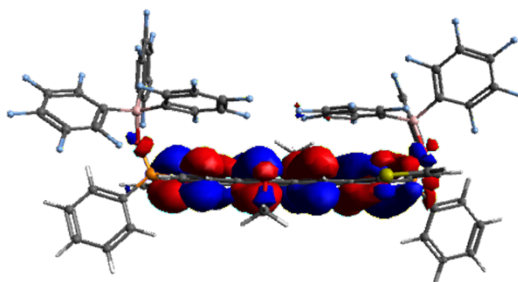


2-cis-2-Me

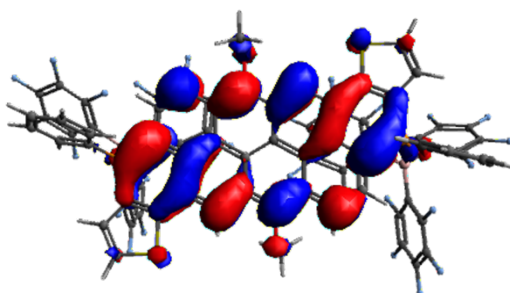


2-*cis*-2-O(BCF)₂

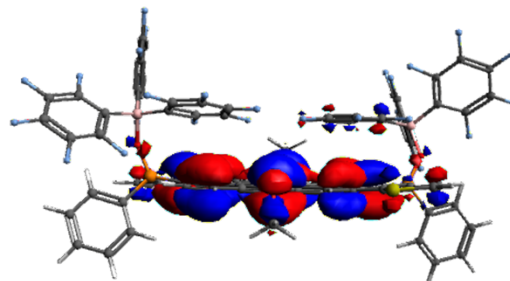
LUMO (side view)



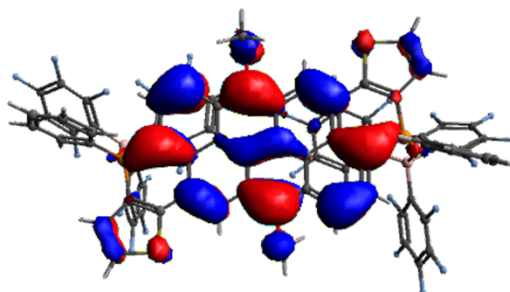
LUMO (top view)



HOMO (side view)



HOMO (top view)



2.4.5. Computational Investigation of the Interaction of 2-cis-2-O with BCF

The new compounds are notable for their distinctive UV-Vis spectra, characterized by peaks at approximately 375 and 510 nm. The P=O groups on these compounds function as exocyclic Lewis bases. When the compounds interact with the Lewis acid tris(pentafluorophenyl)borane (BCF) (Figure S2-5), a red shift of both peaks is observed. Moreover, the peak at 510 nm experiences a more pronounced shift than the peak at 375 nm (Figure S2-6). We performed TD-DFT calculations to provide a deeper understanding for these BCF-induced red shifts.

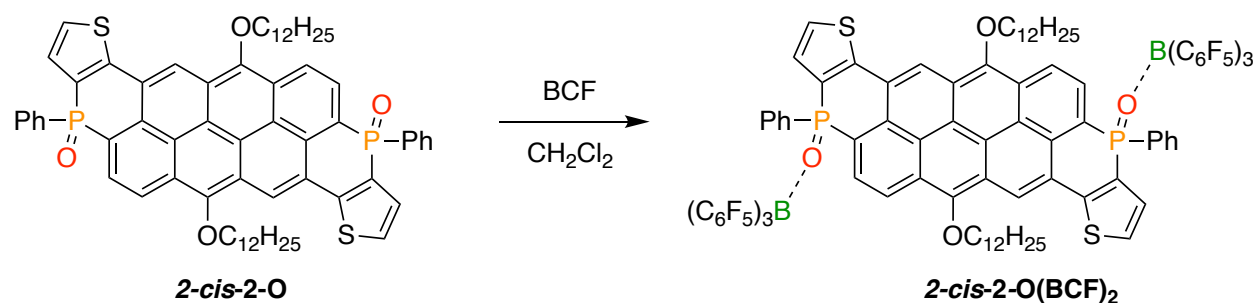


Figure S2-5. The coordination of B(C₆F₅)₃ (BCF) to 2-cis-2-O to form 2-cis-2-O(BCF)₂.

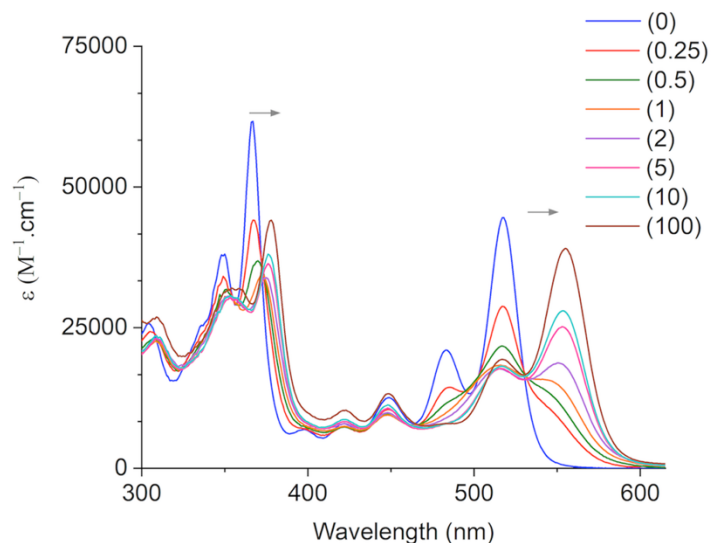


Figure S2-6. Experimental absorption spectra of **2-*cis*-2-O** in the presence of different amounts of BCF indicated by the parenthesized number. (0) means pure **2-*cis*-2-O** and (100) means 100 equiv. of BCF – sufficient for converting all **2-*cis*-2-O** to **2-*cis*-2-O(BCF)₂**.

We performed calculations for **2-*cis*-2-O** and **2-*cis*-2-O(BCF)₂** as representative examples to investigate the origin of the red shift upon BCF coordination. Structural optimizations were performed at the CAM-B3LYP/D3BJ/def2-SVP level, followed by TD-DFT calculations to calculate their vertical excited states and simulate their absorption spectra (Figure S2-7).

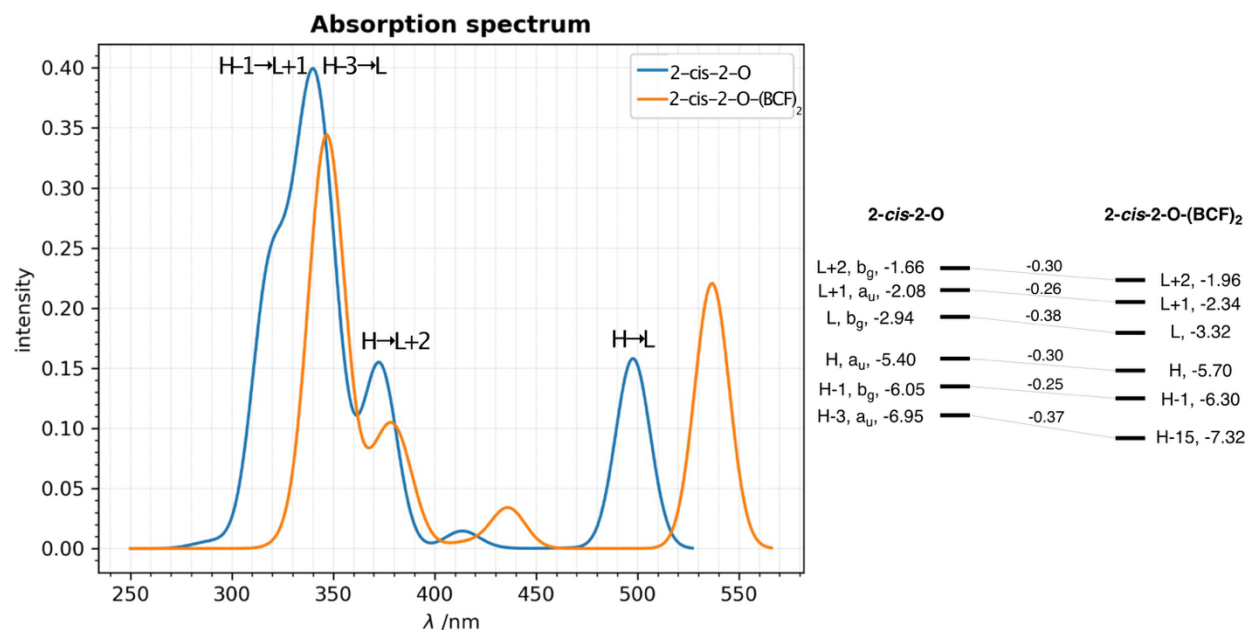


Figure S2-7. TD-DFT simulated absorption spectra of **2-cis-2-O** and **2-cis-2-O(BCF)₂**. Excitation schemes that are responsible for the intense absorptions are added to the **2-cis-2-O** spectrum. The correlation between molecular orbitals in **2-cis-2-O** and **2-cis-2-O(BCF)₂** are given on the right side. H, H-1, and L+1 stand for HOMO, HOMO-1, and LUMO+1, etc.

The simulated absorption spectra of **2-cis-2-O** and **2-cis-2-O(BCF)₂** are in qualitative agreement with the experimental data. Especially, the red shifts for the peaks around 500 and 350 nm upon addition of BCF are captured. Excitation schemes for the intense absorption peaks around the two wavelengths are indicated in the spectrum. In addition to the spectra, the correlations between the frontier orbitals before and after the BCF coordination that are involved in those key excitation schemes, are presented. Naturally, the coordination of the two strong Lewis acidic molecules lowers the energies of all the frontier orbitals. Among them, HOMO-3 and LUMO are stabilized more and to a similar extent (0.37 vs. 0.38 eV). Consequently, the H→L excitation is substantially

red-shifted, dominating the absorption profile around 500 nm. On the contrary, the H-3→L excitation, contributing to the absorption around 350 nm, is only slightly red-shifted. HOMO-1 and LUMO+1 are stabilized to the same extent of about 0.25 eV, while HOMO and LUMO+2 are stabilized to the same extent of 0.30 eV. Consequently, the H-1→L+1 and H→L+2 excitations are also only slightly red-shifted, and these excitations also contribute to the absorptions around 350 nm. The different red shift for the absorption peaks around 500 and 350 nm are fully consistent by the lowered orbital energies induced by the BCF coordination.

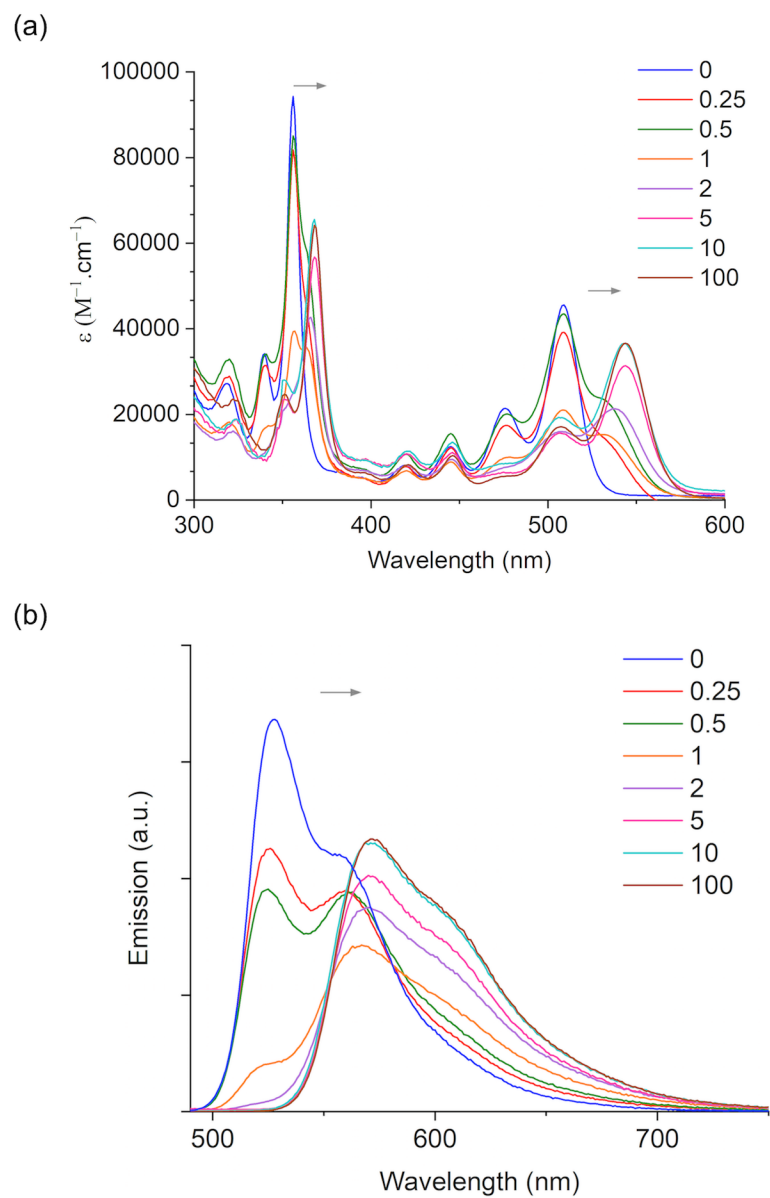


Figure S2-8. Absorption (a) and emission (b) spectra of **2-trans-1-O** upon titration with BCF in CH_2Cl_2 (Solutions with equal concentrations of **2-trans-1-O** with increasing amounts of BCF from 0 to 100 equivalents).

2.5. Steady-state spectroscopy

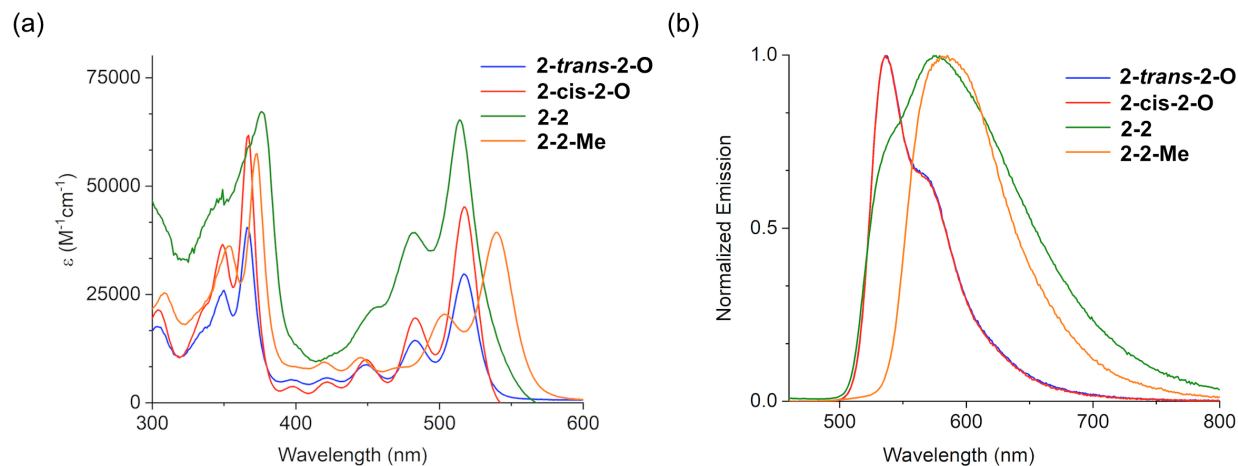


Figure S2-9. Absorption (a) and emission (b) spectra of thieno-fused species in CH_2Cl_2 from isomers **2-trans-2-O**, and **2-cis-2-O** and the isomeric mixtures of P-reduced **2-2**, and P-methylated **2-2-Me**.

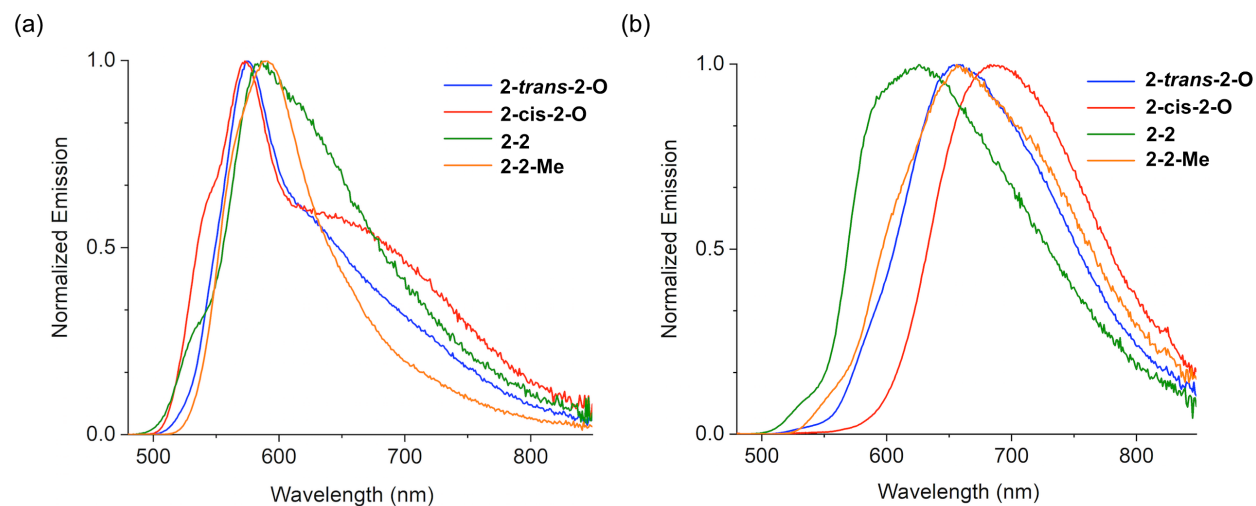


Figure S2-10. Emission spectra of (a) 0.2 wt%, and (b) 1.2 wt% PMMA films of thieno-fused species; separated isomers **2-trans-2-O**, and **2-cis-2-O**, along with isomeric mixtures of P-reduced **2-2**, and P-methylated **2-2-Me**.

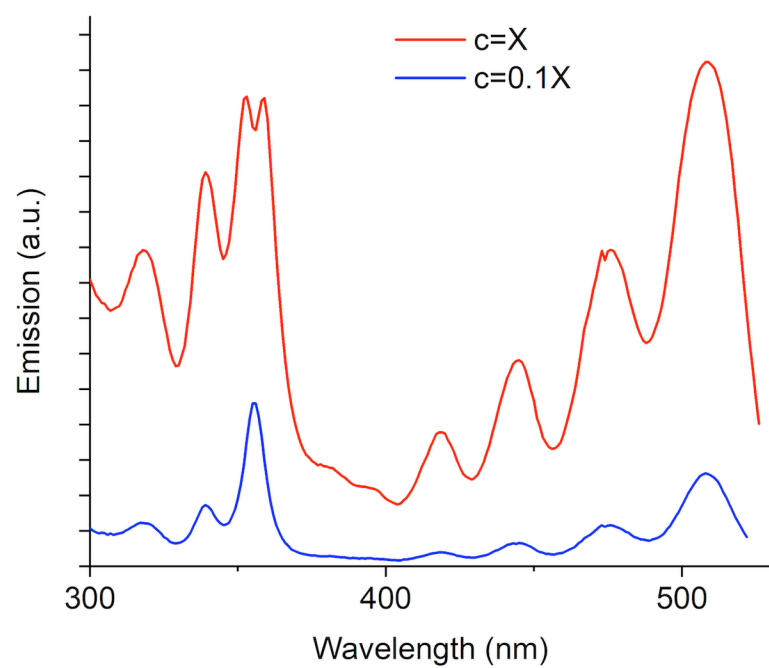


Figure S2-11. Excitation spectra of **2-trans-1-O** in different concentrations ($X = 6.4 \times 10^{-6}$ M).

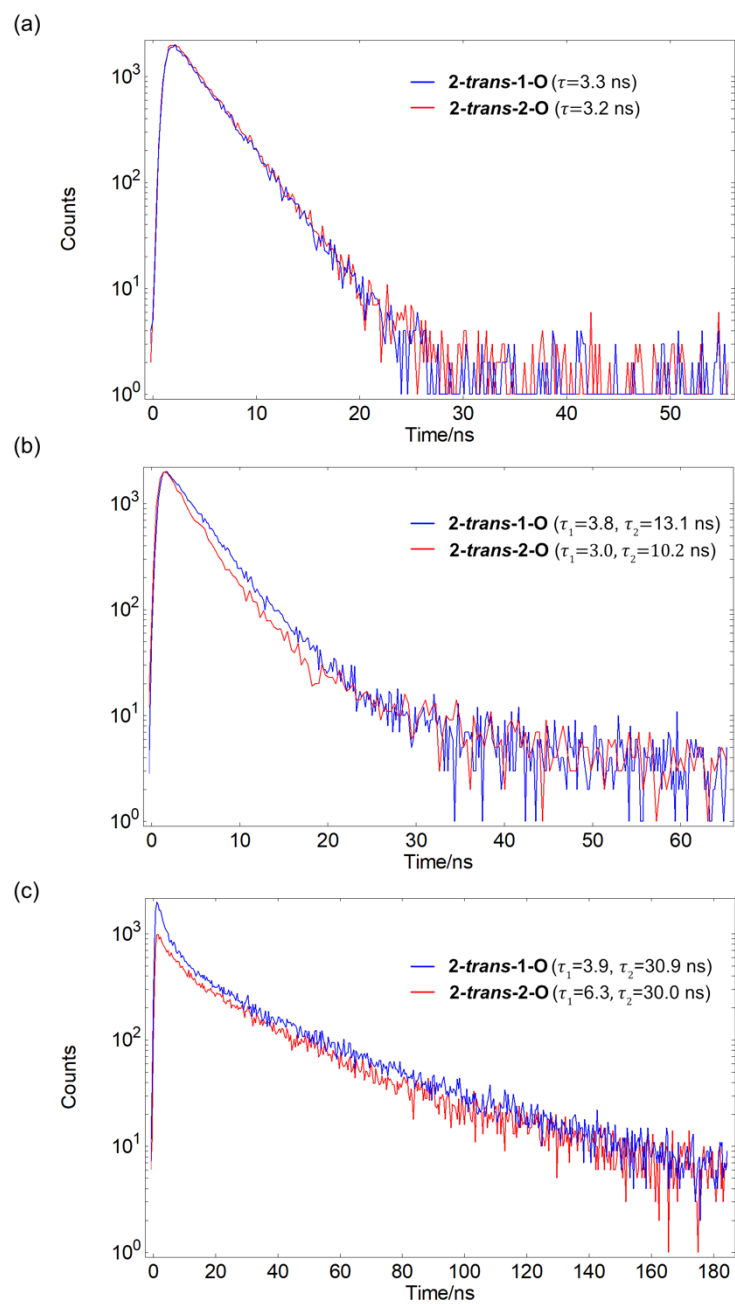


Figure S2-12. Excited-state lifetimes of **2-*trans*-1-O** and **2-*trans*-2-O** from a) DCM solutions, b) 0.2 wt% films in PMMA and c) 1.2 wt % films in PMMA.

2.6. Electrochemical characterization

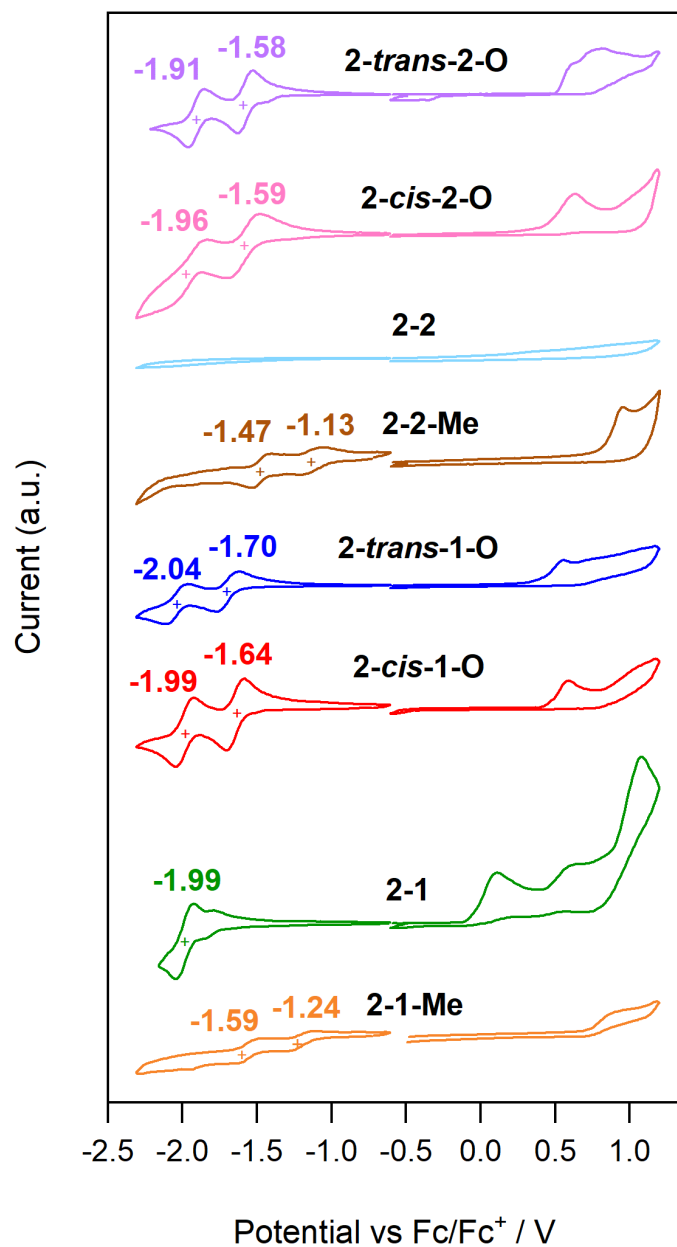


Figure S2-13. Cyclic voltammograms of **2-trans-2-O**, **2-cis-2-O**, **2-2**, **2-2-Me**, and **2-trans-1-O**, **2-cis-1-O**, **2-1**, **2-1-Me**, with scan rate 100 mV s⁻¹, in CH₂Cl₂ with 0.1 M NBu₄PF₆, vs. Fc/Fc⁺.

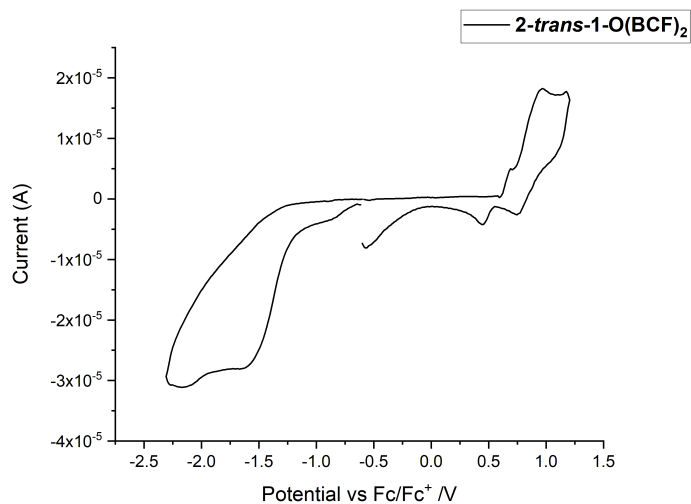


Figure S2-14. Cyclic voltammograms of **2-trans-1-O(BCF)₂**, with scan rate 100 mV s⁻¹, in CH₂Cl₂ with 0.1 M NBu₄PF₆, vs. Fc/Fc⁺.

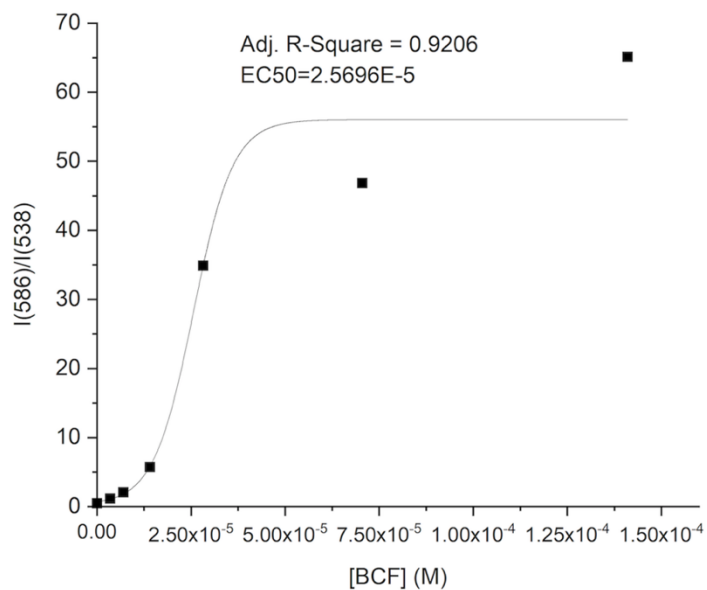
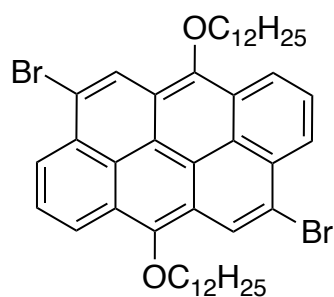
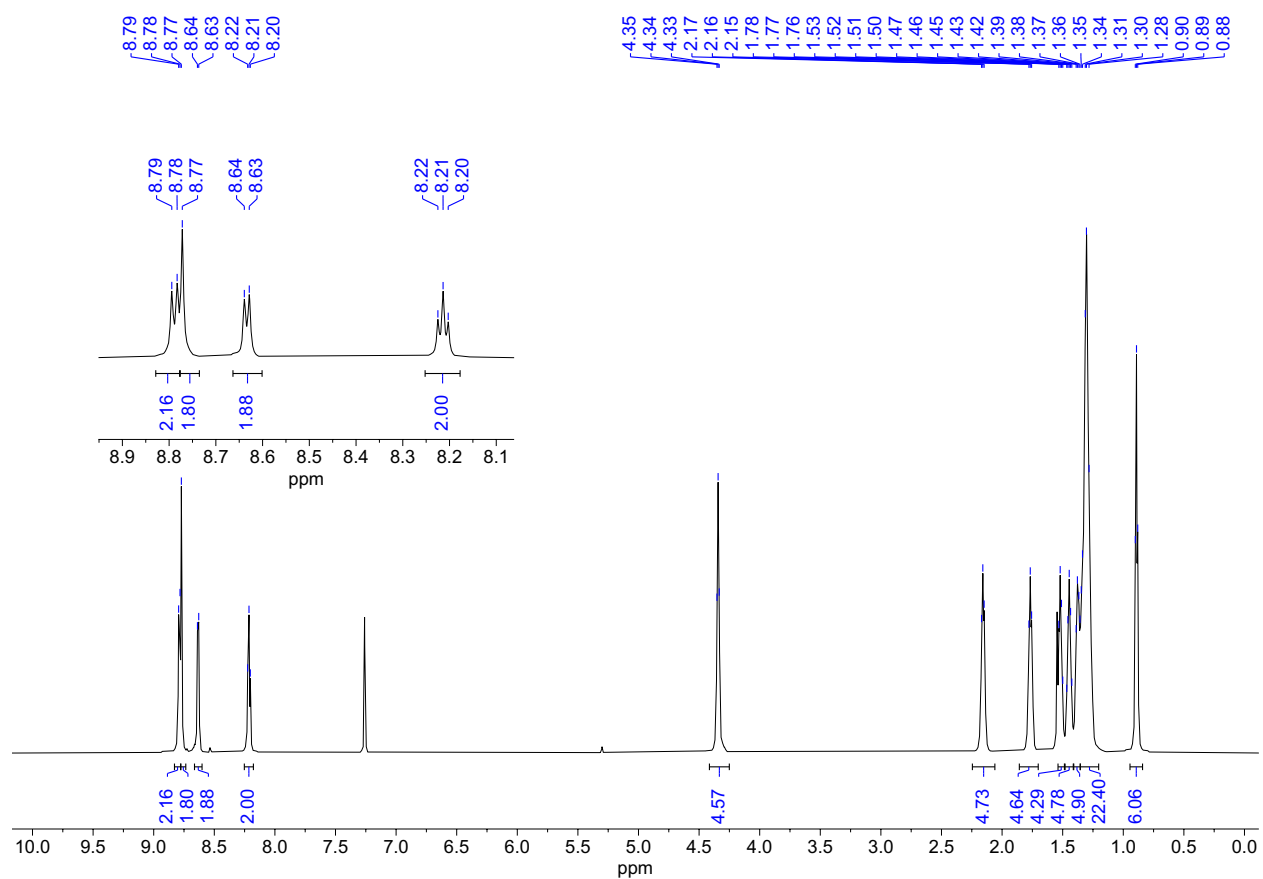


Figure S2-15. Sigmoidal fit of BCF titration of the **2-cis-2-O**. I(586) and I(538) is the intensity of the **2-cis-2-O(BCF)₂** and **2-cis-2-O** at their λ_{max} wavelength. The binding constant (K_{total}) for a full conversion was calculated to be 1.14×10^9 (M⁻¹) based on a method used in our previous work and developed by Lakowicz.^{S2-11, S2-12}

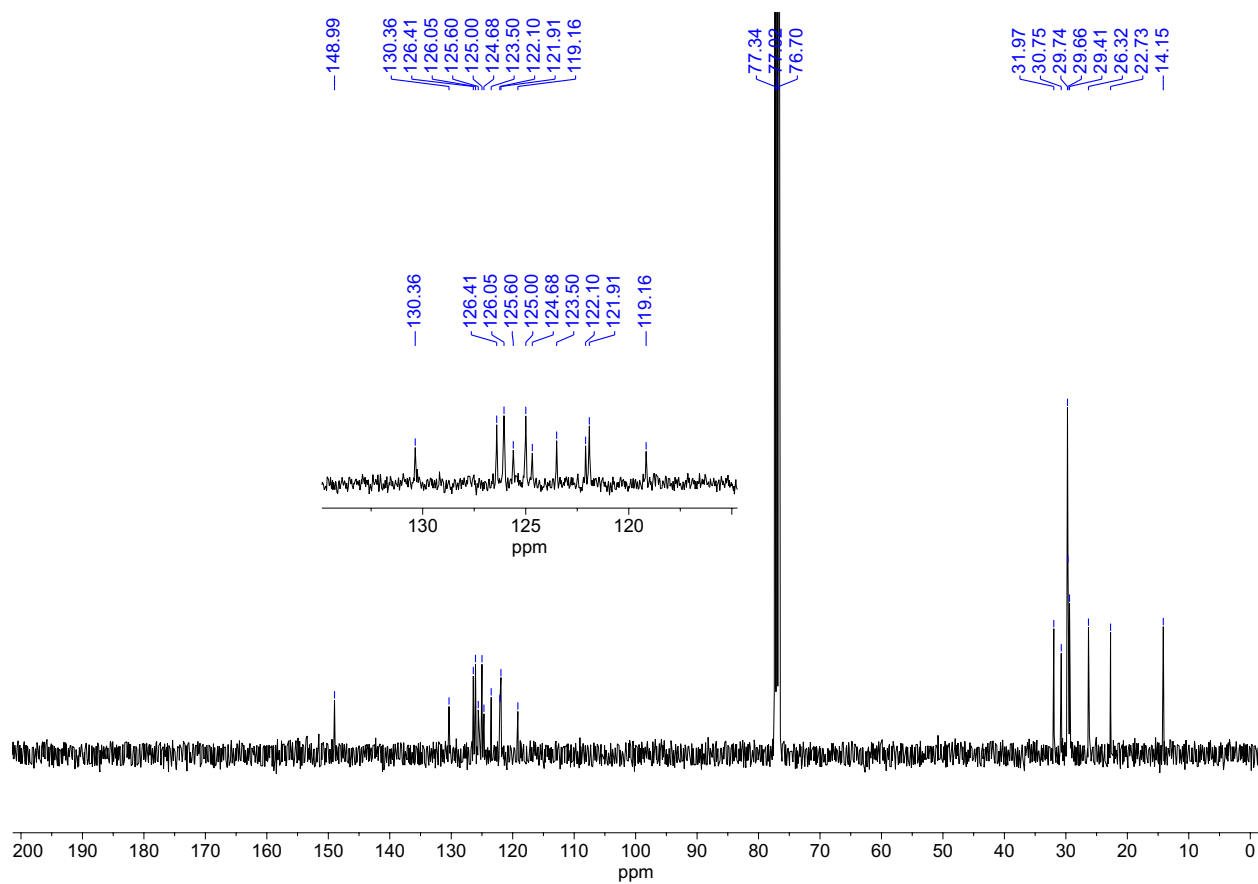
2.7. NMR Spectra

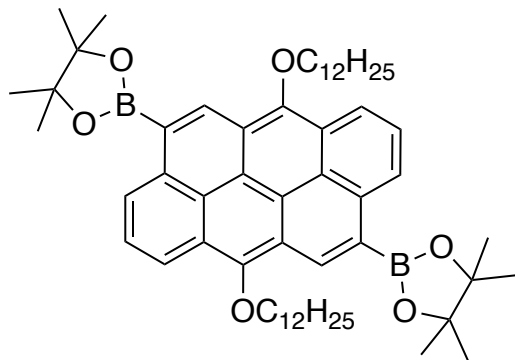


¹H NMR spectrum of **2-S1** measured in CDCl₃ (700 MHz).

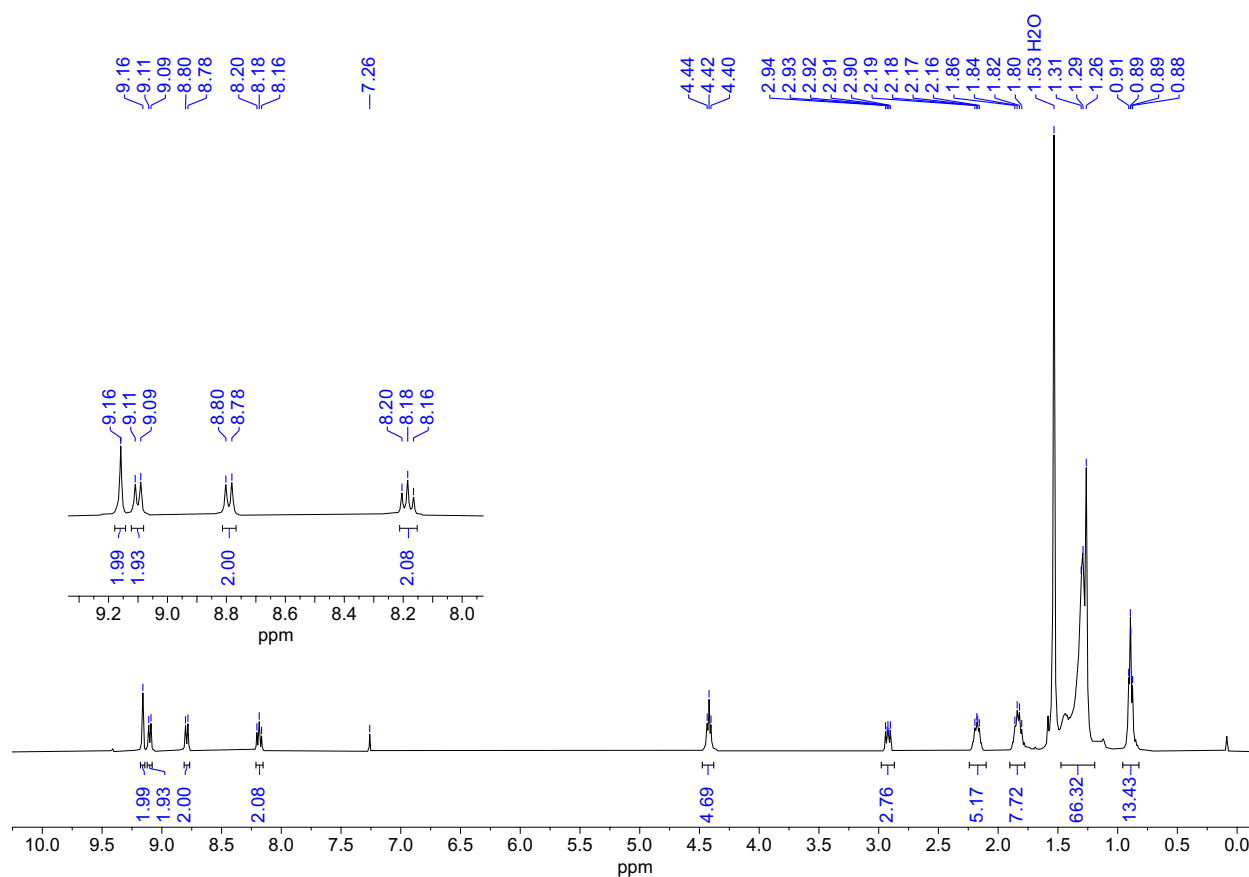


$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2-S1** measured in CDCl_3 (101 MHz).

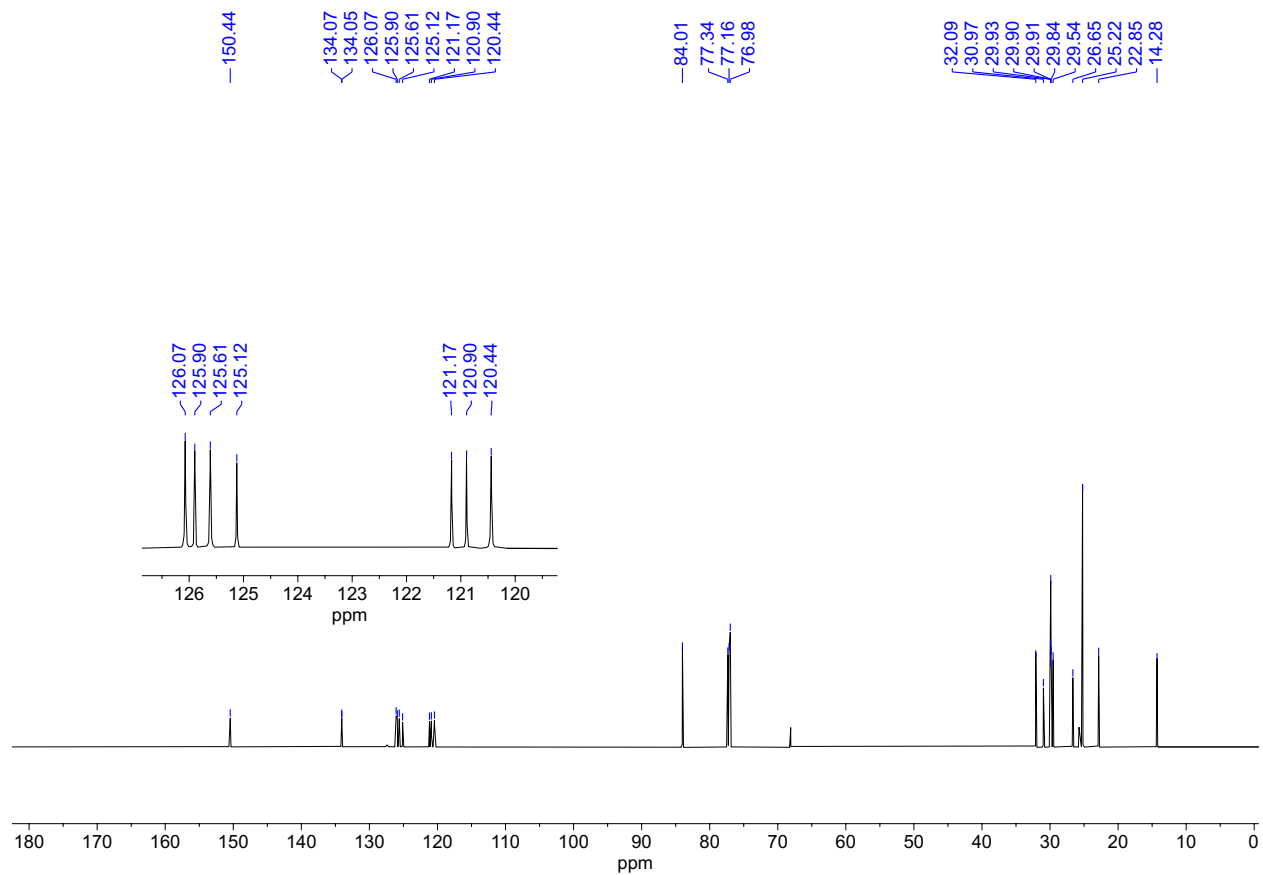


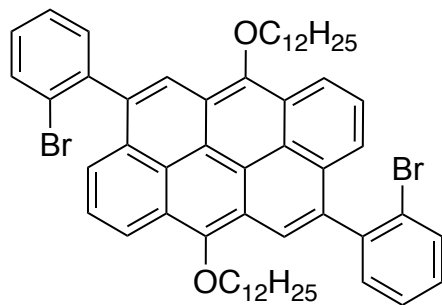


^1H NMR spectrum of **2-S2** measured in CDCl_3 (400 MHz).

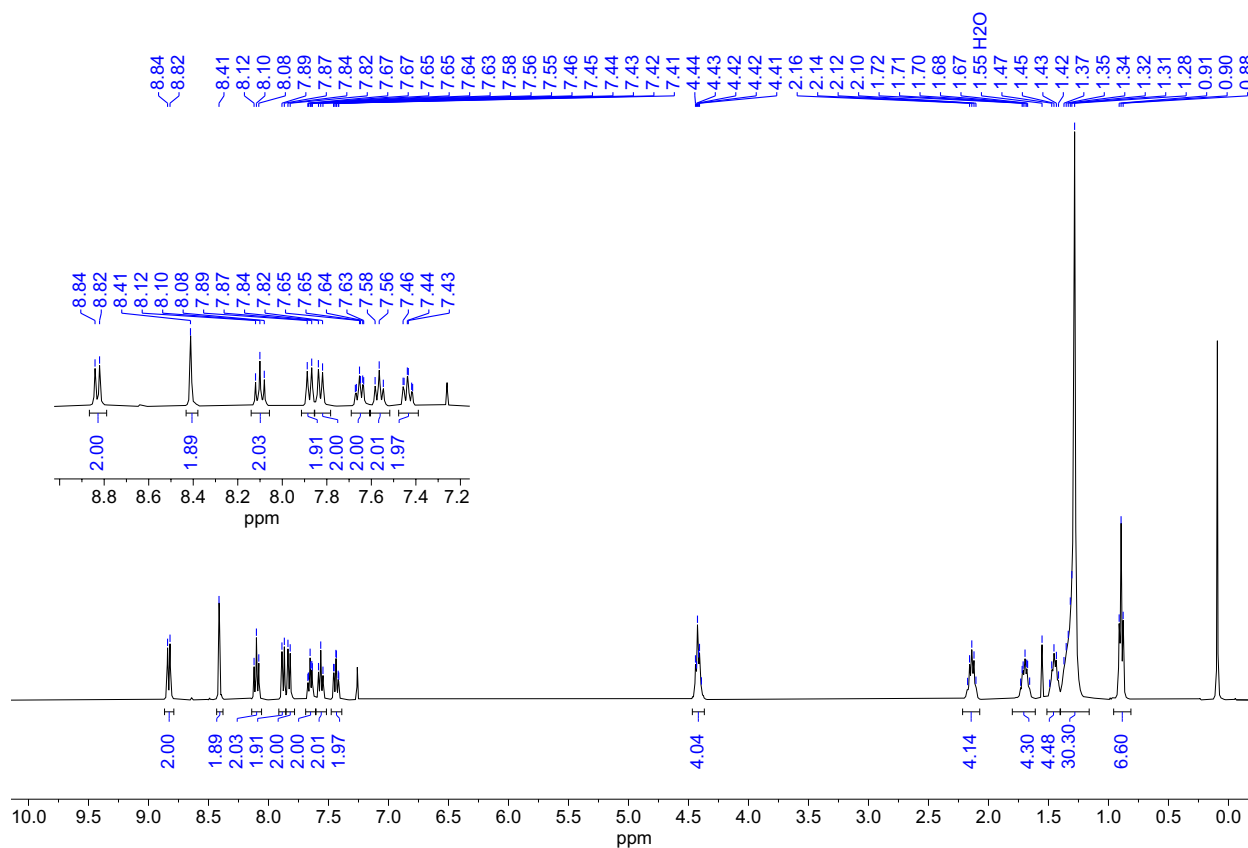


$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2-S2** measured in CDCl_3 (176 MHz).

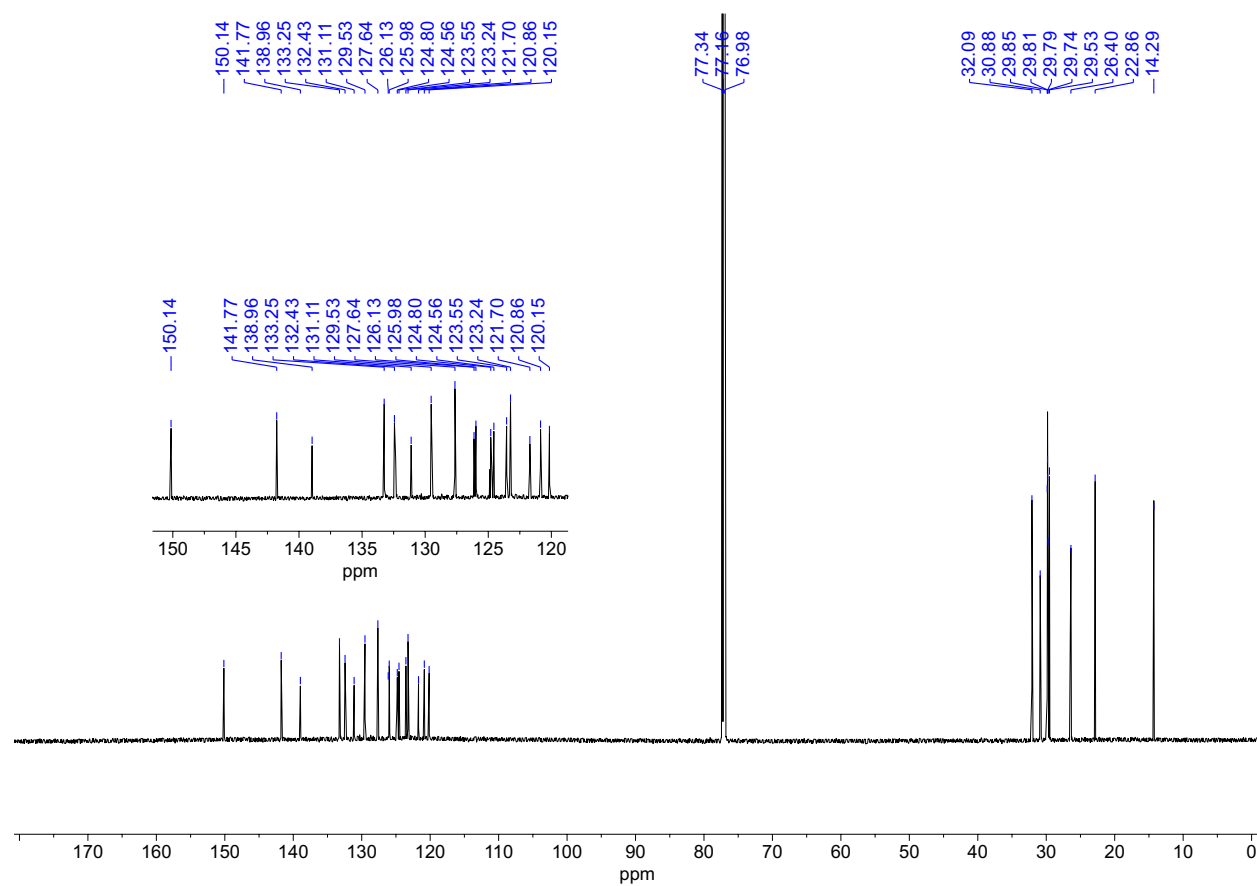


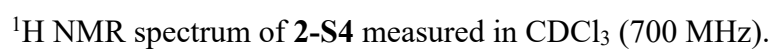


^1H NMR spectrum of **2-S3** measured in CDCl_3 (400 MHz).

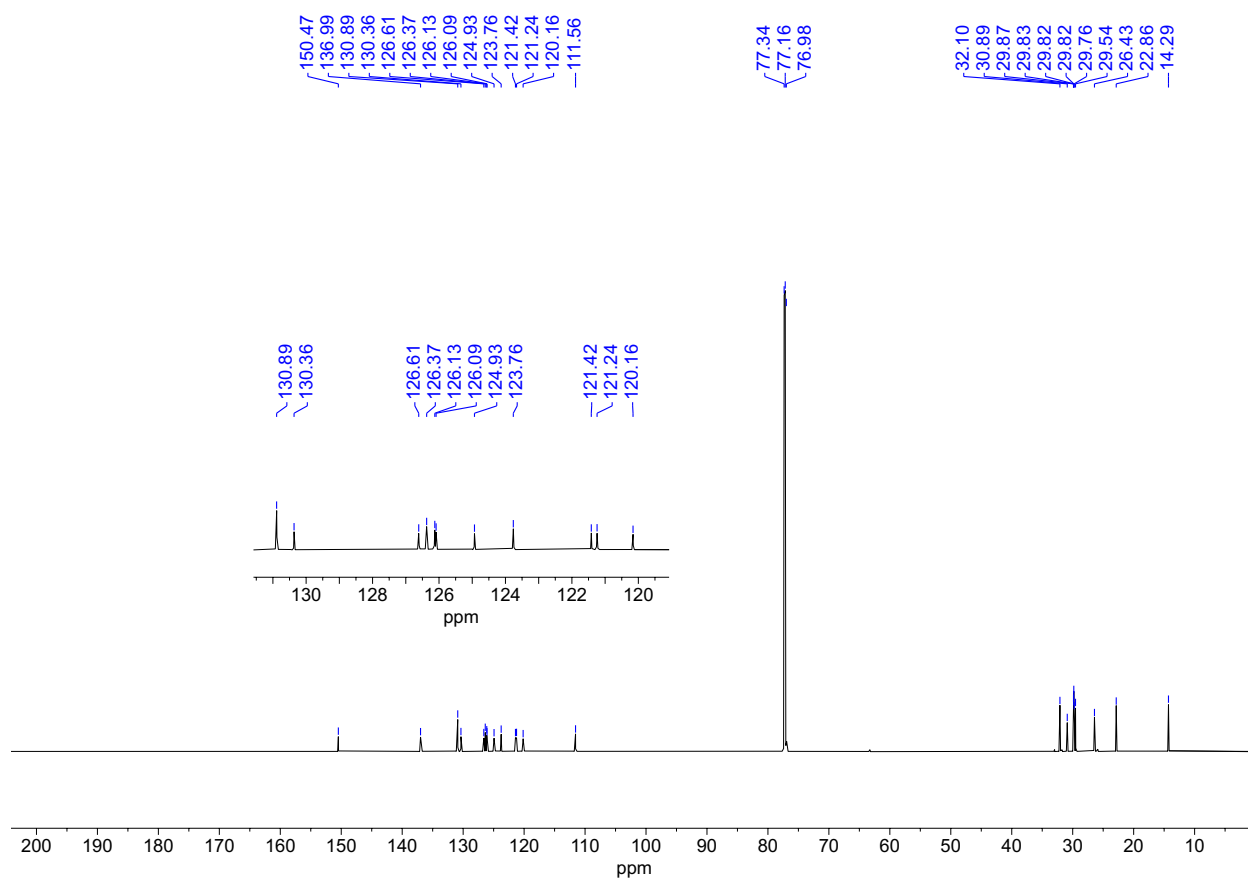


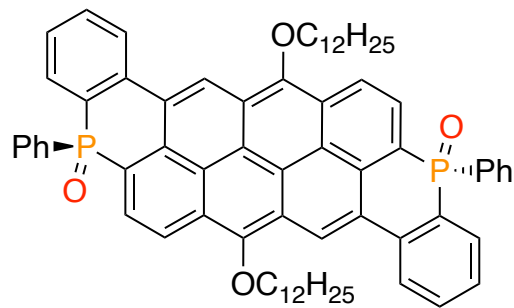
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2-S3** measured in CDCl_3 (176 MHz).



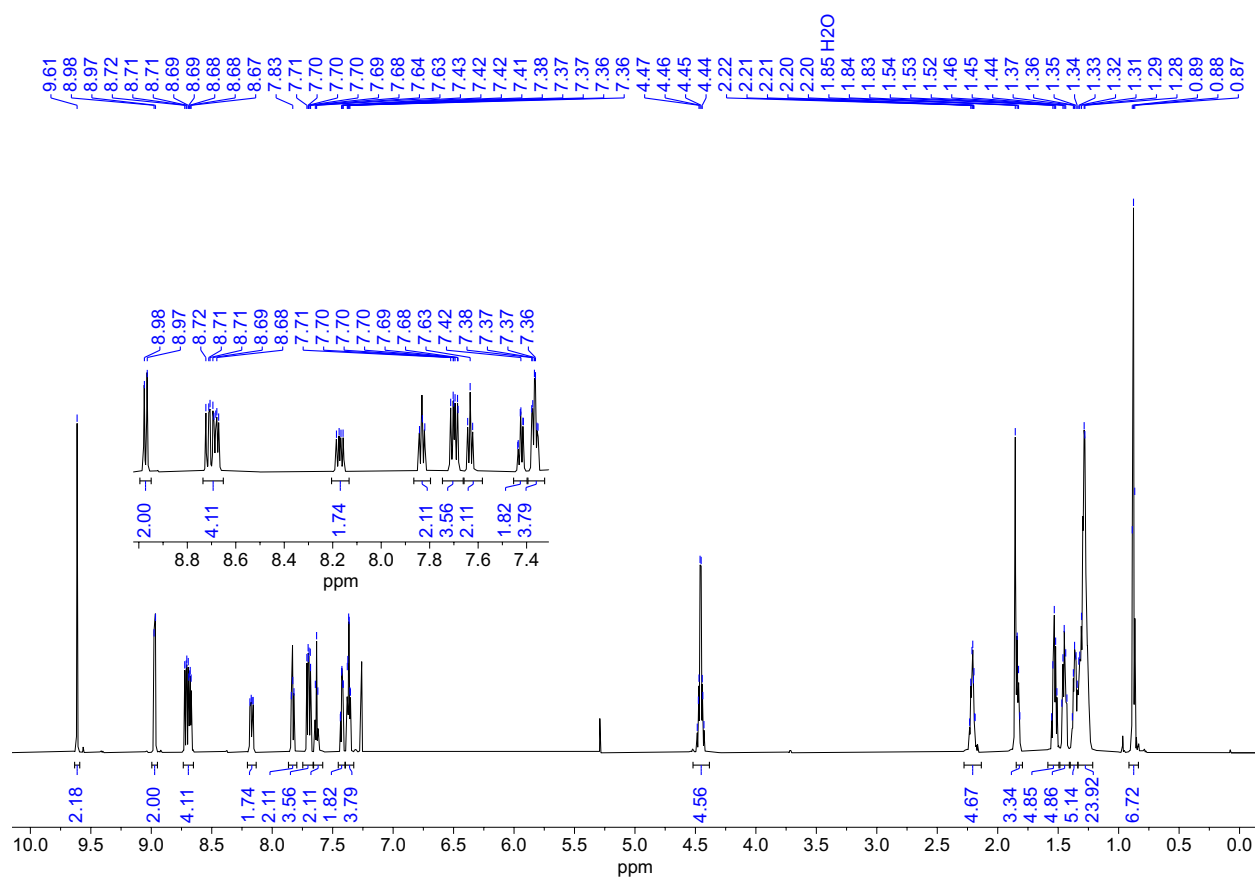


$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2-S4** measured in CDCl_3 (176 MHz).

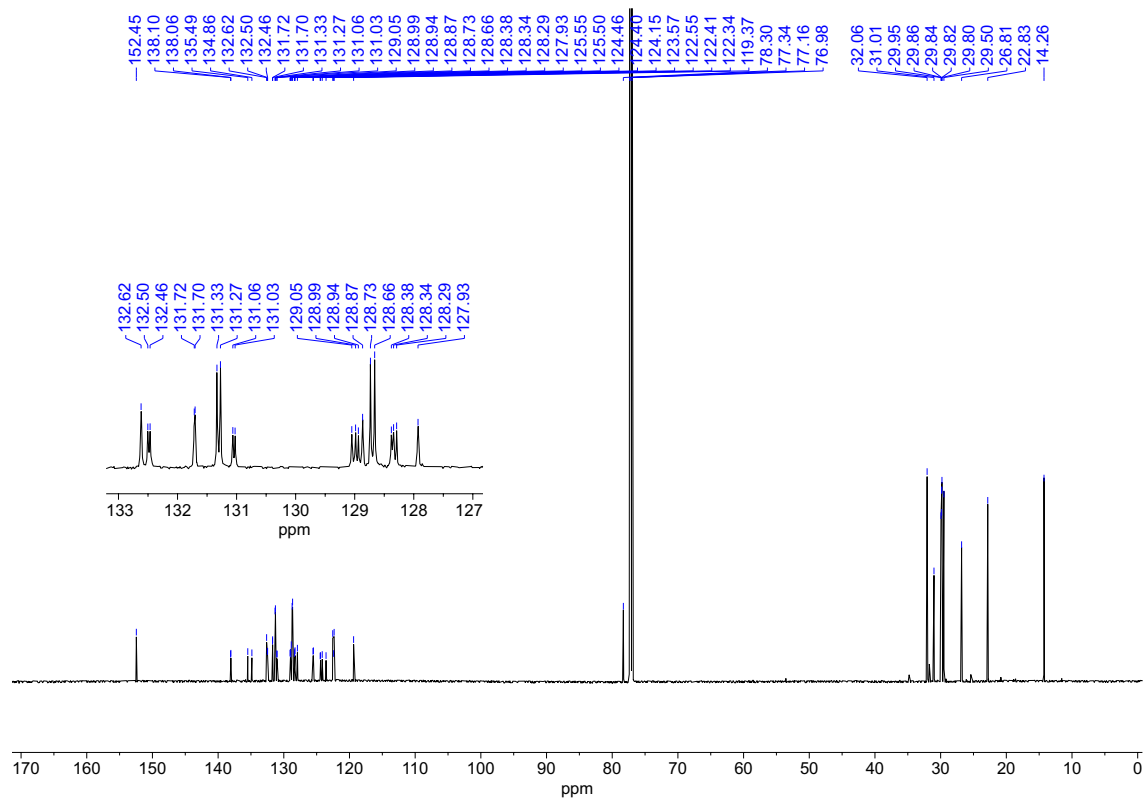




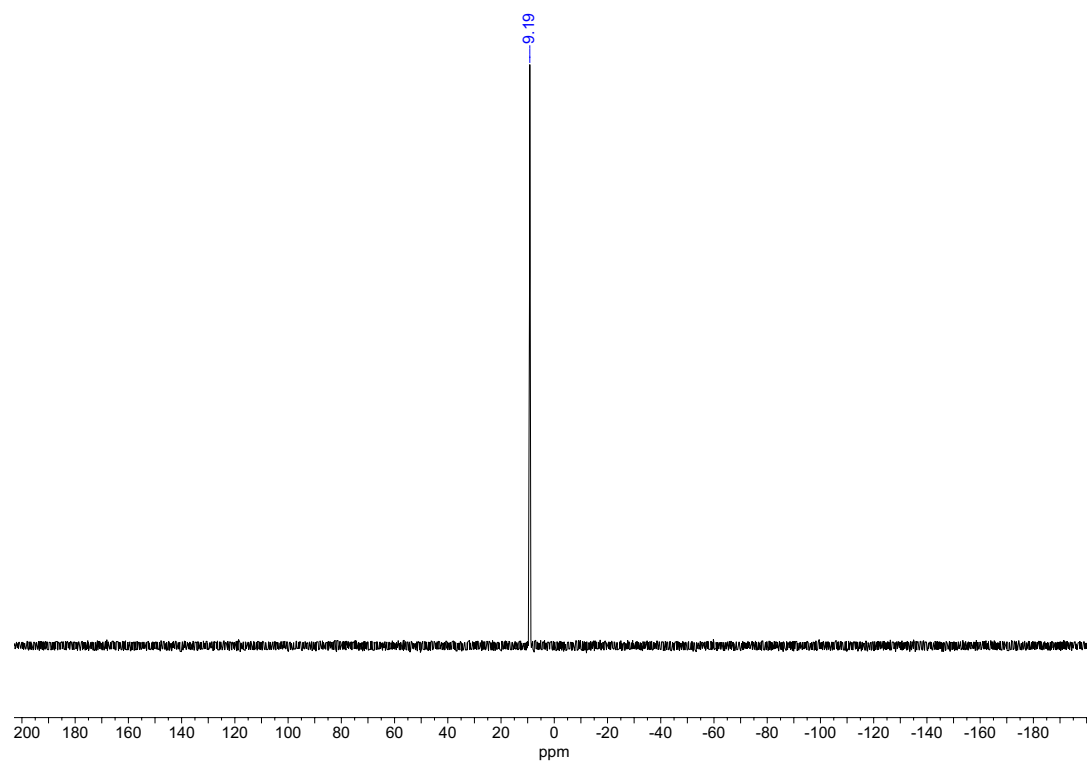
^1H NMR spectrum of **2-trans-1-O** measured in CDCl_3 (700 MHz).



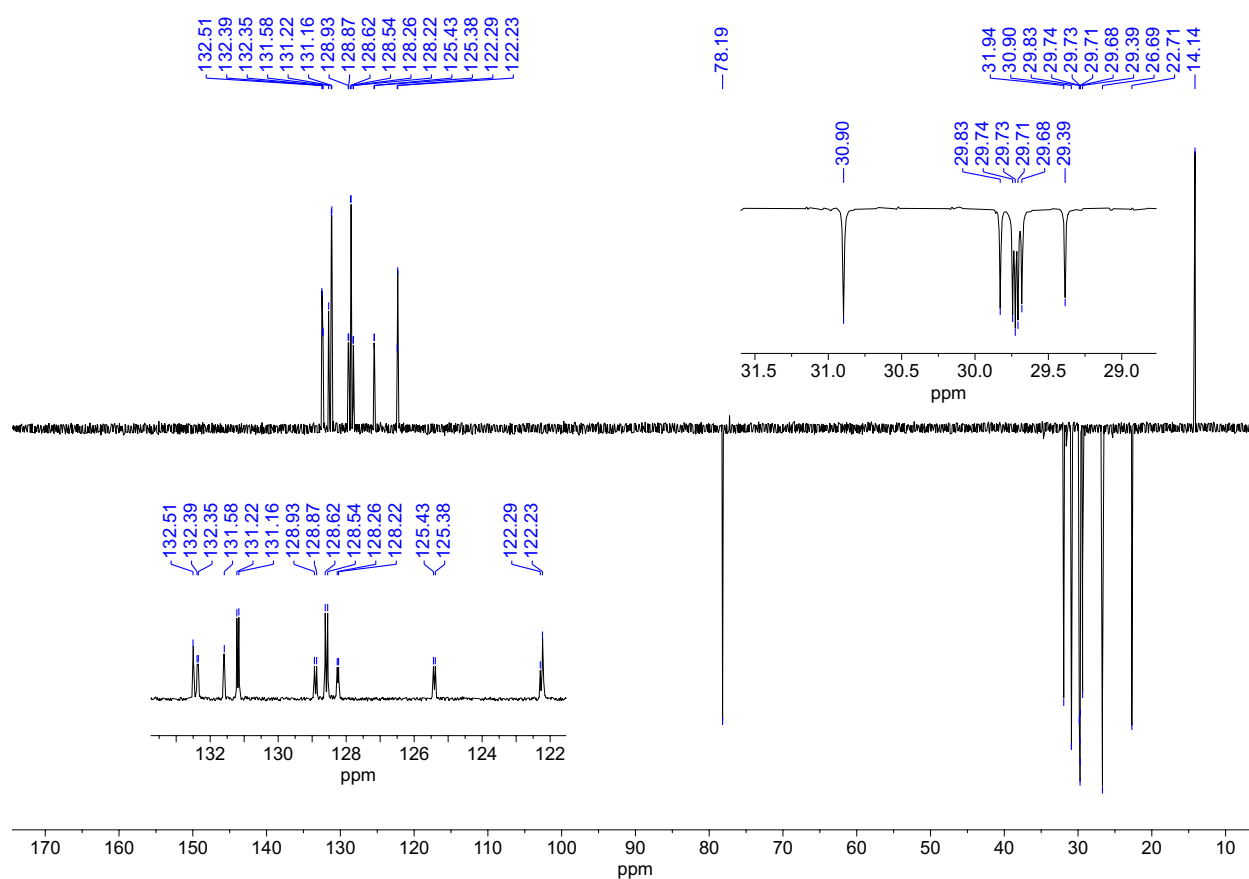
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2-*trans*-1-O** measured in CDCl_3 (176 MHz).



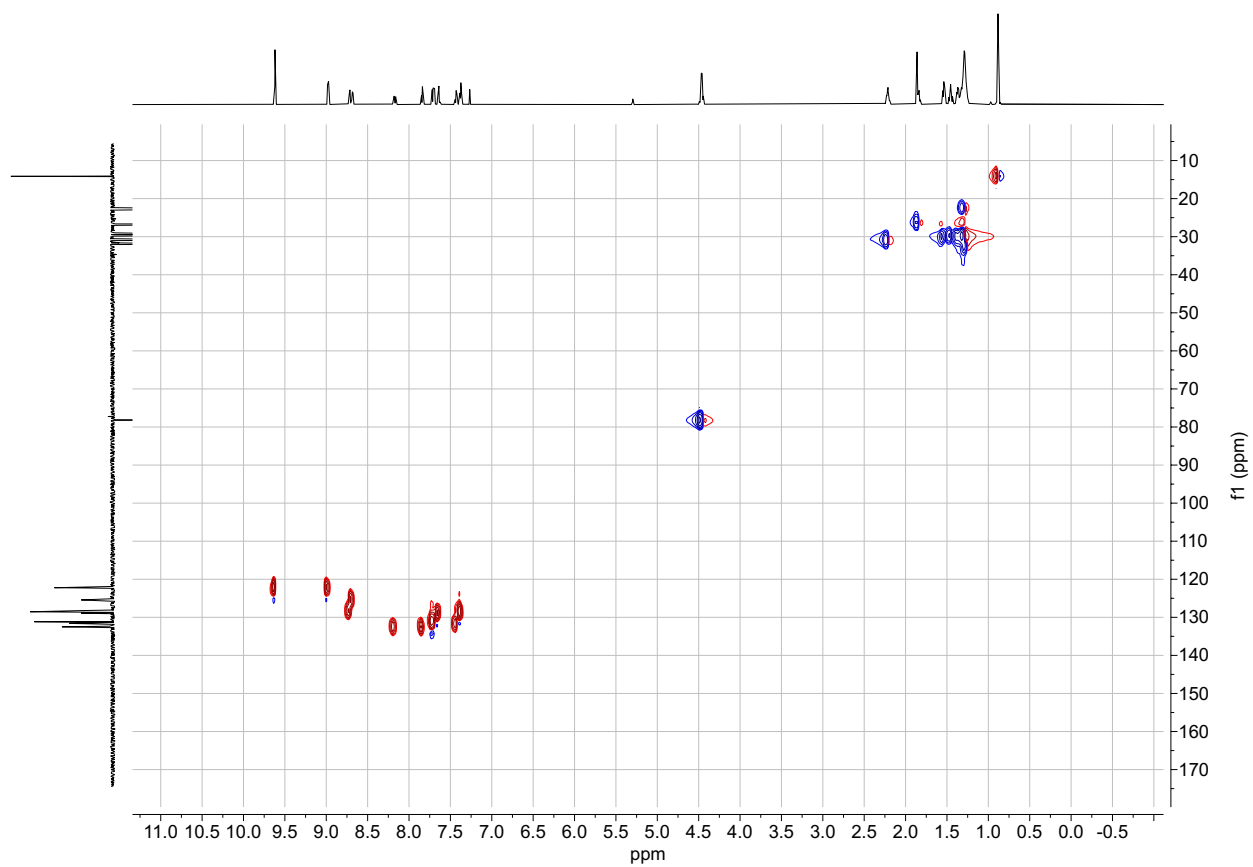
$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2-*trans*-1-O** measured in CDCl_3 (162 MHz).



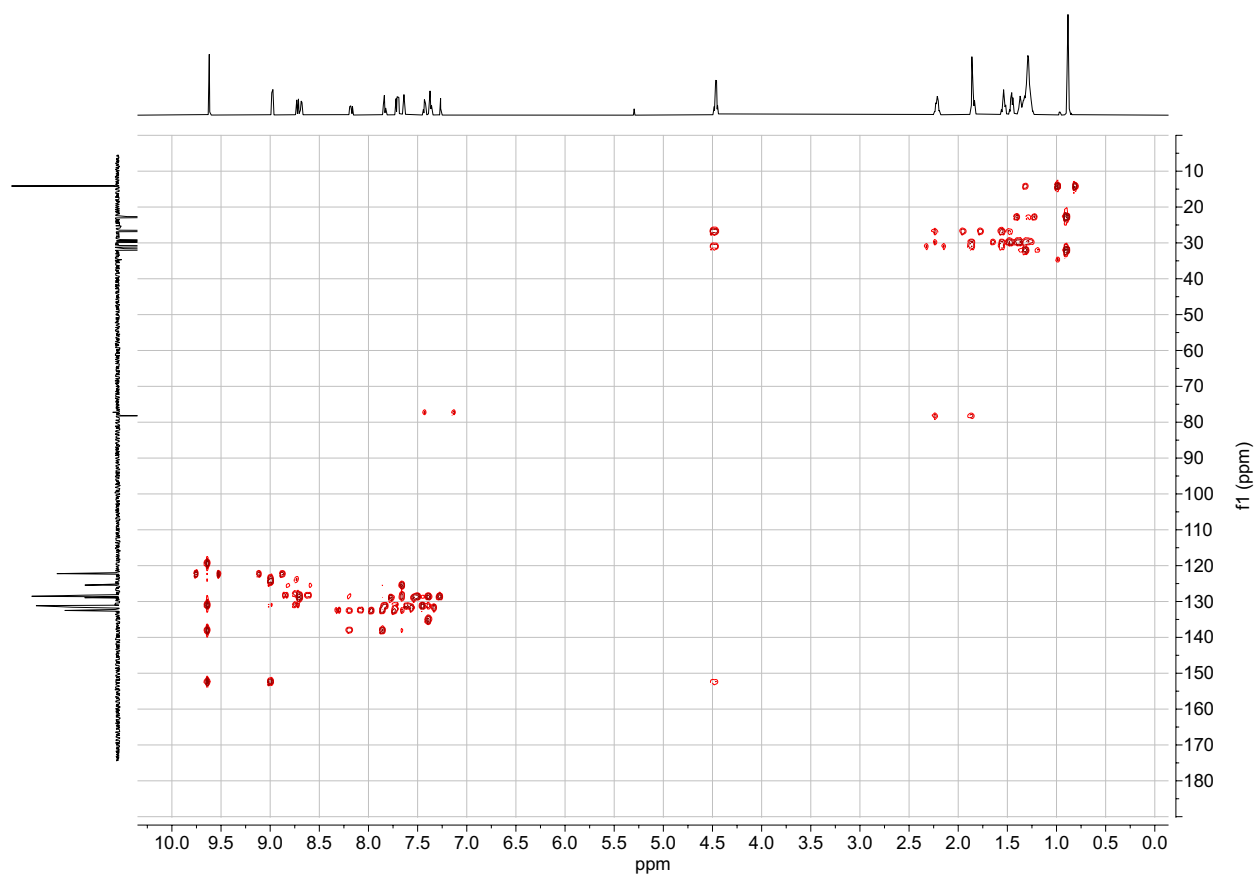
$^{13}\text{C}\{^1\text{H}\}$ DEPT 135 NMR spectrum of **2-*trans*-1-O** measured in CDCl_3 (176 MHz).

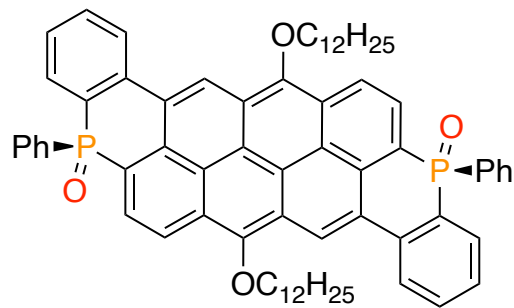


2D HSQC-DEPT 135 NMR spectrum of **2-*trans*-1-O** measured in CDCl₃ (700 MHz).

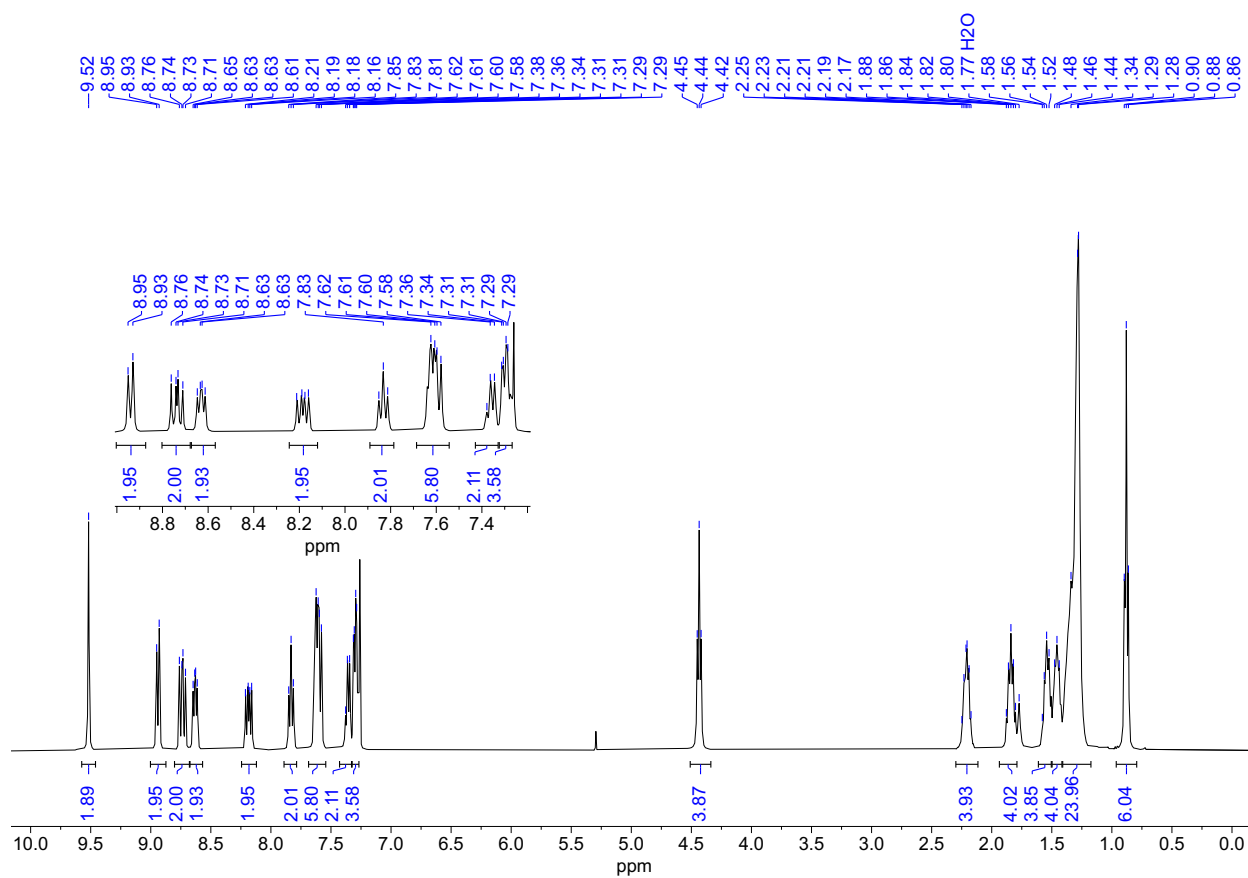


2D HMBC NMR spectrum of **2-*trans*-1-O** measured in CDCl₃ (700 MHz).

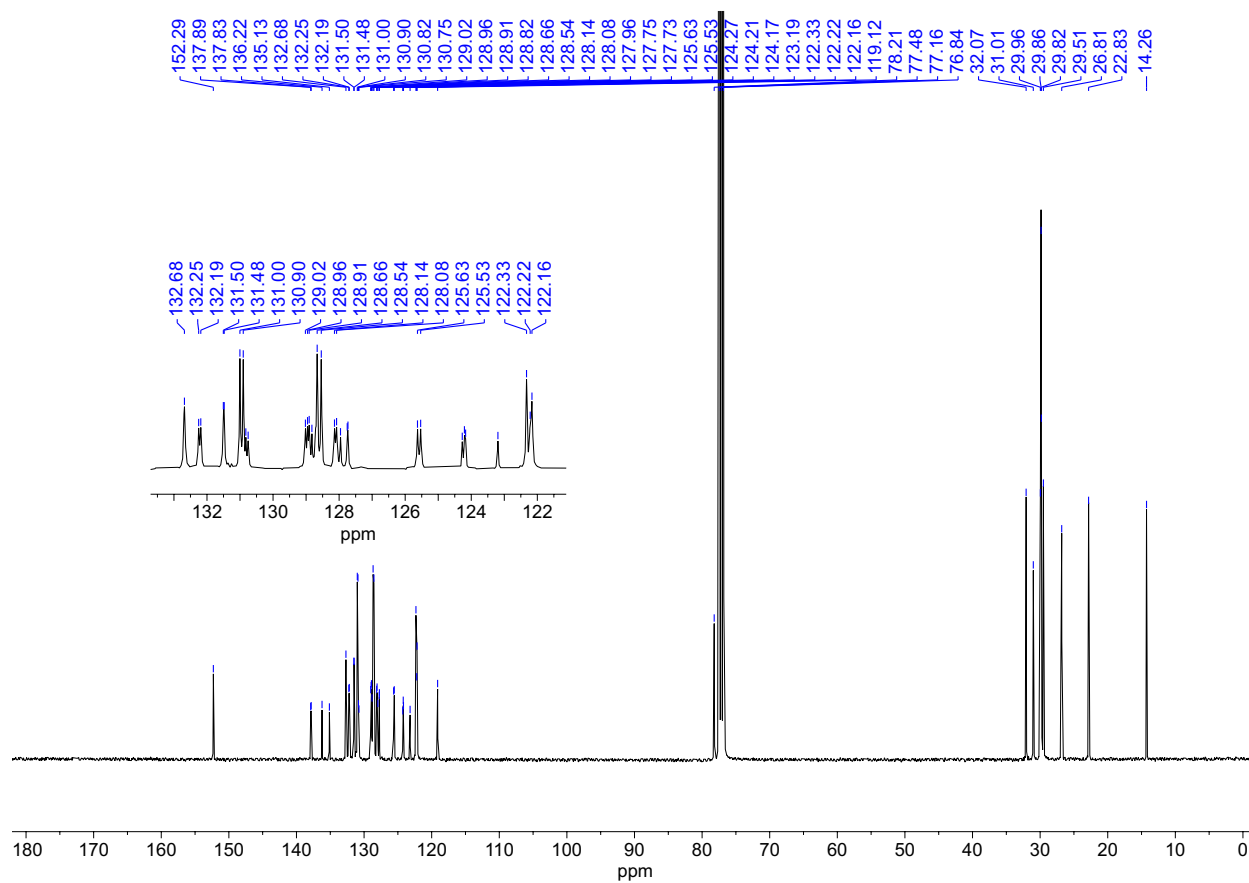




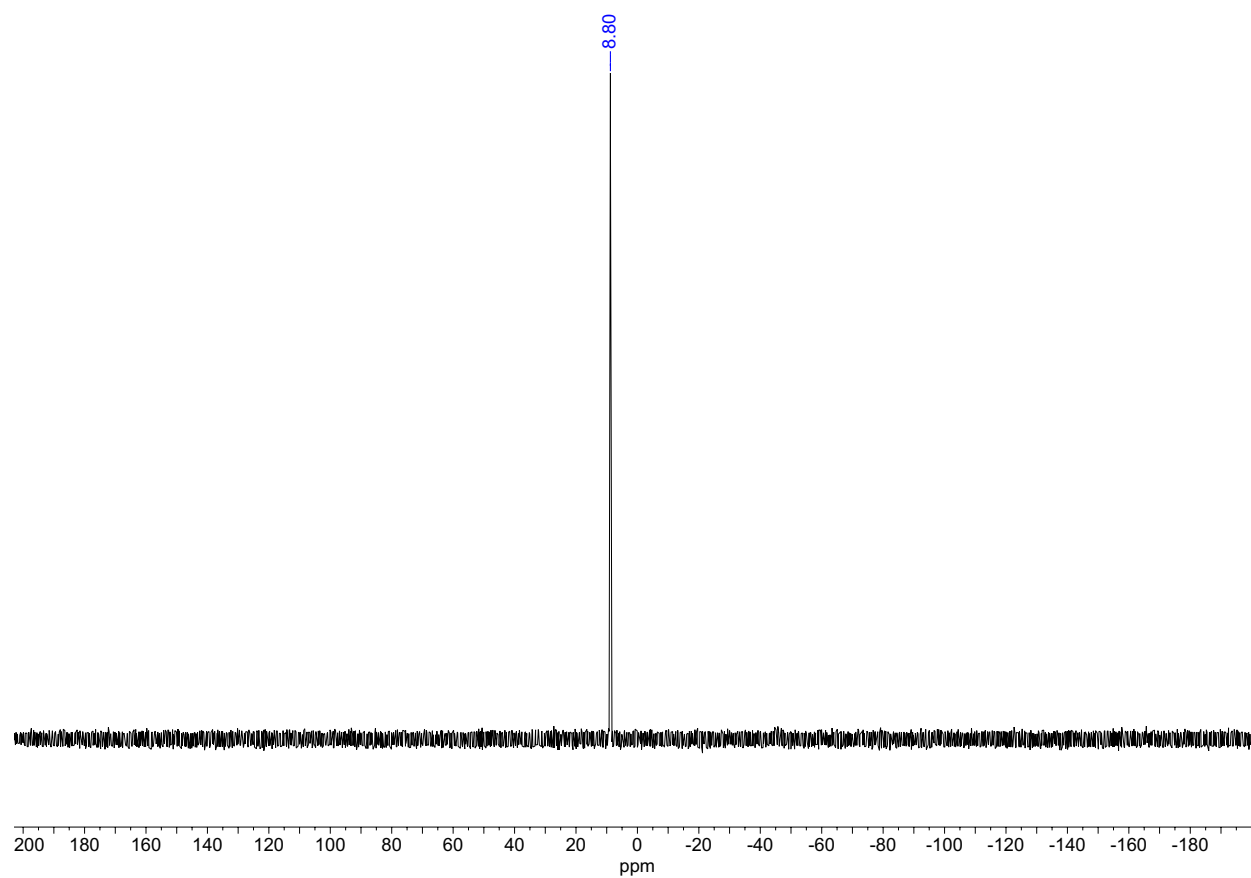
¹H NMR spectrum of **2-*cis*-1-O** measured in CDCl₃ (400 MHz).

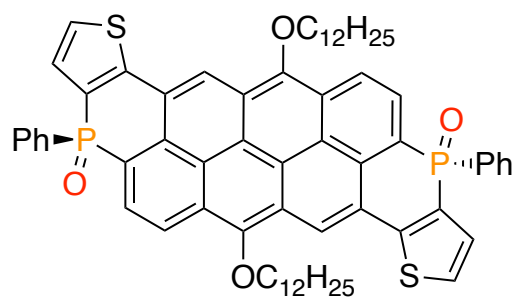


$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2-*cis*-1-O** measured in CDCl_3 (101 MHz).

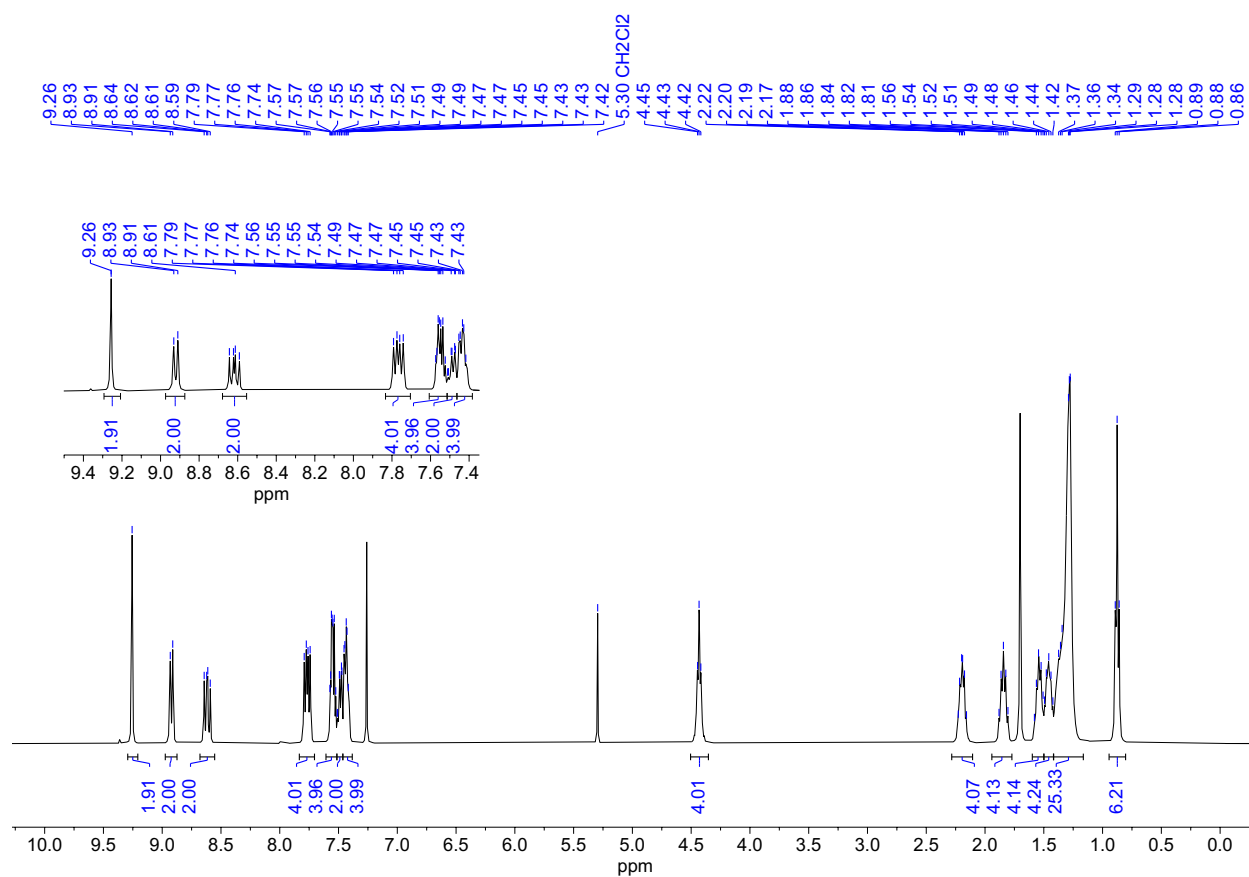


$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2-*cis*-1-O** measured in CDCl_3 (162 MHz).

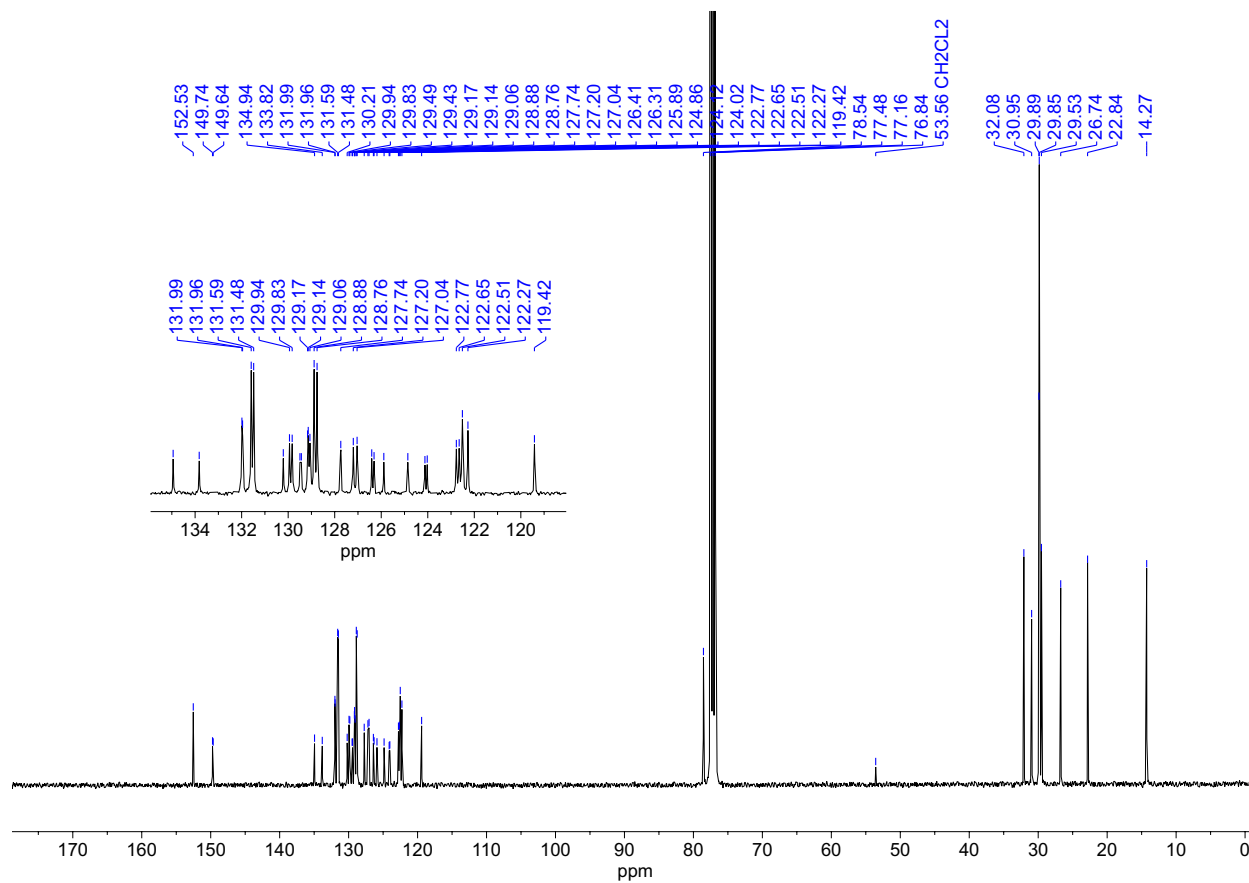




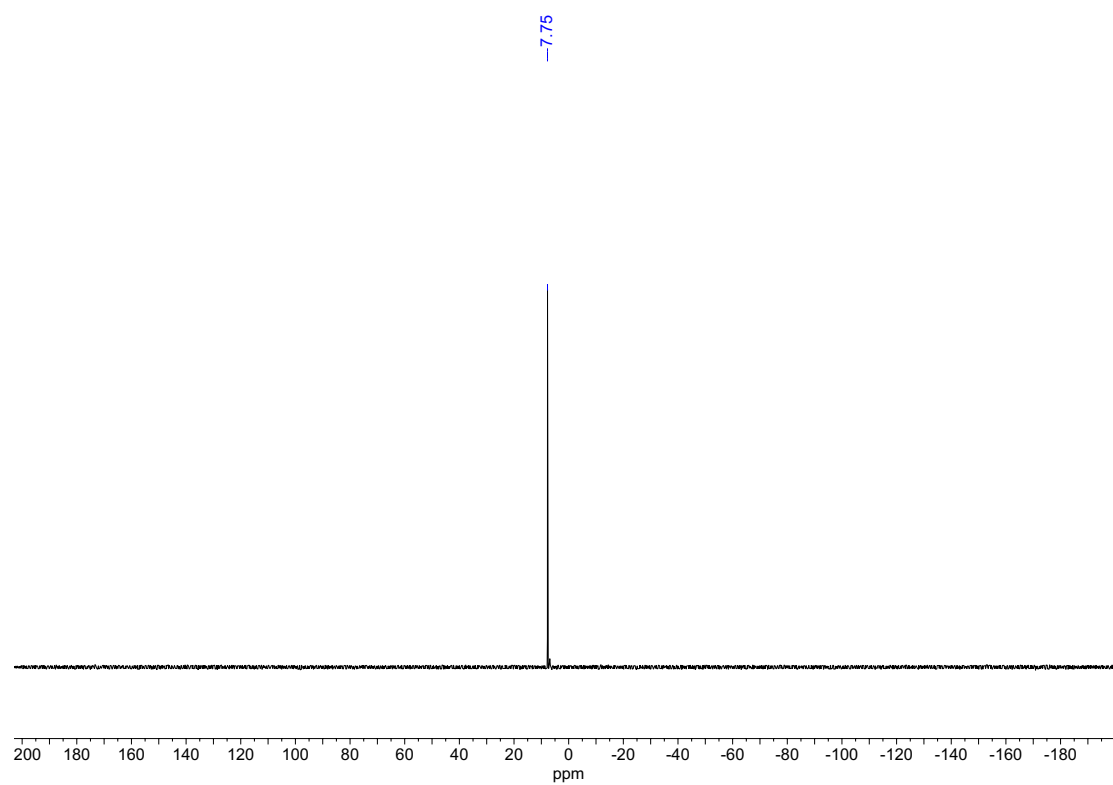
^1H NMR spectrum of **2-trans-2-O** measured in CDCl_3 (400 MHz).



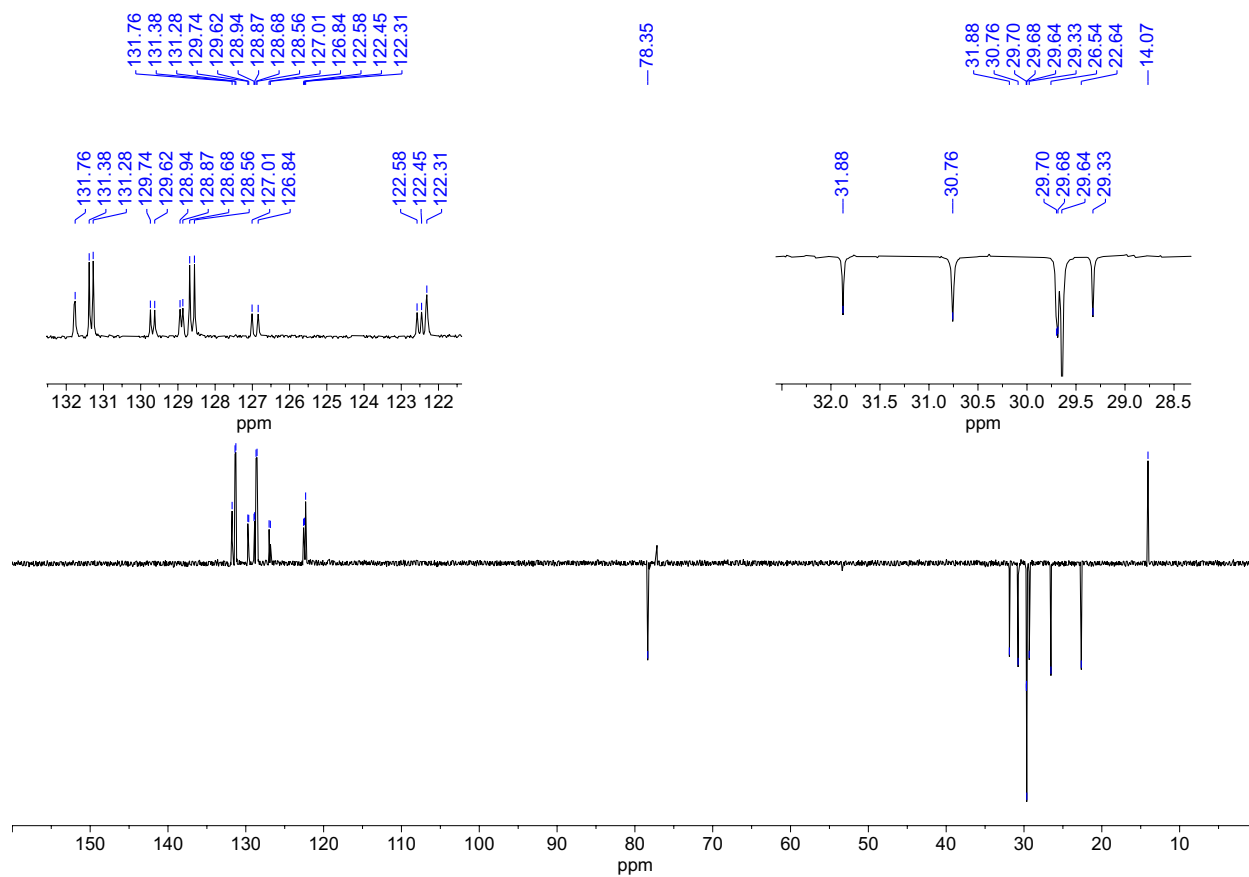
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2-*trans*-2-O** measured in CDCl_3 (101 MHz).

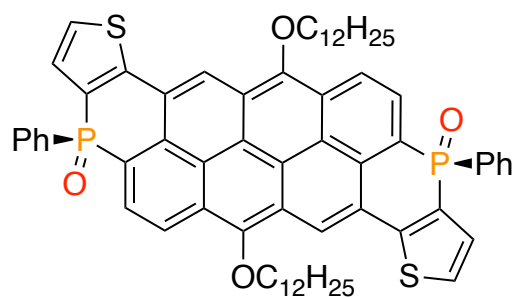


$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2-*trans*-2-O** measured in CDCl_3 (162 MHz).

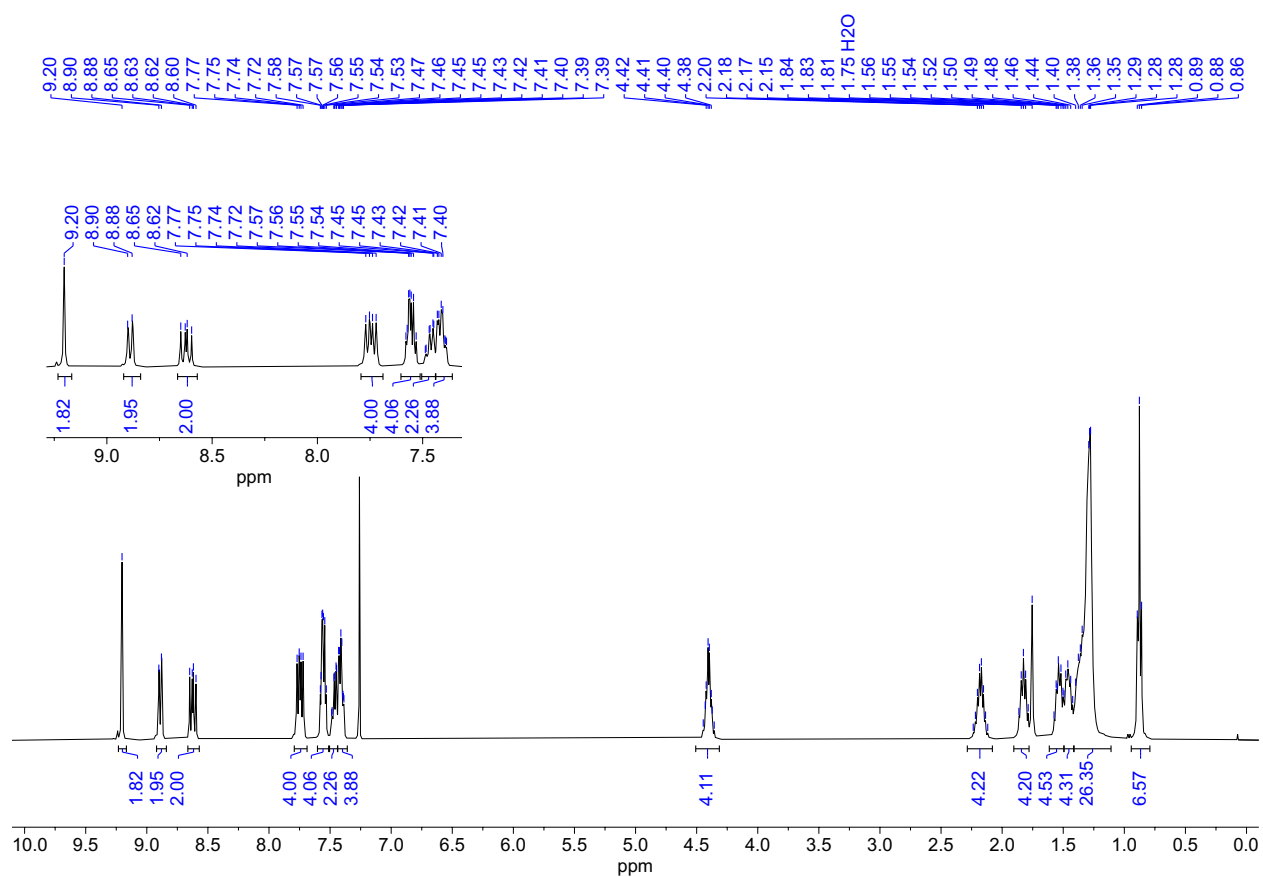


$^{13}\text{C}\{^1\text{H}\}$ DEPT 135 NMR spectrum of **2-*trans*-2-O** measured in CDCl_3 (101 MHz).

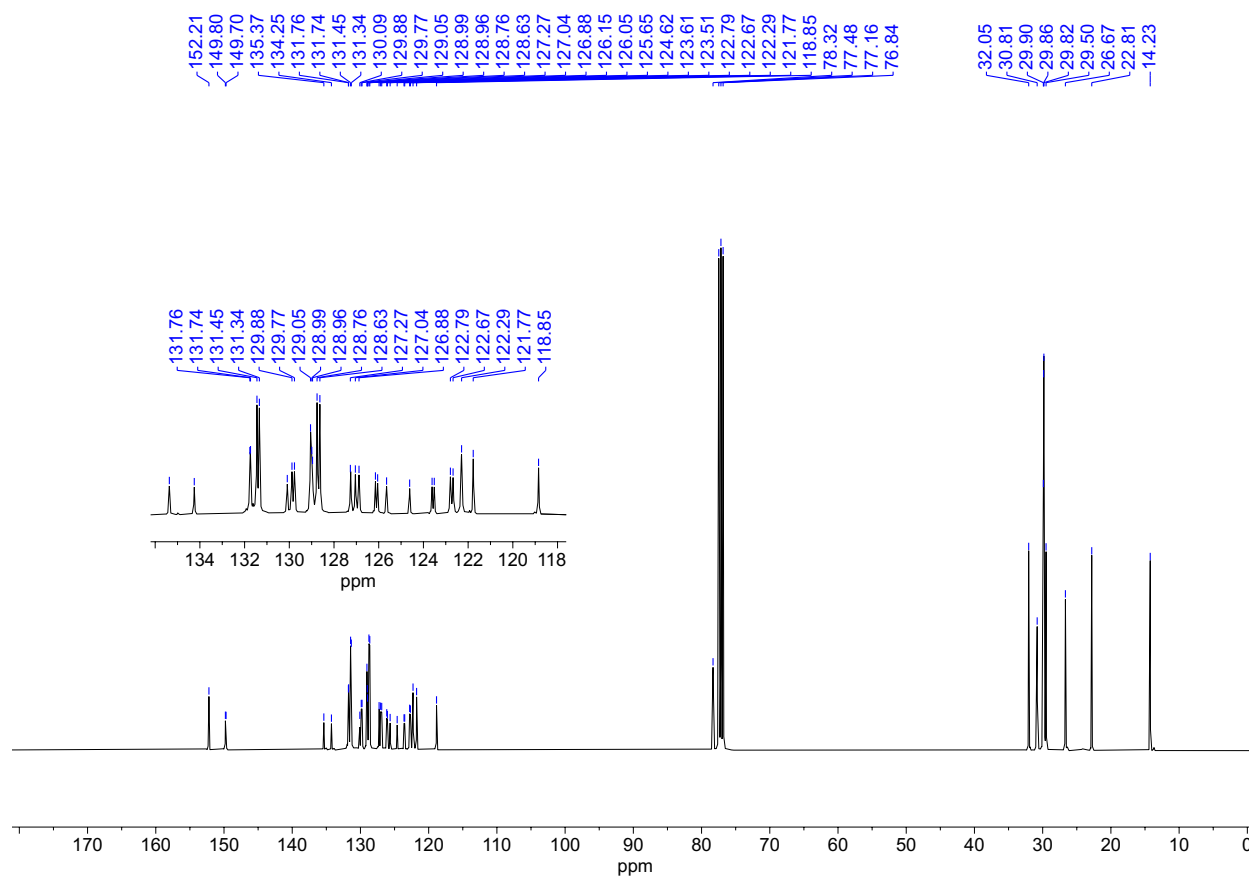




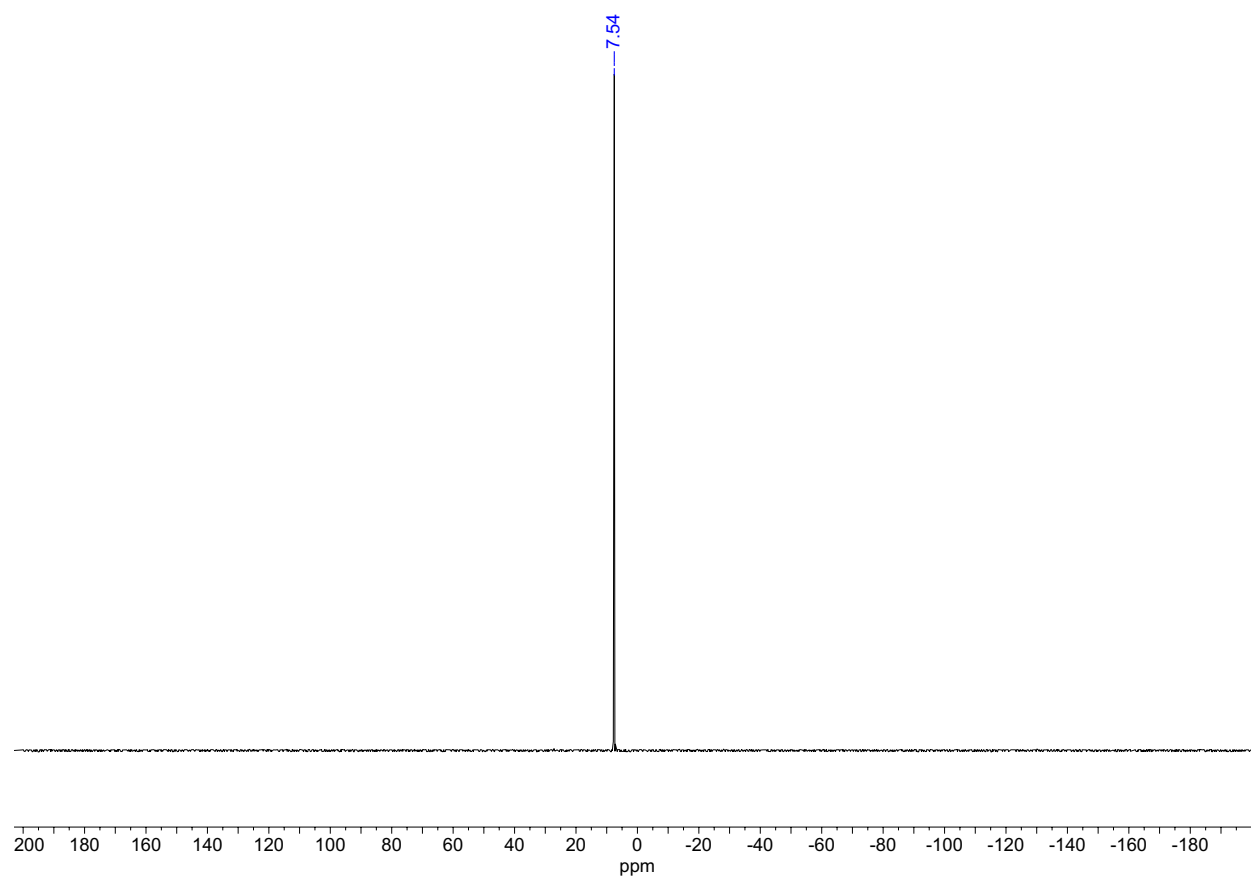
^1H NMR spectrum of **2-*cis*-2-O** measured in CDCl_3 (400 MHz).

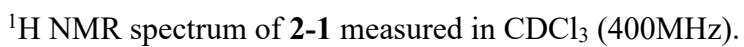


$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2-*cis*-2-O** measured in CDCl_3 (101 MHz).

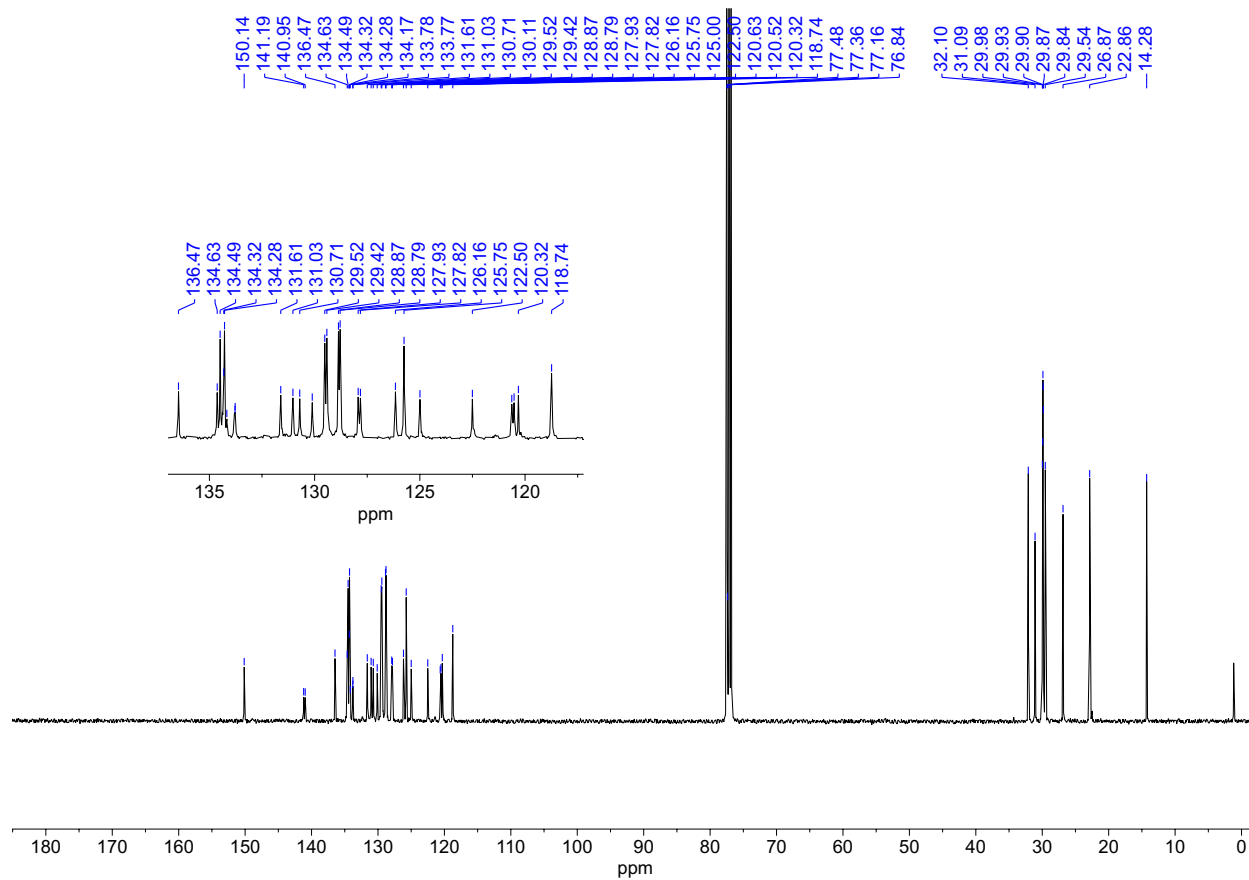


$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2-*cis*-2-O** measured in CDCl_3 (162 MHz).

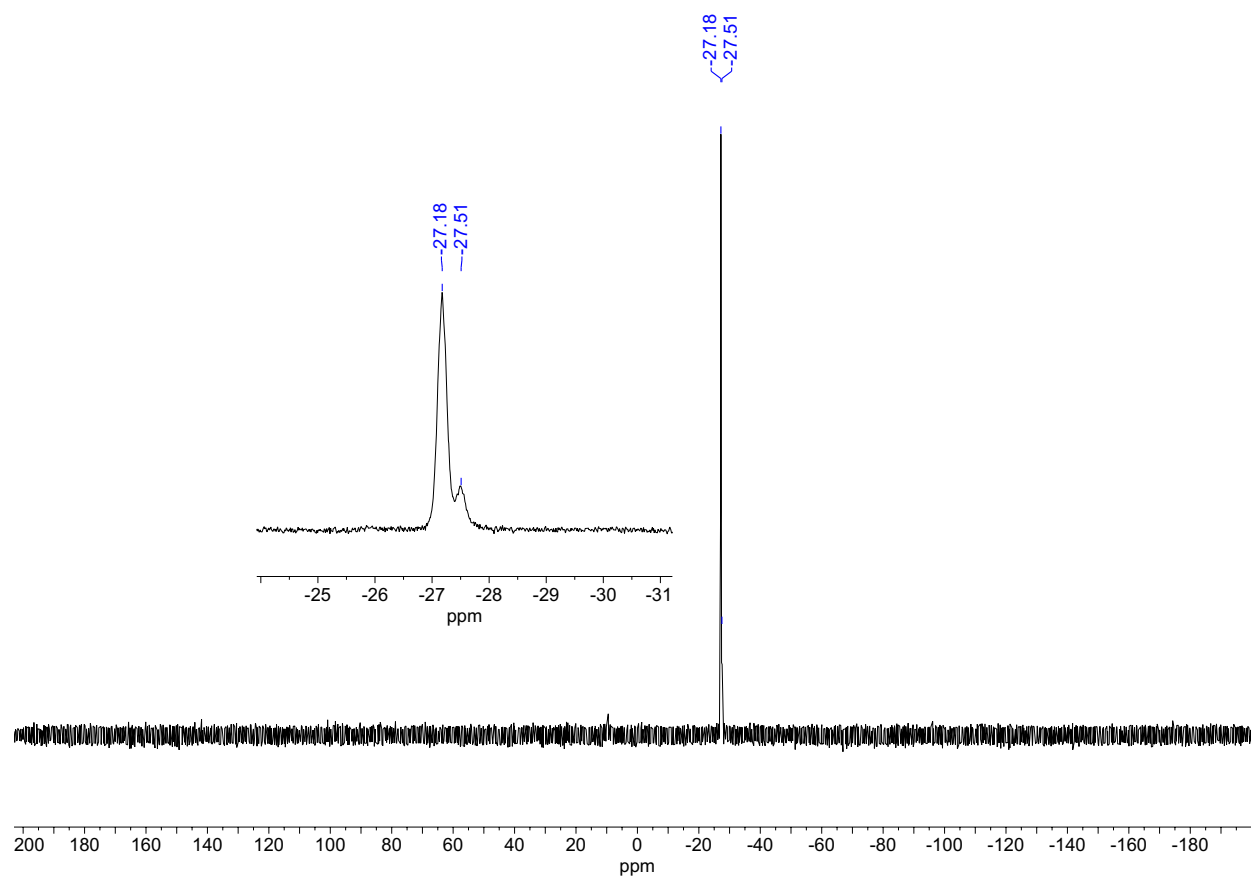


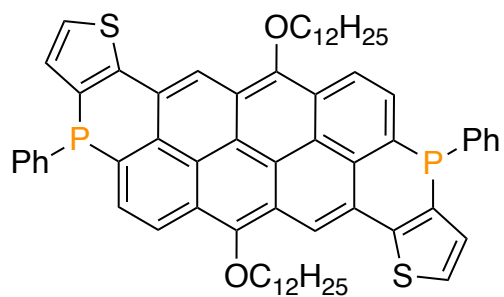


$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2-1** measured in CDCl_3 (101 MHz).

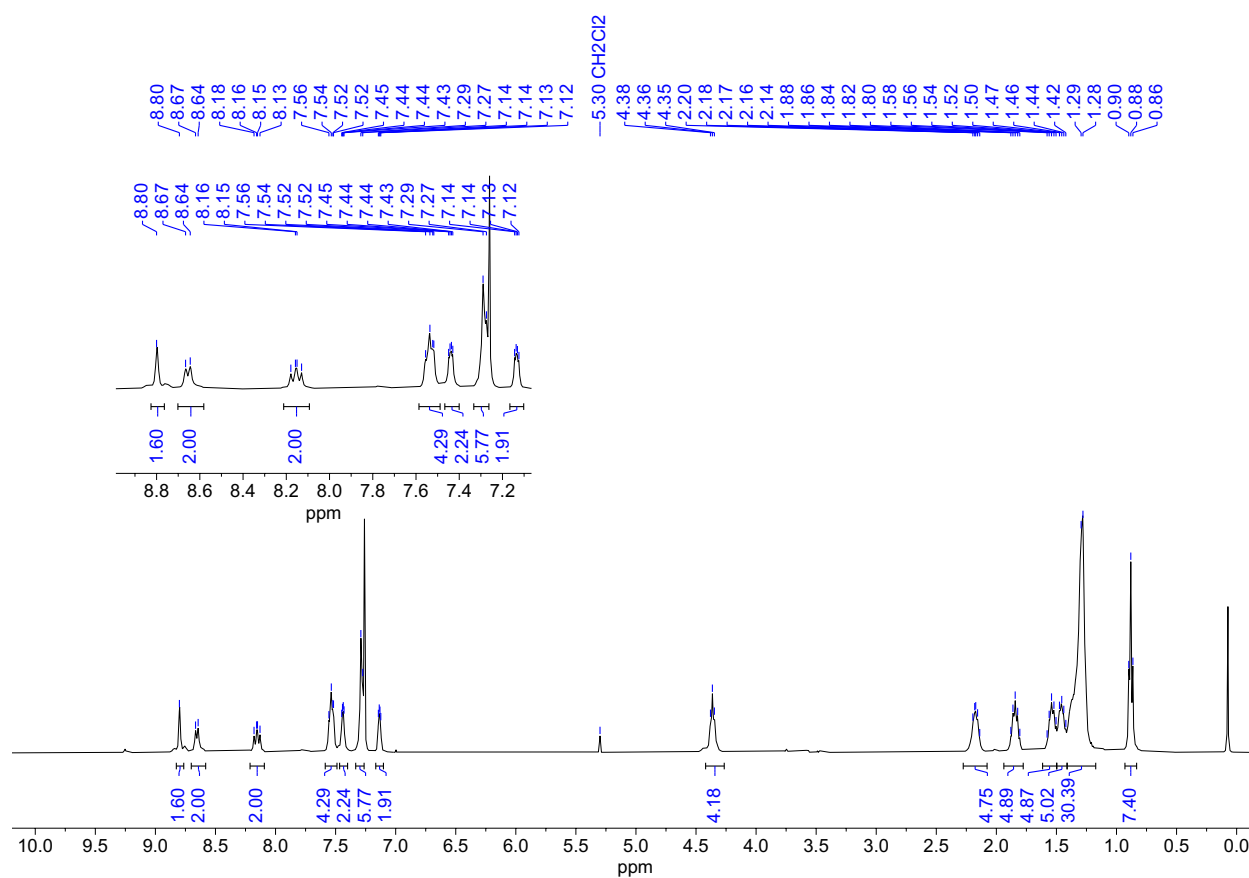


$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2-1** measured in CDCl_3 (162 MHz).

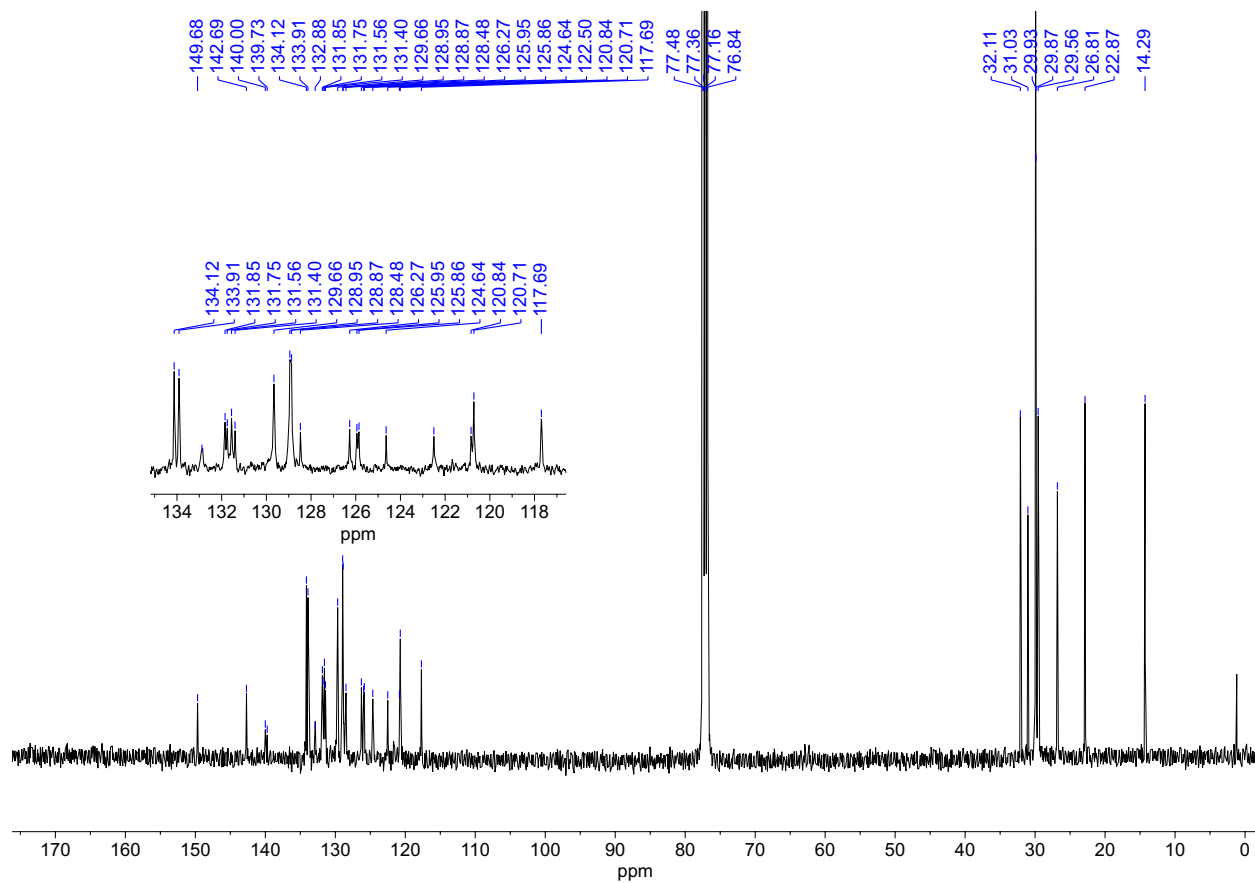




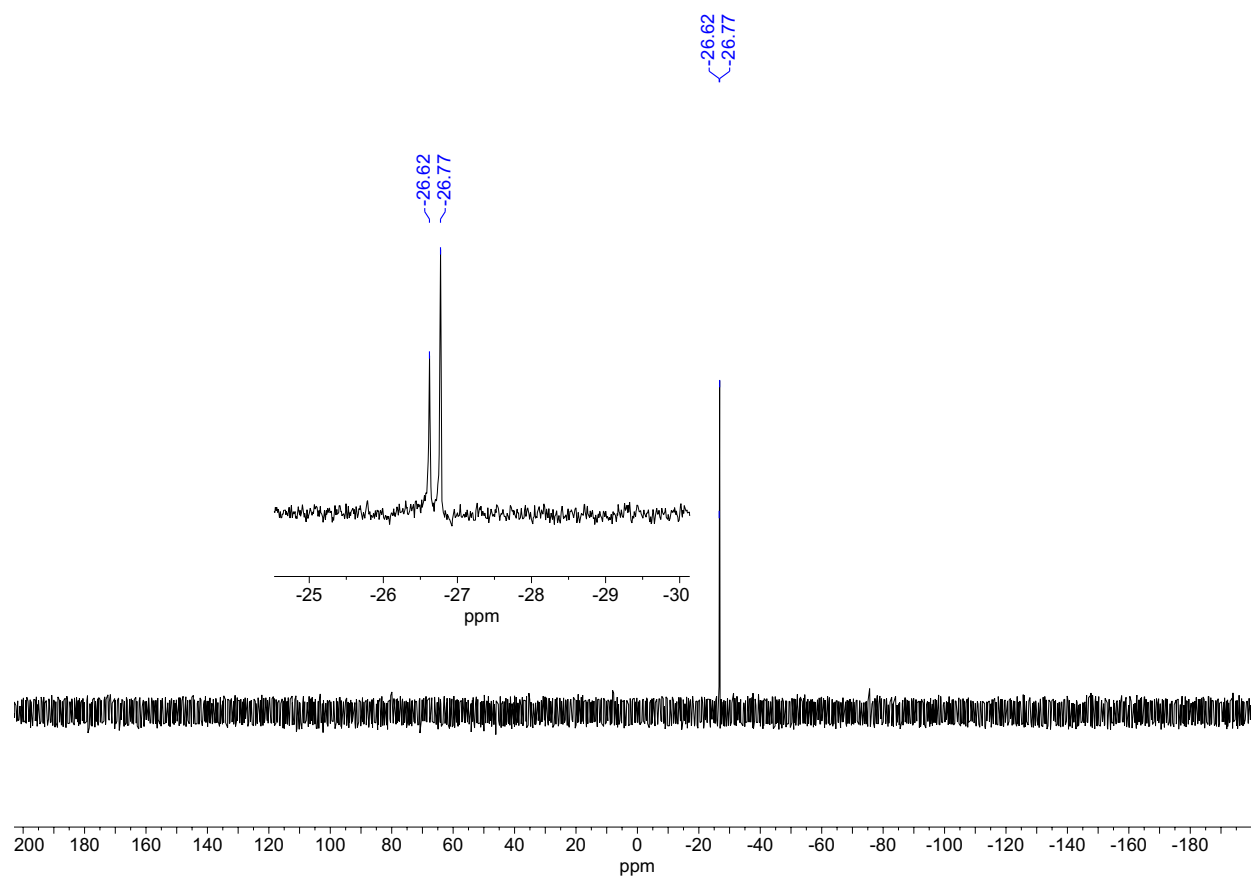
^1H NMR spectrum of **2-2** measured in CDCl_3 (400 MHz).

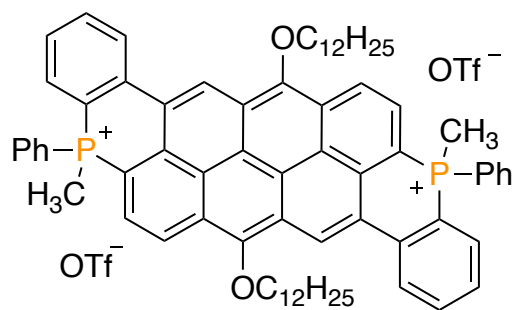


$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2-2** measured in CDCl_3 (101 MHz).

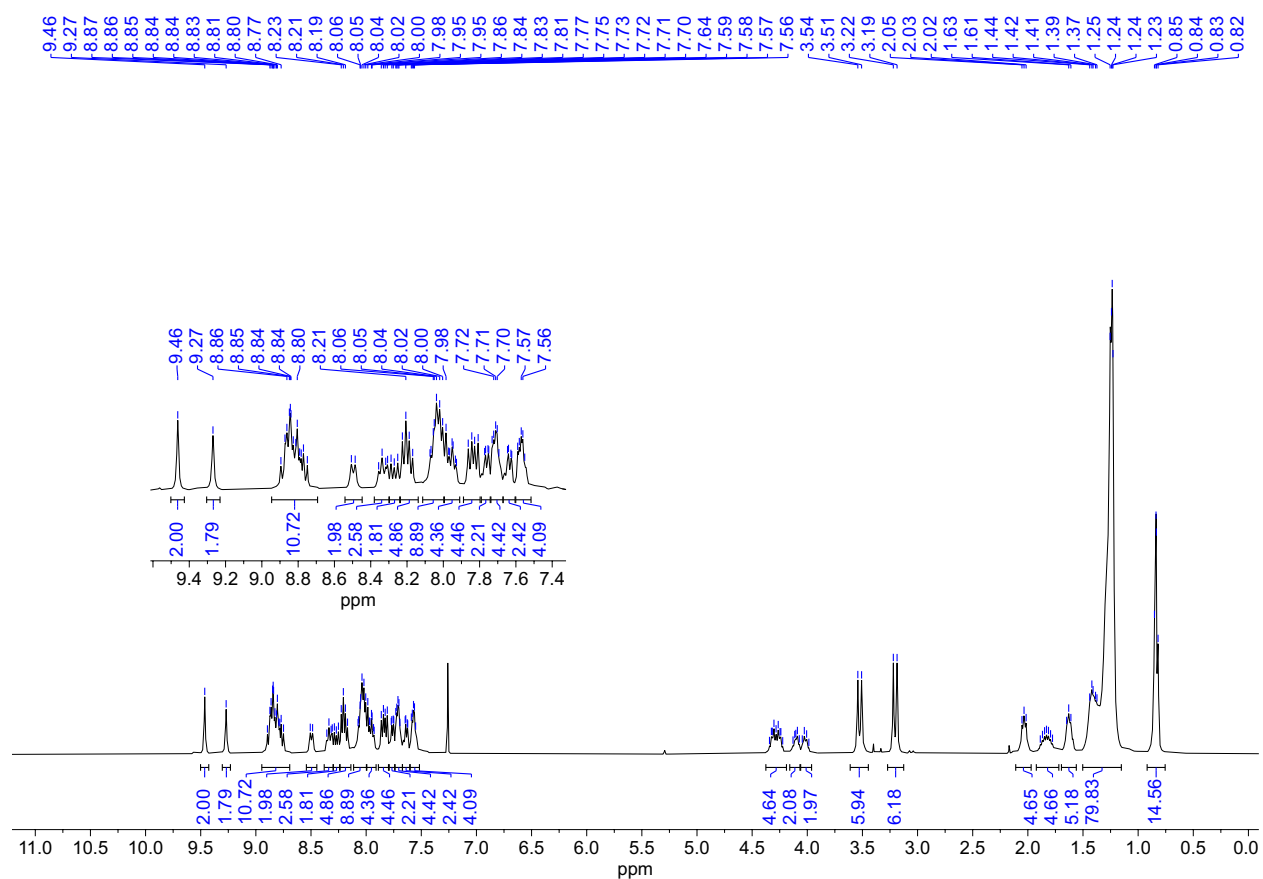


$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2-2** measured in CDCl_3 (162 MHz).

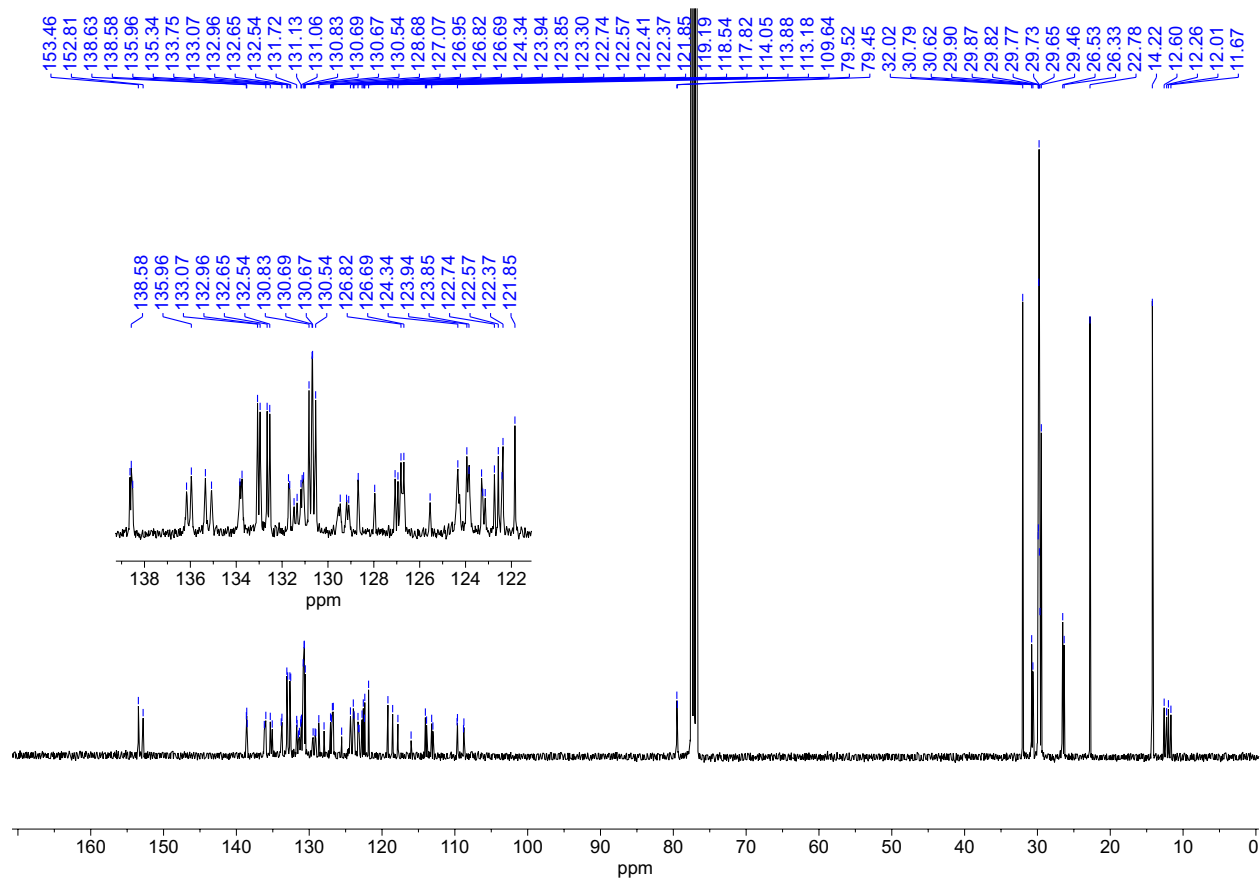




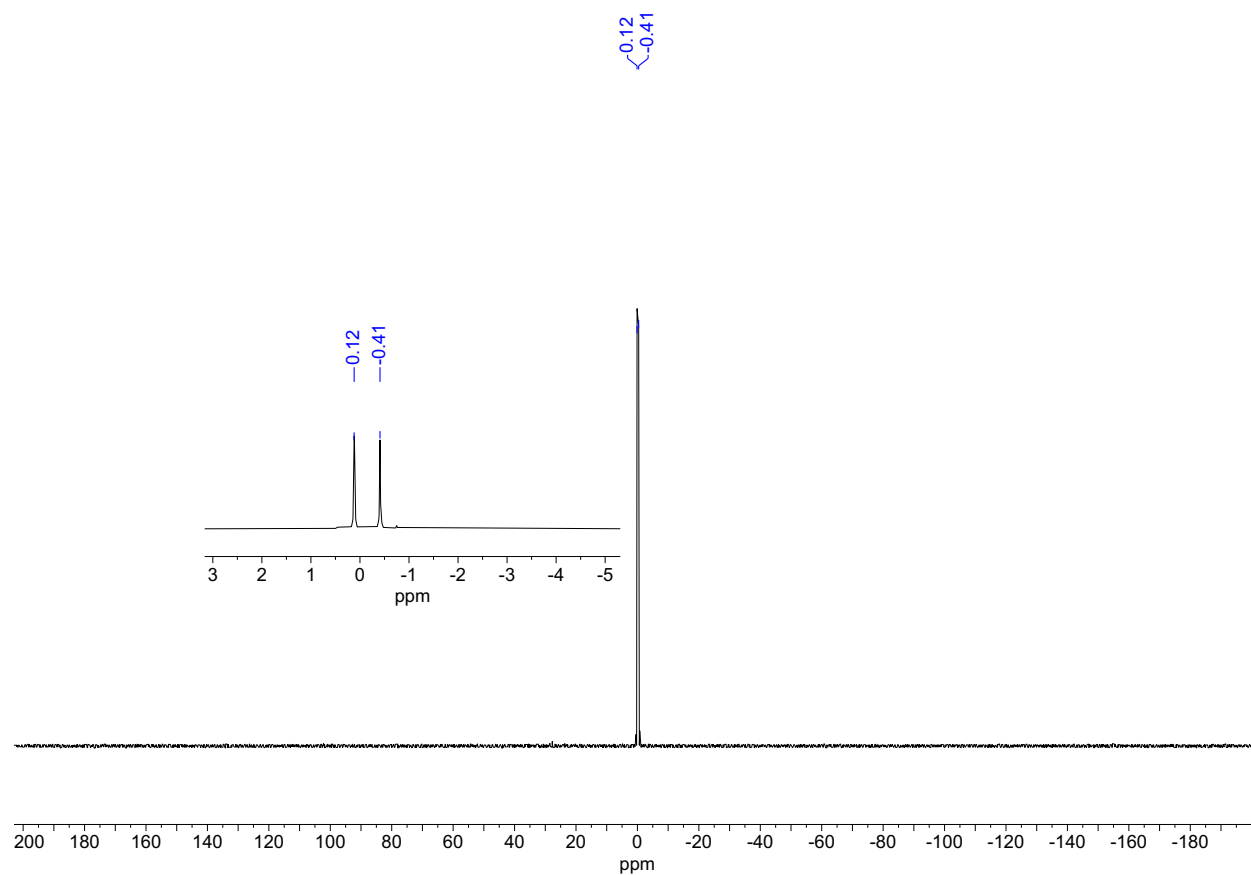
^1H NMR spectrum of **2-1-Me** measured in CDCl_3 (400 MHz).

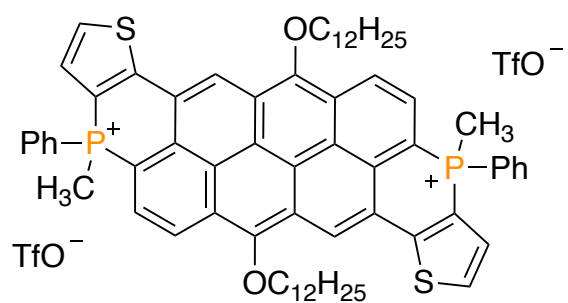


$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2-1-Me** measured in CDCl_3 (101 MHz).

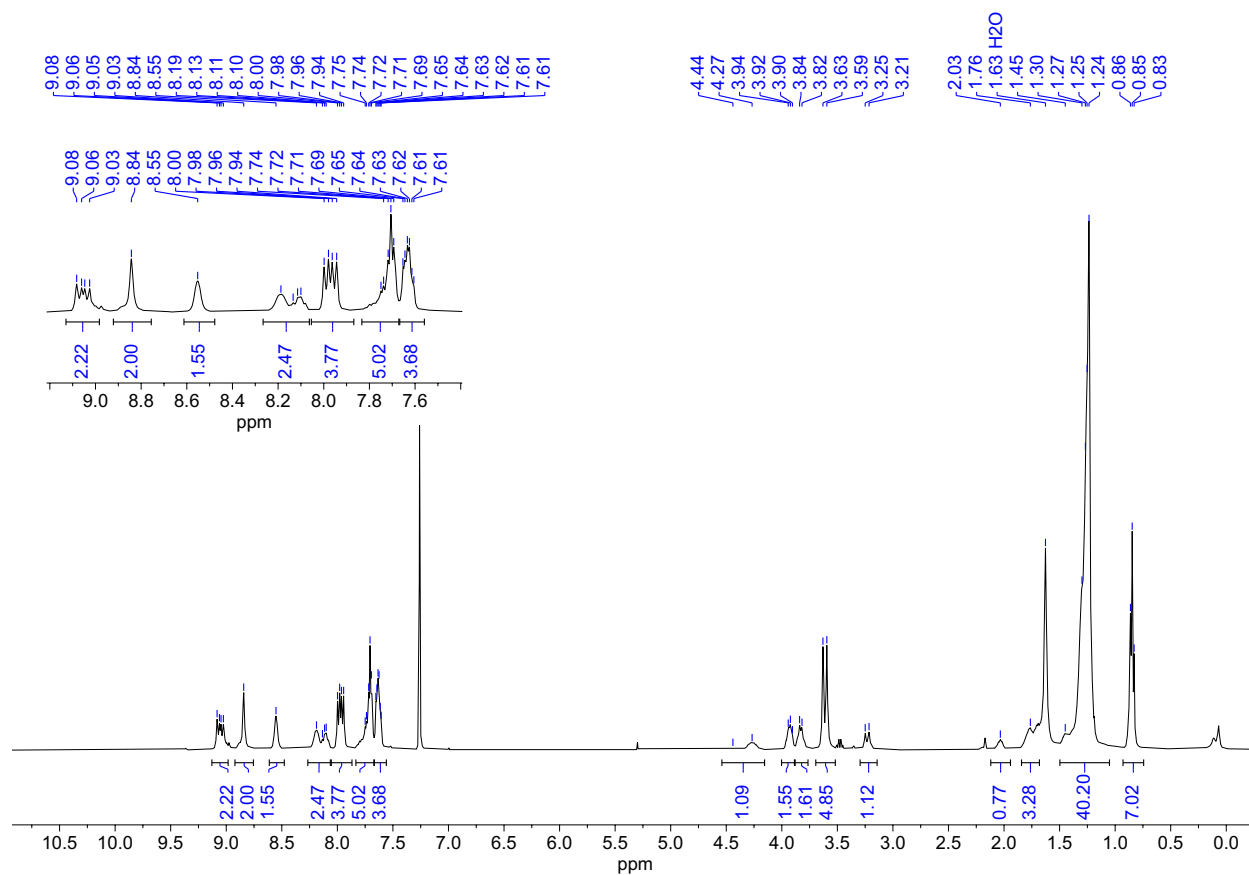


$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2-1-Me** measured in CDCl_3 (162 MHz).

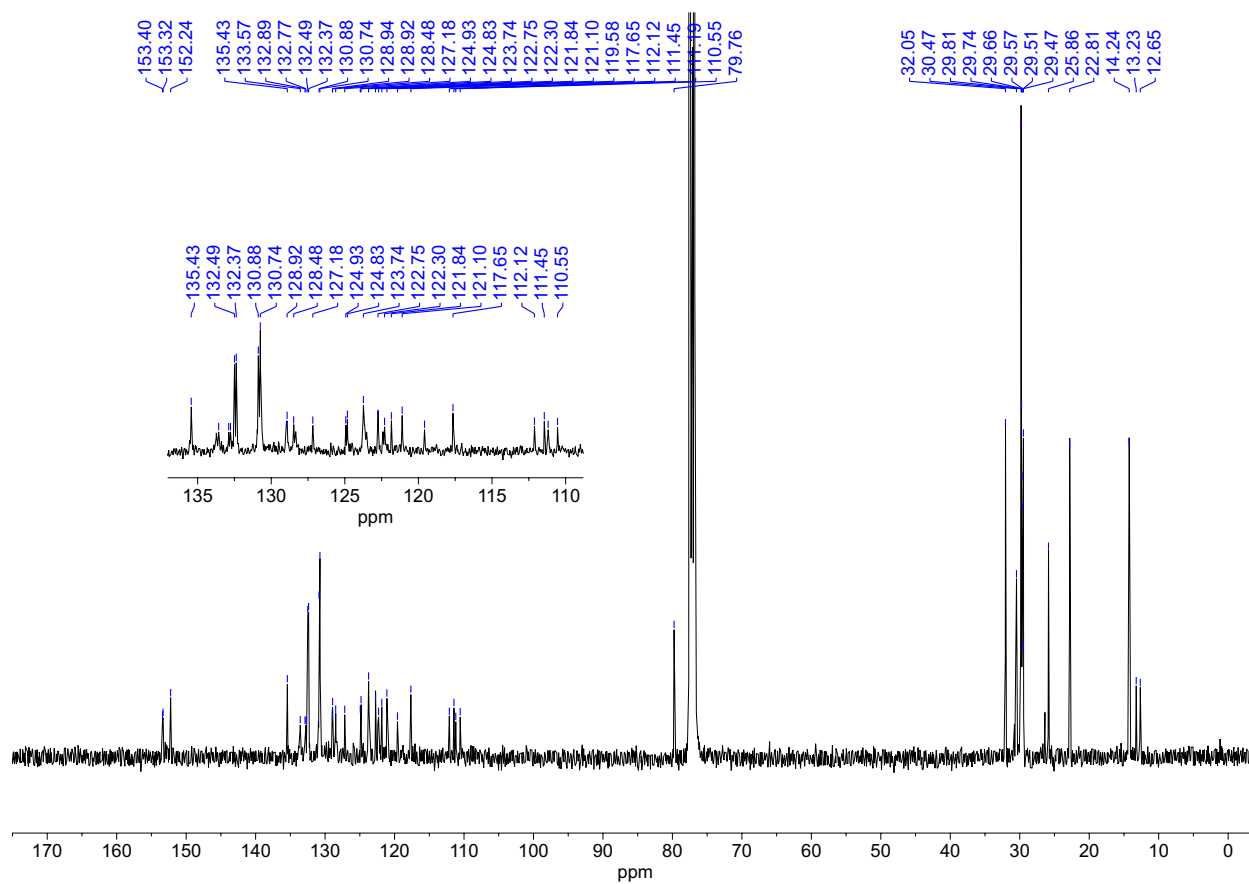




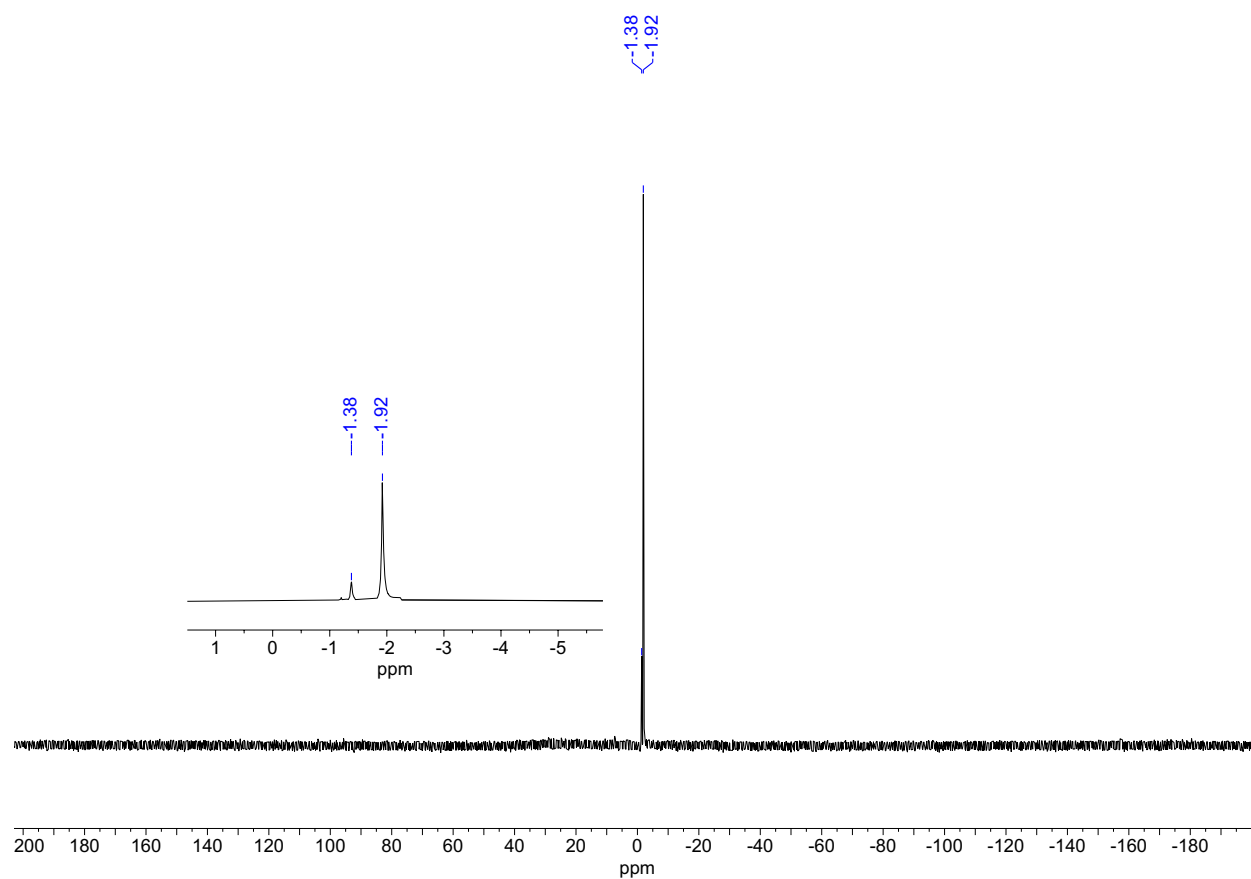
^1H NMR spectrum of **2-2-Me** measured in CDCl_3 (400 MHz).

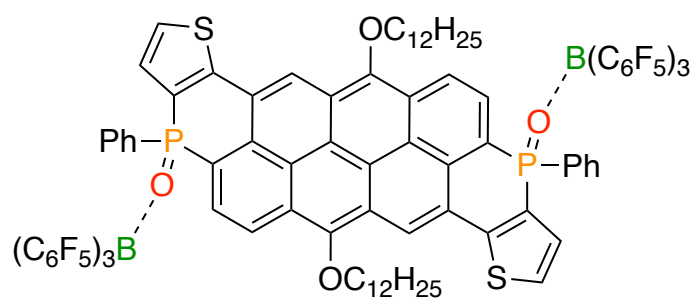


$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2-2-Me** measured in CDCl_3 (101 MHz).

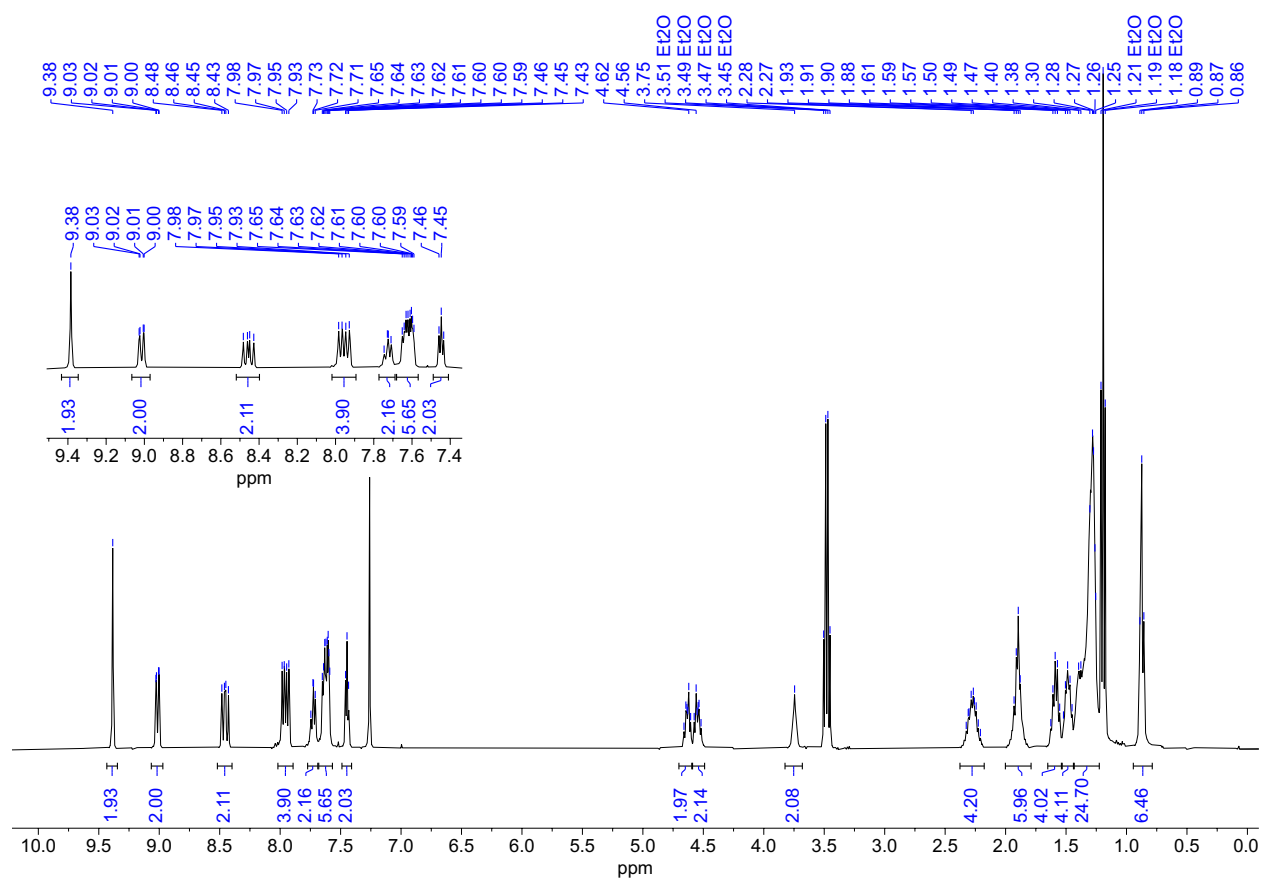


$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2-2-Me** measured in CDCl_3 (162 MHz).

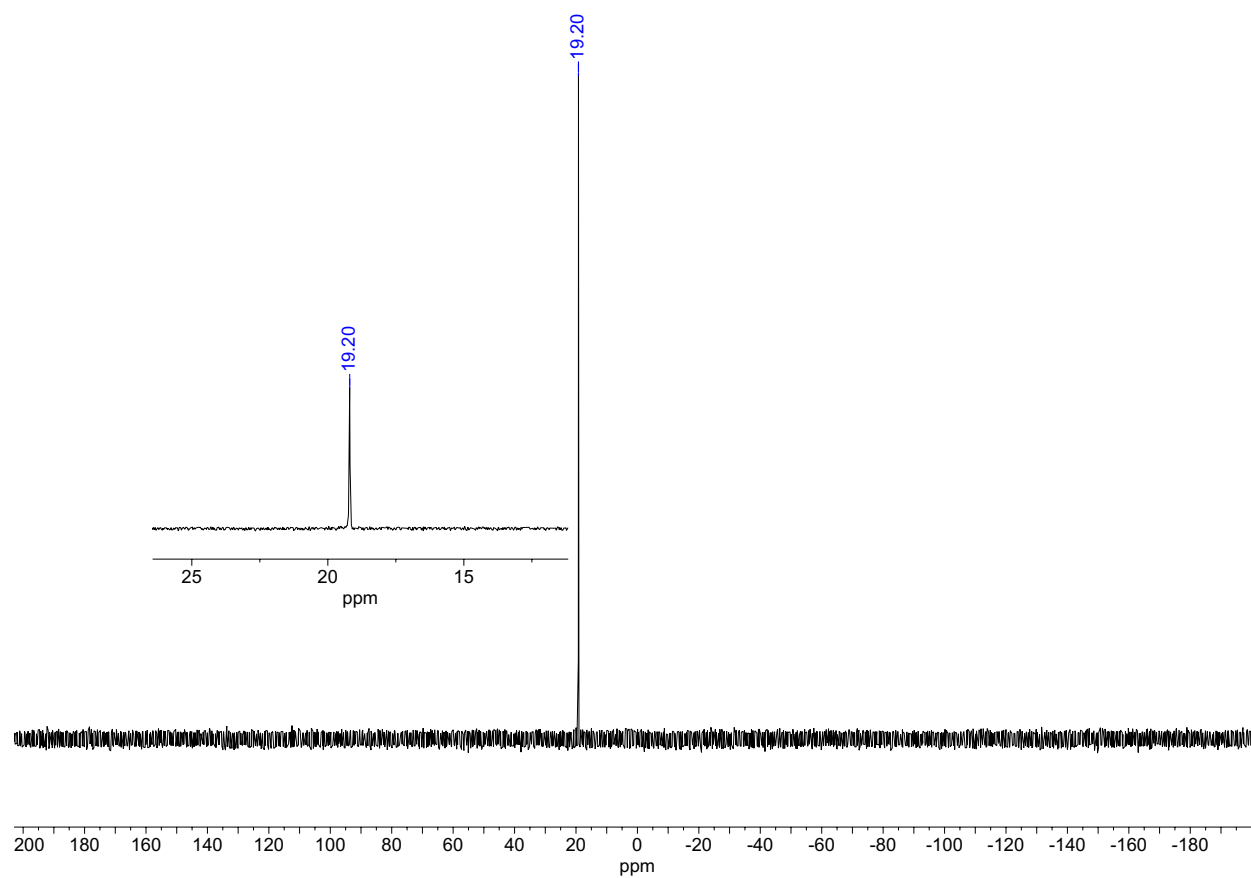




^1H NMR spectrum of **2-cis-2-O(BCF)₂** measured in CDCl_3 (400 MHz).



$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2-*cis*-2-O(BCF)₂** measured in CDCl_3 (162 MHz).



2.8. Coordinates (in Å) of optimized geometries of all 12 vat compounds and *cis*-2-O(BCF)₂

2-*trans*-1-O

C	-3.932480	0.889211	-0.675614
C	-2.837620	0.016246	-0.668045
C	-1.523909	0.589798	-0.532183
C	-1.365834	2.009157	-0.447798
C	-2.506513	2.839426	-0.490818
C	-3.753818	2.283995	-0.597439
C	-0.372357	-0.231601	-0.462902
C	-0.064543	2.557047	-0.308193
C	1.061308	1.746653	-0.223341
C	0.911404	0.331968	-0.304329
C	2.062985	-0.489353	-0.233752
C	3.376966	0.084669	-0.102370
C	3.503923	1.537165	0.016120
C	2.366272	2.289671	-0.046903
H	-2.387551	3.911498	-0.419015
H	-4.623946	2.928755	-0.620095
H	2.418659	3.361088	0.049381
C	1.904439	-1.908984	-0.313059
C	4.472222	-0.788040	-0.090552
C	3.045110	-2.739053	-0.262726
H	2.926017	-3.811568	-0.328046
C	4.292707	-2.183394	-0.158187
H	5.162565	-2.828372	-0.132247
C	0.603158	-2.456805	-0.456397
C	-0.522353	-1.646174	-0.545977
C	-2.964362	-1.435531	-0.795524
C	-1.826886	-2.188369	-0.730219
H	-1.878801	-3.259370	-0.830830
P	-5.639119	0.336602	-0.719453
C	-4.275355	-2.113333	-1.009159
C	-5.506721	-1.430575	-0.984867
C	-6.715664	-2.105426	-1.200931
C	-6.738772	-3.468035	-1.433391
P	6.179399	-0.232649	-0.071479
C	4.815386	2.216872	0.218037
C	6.047253	1.535646	0.184555
C	7.280573	3.576579	0.612921
C	7.257254	2.212942	0.386564
O	0.069451	3.915087	-0.185356
O	0.469348	-3.814981	-0.577910
C	0.361544	4.641066	-1.394401

H	-0.517063	4.678634	-2.042012
H	0.639280	5.646428	-1.084157
H	1.191076	4.178703	-1.932818
C	0.167406	-4.538823	0.630037
H	-0.107893	-5.544734	0.319314
H	1.040844	-4.575272	1.284662
H	-0.666470	-4.075639	1.161010
H	-7.642598	-1.544582	-1.193480
H	-7.676438	-3.981537	-1.603051
H	8.219054	4.092154	0.771240
H	8.184907	1.653469	0.372380
C	6.796555	-0.509453	-1.760602
C	6.216386	0.110107	-2.872586
C	7.848891	-1.408273	-1.942721
C	6.680480	-0.175726	-4.150176
H	5.400589	0.812690	-2.746663
C	8.309999	-1.696169	-3.224018
H	8.299883	-1.879172	-1.079411
C	7.722670	-1.086783	-4.328290
H	6.228037	0.306278	-5.007770
H	9.125792	-2.395948	-3.357410
H	8.079567	-1.316303	-5.324873
O	7.052418	-0.934315	0.920919
O	-6.495672	1.047050	-1.719411
C	-6.285536	0.599704	0.960862
C	-5.688201	0.015530	2.082571
C	-7.388467	1.439526	1.125259
C	-6.184131	0.279145	3.353366
H	-4.833250	-0.641141	1.969623
C	-7.883522	1.702438	2.399086
H	-7.852910	1.883724	0.254919
C	-7.278523	1.128045	3.512366
H	-5.717280	-0.174919	4.218605
H	-8.739702	2.354676	2.519784
H	-7.662169	1.338881	4.503304
C	4.872968	3.603883	0.462657
C	6.072249	4.269507	0.647025
H	3.968586	4.188459	0.526614
H	6.061580	5.335843	0.836335
C	-5.531203	-4.162695	-1.457675
C	-4.332792	-3.499572	-1.258762
H	-5.520270	-5.228371	-1.650808
H	-3.428945	-4.085715	-1.315027

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C	-4.07639	0.75923	-1.00964
C	-2.92536	0.00610	-0.74726
C	-1.66964	0.70731	-0.67671
C	-1.62104	2.11817	-0.90506
C	-2.81544	2.82135	-1.16768
C	-4.00713	2.15032	-1.21687
C	-0.46690	0.02442	-0.37451
C	-0.37561	2.79639	-0.84642
C	0.80017	2.12786	-0.52882
C	0.75760	0.72119	-0.29360
C	1.96371	0.03364	-0.01880
C	3.22107	0.73254	0.02725
C	3.23003	2.18753	-0.12931
C	2.04681	2.80929	-0.41193
H	-2.78389	3.89108	-1.31570
H	-4.91826	2.70050	-1.41787
H	2.01260	3.87625	-0.56025
C	1.91931	-1.38065	0.19055
C	4.38160	-0.02857	0.21024
C	3.12224	-2.09156	0.38695
H	3.09329	-3.16342	0.52097
C	4.31773	-1.42523	0.38162
H	5.23505	-1.98564	0.51510
C	0.66948	-2.05292	0.17084
C	-0.50946	-1.38038	-0.12920
C	-2.93905	-1.44222	-0.53601
C	-1.75926	-2.05838	-0.22781
H	-1.72848	-3.12051	-0.04897
P	-5.73085	0.06576	-1.03180
C	-4.17993	-2.25974	-0.65857
C	-5.45657	-1.69463	-0.84688
C	-6.59992	-2.49744	-0.94926
C	-6.51488	-3.87452	-0.86379
P	6.03064	0.66757	0.09514
C	4.46854	3.00422	0.01860
C	5.74996	2.43594	0.15673
C	6.79785	4.61763	0.28095
C	6.89081	3.23856	0.28469
O	-0.35219	4.14972	-1.06728
O	0.64314	-3.40671	0.39294
C	-0.28489	4.54499	-2.45205
H	-1.06986	4.06081	-3.03462
H	-0.42540	5.62373	-2.47256
H	0.69016	4.28512	-2.87194

C	0.60180	-3.80408	1.77813
H	0.65610	-4.89055	1.78866
H	1.44706	-3.38739	2.32885
H	-0.33108	-3.47167	2.24025
H	-7.56269	-2.02664	-1.10736
H	-7.40421	-4.48662	-0.93976
H	7.68535	5.22884	0.38208
H	7.86118	2.76751	0.38910
C	6.86945	0.19562	1.63814
C	7.98799	-0.63797	1.58779
C	6.37410	0.61003	2.87877
C	8.60278	-1.05756	2.76546
H	8.37162	-0.95921	0.62799
C	6.98868	0.19136	4.05154
H	5.50580	1.25621	2.93369
C	8.10221	-0.64541	3.99537
H	9.46824	-1.70717	2.72061
H	6.59803	0.51538	5.00833
H	8.57617	-0.97680	4.91131
O	6.78813	0.20834	-1.11300
O	-6.53940	0.44080	-2.23335
C	-6.51477	0.67165	0.49282
C	-6.08217	0.24559	1.75161
C	-7.52534	1.63050	0.40068
C	-6.65199	0.77739	2.90160
H	-5.30132	-0.50114	1.83951
C	-8.09308	2.16523	1.55444
H	-7.86274	1.95600	-0.57495
C	-7.65503	1.74021	2.80424
H	-6.31141	0.44086	3.87307
H	-8.87422	2.91139	1.47486
H	-8.09401	2.15711	3.70219
C	4.40526	4.41264	0.03543
C	5.53785	5.19999	0.15748
H	3.45492	4.91934	-0.03671
H	5.43496	6.27832	0.16502
C	-5.25963	-4.45456	-0.69051
C	-4.12439	-3.66733	-0.59771
H	-5.16242	-5.53188	-0.63201
H	-3.17898	-4.17496	-0.48303

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C	-3.830484	0.912218	-0.503612
C	-2.739011	0.039012	-0.577738
C	-1.415402	0.592055	-0.434739
C	-1.242922	1.987210	-0.173582
C	-2.381611	2.815074	-0.078024
C	-3.630530	2.286206	-0.262430
C	-0.263202	-0.225506	-0.547505
C	0.063772	2.513686	-0.022986
C	1.191896	1.712633	-0.138250
C	1.031754	0.321508	-0.406487
C	2.183991	-0.496014	-0.519234
C	3.507638	0.056866	-0.375315
C	3.645692	1.496086	-0.151714
C	2.508987	2.240912	-0.016991
H	-2.259715	3.867165	0.137945
H	-4.493351	2.940983	-0.212747
H	2.572582	3.293573	0.200056
C	2.011620	-1.890966	-0.781650
C	4.599142	-0.816284	-0.450485
C	3.150295	-2.718699	-0.878254
H	3.028371	-3.770564	-1.095335
C	4.399238	-2.190004	-0.693413
H	5.262067	-2.844731	-0.743576
C	0.704942	-2.417524	-0.931942
C	-0.423273	-1.616666	-0.815655
C	-2.876980	-1.400404	-0.799948
C	-1.740391	-2.145169	-0.935931
H	-1.804049	-3.197776	-1.153461
P	-5.556633	0.433258	-0.790726
C	-4.203216	-2.077926	-0.865935
C	-5.423669	-1.377825	-0.850388
C	-6.640478	-2.069512	-0.937362
C	-6.684543	-3.449850	-1.005209
P	6.324836	-0.337766	-0.161072
C	4.972054	2.173619	-0.084321
C	6.192399	1.473405	-0.100659
C	7.453791	3.545106	0.054367
C	7.409445	2.164793	-0.014242
O	0.208337	3.843914	0.295930
O	0.560257	-3.747634	-1.251466
C	0.363616	4.745625	-0.811226
H	-0.552762	4.798070	-1.403397
H	0.580146	5.721180	-0.379573
H	1.191204	4.436201	-1.453602

C	0.407058	-4.650011	-0.144498
H	0.191131	-5.625617	-0.576356
H	1.324008	-4.701792	0.446828
H	-0.420285	-4.341650	0.498691
H	-7.566606	-1.505328	-0.946791
H	-7.633872	-3.967279	-1.065909
H	8.403247	4.062349	0.114661
H	8.335520	1.600460	-0.005917
C	7.064833	-0.631451	-1.833669
C	6.500791	-0.111120	-3.003991
C	8.206925	-1.428925	-1.927012
C	7.063652	-0.393600	-4.241626
H	5.614497	0.509776	-2.950173
C	8.774361	-1.711523	-3.169045
H	8.653453	-1.835223	-1.026965
C	8.200253	-1.198199	-4.325858
H	6.615842	0.010632	-5.141549
H	9.659646	-2.332647	-3.229341
H	8.634545	-1.423904	-5.292243
C	-6.293976	0.728161	0.882794
C	-5.729526	0.207470	2.052752
C	-7.433857	1.528731	0.977167
C	-6.289663	0.492767	3.291010
H	-4.844664	-0.415389	1.998311
C	-7.998482	1.814257	2.219817
H	-7.880417	1.935596	0.077406
C	-7.423867	1.300534	3.376229
H	-5.841550	0.088280	4.190669
H	-8.881963	2.437854	2.280955
H	-7.856088	1.528335	4.343066
C	5.048195	3.581256	-0.017557
C	6.254559	4.255301	0.048704
H	4.149624	4.178039	-0.028671
H	6.259221	5.337427	0.099222
C	-5.485213	-4.159889	-0.998096
C	-4.279069	-3.485589	-0.931609
H	-5.489656	-5.242050	-1.047987
H	-3.380346	-4.082136	-0.919506

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C	-4.06286	0.75861	-0.94423
C	-2.90405	0.00511	-0.71704
C	-1.64492	0.70528	-0.65240
C	-1.59919	2.12369	-0.82904
C	-2.80125	2.83232	-1.03519
C	-3.98884	2.15688	-1.10068
C	-0.43127	0.01437	-0.40910
C	-0.35379	2.79889	-0.78979
C	0.83249	2.12469	-0.53384
C	0.79746	0.71011	-0.34407
C	2.01340	0.01665	-0.12263
C	3.27403	0.71549	-0.08044
C	3.27291	2.17551	-0.19448
C	2.08262	2.80293	-0.43210
H	-2.77611	3.90735	-1.14296
H	-4.90184	2.71400	-1.27770
H	2.04132	3.87385	-0.54526
C	1.97049	-1.40254	0.04565
C	4.44294	-0.04260	0.05969
C	3.18088	-2.11504	0.18713
H	3.15850	-3.19177	0.28070
C	4.37435	-1.44652	0.17197
H	5.29520	-2.01259	0.25529
C	0.72172	-2.07377	0.04180
C	-0.46722	-1.39836	-0.20591
C	-2.91176	-1.44768	-0.53157
C	-1.72199	-2.07191	-0.27822
H	-1.68546	-3.13727	-0.12124
P	-5.73891	0.07683	-1.09976
C	-4.16619	-2.25483	-0.59999
C	-5.44139	-1.68173	-0.77352
C	-6.58776	-2.48905	-0.80463
C	-6.51317	-3.86138	-0.65929
P	6.12407	0.63608	-0.02215
C	4.51461	2.98887	-0.04243
C	5.79461	2.41745	0.08575
C	6.83257	4.61030	0.23425
C	6.92887	3.23167	0.21292
O	-0.34107	4.16323	-0.96913
O	0.70591	-3.43632	0.23398
C	-0.31037	4.59481	-2.34175
H	-1.10511	4.11892	-2.91887
H	-0.46120	5.67275	-2.33268
H	0.65599	4.35672	-2.79422

C	0.73200	-3.85707	1.61050
H	0.86997	-4.93671	1.60372
H	1.55660	-3.38613	2.14859
H	-0.21099	-3.60494	2.10323
H	-7.55409	-2.02089	-0.95666
H	-7.41065	-4.46667	-0.67964
H	7.72051	5.22114	0.33746
H	7.90428	2.76451	0.29378
C	6.77041	0.20244	1.65644
C	7.90105	-0.61429	1.72756
C	6.14946	0.60733	2.84375
C	8.40115	-1.03130	2.95945
H	8.38975	-0.93301	0.81436
C	6.64843	0.19407	4.07218
H	5.27123	1.24130	2.80914
C	7.77304	-0.62929	4.13229
H	9.27584	-1.66899	3.00006
H	6.15926	0.51077	4.98554
H	8.15667	-0.95535	5.09156
C	-6.51112	0.69206	0.46753
C	-6.11854	0.24757	1.73401
C	-7.49083	1.68281	0.37266
C	-6.68826	0.79232	2.87825
H	-5.36306	-0.52334	1.83000
C	-8.05836	2.23548	1.52021
H	-7.81126	2.03022	-0.60304
C	-7.65629	1.79071	2.77396
H	-6.37211	0.44047	3.85311
H	-8.81268	3.00800	1.43085
H	-8.09452	2.21735	3.66783
C	4.44650	4.39837	-0.01257
C	5.57189	5.19314	0.11925
H	3.49368	4.90059	-0.08375
H	5.46427	6.27095	0.13521
C	-5.25758	-4.44709	-0.50863
C	-4.11841	-3.66121	-0.48569
H	-5.16462	-5.52213	-0.41239
H	-3.17266	-4.16910	-0.37555

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C	-3.917325	0.907495	-0.210578
C	-2.805883	0.017504	-0.427129
C	-1.486359	0.570919	-0.356708
C	-1.285828	1.973787	-0.047058
C	-2.438565	2.805013	0.172434
C	-3.686316	2.280248	0.084464
C	-0.341216	-0.244694	-0.581984
C	-0.002666	2.476636	0.034994
C	1.150201	1.674377	-0.188103
C	0.974785	0.296444	-0.504064
C	2.119987	-0.521389	-0.721257
C	3.440287	0.024693	-0.621646
C	3.588184	1.423303	-0.338323
C	2.442497	2.188733	-0.113177
H	-2.296338	3.847089	0.420467
H	-4.539006	2.930040	0.256119
H	2.533555	3.226088	0.161732
C	1.919578	-1.920239	-1.048371
C	4.553118	-0.868322	-0.821993
C	3.072975	-2.748155	-1.277946
H	2.930512	-3.782601	-1.555741
C	4.321855	-2.232130	-1.156062
H	5.175062	-2.881095	-1.327876
C	0.636374	-2.421909	-1.135532
C	-0.516194	-1.622824	-0.897459
C	-2.952751	-1.382703	-0.703511
C	-1.807279	-2.141777	-0.952600
H	-1.897221	-3.179527	-1.225596
P	-5.556397	0.395761	-0.375588
C	-4.264047	-2.052706	-0.717718
C	-5.499668	-1.365961	-0.618781
C	-6.723774	-2.054930	-0.654553
C	-6.769245	-3.428474	-0.773006
P	6.181225	-0.380424	-0.525893
C	4.902397	2.085990	-0.293590
C	6.134698	1.388778	-0.333389
C	7.412982	3.445389	-0.180362
C	7.362241	2.069539	-0.270569
O	0.191589	3.804228	0.398295
O	0.440856	-3.745941	-1.511973
C	0.306041	4.721739	-0.693407
H	-0.642888	4.814712	-1.229224
H	0.577595	5.686165	-0.263962
H	1.082970	4.405616	-1.394721

C	0.347117	-4.677667	-0.430280
H	0.075947	-5.638368	-0.868225
H	1.303644	-4.771200	0.091660
H	-0.422398	-4.375002	0.284889
H	-7.651762	-1.501588	-0.571608
H	-7.718162	-3.948552	-0.798460
H	8.364123	3.959965	-0.133591
H	8.287934	1.507307	-0.308946
C	7.297815	-0.787028	-1.910757
C	6.813972	-0.622738	-3.213805
C	8.634798	-1.146974	-1.719740
C	7.657482	-0.791598	-4.303737
H	5.776574	-0.354261	-3.371956
C	9.479533	-1.307406	-2.814035
H	9.031668	-1.297620	-0.725000
C	8.994503	-1.125297	-4.105194
H	7.271100	-0.657756	-5.306603
H	10.515724	-1.579113	-2.655948
H	9.653948	-1.248127	-4.955352
C	-6.559314	0.751308	1.111128
C	-5.930532	0.669628	2.357970
C	-7.935599	0.996099	1.055368
C	-6.665520	0.815495	3.527953
H	-4.863832	0.487980	2.410982
C	-8.671096	1.129010	2.229638
H	-8.445988	1.080999	0.105296
C	-8.039031	1.034586	3.465568
H	-6.166416	0.751179	4.486898
H	-9.737273	1.311913	2.176660
H	-8.613501	1.138079	4.377792
C	5.000464	3.496636	-0.224167
C	6.210702	4.158254	-0.166542
H	4.104712	4.097258	-0.231834
H	6.221850	5.240704	-0.117180
C	-5.563320	-4.131678	-0.844211
C	-4.356562	-3.462347	-0.815468
H	-5.568672	-5.212728	-0.918233
H	-3.458110	-4.057154	-0.856815
C	-6.435462	1.194367	-1.757475
H	-7.438865	0.789298	-1.889644
H	-6.500473	2.267947	-1.574604
H	-5.853721	1.014352	-2.661495
C	6.933223	-1.143243	0.951423
H	7.026360	-2.220194	0.805657
H	7.913037	-0.717946	1.169017
H	6.264593	-0.948181	1.789842

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C	-4.001629	0.752322	-0.408660
C	-2.835894	-0.018377	-0.291831
C	-1.590572	0.690802	-0.191561
C	-1.578253	2.119837	-0.143026
C	-2.794581	2.831601	-0.180780
C	-3.975587	2.157938	-0.336477
C	-0.361315	-0.007888	-0.152233
C	-0.339008	2.807078	-0.057940
C	0.867131	2.117434	-0.033623
C	0.860285	0.693542	-0.082429
C	2.092229	-0.001323	-0.075727
C	3.341060	0.712754	-0.036385
C	3.326785	2.175045	0.007918
C	2.114172	2.801877	0.022969
H	-2.791231	3.908104	-0.094696
H	-4.900356	2.716790	-0.397442
H	2.051868	3.875507	0.084764
C	2.077889	-1.430688	-0.121883
C	4.513342	-0.055130	-0.041199
C	3.296580	-2.140944	-0.144780
H	3.290175	-3.218990	-0.210338
C	4.482936	-1.462434	-0.096291
H	5.409314	-2.022862	-0.101255
C	0.836884	-2.120446	-0.164582
C	-0.370877	-1.432278	-0.194575
C	-2.829303	-1.479843	-0.274087
C	-1.620172	-2.114741	-0.248137
H	-1.567109	-3.191077	-0.271481
P	-5.556452	-0.013059	-0.801263
C	-4.080480	-2.287723	-0.234120
C	-5.367324	-1.732351	-0.390131
C	-6.527359	-2.511485	-0.311725
C	-6.443728	-3.873442	-0.091971
P	6.124208	0.689738	0.047762
C	4.569057	2.998039	0.036684
C	5.864086	2.445113	0.066455
C	6.913964	4.621399	0.091309
C	7.014393	3.244396	0.099242
O	-0.345799	4.167558	0.057251
O	0.840724	-3.482767	-0.251743
C	-0.440994	4.926364	-1.166166
H	-1.233963	4.539035	-1.807355
H	-0.670875	5.947131	-0.869015
H	0.508695	4.895950	-1.704377

C	0.985941	-4.214621	0.983773
H	1.225010	-5.237586	0.701822
H	1.790231	-3.800105	1.592936
H	0.051731	-4.188897	1.548944
H	-7.498364	-2.045133	-0.423706
H	-7.340879	-4.474631	-0.029772
H	7.803395	5.236503	0.113382
H	7.992643	2.780844	0.134989
C	6.963954	0.156028	1.551273
C	8.044433	-0.728931	1.515148
C	6.470076	0.611746	2.779429
C	8.626620	-1.157383	2.704045
H	8.439446	-1.088286	0.574971
C	7.055874	0.178953	3.959533
H	5.635651	1.301698	2.817771
C	8.131719	-0.706033	3.922000
H	9.464600	-1.841844	2.674512
H	6.673109	0.533455	4.907838
H	8.584664	-1.043524	4.845681
C	-6.891180	0.782637	0.105777
C	-6.733545	1.026074	1.476309
C	-8.063223	1.180959	-0.543782
C	-7.736958	1.671646	2.183580
H	-5.827289	0.725344	1.987497
C	-9.065893	1.823172	0.174409
H	-8.203936	1.000359	-1.601022
C	-8.903646	2.069285	1.532811
H	-7.606172	1.871090	3.239496
H	-9.969813	2.135603	-0.332291
H	-9.684139	2.575329	2.086891
C	4.507849	4.405890	0.030764
C	5.645357	5.195321	0.054894
H	3.557100	4.913854	-0.000175
H	5.538939	6.272918	0.045422
C	-5.184290	-4.449079	0.057252
C	-4.036906	-3.675198	-0.001576
H	-5.094477	-5.512527	0.240181
H	-3.093110	-4.173303	0.156311
C	7.097212	0.207827	-1.391901
H	7.192928	-0.876777	-1.443075
H	6.574215	0.565256	-2.278259
H	8.087623	0.658811	-1.343018
C	-5.859575	0.141781	-2.572329
H	-6.776297	-0.378169	-2.849750
H	-5.926945	1.193142	-2.852232
H	-5.018997	-0.320540	-3.089220

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C	-3.969847	1.140785	-0.646081
C	-2.897233	0.242203	-0.726830
C	-1.561598	0.760401	-0.652773
C	-1.350920	2.171789	-0.561268
C	-2.464812	3.038261	-0.536853
C	-3.736665	2.527375	-0.567912
C	-0.440933	-0.109030	-0.650307
C	-0.025895	2.670310	-0.477704
C	1.069272	1.816399	-0.431466
C	0.865860	0.405186	-0.523647
C	1.985201	-0.465096	-0.488048
C	3.318169	0.049089	-0.349204
C	3.491486	1.493816	-0.238112
C	2.396874	2.306964	-0.281637
H	-2.305696	4.105388	-0.468230
H	-4.582437	3.202912	-0.530804
H	2.518352	3.376691	-0.179817
C	1.774561	-1.875128	-0.591029
C	4.388084	-0.855335	-0.319710
C	2.886760	-2.743896	-0.569407
H	2.731034	-3.809021	-0.669177
C	4.154277	-2.239797	-0.431788
H	4.995364	-2.922335	-0.406605
C	0.451750	-2.371787	-0.717241
C	-0.644885	-1.519221	-0.756193
C	-3.071367	-1.197468	-0.895424
C	-1.974144	-2.008744	-0.905612
H	-2.095939	-3.074886	-1.040266
P	-5.704142	0.643542	-0.606750
C	-4.405732	-1.758390	-1.072279
C	-5.613850	-1.101787	-0.964711
C	-6.742057	-1.945998	-1.180599
C	-6.384921	-3.228187	-1.461951
S	-4.677675	-3.430523	-1.471835
P	6.119643	-0.380254	-0.114436
C	4.821449	2.065757	-0.072534
C	6.024377	1.396123	0.004249
C	6.790793	3.573509	0.200493
C	7.147248	2.260781	0.164034
S	5.090699	3.780644	0.050637
O	0.168175	4.021344	-0.367437
O	0.261582	-3.720159	-0.857841
C	0.431332	4.727053	-1.595842
H	-0.472023	4.785292	-2.206707

H	0.751814	5.726339	-1.308459
H	1.222843	4.233414	-2.162907
C	-0.006944	-4.455899	0.351266
H	-0.316947	-5.450529	0.037435
H	0.891118	-4.521837	0.969019
H	-0.807270	-3.981468	0.922069
H	-7.767832	-1.608451	-1.134405
H	-7.025736	-4.069266	-1.674411
H	7.428257	4.436283	0.312382
H	8.168431	1.916169	0.246670
C	6.941020	-0.739382	-1.697125
C	6.429587	-0.240229	-2.899061
C	8.098603	-1.519837	-1.710627
C	7.065159	-0.526337	-4.100094
H	5.533116	0.368472	-2.902369
C	8.736544	-1.802203	-2.916293
H	8.494709	-1.903422	-0.779328
C	8.218837	-1.308693	-4.108658
H	6.661226	-0.140753	-5.027989
H	9.634869	-2.406875	-2.922176
H	8.711437	-1.534560	-5.046521
O	6.808709	-1.064538	1.023853
O	-6.596713	1.418168	-1.524035
C	-6.260514	0.794923	1.119441
C	-5.387510	0.664747	2.203272
C	-7.620199	1.018634	1.356801
C	-5.867545	0.765137	3.504605
H	-4.331022	0.491790	2.038412
C	-8.099183	1.105673	2.659370
H	-8.299124	1.133735	0.521478
C	-7.222703	0.983874	3.733585
H	-5.183776	0.672907	4.339215
H	-9.154017	1.278242	2.834965
H	-7.595655	1.061151	4.747630

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C	-4.191320	1.031072	-0.453401
C	-3.117921	0.135800	-0.540410
C	-1.782747	0.659338	-0.493031
C	-1.575293	2.068463	-0.371279
C	-2.691279	2.929879	-0.300947
C	-3.960847	2.416125	-0.342720
C	-0.658272	-0.201617	-0.562747
C	-0.251304	2.572290	-0.314912
C	0.850705	1.727397	-0.362630
C	0.650236	0.319688	-0.498763
C	1.774717	-0.540769	-0.573390
C	3.110083	-0.018247	-0.516891
C	3.282858	1.421424	-0.351537
C	2.181964	2.223690	-0.276370
H	-2.535154	3.994874	-0.200745
H	-4.806998	3.090552	-0.288091
H	2.303563	3.288601	-0.133881
C	1.567029	-1.948503	-0.708666
C	4.183539	-0.912180	-0.616745
C	2.682589	-2.807641	-0.803165
H	2.526055	-3.870631	-0.922019
C	3.952056	-2.293995	-0.760317
H	4.796978	-2.967134	-0.843906
C	0.243199	-2.453552	-0.754467
C	-0.858868	-1.609709	-0.695028
C	-3.290908	-1.305792	-0.688622
C	-2.190167	-2.107719	-0.766774
H	-2.312435	-3.173605	-0.901020
P	-5.928315	0.544084	-0.499974
C	-4.626092	-1.886122	-0.756538
C	-5.834197	-1.228288	-0.657423
C	-6.963950	-2.094422	-0.745448
C	-6.607550	-3.396953	-0.910708
S	-4.899481	-3.592256	-0.966315
P	5.920513	-0.417997	-0.620607
C	4.618339	2.000340	-0.270516
C	5.827105	1.342310	-0.360921
C	6.598971	3.510373	-0.098943
C	6.956243	2.208203	-0.265222
S	4.890745	3.706001	-0.055429
O	-0.063446	3.917438	-0.145723
O	0.054701	-3.798171	-0.927506
C	0.168153	4.687780	-1.340593
H	-0.749413	4.773477	-1.926411

H	0.490572	5.672192	-1.007560
H	0.948175	4.230102	-1.951551
C	-0.164038	-4.574587	0.265529
H	-0.490196	-5.557274	-0.069071
H	0.759595	-4.663802	0.841277
H	-0.937523	-4.120359	0.887385
H	-7.989536	-1.757478	-0.689812
H	-7.248981	-4.258182	-1.011263
H	7.239818	4.371432	0.006479
H	7.982078	1.872056	-0.321454
C	6.641683	-1.139430	0.884897
C	6.174583	-0.760903	2.147551
C	7.648710	-2.100239	0.783766
C	6.710511	-1.336228	3.292152
H	5.392967	-0.015770	2.241083
C	8.183779	-2.678208	1.933249
H	8.011935	-2.392047	-0.193202
C	7.714657	-2.297233	3.185910
H	6.344041	-1.034604	4.265768
H	8.964749	-3.423830	1.848342
H	8.130502	-2.746035	4.079605
O	6.666760	-0.836284	-1.848335
O	-6.719630	1.232471	-1.566011
C	-6.614986	0.907644	1.142037
C	-6.030881	0.401727	2.307368
C	-7.746662	1.720611	1.232107
C	-6.570068	0.715318	3.548330
H	-5.153848	-0.232368	2.249951
C	-8.286721	2.031113	2.476817
H	-8.197065	2.107121	0.327376
C	-7.696676	1.532185	3.633267
H	-6.112872	0.324220	4.448629
H	-9.165018	2.661407	2.540936
H	-8.114356	1.779501	4.601558

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C	-4.331647	0.886495	-0.337134
C	-3.254407	0.004486	-0.498536
C	-1.917144	0.530179	-0.496737
C	-1.702249	1.929744	-0.304817
C	-2.818055	2.778835	-0.139598
C	-4.087429	2.265300	-0.174432
C	-0.795332	-0.321207	-0.680259
C	-0.379459	2.434478	-0.289446
C	0.719308	1.605075	-0.467224
C	0.514881	0.204751	-0.670196
C	1.636689	-0.646661	-0.853629
C	2.973973	-0.120981	-0.851692
C	3.143601	1.317179	-0.675742
C	2.050924	2.108007	-0.471596
H	-2.661690	3.837477	0.014880
H	-4.930060	2.938340	-0.061993
H	2.182073	3.167842	-0.304593
C	1.421890	-2.046229	-1.045573
C	4.051327	-1.002916	-1.013048
C	2.537768	-2.895253	-1.210758
H	2.381458	-3.953886	-1.365355
C	3.807148	-2.381686	-1.175854
H	4.649744	-3.054776	-1.288310
C	0.099079	-2.550962	-1.060917
C	-0.999691	-1.721549	-0.883171
C	-3.424058	-1.433721	-0.674396
C	-2.331357	-2.224509	-0.878696
H	-2.462531	-3.284320	-1.045834
P	-6.096753	0.418550	-0.409851
C	-4.751592	-2.025589	-0.599299
C	-5.951431	-1.379253	-0.404786
C	-7.064918	-2.271378	-0.343435
C	-6.702232	-3.576397	-0.481193
S	-5.006266	-3.748813	-0.703221
P	5.816491	-0.534755	-0.940254
C	4.471081	1.909085	-0.750668
C	5.671029	1.262969	-0.945298
C	6.421331	3.460255	-0.868639
C	6.784312	2.155332	-1.006560
S	4.725396	3.632281	-0.646151
O	-0.181623	3.770279	-0.032416
O	-0.098815	-3.886745	-1.317987
C	-0.044434	4.625769	-1.179142
H	-0.998197	4.730667	-1.701412

H	0.276764	5.594004	-0.799124
H	0.705498	4.236186	-1.870732
C	-0.236011	-4.742321	-0.171335
H	-0.556909	-5.710609	-0.551475
H	0.717676	-4.847017	0.351114
H	-0.986176	-4.352974	0.520137
H	-8.087269	-1.949346	-0.199132
H	-7.335037	-4.449850	-0.471431
H	7.053963	4.333830	-0.878384
H	7.806729	1.833556	-1.150960
C	6.401251	-0.938193	-2.647137
C	5.816977	-0.405977	-3.802279
C	7.458432	-1.841507	-2.772887
C	6.280871	-0.779752	-5.057026
H	4.995928	0.297037	-3.722391
C	7.923378	-2.218201	-4.031077
H	7.919058	-2.254795	-1.883424
C	7.332149	-1.689393	-5.172813
H	5.821424	-0.365277	-5.946301
H	8.742717	-2.921594	-4.116485
H	7.689720	-1.983819	-6.152178
C	-6.681627	0.821804	1.297070
C	-6.097424	0.289481	2.452196
C	-7.738969	1.724923	1.422854
C	-6.561511	0.662940	3.706973
H	-5.276222	-0.413354	2.372264
C	-8.204099	2.101292	2.681070
H	-8.199541	2.138323	0.533411
C	-7.612978	1.572378	3.822816
H	-6.102127	0.248345	4.596224
H	-9.023584	2.804513	2.766483
H	-7.970758	1.866579	4.802166

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C	-4.279073	0.881021	-0.493050
C	-3.192614	-0.004967	-0.516185
C	-1.858066	0.526969	-0.472222
C	-1.656770	1.938913	-0.378904
C	-2.782425	2.790661	-0.333793
C	-4.046858	2.269275	-0.408629
C	-0.724868	-0.327729	-0.525767
C	-0.337665	2.452340	-0.339831
C	0.772893	1.620350	-0.396485
C	0.582137	0.206815	-0.498877
C	1.714715	-0.646543	-0.579674
C	3.048911	-0.111654	-0.584104
C	3.208343	1.332807	-0.444602
C	2.102907	2.128426	-0.352727
H	-2.636543	3.858732	-0.247605
H	-4.895378	2.944401	-0.398668
H	2.221155	3.196329	-0.231059
C	1.512998	-2.059168	-0.662863
C	4.132296	-0.992636	-0.710717
C	2.636346	-2.908652	-0.762382
H	2.488290	-3.977418	-0.834946
C	3.898937	-2.380118	-0.800777
H	4.745227	-3.049658	-0.906207
C	0.194801	-2.575077	-0.662922
C	-0.915206	-1.742470	-0.612567
C	-3.350081	-1.454546	-0.588878
C	-2.244105	-2.252219	-0.645568
H	-2.362088	-3.323677	-0.730118
P	-6.034745	0.408304	-0.665496
C	-4.681332	-2.043498	-0.586545
C	-5.890520	-1.387407	-0.566203
C	-7.010242	-2.272725	-0.556204
C	-6.645075	-3.584127	-0.555417
S	-4.935465	-3.770004	-0.582523
P	5.885360	-0.498915	-0.871531
C	4.542208	1.916181	-0.391952
C	5.749351	1.265324	-0.517736
C	6.511303	3.442400	-0.244573
C	6.871141	2.144925	-0.442822
S	4.803435	3.626028	-0.159746
O	-0.159741	3.806012	-0.185171
O	0.015719	-3.931885	-0.789415
C	0.045715	4.562929	-1.390049
H	-0.880919	4.634460	-1.964211

H	0.364155	5.555327	-1.075767
H	0.820544	4.106787	-2.009213
C	-0.174196	-4.663218	0.433891
H	-0.496175	-5.662224	0.145267
H	0.759682	-4.722034	0.997800
H	-0.941310	-4.194104	1.053358
H	-8.039608	-1.940887	-0.547503
H	-7.280946	-4.455319	-0.544469
H	7.150520	4.305206	-0.142615
H	7.898230	1.818452	-0.534526
C	6.613830	-1.185141	0.686072
C	6.199999	-0.768489	1.955461
C	7.591387	-2.176611	0.583802
C	6.751012	-1.337604	3.096455
H	5.443734	0.001264	2.054405
C	8.142774	-2.751714	1.728714
H	7.924241	-2.505156	-0.394171
C	7.722256	-2.332316	2.985129
H	6.420286	-1.006046	4.073619
H	8.898045	-3.522696	1.635358
H	8.148670	-2.775944	3.876469
C	-6.734521	0.852522	0.988435
C	-6.155330	0.438288	2.192767
C	-7.887486	1.639562	1.024505
C	-6.718702	0.809900	3.406465
H	-5.260958	-0.173277	2.183080
C	-8.454929	2.011020	2.242115
H	-8.343729	1.965701	0.097117
C	-7.868931	1.598614	3.432833
H	-6.261997	0.484932	4.333598
H	-9.349303	2.621754	2.257226
H	-8.304771	1.890056	4.380722

2-trans-2-Me

C	-4.381921	0.802115	-0.144956
C	-3.258952	-0.071716	-0.349567
C	-1.950521	0.499687	-0.413971
C	-1.767711	1.929018	-0.263552
C	-2.926167	2.754388	-0.050628
C	-4.164696	2.200917	0.003157
C	-0.805268	-0.324000	-0.622337
C	-0.494077	2.460240	-0.318359
C	0.659193	1.657722	-0.531219
C	0.498166	0.244742	-0.686022
C	1.643492	-0.578898	-0.894361
C	2.951978	-0.007499	-0.958246
C	3.074795	1.414190	-0.819088
C	1.941468	2.197606	-0.600211
H	-2.794795	3.819152	0.081078
H	-5.017703	2.850653	0.173207
H	2.052545	3.264798	-0.464692
C	1.460742	-2.008189	-1.045097
C	4.075103	-0.881238	-1.162342
C	2.619299	-2.833424	-1.258116
H	2.487987	-3.898147	-1.390228
C	3.857886	-2.279976	-1.311170
H	4.710945	-2.929712	-1.480974
C	0.187065	-2.539433	-0.990428
C	-0.966230	-1.736989	-0.777153
C	-3.381796	-1.493435	-0.488406
C	-2.248511	-2.276851	-0.707768
H	-2.359647	-3.344067	-0.843067
P	-6.025901	0.242838	-0.095293
C	-4.674289	-2.119135	-0.372906
C	-5.908621	-1.511080	-0.172378
C	-6.997101	-2.433117	-0.068389
C	-6.598137	-3.725290	-0.194016
S	-4.893202	-3.849088	-0.438702
P	5.719206	-0.321993	-1.209784
C	4.367338	2.039916	-0.933638
C	5.601856	1.431917	-1.133122
C	6.291280	3.646136	-1.110693
C	6.690396	2.353995	-1.236192
S	4.586085	3.769868	-0.867844
O	-0.306551	3.816861	-0.091554
O	-0.000491	-3.896013	-1.217521
C	-0.273154	4.639642	-1.263211
H	-1.262872	4.705474	-1.723738

H	0.044539	5.630409	-0.938261
H	0.438102	4.252486	-1.997439
C	-0.033959	-4.719087	-0.046062
H	-0.351940	-5.709695	-0.371216
H	0.955790	-4.785298	0.414347
H	-0.745039	-4.331926	0.688333
H	-8.024324	-2.140543	0.101725
H	-7.201372	-4.618221	-0.154096
H	6.894526	4.539091	-1.149883
H	7.717790	2.061448	-1.405292
C	6.584481	-0.841003	-2.730275
C	6.017048	-0.472031	-3.955364
C	7.753721	-1.605828	-2.720071
C	6.612887	-0.857479	-5.147904
H	5.104165	0.111271	-3.975778
C	8.346736	-1.995224	-3.918202
H	8.209794	-1.907764	-1.787496
C	7.777565	-1.622830	-5.130327
H	6.166540	-0.565218	-6.090172
H	9.250790	-2.590739	-3.900759
H	8.237761	-1.930170	-6.061234
C	-6.888830	0.761689	1.426610
C	-6.320308	0.391143	2.650736
C	-8.057026	1.528112	1.418401
C	-6.914144	0.776540	3.844272
H	-5.408163	-0.193364	2.669581
C	-8.648011	1.917483	2.617537
H	-8.513785	1.831373	0.486596
C	-8.077807	1.543458	3.828677
H	-6.467068	0.482982	4.785798
H	-9.551260	2.514261	2.601658
H	-8.536419	1.850789	4.760370
C	6.734020	-0.946514	0.166925
H	7.745110	-0.538921	0.126924
H	6.252722	-0.627560	1.090928
H	6.778744	-2.036201	0.145144
C	-7.042826	0.867633	-1.470314
H	-8.053841	0.459965	-1.428850
H	-7.087598	1.957310	-1.448172
H	-6.562953	0.548936	-2.395147

2-cis-2-Me

C	-4.191120	1.099809	-0.302752
C	-3.096265	0.169003	-0.370426
C	-1.762017	0.675777	-0.295172
C	-1.525572	2.097364	-0.144735
C	-2.658372	2.979276	-0.058873
C	-3.921445	2.488722	-0.143816
C	-0.641968	-0.203564	-0.370711
C	-0.228117	2.566433	-0.086356
C	0.900391	1.709469	-0.185355
C	0.687542	0.302935	-0.328303
C	1.807119	-0.573468	-0.431853
C	3.140235	-0.058589	-0.428098
C	3.316732	1.357794	-0.290445
C	2.206879	2.191138	-0.157336
H	-2.489396	4.038252	0.077580
H	-4.754071	3.182286	-0.079388
H	2.355524	3.253800	-0.024697
C	1.572189	-1.998597	-0.546699
C	4.233308	-0.981380	-0.560733
C	2.705972	-2.878660	-0.640126
H	2.538625	-3.943855	-0.718683
C	3.967462	-2.377060	-0.649583
H	4.800462	-3.069118	-0.724689
C	0.275098	-2.471621	-0.568755
C	-0.853975	-1.611592	-0.501786
C	-3.271638	-1.247294	-0.511990
C	-2.160653	-2.088637	-0.570445
H	-2.307429	-3.152664	-0.696334
P	-5.854294	0.622185	-0.434522
C	-4.596648	-1.805943	-0.589893
C	-5.811533	-1.132094	-0.586989
C	-6.949621	-1.994642	-0.659419
C	-6.605845	-3.307050	-0.717828
S	-4.892975	-3.523568	-0.688565
P	5.898410	-0.485885	-0.591888
C	4.639664	1.926379	-0.302557
C	5.854853	1.265686	-0.439030
C	6.642277	3.441814	-0.299840
C	6.989379	2.136364	-0.438783
S	4.932269	3.641782	-0.166311
O	0.006124	3.917222	0.125190
O	0.043156	-3.829021	-0.736610
C	0.193808	4.700118	-1.059116
H	-0.745948	4.811331	-1.606990

H	0.545411	5.679220	-0.734065
H	0.939119	4.246140	-1.716697
C	-0.147382	-4.570471	0.473927
H	-0.497293	-5.560846	0.182942
H	0.791400	-4.661768	1.027488
H	-0.894379	-4.093842	1.113468
H	-7.974131	-1.648695	-0.661672
H	-7.255640	-4.165510	-0.779089
H	7.289049	4.303986	-0.264302
H	8.012220	1.799680	-0.538017
C	6.857444	-1.215755	0.781593
C	6.510988	-0.815938	2.077814
C	7.839533	-2.193823	0.608818
C	7.135340	-1.383253	3.179754
H	5.745537	-0.063277	2.226806
C	8.460493	-2.767354	1.717521
H	8.126644	-2.522259	-0.381147
C	8.110212	-2.363601	3.000836
H	6.857512	-1.062279	4.176144
H	9.216756	-3.529204	1.574088
H	8.592887	-2.811310	3.860532
C	-6.850958	1.071339	1.030501
C	-6.225719	1.043229	2.281005
C	-8.223523	1.331432	0.957198
C	-6.961666	1.258969	3.439538
H	-5.162091	0.847529	2.346423
C	-8.959946	1.533897	2.120744
H	-8.729845	1.372939	0.002044
C	-8.331413	1.495262	3.361239
H	-6.466263	1.237704	4.402376
H	-10.023333	1.728538	2.055582
H	-8.905773	1.654541	4.265418
C	6.754010	-0.965810	-2.123722
H	6.684896	-2.043701	-2.276697
H	6.248538	-0.458460	-2.944377
H	7.803191	-0.668101	-2.099502
C	-6.710345	1.376171	-1.854799
H	-7.713085	0.965472	-1.976664
H	-6.776856	2.456378	-1.719204
H	-6.121770	1.155459	-2.744793

2-cis-2-O(BCF)₂

C	-4.055489	0.555530	-1.113006
C	-2.908149	-0.243957	-1.016821
C	-1.633058	0.402261	-1.090379
C	-1.565189	1.809981	-1.291790
C	-2.747877	2.577834	-1.319057
C	-3.966732	1.959814	-1.221107
C	-0.427789	-0.347408	-1.016960
C	-0.296605	2.430591	-1.469124
C	0.875300	1.704870	-1.346556
C	0.817439	0.296910	-1.113493
C	2.023610	-0.448522	-1.031476
C	3.296520	0.198071	-1.156894
C	3.322397	1.651825	-1.322470
C	2.153627	2.338754	-1.433807
H	-2.678228	3.659070	-1.429107
H	-4.880235	2.553745	-1.259980
H	2.158071	3.420771	-1.566705
C	1.956135	-1.859526	-0.850534
C	4.449150	-0.598705	-1.118051
C	3.147681	-2.616029	-0.796566
H	3.088815	-3.696751	-0.676118
C	4.362968	-1.995467	-0.926287
H	5.273699	-2.591782	-0.900809
C	0.684739	-2.495419	-0.754848
C	-0.489017	-1.764354	-0.846334
C	-2.939680	-1.701971	-0.896055
C	-1.771912	-2.397478	-0.808855
H	-1.781766	-3.485162	-0.739680
P	-5.696549	-0.128345	-1.292530
C	-4.217996	-2.411483	-0.916507
C	-5.476930	-1.865809	-1.069766
C	-6.526891	-2.835432	-1.088262
C	-6.046377	-4.100943	-0.946001
S	-4.332573	-4.133726	-0.790301
P	6.077315	0.080324	-1.438349
C	4.594499	2.370545	-1.328520
C	5.860415	1.825306	-1.310766
C	6.416116	4.066772	-1.277860
C	6.907584	2.798145	-1.282284
S	4.693954	4.099356	-1.303557
O	-0.253350	3.754062	-1.762326
O	0.636661	-3.842468	-0.599218
C	-0.334025	4.051816	-3.157925
H	-1.229122	3.593277	-3.605356

H	-0.388187	5.142809	-3.250027
H	0.559604	3.678481	-3.682866
C	0.636701	-4.314840	0.745892
H	0.619381	-5.410057	0.699014
H	1.541540	-3.984700	1.279858
H	-0.253746	-3.955625	1.285754
H	-7.582578	-2.590876	-1.207224
H	-6.608137	-5.033694	-0.922854
H	6.973116	5.002494	-1.260943
H	7.969546	2.553041	-1.275627
C	7.229418	-0.506523	-0.192605
C	6.813100	-0.645366	1.135614
C	8.548681	-0.792972	-0.554109
C	7.716728	-1.086277	2.096080
H	5.783080	-0.418766	1.420009
C	9.446269	-1.235433	0.412760
H	8.867867	-0.675620	-1.589833
C	9.030199	-1.383975	1.734194
H	7.392959	-1.202721	3.132060
H	10.475067	-1.467105	0.130673
H	9.735507	-1.734674	2.490540
O	6.688637	-0.265808	-2.816063
O	-6.347576	0.212456	-2.664015
C	-6.813436	0.521254	-0.052649
C	-6.376298	0.632614	1.271381
C	-8.119184	0.870635	-0.406855
C	-7.250989	1.105252	2.243033
H	-5.353997	0.357935	1.542627
C	-8.988355	1.336872	0.575163
H	-8.440321	0.785811	-1.444778
C	-8.555131	1.456034	1.894150
H	-6.913671	1.202856	3.276593
H	-10.009624	1.613537	0.306361
H	-9.239765	1.827572	2.659583
B	6.665016	-1.038433	-4.130467
C	7.980527	-2.011915	-4.010882
C	9.149151	-1.912961	-4.758592
F	9.264858	-1.045475	-5.768513
C	10.284664	-2.684097	-4.510257
F	11.373737	-2.536366	-5.257246
C	10.281351	-3.599558	-3.470565
F	11.355666	-4.333904	-3.215943
C	9.137701	-3.735513	-2.693233
F	9.116548	-4.600926	-1.685538
C	8.037409	-2.943867	-2.978153
F	6.976739	-3.098567	-2.170827

C	6.739158	0.005531	-5.383590
C	6.829927	1.388386	-5.308315
F	6.933471	2.021417	-4.135788
C	6.818866	2.211440	-6.432599
F	6.903691	3.532235	-6.299985
C	6.717109	1.650260	-7.695579
F	6.708221	2.423155	-8.774693
C	6.631676	0.268605	-7.820064
F	6.545059	-0.285571	-9.025428
C	6.640190	-0.509868	-6.672570
F	6.577428	-1.837745	-6.842262
C	5.217223	-1.802862	-4.233928
C	4.060969	-1.031723	-4.153503
F	4.158273	0.301650	-4.032505
C	2.774331	-1.552579	-4.138332
F	1.722081	-0.750239	-4.018746
C	2.610427	-2.929209	-4.214525
F	1.404982	-3.474911	-4.150114
C	3.729641	-3.738926	-4.346131
F	3.579476	-5.055844	-4.440760
C	4.997632	-3.167856	-4.373952
F	6.014303	-4.019027	-4.532602
B	-5.906998	0.499705	-4.099847
C	-4.402679	-0.135337	-4.250644
C	-3.212712	0.583085	-4.318330
F	-3.209793	1.919974	-4.390463
C	-1.954909	-0.011108	-4.253470
F	-0.852287	0.733834	-4.247492
C	-1.857893	-1.385814	-4.115384
F	-0.680739	-1.970849	-3.976780
C	-3.015463	-2.148295	-4.061974
F	-2.930321	-3.459978	-3.871265
C	-4.245571	-1.515336	-4.132758
F	-5.320790	-2.305014	-4.034783
C	-5.989231	2.105855	-4.399573
C	-6.472650	3.089331	-3.547696
F	-6.858740	2.809661	-2.293763
C	-6.574077	4.431588	-3.907026
F	-7.039137	5.326111	-3.040284
C	-6.190706	4.830889	-5.176808
F	-6.282719	6.104117	-5.538306
C	-5.701386	3.882040	-6.067671
F	-5.317260	4.253260	-7.284160
C	-5.626973	2.557252	-5.666282
F	-5.149970	1.679831	-6.558681
C	-7.043429	-0.207793	-5.045738

C	-8.390007	-0.016606	-4.745323
F	-8.751725	0.779032	-3.729530
C	-9.430080	-0.605917	-5.453887
F	-10.695942	-0.402338	-5.102194
C	-9.135661	-1.401265	-6.552588
F	-10.112051	-1.978003	-7.241193
C	-7.810263	-1.586308	-6.919142
F	-7.513834	-2.335544	-7.976591
C	-6.801091	-0.982246	-6.175362
F	-5.554675	-1.202749	-6.604379

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Chapter Three: From Aqua Green to Deep Red in One Step: Targeted Design of a Highly Luminescent Phosphocyclic Vat Orange 3

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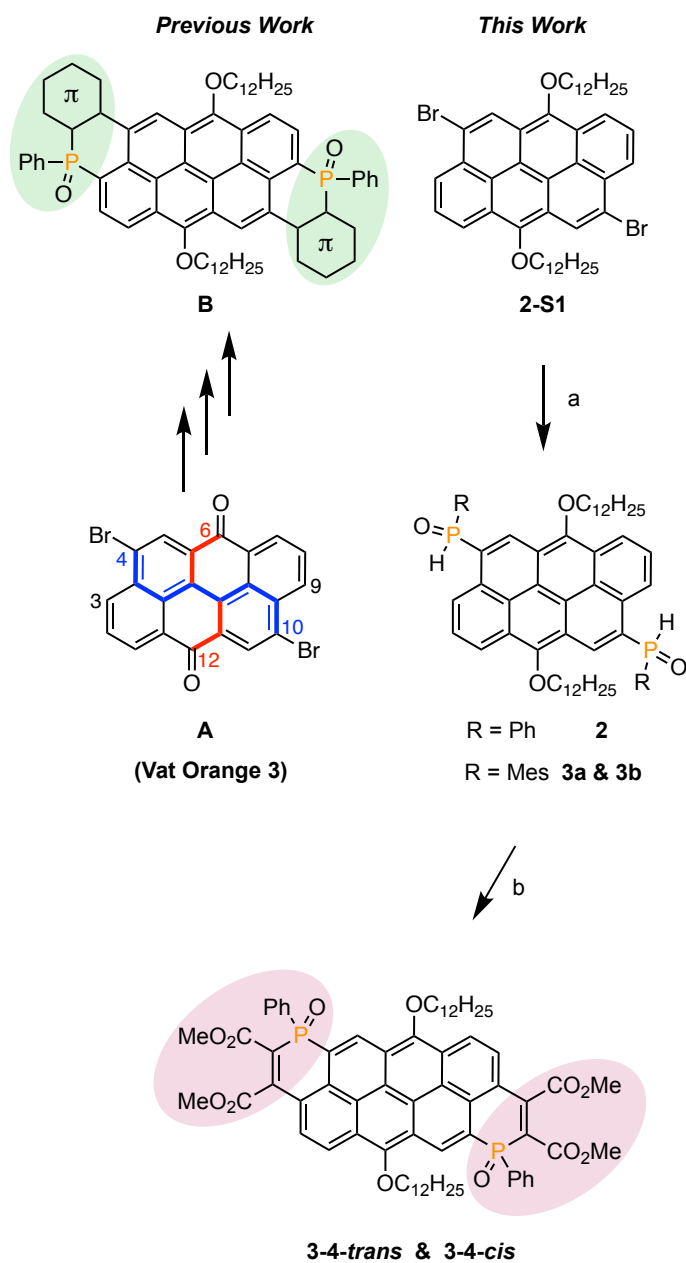
Important Note: Number **3** before every number, scheme, and figure in this chapter indicates they belong to **Chapter Three**.

3.1. Introduction

Red luminescent materials have gained widespread utility in bioimaging, photodynamic therapy,¹⁻³ and materials science (OLEDs, sensors).⁴⁻⁶ While reports on efficient red-light emitters have been steadily increasing in recent years, maintaining intense fluorescence remains challenging, as it shifts into the deep-red region (650-700 nm). This is attributed to increasing non-radiative decay processes as the energy difference between the excited and ground states narrows,⁷ and this is further exacerbated in the near-IR (NIR) region.^{8,9} As a result, organic conjugated systems capable of achieving quantum yields above 40% in these regions remain scarce, despite being highly advantageous for a variety of applications.¹⁰⁻¹² Designing conjugated materials with tailored luminescence features therefore continues to be an active area of research, as detailed in chapter 1.

Vat dyes are a distinct class of polyaromatic hydrocarbons with a long history in the textile industry owing to their intense absorption in the UV-vis region and resulting vibrant colors.¹³ Among them, Vat Orange 3 (VO3, **A**, Scheme 3-1) has proven to be a valuable building block for conjugated materials with notable functional properties, such as pronounced luminescence. The key to activating luminescence in VO3-based scaffolds lies in precise functionalization of the sites bearing the keto and bromo functional groups.^{14,15} Furthermore, embedding phosphorus into the backbone of π -conjugated structures is a versatile tool to tailor the overall electronics of organic systems. Studies suggest that this effect is largely governed by the interactions between external P-substituents and the π -conjugated system in the P-heterocycle, typically resulting in a lowered LUMO.^{16,17} Indeed, numerous examples of phosphorus-containing conjugated materials with advanced light-emitting and electron-acceptor behaviour—developed by us and other groups—are well documented in the literature, and detailed in Chapter 1.^{16,18-20} Our initial study on phosphorus-

modified VO3, provided in Chapter 2, led to a series of conjugated materials (**B**, Scheme 3-1) with highly tunable optical and electrochemical properties via phosphorus modification.²¹



Scheme 3-1. Previous and current target structures along with the attempted synthetic route. (a) 1: *n*-BuLi, PhPCl₂ (MesPCl₂ for **3**), THF, 6h; 2: H₂O 1h (70 %). (b) Ag₂O, DMAD, CH₃CN, 100 °C, overnight (17 %).

The phosphorus moieties installed at the 3- and 9-positions of VO3 (Scheme 3-1) have a pronounced impact on the optical and electronic properties of the inherently green-emissive framework, despite the small phosphorus-to-hydrocarbon ratio within the scaffold.

Conversely, the majority of reported core-substituted VO3 derivatives (see Chapter 1.3) confirm that modulation of the frontier molecular orbital (FMO) energy values are more substantial when substituents are installed along the 6-12 and 4-10 conjugation pathways (Scheme 3-1).^{22,23} Consequently, we envisioned that placing phosphorus at the 4- and 10-positions would exert a more pronounced stabilizing effect on the LUMO energy level, thereby effectively decreasing the energy gap. To ensure the success of this approach, we selected dimethyl acetylenedicarboxylate (DMAD) as the ring-expanding partner, as its electron-withdrawing ester groups were expected to further lower the LUMO energy level and shift the emission of the scaffold well into the red region and beyond (**3-4**, Scheme 3-1).

3.2. Synthesis and Characterization

The synthetic strategy toward **3-4-trans** and **3-4-cis** (defined by the stereochemistry of the two P-centers) involves precursor **2-S1**²¹ (Chapter 2) that enhances the solubility of native VO3 and also suppresses side reactions involving the keto groups. Lithiation of **2-S1** with *n*-butyl lithium, followed by addition of PhPCl₂ for the direct attachment of PhPCl-moieties to the main framework was explored. Due to the low solubility of **2-S1** in THF at -78°C, the reaction mixture was stirred at elevated temperatures for an extended period after addition of *n*-BuLi at low temperature, to ensure complete lithiation. Optimization of this step, followed by hydrolysis of the PhPCl moieties and rearrangement into the PhP(O)H functional groups provided **3-2** in up to 70% at a gram scale. Interestingly, the ³¹P{¹H} NMR spectrum of **3-2** revealed two barely separated singlets at δ³¹P:

25.3 and 26.0 ppm suggesting of the presence of isomeric species (i.e., diastereomers). To confirm this assumption, variable-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy was performed on **3-2**, revealing the coalescence of the two singlets at 100 °C and re-emergence of the original signals upon cooling (Figure S3-1). To be able to isolate these isomers, we surmised increasing the sterics around the P-center would be beneficial. Indeed, using mesityl group instead of phenyl on the phosphorus, rendered the separation of the diastereomers of **3-3** possible. The blue luminescent compounds **3-3a** and **3-3b** were separated using column chromatography (CHCl_3 :acetone-10:0.8) with $^{31}\text{P}\{^1\text{H}\}$ NMR shifts at 11.2 and 11.1 ppm.

Ag-mediated oxidative coupling^{24,25} between the phosphorylated **3-2** and DMAD led to the formation of phosphacycles on each side of the framework. Due to the radical nature of the reaction, the target species **3-4** was afforded as mixture of the two possible isomers with *trans*- and *cis*-configured P-Ph groups with respect to the plane of the conjugated scaffold. Both isomers are deep blue in colour, indicative of a small energy gap, but highly stable under ambient conditions. We were able to separate **3-4-trans** and **3-4-cis** through column chromatography (CHCl_3 :acetone-10:1) and the species were characterized by respective singlets at $\delta^{31}\text{P}$: 6.9 and 6.8 ppm and their corresponding ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra.

Single crystals of **3-4-trans** were grown from acetone that confirmed the structural attributes of this species via X-ray diffraction (Figure 3-1). Contrary to **B** (Chapter 2),²¹ the fused scaffold of **3-4-trans** is entirely flat with the merged phosphacycles deviating only 1° from planarity, suggesting effective conjugation throughout the π -system. The terminal ester groups proximal to the phosphorus centers are coplanar and consequently involved in conjugation, while the distal ester groups are perpendicular to the main scaffold, likely due to steric pressure. Furthermore, the packing in the solid state (Figure S3-4) shows isolated slipped stacks in an overall herringbone

pattern without any π -stacking interactions. As in our previous P-modified VO₃ species **B** (Chapter 2), the extended π -systems are separated by intercalated dodecyl chains from neighboring molecules in a different stack.

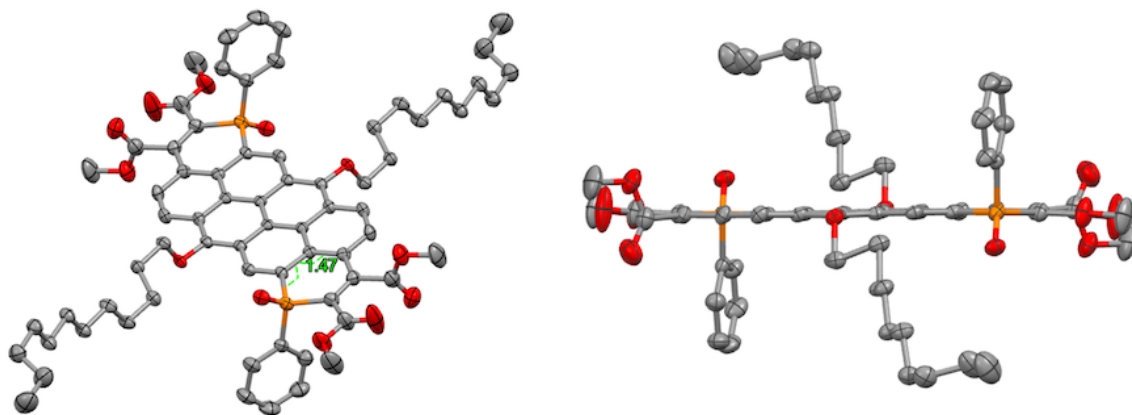


Figure 3-1. Different views of **3-4-*trans*** in the solid state (ellipsoids at 50% probability, H atoms omitted for clarity).

However, it should be noted that the reaction also provided a significant number of difficult-to-separate byproducts, requiring the optimization of the reaction conditions (see SI), that ultimately improved the yield to 17% overall using CH₃CN as solvent at 100 °C. Isolation of some of the purple byproducts from the reaction mixture by preparative thin layer chromatography (TLC) revealed their identity as partially ring-closed species **C** and **D** using HRMS (Figure S3-2).

Furthermore, we presumed that the ring closure could also occur on the exocyclic P-Ph (**E**, Figure S3-2) adding to the complexity of this reaction. The Mes-P moieties in compound **3-3** were expected to block the active positions on the exocyclic substituent and the ring closure was thus attempted with **3-3** as well. Unfortunately, this strategy did not result in the desired outcome, rather leading to an even more complex mixture (Figure S3-3), which is probably due to ineffective

production of the P-centered radical or its ineffective attack on DMAD due to the increased steric profile of Mes vs. Ph.

3.3. DFT calculations and Photophysics

DFT calculations at the B3LYP/6-31+G(d) level of theory confirmed involvement of the entire conjugated core in the π -system across all synthesized species. Moving from **2-S1** to **3-2**, only a minimal stabilization effect from the phosphoryl groups on the LUMO was noted ($-2.64 \rightarrow -2.75$ eV). While the small influence can be linked to the electron-accepting nature of the phosphoryl groups, the limited conjugation between phosphorus and the π -system suggests only a modest effect (Figures 3-2, top and S3-5). However, stark differences are observed after ring closure; in **3-4-trans** (and **3-4-cis**), the P-centre shows significant contribution to the LUMO, and participation of the adjacent ester groups is also evident (Figure 3-2, top). This stabilizes the LUMO substantially—from -2.75 to -3.72 eV—along with a lesser impact on the HOMO level. This decreases the overall FMO energy gap from 2.71 eV in **3-2** to 2.04 eV in **3-4-trans**, highlighting the effectiveness of the employed strategy (see Figure S3-5 for other precursors and isomers).

The photophysical properties of the synthesized species were investigated in dichloromethane (Table S3-4). Both **2-S1** and **3-2** exhibit two distinct absorption bands around 320 and 460 nm, respectively, red-shifted by only 5 nm from **2-S1** to **3-2**, as supported by DFT (Figure S3-6). Furthermore, the extinction coefficients of both compounds exceed $90,000 \text{ M}^{-1} \text{ cm}^{-1}$, confirming the significant absorption features of vat-dye-based scaffolds. Notably, the absorption spectrum of **3-4-trans** (similar to **3-4-cis**) is comprised of three sets of bands around 375, 474, and 637 nm, respectively, featuring light-absorption that covers the entire visible region and extending into the

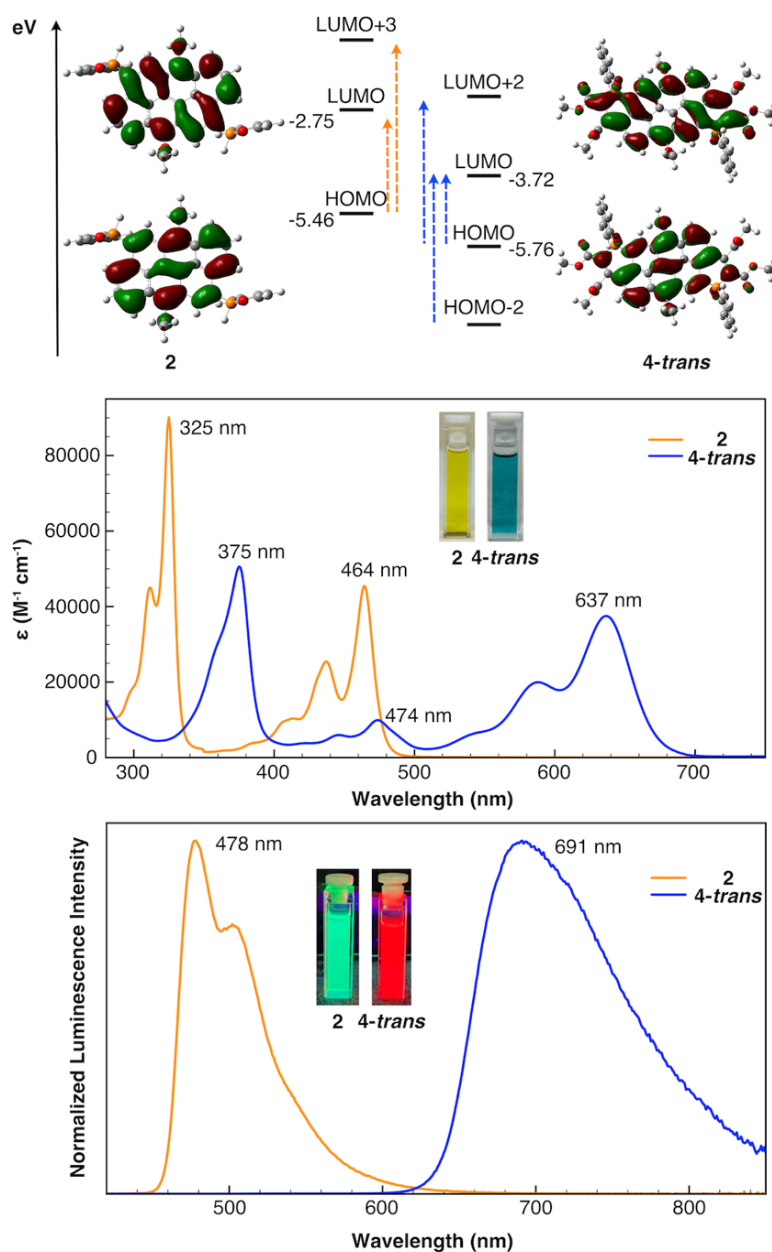


Figure 3-2. FMOs along with the involved electronic transitions (top), absorption (middle), and emission (bottom) spectra of **3-2** and **3-4-trans** in CH_2Cl_2 .

UV (Figure 3-2, middle). Comparison between **3-2** and **3-4-trans** confirms that the phosphacycles induce a remarkable red-shift of 173 nm for the low-energy absorption ($464 \rightarrow 637$ nm) that is

achieved with a relatively small structural change. The extinction coefficients for **3-4-trans** are up to 50,600 M⁻¹ cm⁻¹ with a strong absorption beyond 600 nm that makes it a potential conjugated material for photovoltaics as this region has a great overlap with solar emissions. It is worth noting that the optical properties of diastereomers **3-3a** and **3-3b** are nearly identical and resemble that of their phenyl congener **3-2**, which is expected given the structural similarity among these species (Figure S3-7).

To obtain deeper insight into the nature of the observed absorption features, time-dependent TD-DFT calculations were performed that align well with the experimental data. The low-energy bands for both **3-2** and **3-4-trans** are results of HOMO→LUMO transitions ($\pi\rightarrow\pi^*$) with respective oscillator strengths of $f=0.45$ and 0.74 , confirming the intense absorption in the red-shifted area (Figure 3-2, top). The high-energy features can be attributed to a combination of transitions, with the most significant contributions arising from HOMO→LUMO+3 for **3-2**, and HOMO→LUMO+2 for **3-4-trans** with $f=0.61$ and 0.85 . The emerging third absorption band for **3-4-trans** (474 nm) receives a strong contribution from HOMO-2→LUMO with $f=0.30$ (see Figure S3-5 for other species).

The small red-shift in the emission between **2-S1** and **3-2** (470 → 478 nm) is due to the largely unaffected electronics in these systems (Figure S3-6). However, replacing bromine in the weakly emissive **2-S1** with P-based moieties in **3-2** results in a drastic increase in quantum yield (QY; **2-S1**: 2% vs. **3-2**: 56%), due to the suppression of non-radiative relaxation pathways; this is an established effect of phosphoryl moieties in organic materials.²⁶ Compounds **3-4-trans** and **3-4-cis** exhibit a surprisingly large red-shift of 213 nm for their emission maxima at 691 nm—at the trailing edge of the deep-red region—that is accomplished through a single synthetic step (Figure 3-2, bottom and S3-6). Moreover, the emission profile expands into NIR region, progressing past

800 nm. Impressively, **3-4-*trans*** and **3-4-*cis*** are strongly luminescent, with QY values of up to 70%. This is rare for compounds (organic and inorganic) emitting in this spectral region (likely due to the highly planarity of this system), supporting its high value for applications in biological and materials sciences.

Table 3-1. Photophysical, electrochemical, and DFT calculation data of all the synthesised species.

Comp.	λ_{abs} (nm)	ϵ ($\text{M}^{-1} \text{cm}^{-1}$)	λ_{em} (nm)	Φ_{f} (%)	E_{red} (V)	$E_{\text{LUMO}}, E_{\text{HOMO}}$ (eV)	E_{g} (eV)
2-S1	320, 459	94 800	470	2	—	-2.65, -5.38	2.73
3-2	325, 464	90 100	478	56	-1.96	-2.75, -5.46	2.71
3-3a	324, 465	43 800	478	45	—	-2.68, -5.42	2.74
3-3b	324, 465	42 400	479	50	—	-2.69, -5.42	2.73
3-4-<i>trans</i>	375, 474, 637	50 600	691	70	-1.04	-3.72, -5.76	2.04
3-4-<i>cis</i>	375, 474, 636	41 900	691	69	-0.98, -1.11	-3.75, -5.77	2.02

Photophysical and electrochemical data were recorded from DCM solutions.

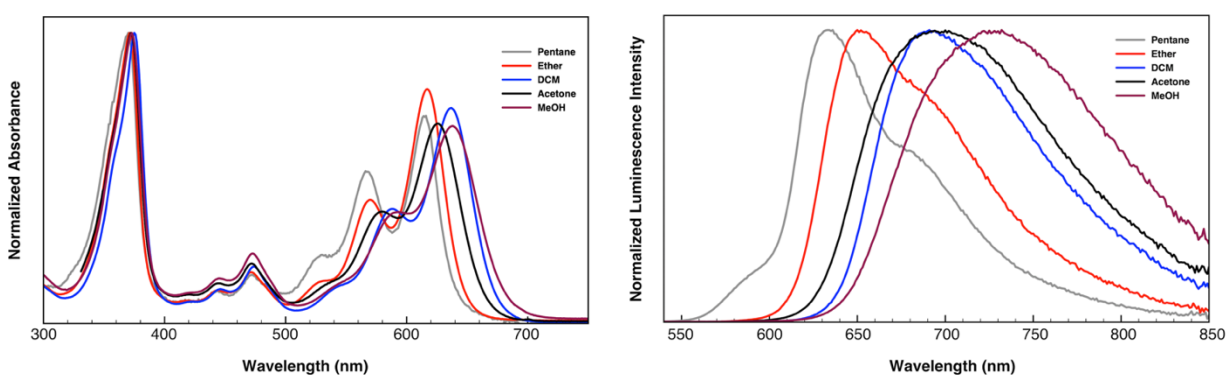


Figure 3-3. Absorption (left), and emission (right) spectra of **3-4-*trans*** in pentane, diethyl ether, dichloromethane, acetone, and methanol.

Positive solvatochromism was representatively confirmed for **3-4-trans** (see Figure 3-3). In less polar solvents such as pentane and diethyl ether, **3-4-trans** exhibits blue-shifted emissions at 634 and 650 nm, respectively. More polar solvents and those capable of hydrogen bonding, such as acetone and methanol, red-shift the emission to 700 and 732 nm, respectively. The overall emission range across the solvents tested reaches an impressive value of almost 100 nm. In methanol, most of the emission profile of **3-4-trans** notably falls into the NIR region, with a relatively high QY of 16 %. A similar positive solvatochromism is observed in the absorption spectra, albeit with less pronounced shifts overall.

Table 3-2. Photophysical data of **3-4-trans** in different solvents.

Solvent	λ_{abs} (nm)	λ_{em} (nm)	Φ_f (%)
Pentane	370, 472, 616	634	64
Diethyl ether	371, 471, 617	650	44
Dichloromethane	373, 474, 637	691	70
Acetone	372, 472, 626	700	55
Methanol	375, 473, 638	732	16

3.4. Electrochemical properties

Given the beneficial electrochemical properties of the phosphorus-modified VO₃ species **B** in Chapter 2 with reversible reductions at -1.7 and -2.0 V (vs. Fc/Fc⁺) respectively,²¹ cyclic voltammetry was conducted on the new species as well (Figure 3-4). The voltammogram of **3-2** shows a fully reversible reduction peak at relatively high potential of -1.96 V (vs. Fc/Fc⁺) that is

likely comprised of a one-step two-electron reduction process (due to the presence of two P-components).²¹

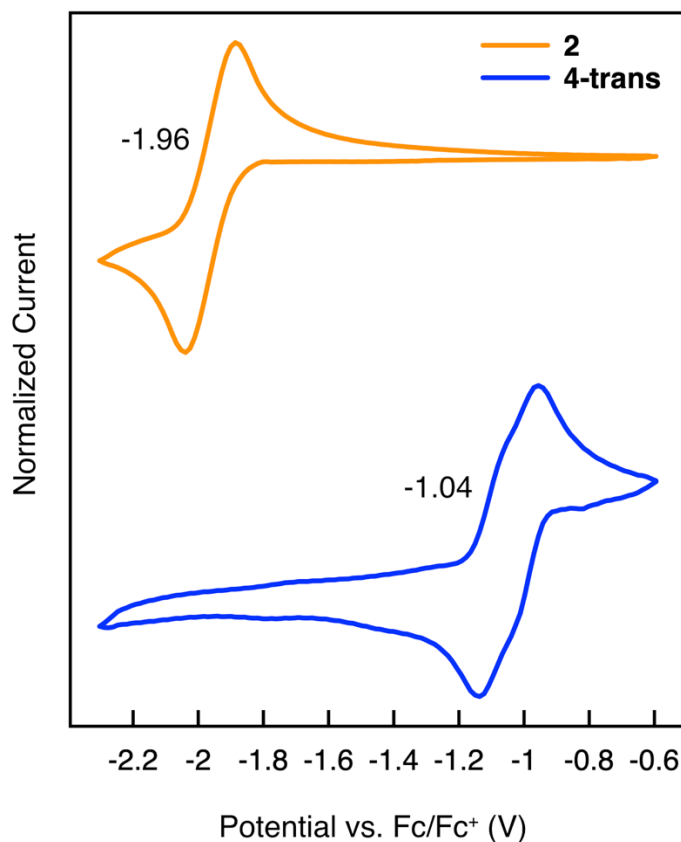


Figure 3-4. Cyclic voltammograms of **3-2** and **3-4-trans** in CH₂Cl₂; scan rate: 100 mVs⁻¹, 0.1 M *n*-Bu₄PF₆, vs. Fc/Fc⁺.

As the LUMO energy level experiences a meaningful decrease in **3-4-trans**, the reduction events undergo a substantial potential shift to -1.04 V (vs. Fc/Fc⁺) while retaining their reversibility, confirming the high stability of these species upon electron uptake. However, the two reduction events appear at slightly different potentials, as the reduction events in **3-4-trans** begin to show signs of separation, supporting electronic communication across the scaffold. This phenomenon is more pronounced in **3-4-cis**, as the reduction events occurring at -0.98 and -1.11 V (Figure S3-8)

are fully resolved, with a center aligning with the reduction feature of **3-4-*trans***. Also, the new species exhibit no reversible oxidation, which is a common observation for such species (Figure S3-9).²¹

3.5. Conclusion

In summary, we successfully developed a ring-fusion methodology for diminishing the LUMO level and narrowing the FMO energy gap of the VO3 scaffold using phosphoryl and alkyne building blocks. The resulting phosphacyclic materials experience an almost 1 eV reduction for their energy gap in one synthetic step. The absorption features disclose intense absorption throughout the visible spectrum especially past 600 nm. More impressively, the new species turned out to be high-performing luminescent emitters with quantum yields of up to 70% and pronounced positive solvatochromism in the red-NIR region. The new functional materials also exhibit enhanced electron-accepting properties with low reduction thresholds that confirm the potentially broad utility of these species in materials chemistry. To round out the initial elaboration the scaffold toward practical applicability, the next Chapter will focus on the effects of modifying the 6-, 12-positions of the scaffold.

3.6. References:

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Appendix B: Chapter Three

From Aqua Green to Deep Red in One Step: Targeted Design of a Highly Luminescent Phosphacyclic Vat Orange 3 Dye

3.1. General Section

Reactions were carried out in dry glassware and under an inert atmosphere of purified argon using Schlenk techniques. Anhydrous solvents such as CH_2Cl_2 and THF were used directly from a solvent purification system (MBraun) or, in case of reactions or column chromatography, were purchased from commercial suppliers and used as received. Standard solvents such as MeCN, chloroform (CHCl_3), CH_2Cl_2 , diethyl ether, hexanes, and methanol (MeOH), were purchased from commercial suppliers and used as received. Deuterated solvents such as chloroform-d and toluene-d₈ were purchased from commercial suppliers and used as received. Silica gel, preparatory TLC plates (silica coated), Celite[®], sodium sulfate (Na_2SO_4), *n*-butyllithium (*n*-BuLi) (2.5 M solution in hexanes), sodium bicarbonate (NaHCO_3), sodium hydroxide (NaOH), dichlorophenylphosphine PhPCl_2 , dimethyl acetylenedicarboxylate (DMAD), silver oxide (Ag_2O) were purchased from commercial suppliers and used as received. MesPCl_2 were prepared according to the adopted procedure found in the literature.^{S3-1} The synthetic procedure and spectral data of compound **1** can be found in the literature.^{S3-2}

NMR: ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker NEO 700 and 300 spectrometers (700 MHz (^1H), 176 MHz (^{13}C); 121 MHz (^{31}P) respectively). The chemical shift δ values were corrected to CDCl_3 (δ 7.26 ppm for ^1H , δ 77.16 ppm for ^{13}C). Signal descriptions include: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. All coupling constants are absolute values and J values are expressed in Hertz (Hz). All ^{13}C signals are singlets unless stated otherwise.

X-Ray crystallography: X-ray crystal structure analyses were measured at 173 K on a Bruker DQ Quest eco instrument. The structure was solved and refined using OLEX2 and SHELXL. CCDC 2468570 (**3-4-trans**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Theoretical calculations: Molecular optimizations were carried out at the B3LYP/6-31+G(d) scrf=(solvent=dichloromethane) level by using the ORCA suite of programs.

Steady-state spectroscopy: Absorption and emission spectra were recorded from CH_2Cl_2 solutions using an Agilent Technologies Cary 5000 UV-Vis spectrometer and Edinburgh FS5 instrument spectrometer with a SC-05 standard cuvette holder, respectively.

Fluorescence quantum yields Φ : Quantum yields were determined using an integrating sphere.

Electrochemistry: Cyclic voltammograms were recorded using a Metrohm Autolab potentiostat from CH₂Cl₂ solutions using tetrabutylammonium hexafluorophosphate as electrolyte, glassy carbon as working electrode, platinum wire as counter electrode and silver/silver chloride (Ag/Ag⁺) as pseudo-reference electrode. Scan rate is 100 mV s⁻¹. The curves were calibrated using ferrocene as standard ($E_{1/2} = 0.60$ V). The voltammogram was recorded using the NOVA software package.

3.2. Experimental Data

3.2.1. Synthesis

Compound 3-2

Compound **2-S1** (1.0 g, 1.2 mmol) was dissolved in 250 ml dry THF in a 500 ml Schlenk flask under argon and the solution was brought down to -78 °C while being stirred rapidly. Immediately after the temperature was brought down, the *n*-BuLi (3 eq, 3.7 mmol, 1.5 ml, 2.5 M) was added to the mixture in span of 3 minutes and the temperature was quickly brought up to 0 °C, and the mixture was stirred for 30 minutes. Next, the reaction mixture was stirred at room temperature for another 30 minutes and was brought back to -78 °C and PhPCl₂ (3 eq, 3.7 mmol, 0.5 ml) was added. The mixture was stirred for one hour at low temperature and four hours at room temperature. Then, 5 ml water was added, and stirring was continued for one hour. The solution was concentrated and separated using DCM/water (200 ml each). The organic phase was washed with water, sodium bicarbonate solution, and brine and was dried using sodium sulfate. The solvent was evaporated under reduced pressure and the product was separated using flash column chromatography (silica) with chloroform and acetone (10:1) and recrystallized from acetone to form an orange solid (70% yield, 0.78 g).

Note: the excess amount of *n*-BuLi is necessary for achieving higher yields. Accordingly, 3 eq of PhPCl₂ was used to ensure the consumption of the lithiated species. The excess phosphine is easily separable by column chromatography.

¹H NMR (300 MHz, CDCl₃) δ 8.98 (dd, *J* = 21.6, 6.7 Hz, 2H), 8.78 (t, *J* = 7.7 Hz, 4H), 8.63 (dd, *J* = 486.0, 2.4 Hz, 2H), 8.13 (t, *J* = 7.8 Hz, 2H), 7.93 (ddd, *J* = 13.7, 6.8, 1.4 Hz, 4H), 7.57 (dt, *J* = 7.3, 1.5 Hz, 2H), 7.51 (td, *J* = 7.3, 2.8 Hz, 4H), 4.40 – 4.29 (m, 4H), 2.19 – 2.00 (m, 4H), 1.76 – 1.59 (m, 4H), 1.54 – 1.15 (m, 32H), 0.87 (t, *J* = 6.9, 6H).

³¹P{¹H} NMR (121 MHz, CDCl₃) δ 26.0, 25.3.

¹³C{¹H} NMR (176 MHz, CDCl₃) δ 152.1, 132.8, 131.5 (d, *J* = 7.0 Hz), 131.4 (d, *J* = 5.3 Hz), 131.0 (d, *J* = 84.5 Hz), 131.1 (d, *J* = 7.0 Hz), 131.1 (d, *J* = 5.3 Hz), 129.5 (d, *J* = 7.0 Hz), 129.4 (d, *J* = 8.8 Hz), 129.2 (d, *J* = 12.3 Hz), 128.6 (d, *J* = 100.3 Hz), 126.7, 126.1, 125.9 (d, *J* = 5.3 Hz), 125.9 (d, *J* = 5.3 Hz), 124.7 (d, *J* = 7.0 Hz), 124.6 (d, *J* = 7.0 Hz), 122.2, 120.5, 120.3 (d, *J* = 15.8 Hz), 77.8, 32.0, 30.8, 29.8, 29.8, 29.8, 29.8, 29.5, 26.4, 26.4, 22.8, 14.3.

HRMS (ESI, *m/z*): [M+H]⁺ calculated for: C₅₈H₇₀O₄P₂, *m/z*=893.4822; Found [M+H]⁺ *m/z*=893.4800.

Compound 3-3

Compound **3-3** was synthesized according to a similar procedure to that used for compound **3-2**. MesPCl₂ was used as the phosphine, and a mixture of chloroform to acetone (10:0.8) was used as eluent in the column chromatography for separation. Each diastereomer was washed with acetone and ether, and isolated as a yellow solid powder (54%, 0.66 g).

Note: **3-3a** and **3-3b** can be separated using column chromatography, but some of the fractions involve both isomers as a mixture, so the total yield of both diastereomer is reported here.

Isomer 3-3a

¹H NMR (700 MHz, CDCl₃) δ 9.12 (d, *J* = 483.0 Hz, 2H), 9.01 (d, *J* = 7.4 Hz, 2H), 8.82 (d, *J* = 8.2 Hz, 2H), 8.62 (d, *J* = 18.4 Hz, 2H), 8.25 (t, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 3.7 Hz, 4H), 4.21 – 4.12 (m, 4H), 2.66 (s, 12H), 2.45 (s, 6H), 1.91 – 1.84 (m, 4H), 1.58 – 1.51 (m, 4H), 1.48 – 1.24 (m, 32H), 0.91 (t, *J* = 6.9 Hz, 6H).

³¹P{¹H} NMR (121 MHz, CDCl₃) δ 11.2.

¹³C{¹H} NMR (176 MHz, CDCl₃) δ 151.9, 143.1, 142.9 (d, *J* = 8.8 Hz), 130.9 (d, *J* = 12.3 Hz), 130.8 (d, *J* = 10.6 Hz), 130.4 (d, *J* = 8.8 Hz), 128.8 (d, *J* = 95.0 Hz), 126.8, 126.1, 125.7 (d, *J* = 8.8 Hz), 124.0 (d, *J* = 7.0 Hz), 123.0 (d, *J* = 105.6 Hz), 121.9, 120.4, 120.4, 77.8, 32.1, 30.6, 29.9, 29.8, 29.8, 29.8, 29.5, 26.2, 22.8, 21.8, 21.8, 21.6, 14.3.

HRMS (ESI, *m/z*): [M+H]⁺ calculated for: C₆₄H₈₂O₄P₂, *m/z*=977.5761; Found [M+H]⁺ *m/z*=977.5762.

Isomer 3-3b

¹H NMR (700 MHz, CDCl₃) δ 9.09 (d, *J* = 483.0 Hz, 2H), 8.98 (d, *J* = 7.4 Hz, 2H), 8.79 (d, *J* = 8.2 Hz, 2H), 8.60 (d, *J* = 18.5 Hz, 2H), 8.22 (t, *J* = 7.8 Hz, 2H), 7.06 (d, *J* = 3.6 Hz, 4H), 4.18 – 4.13 (m, 4H), 2.63 (s, 12H), 2.42 (s, 6H), 1.88 – 1.81 (m, 4H), 1.57 – 1.49 (m, 4H), 1.44 – 1.23 (m, 32H), 0.89 (t, *J* = 6.8 Hz, 6H).

³¹P{¹H} NMR (121 MHz, CDCl₃) δ 11.1.

$^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, CDCl_3) δ 151.9, 143.2, 142.9 (d, $J = 8.8$ Hz), 131.0 (d, $J = 12.3$ Hz), 130.8 (d, $J = 10.6$ Hz), 130.5 (d, $J = 8.8$ Hz), 128.9 (d, $J = 95.0$ Hz), 126.8, 126.1, 125.7 (d, $J = 7.0$ Hz), 124.0 (d, $J = 7.0$ Hz), 123.1 (d, $J = 105.6$ Hz), 121.9, 120.5, 120.4 (d, $J = 12.3$ Hz), 77.9, 32.1, 30.6, 29.9, 29.9, 29.8, 29.8, 29.5, 26.3, 22.8, 21.8, 21.8, 21.6, 14.3.

HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ calculated for: $\text{C}_{64}\text{H}_{82}\text{O}_4\text{P}_2$, $m/z=977.5761$; Found $[\text{M}+\text{H}]^+$ $m/z=977.5739$

Compound 3-4

A Schlenk tube was charged with **3-2** (50 mg, 0.06 mmol), dimethyl acetylenedicarboxylate (2 eq, 0.11 mmol, 0.014 ml), Ag_2O (4 eq, 0.22 mmol, 52 mg), and 1.5 ml of acetonitrile under argon, and was reacted at 100 °C overnight in a confined environment (static argon). After completion, the solvent was evaporated under reduced pressure and the crude mixture was passed through celite using DCM. The resulted mixture was separated using flash column chromatography (CHCl_3 :acetone, 10:1) and fractions including the blue compounds (**3-4-trans** and **3-4-cis**) were isolated. The compounds (containing purple side products) were isolated using preparative TLC run with CHCl_3 :acetone, 10:0.8 as eluent. The clean blue bands (**3-4-trans** and **3-4-cis**) were separated, washed with acetone and the silica was filtered. Acetone was evaporated and the isolated blue compounds was recrystallized in diethyl ether (**3-4-trans**) and diethyl ether/hexanes, 2:1 (**3-4-cis**).

Note 1: For optimizing the conditions of this reactions, solvents such as DMF and CH_3CN , along with variation in the equivalents of DMAD (1, 2, 4 eq.), and Ag_2O (2, 4, 8 eq.), as well as the reaction time (from 2 h to overnight) and temperature (80, 100, and 120 °C) were varied. The

efficiency of each condition was established using thin layer chromatography and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy of the crude mixture.

Note 2: Column chromatography with different ratios of solvents as eluent was attempted to simplify the purification procedure, but the use of preparative TLC is required for isolation of the target blue compounds from the purple side products.

Isomer 3-4-*trans*: (11%, 7 mg)

^1H NMR (700 MHz, CDCl_3) δ 9.21 (d, $J = 16.0$ Hz, 2H), 8.92 (d, $J = 8.9$ Hz, 2H), 8.23 (d, $J = 8.8$ Hz, 2H), 7.89 (dd, $J = 13.4, 7.6$ Hz, 4H), 7.56 (t, $J = 7.5$ Hz, 2H), 7.50 (td, $J = 7.7, 2.7$ Hz, 4H), 4.40 – 4.34 (m, 2H), 4.17 (s, 6H), 4.14 – 4.08 (m, 2H), 3.73 (s, 6H), 1.95 – 1.85 (m, 4H), 1.56 – 1.48 (m, 2H), 1.47 – 1.39 (m, 2H), 1.39 – 1.27 (m, 32H), 0.89 (t, $J = 6.9$ Hz, 6H).

$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CDCl_3) δ 6.9.

$^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, CDCl_3) δ 168.4 (d, $J = 14.1$ Hz), 164.6 (d, $J = 5.3$ Hz), 154.2, 154.2, 136.4 (d, $J = 8.8$ Hz), 134.3 (d, $J = 119.7$ Hz), 132.2, 131.7 (d, $J = 10.6$ Hz), 129.0 (d, $J = 103.9$ Hz), 128.6, 128.5, 128.5, 127.5, 124.7 (d, $J = 8.8$ Hz), 123.4, 123.1 (d, $J = 12.3$ Hz), 122.6 (d, $J = 14.1$ Hz), 121.0 (d, $J = 93.3$ Hz), 120.1, 79.4, 53.5, 52.9, 32.1, 30.6, 29.9, 29.8, 29.8, 29.7, 29.5, 26.2, 22.9, 14.3.

HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ calculated for: $\text{C}_{70}\text{H}_{78}\text{O}_{12}\text{P}_2$, $m/z=1173.5041$; Found $[\text{M}+\text{H}]^+$ $m/z=1173.5011$

Isomer 3-4-*cis*: (6%, 4 mg)

^1H NMR (700 MHz, CDCl_3) δ 9.21 (d, $J = 16.0$ Hz, 2H), 8.92 (d, $J = 8.9$ Hz, 2H), 8.23 (d, $J = 8.8$ Hz, 2H), 7.90 – 7.82 (m, 4H), 7.58 – 7.53 (m, 2H), 7.48 (td, $J = 7.6, 2.8$ Hz, 4H), 4.40 – 4.34 (m, 2H), 4.17 (s, 6H), 4.16 – 4.12 (m, 2H), 3.73 (s, 6H), 1.98 – 1.86 (m, 4H), 1.58 – 1.51 (m, 2H), 1.50 – 1.43 (m, 2H), 1.40 – 1.23 (m, 32H), 0.89 (t, $J = 7.0$ Hz, 6H).

$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CDCl_3) δ 6.8.

$^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, CDCl_3) δ 168.4 (d, $J = 15.9$ Hz), 164.6 (d, $J = 5.3$ Hz), 154.2, 154.1, 136.3 (d, $J = 7.0$ Hz), 134.3 (d, $J = 117.9$ Hz), 132.2 (d, $J = 3.5$ Hz), 131.7 (d, $J = 10.6$ Hz), 128.9 (d, $J = 102.1$ Hz), 128.6 (d, $J = 12.3$ Hz), 128.5, 128.5, 127.5, 124.7 (d, $J = 7.0$ Hz), 123.4, 123.1 (d, $J = 10.6$ Hz), 122.6 (d, $J = 14.1$ Hz), 121.0 (d, $J = 93.3$ Hz), 120.1, 79.4, 53.6, 52.9, 32.1, 30.6, 29.9, 29.8, 29.8, 29.7, 29.5, 26.2, 22.9, 14.3.

HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ calculated for: $\text{C}_{70}\text{H}_{78}\text{O}_{12}\text{P}_2$, $m/z=1173.5041$; Found $[\text{M}+\text{H}]^+$ $m/z=1173.5043$.

3.2.2. Variable-Temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy of compound 3-2.

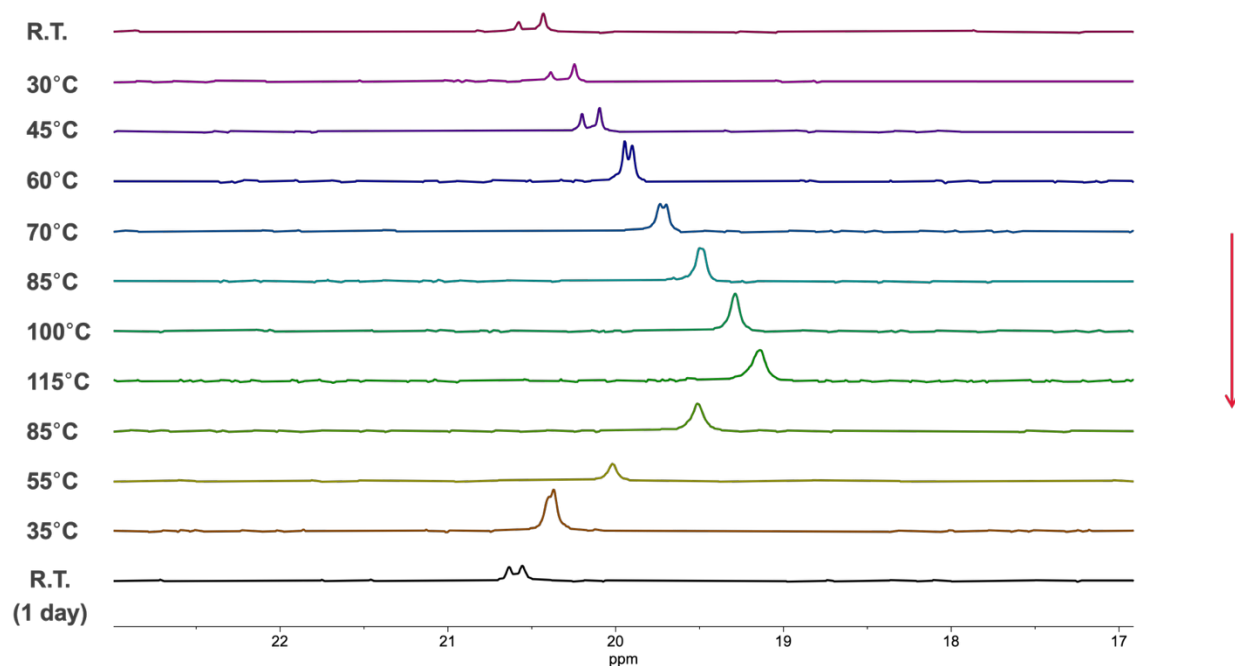


Figure S3-1. VT $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy of compound **3-2** in toluene- d_8 .

3.2.3. Chemical structures of byproducts along with the TLCs of the final reaction step

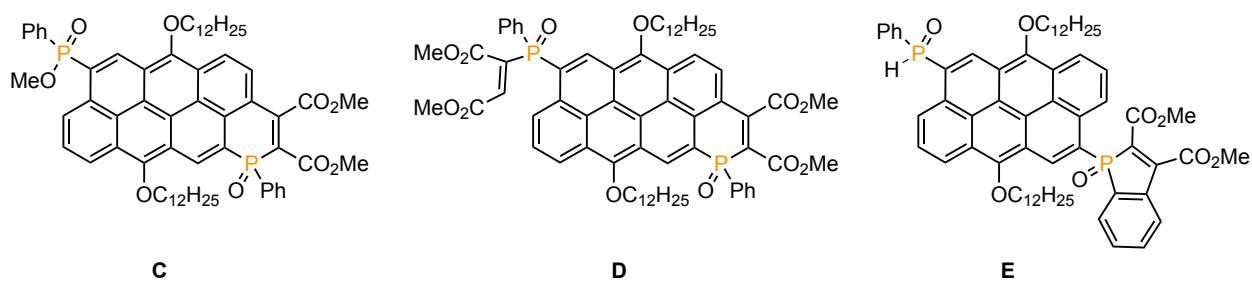
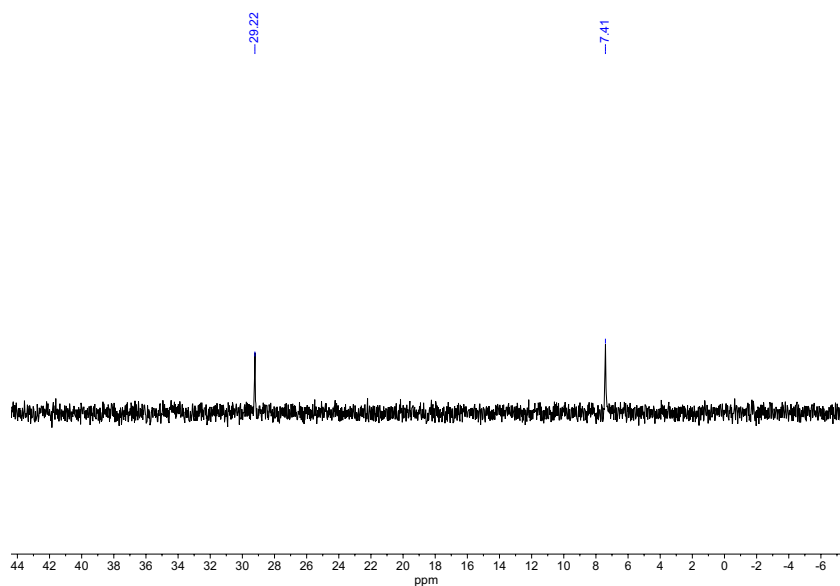


Figure S3-2. Structures of purple byproducts **C** and **D** formed in the final step and confirmed by HRMS, and the structure of the potential byproduct **E** due the ring closure occurring on the exocyclic P-Ph.

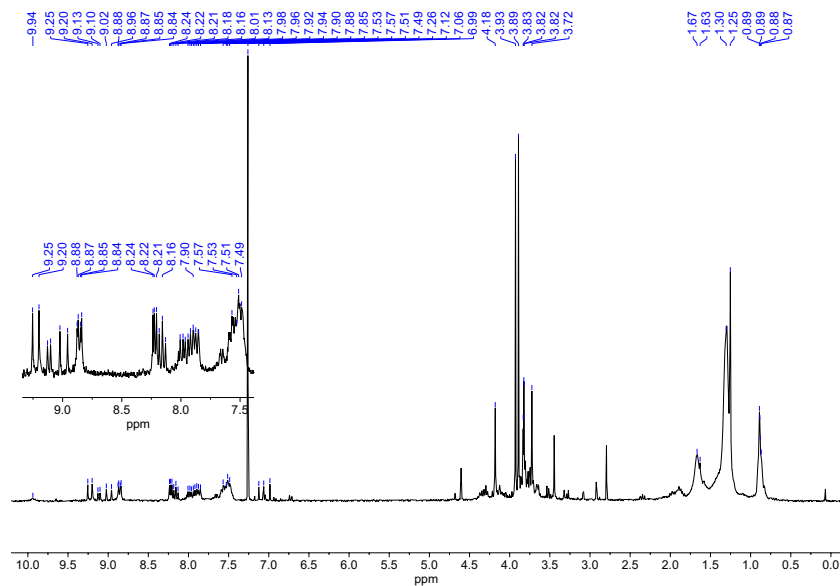
Compound **C**: **HRMS** (ESI, m/z): $[M+H]^+$ calculated for: $C_{65}H_{76}O_9P_2$, $m/z=1063.5037$; Found $[M+H]^+$ $m/z= 1063.50$

Compound **D**: **HRMS** (ESI, m/z): $[M+H]^+$ calculated for: $C_{70}H_{80}O_{12}P_2$, $m/z=1175.5198$; Found $[M+H]^+$ $m/z= 1175.5199$

$^{31}P\{^1H\}$ NMR spectrum of **C** measured in $CDCl_3$ (121 MHz).



1H NMR spectrum of **C** measured in $CDCl_3$ (300 MHz).



Note: After performing a similar purification procedure as compound **3-4** for compound **C**, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the isolated species shows only two singlets with same intensity, suggestive of the presence of two phosphorus atoms in different environment. While this result was promising, the ^1H NMR spectrum of the same solution displays a complex mixture of products (likely including non-phosphorus-containing species) that render characterization of these species impossible. Further chromatography or recrystallization methods did not resolve the complexity of the issue for either of the separated species, **C** and **D**.

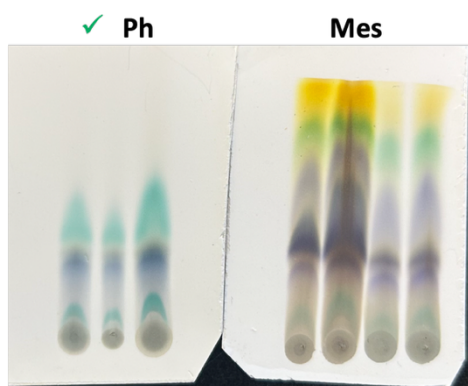


Figure S3-3. TLC of the crude reaction mixture (after celite filtration) of the attempted final step with **3-2** (bearing P-Ph, left) and **3-3** (bearing P-Mes, right) as precursors.

3.2.4. Molecular packing of 3-4-*trans* and the relevant structural data in solid-state.

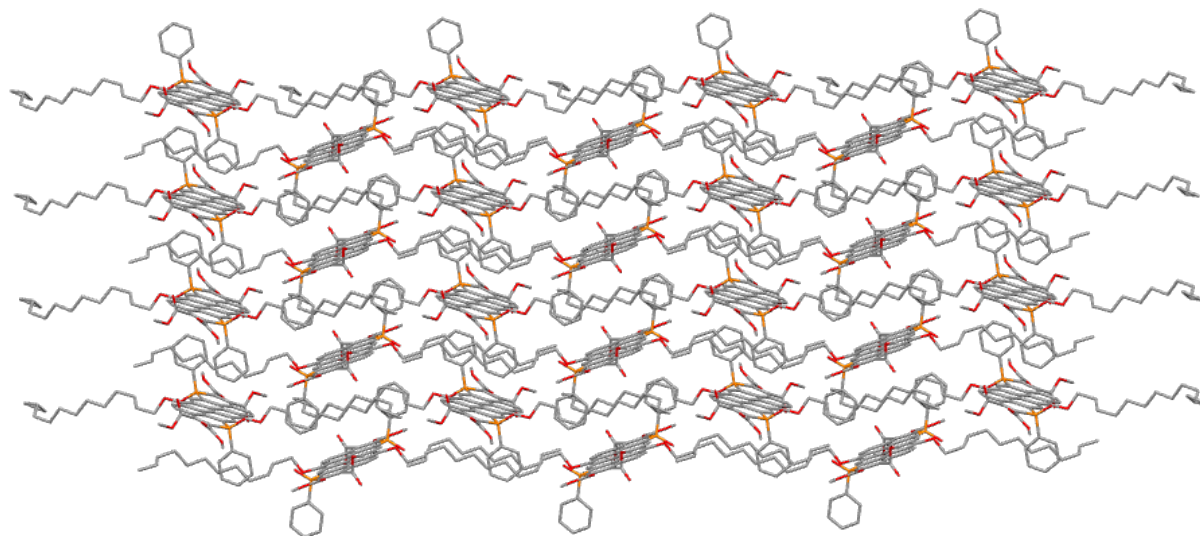


Figure S3-4. Solid-state molecular packing of **3-4-*trans*** (H atoms omitted for clarity).

Table S3-1. Crystal data and structure refinement for 3-4-trans.

Identification code	CCDC 2468570
Empirical formula	C ₇₀ H ₇₈ O ₁₂ P ₂
Formula weight	1173.26
Temperature/K	173.00
Crystal system	triclinic
Space group	P-1
a/Å	8.5368(3)
b/Å	18.5817(7)
c/Å	21.2141(8)
α/°	69.506(2)
β/°	88.807(2)
γ/°	82.570(2)
Volume/Å ³	3124.6(2)
Z	2
ρ _{calc} /g/cm ³	1.247
μ/mm ⁻¹	0.132
F(000)	1248.0
Crystal size/mm ³	0.25 × 0.25 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.438 to 54.968
Index ranges	-11 ≤ h ≤ 11, -24 ≤ k ≤ 24, -27 ≤ l ≤ 27
Reflections collected	102420
Independent reflections	14323 [R _{int} = 0.1166, R _{sigma} = 0.0806]
Data/restraints/parameters	14323/3/804
Goodness-of-fit on F ²	1.025
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0673, wR ₂ = 0.1355
Final R indexes [all data]	R ₁ = 0.1392, wR ₂ = 0.1727
Largest diff. peak/hole / e Å ⁻³	0.49/-0.36

Table S3-2. Bond Lengths for 3-4-*trans*.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P1	O4	1.478(2)	C26	C27	1.499(4)
P1	C26	1.789(3)	C27	O5A	1.219(7)
P1	C30	1.797(3)	C29	C30	1.367(4)
P1	C31	1.796(3)	C31	C32	1.390(5)
P2	O10	1.479(2)	C31	C33	1.387(4)
P2	C54	1.800(3)	C32	C36	1.384(5)
P2	C55	1.783(3)	C33	C34	1.384(5)
P2	C65	1.789(3)	C34	C35	1.375(5)
O1	C12	1.452(3)	C35	C36	1.384(5)
O1	C13	1.379(3)	C37	C38	1.517(14)
O2	C23	1.200(4)	C37	C24	1.60(2)
O3	C27	1.311(4)	C38	C39	1.523(5)
O3	C28	1.455(4)	C38	C37A	1.505(12)
O5	C27	1.217(15)	C39	C40	1.485(5)
O6	C47	1.451(3)	C40	C41	1.536(5)
O6	C48	1.376(3)	C41	C42	1.513(5)
O7	C56	1.320(4)	C42	C43	1.526(4)
O7	C57	1.454(4)	C43	C44	1.525(4)
O8	C56	1.218(8)	C44	C45	1.527(4)
O9	C62	1.196(5)	C45	C46	1.508(4)
C70	C2	1.505(6)	C46	C47	1.501(4)
C2	C3	1.529(5)	C48	C49 ²	1.385(4)
C3	C4	1.521(5)	C48	C51	1.411(4)
C4	C5	1.510(5)	C49	C50	1.435(4)
C5	C6	1.526(4)	C49	C71	1.430(4)
C6	C7	1.514(4)	C50	C50 ²	1.414(5)
C7	C8	1.518(4)	C50	C52	1.420(4)
C9	C10	1.525(4)	C51	C52	1.425(4)
C9	C8	1.527(4)	C51	C61	1.414(4)
C10	C11	1.514(4)	C52	C53	1.432(4)
C11	C12	1.504(4)	C53	C54	1.441(4)
C13	C14	1.384(4)	C53	C59	1.410(4)
C13	C17 ¹	1.411(4)	C54	C71	1.359(4)
C14	C15	1.433(4)	C55	C56	1.498(4)

Table S3-2. Bond Lengths for 3-4-*trans*.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C14	C29	1.430(4)	C55	C58	1.349(4)
C15	C1.5 ¹	1.409(5)	C56	O8A	1.214(16)
C15	C16	1.422(4)	C58	C59	1.474(4)
C16	C17	1.427(4)	C58	C62	1.507(5)
C16	C18	1.437(4)	C59	C60	1.411(4)
C17	C21	1.411(4)	C60	C61	1.367(4)
C18	C19	1.408(4)	C62	O63	1.328(5)
C18	C30	1.439(4)	O63	C64	1.507(6)
C19	C20	1.412(4)	C65	C66	1.389(4)
C19	C22	1.470(4)	C65	C1	1.389(4)
C20	C21	1.366(4)	C66	C67	1.386(5)
C22	C23	1.522(5)	C67	C68	1.377(5)
C22	C26	1.356(4)	C68	C69	1.380(5)
C23	O24	1.328(4)	C69	C1	1.380(5)
O24	C25	1.468(4)	C37A	C63	1.49(2)

¹-X,1-Y,1-Z; ²1-X,1-Y,2-Z**Table S3-3. Bond Angles for 3-4-*trans*.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O4	P1	C26	116.81(15)	C33	C31	C32	118.9(3)
O4	P1	C30	112.29(14)	C36	C32	C31	120.5(3)
O4	P1	C31	113.64(14)	C34	C33	C31	120.6(3)
C26	P1	C30	102.09(14)	C35	C34	C33	120.0(4)
C26	P1	C31	106.15(15)	C34	C35	C36	120.2(3)
C31	P1	C30	104.53(13)	C35	C36	C32	119.8(4)
O10	P2	C54	113.85(13)	C38	C37	C24	110.6(11)
O10	P2	C55	114.02(14)	C37	C38	C39	106.4(7)
O10	P2	C65	113.29(14)	C37A	C38	C39	123.1(7)
C55	P2	C54	102.21(14)	C40	C39	C38	115.5(4)

Table S3-3. Bond Angles for 3-4-*trans*.

Atom Atom Atom	Angle/°	Atom Atom Atom	Angle/°
C55 P2 C65	108.66(15)	C39 C40 C41	113.8(3)
C65 P2 C54	103.77(13)	C42 C41 C40	113.3(3)
C13 O1 C12	112.0(2)	C41 C42 C43	113.6(3)
C27 O3 C28	116.6(3)	C44 C43 C42	112.5(3)
C48 O6 C47	111.5(2)	C43 C44 C45	113.9(3)
C56 O7 C57	116.6(3)	C46 C45 C44	113.9(3)
C70 C2 C3	113.3(4)	C47 C46 C45	114.6(3)
C4 C3 C2	114.0(3)	O6 C47 C46	109.3(2)
C5 C4 C3	114.6(3)	O6 C48 C49 ²	119.8(2)
C4 C5 C6	113.1(3)	O6 C48 C51	118.7(3)
C7 C6 C5	114.1(3)	C49 ² C48 C51	121.6(3)
C6 C7 C8	113.6(3)	C48 ² C49 C50	119.4(3)
C10 C9 C8	113.9(3)	C48 ² C49 C71	122.6(3)
C11 C10 C9	113.5(3)	C71 C49 C50	118.0(3)
C12 C11 C10	114.3(3)	C50 ² C50 C49	119.8(3)
O1 C12 C11	109.1(2)	C50 ² C50 C52	120.2(3)
O1 C13 C14	119.5(3)	C52 C50 C49	120.0(2)
O1 C13 C17 ¹	118.7(3)	C48 C51 C52	119.6(3)
C14 C13 C17 ¹	121.8(3)	C48 C51 C61	121.4(3)
C13 C14 C15	119.6(3)	C61 C51 C52	119.0(3)
C13 C14 C29	122.2(3)	C50 C52 C51	119.3(2)
C29 C14 C15	118.1(3)	C50 C52 C53	120.5(3)
C15 ¹ C15 C14	119.6(3)	C51 C52 C53	120.2(3)
C15 ¹ C15 C16	120.3(3)	C52 C53 C54	118.2(3)
C16 C15 C14	120.1(3)	C59 C53 C52	119.1(3)
C15 C16 C17	119.6(3)	C59 C53 C54	122.7(3)
C15 C16 C18	120.5(3)	C53 C54 P2	123.6(2)
C17 C16 C18	119.9(3)	C71 C54 P2	115.6(2)
C13 ¹ C17 C16	119.0(3)	C71 C54 C53	120.8(3)
C21 C17 C13 ¹	122.3(3)	C56 C55 P2	118.3(2)
C21 C17 C16	118.7(3)	C58 C55 P2	122.9(2)
C16 C18 C30	118.0(3)	C58 C55 C56	118.7(3)
C19 C18 C16	119.5(3)	O7 C56 C55	110.5(3)
C19 C18 C30	122.5(3)	O8 C56 O7	124.3(7)

Table S3-3. Bond Angles for 3-4-*trans*.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C18	C19	C20	119.0(3)	O8	C56	C55	124.4(7)
C18	C19	C22	122.2(3)	O8A	C56	O7	118(2)
C20	C19	C22	118.8(3)	O8A	C56	C55	123.8(18)
C21	C20	C19	122.0(3)	C55	C58	C59	126.7(3)
C20	C21	C17	120.9(3)	C55	C58	C62	118.6(3)
C19	C22	C23	114.4(3)	C59	C58	C62	114.7(3)
C26	C22	C19	126.4(3)	C53	C59	C58	121.6(3)
C26	C22	C23	119.0(3)	C53	C59	C60	119.2(3)
O2	C23	C22	123.0(4)	C60	C59	C58	119.1(3)
O2	C23	O24	125.1(4)	C61	C60	C59	122.3(3)
O24	C23	C22	111.6(3)	C60	C61	C51	120.3(3)
C23	O24	C25	114.7(3)	O9	C62	C58	124.7(4)
C22	C26	P1	122.8(2)	O9	C62	O63	125.1(4)
C22	C26	C27	118.8(3)	O63	C62	C58	110.1(4)
C27	C26	P1	118.4(2)	C62	O63	C64	111.0(5)
O3	C27	C26	111.1(3)	C66	C65	P2	118.8(2)
O5	C27	O3	121.6(17)	C66	C65	C1	119.0(3)
O5	C27	C26	121(3)	C1	C65	P2	122.0(2)
O5A	C27	O3	123.6(6)	C67	C66	C65	120.5(3)
O5A	C27	C26	124.6(9)	C68	C67	C66	119.8(3)
C30	C29	C14	122.2(3)	C67	C68	C69	120.2(3)
C18	C30	P1	123.9(2)	C68	C69	C1	120.1(3)
C29	C30	P1	115.0(2)	C69	C1	C65	120.4(3)
C29	C30	C18	121.0(3)	C54	C71	C49	122.4(3)
C32	C31	P1	122.0(2)	C7	C8	C9	113.3(3)
C33	C31	P1	119.0(3)	C63	C37A	C38	107.7(13)

¹-X,1-Y,1-Z; ²1-X,1-Y,2-Z

3.2.5. DFT and TD-DFT data of precursor and target species.

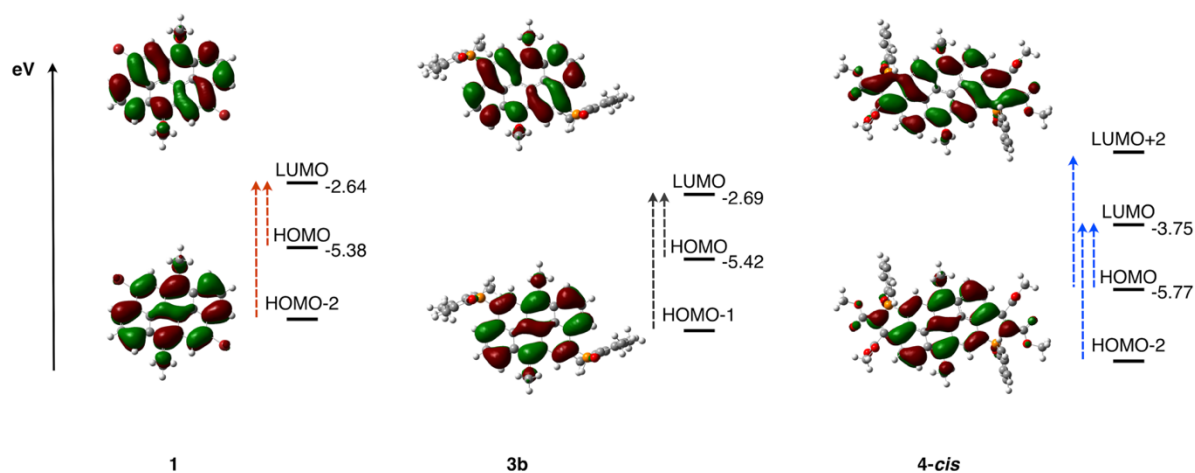


Figure S3-5. FMOs along with the involved electronic transitions based on TD-DFT calculations of **2-S1**, **3-3b**, **3-4-cis**. The oscillator strength of **3-1** for $H \rightarrow L$, and $H-2 \rightarrow L$ are $f = 0.47$ and 0.86 ; of **3-3b** for $H \rightarrow L$, and $H-1 \rightarrow L$ are $f = 0.44$ and $f = 0.58$; and of **3-4-cis** for $H \rightarrow L$, $H-2 \rightarrow L$, $H \rightarrow L+2$ are $f = 0.75$, $f = 0.32$, and $f = 0.89$, respectively.

3.2.6. Absorption and emission spectra of all species.

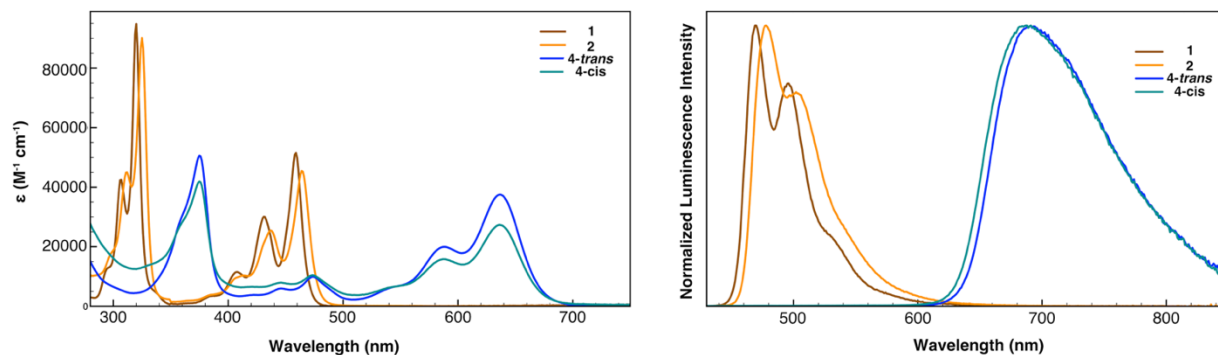


Figure S3-6. Absorption (left), and emission (right) spectra of **2-S1**, **3-2**, **3-4-cis**, and **3-4-trans** in CH_2Cl_2 .

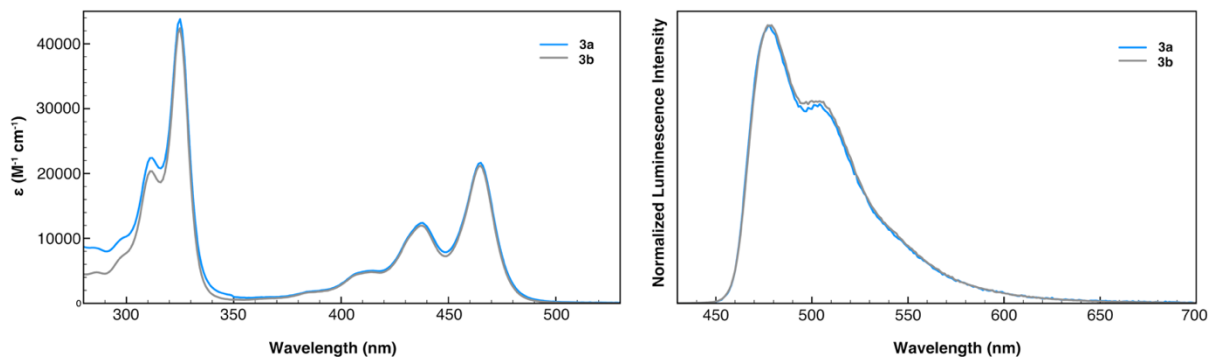


Figure S3-7. Absorption (left), and emission (right) spectra of **3-3a** and **3-3b** in CH_2Cl_2 .

3.2.7. Cyclic voltammetry of 3-4-*cis*.

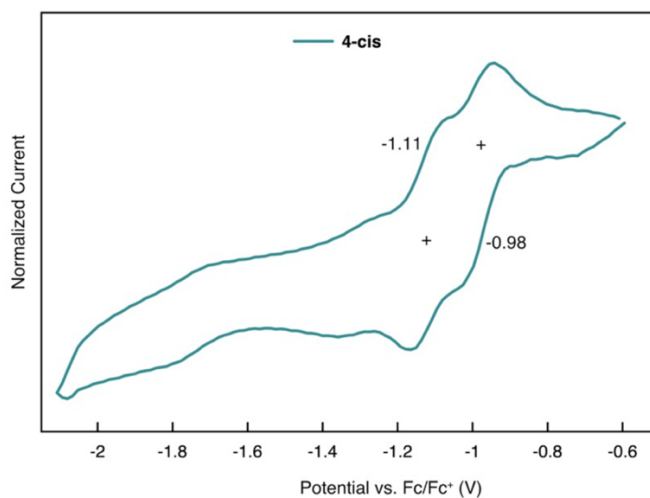


Figure S3-8. Cyclic voltammograms of **3-4-*cis*** run in CH₂Cl₂; scan rate: 100 mVs⁻¹, electrolyte: 0.1 M *n*-Bu₄PF₆, vs Fc/Fc⁺.

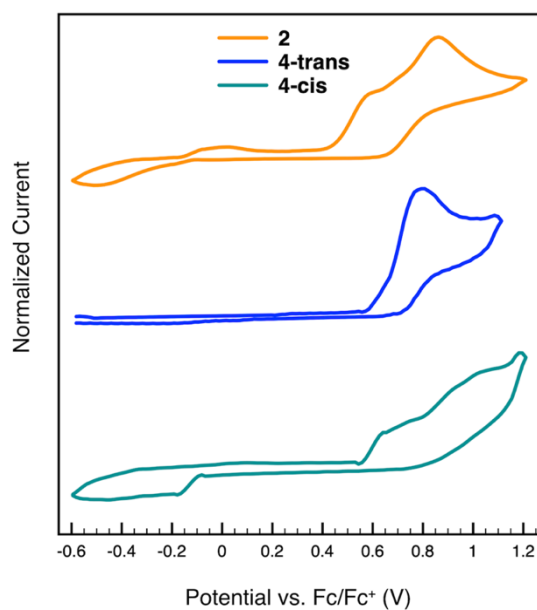
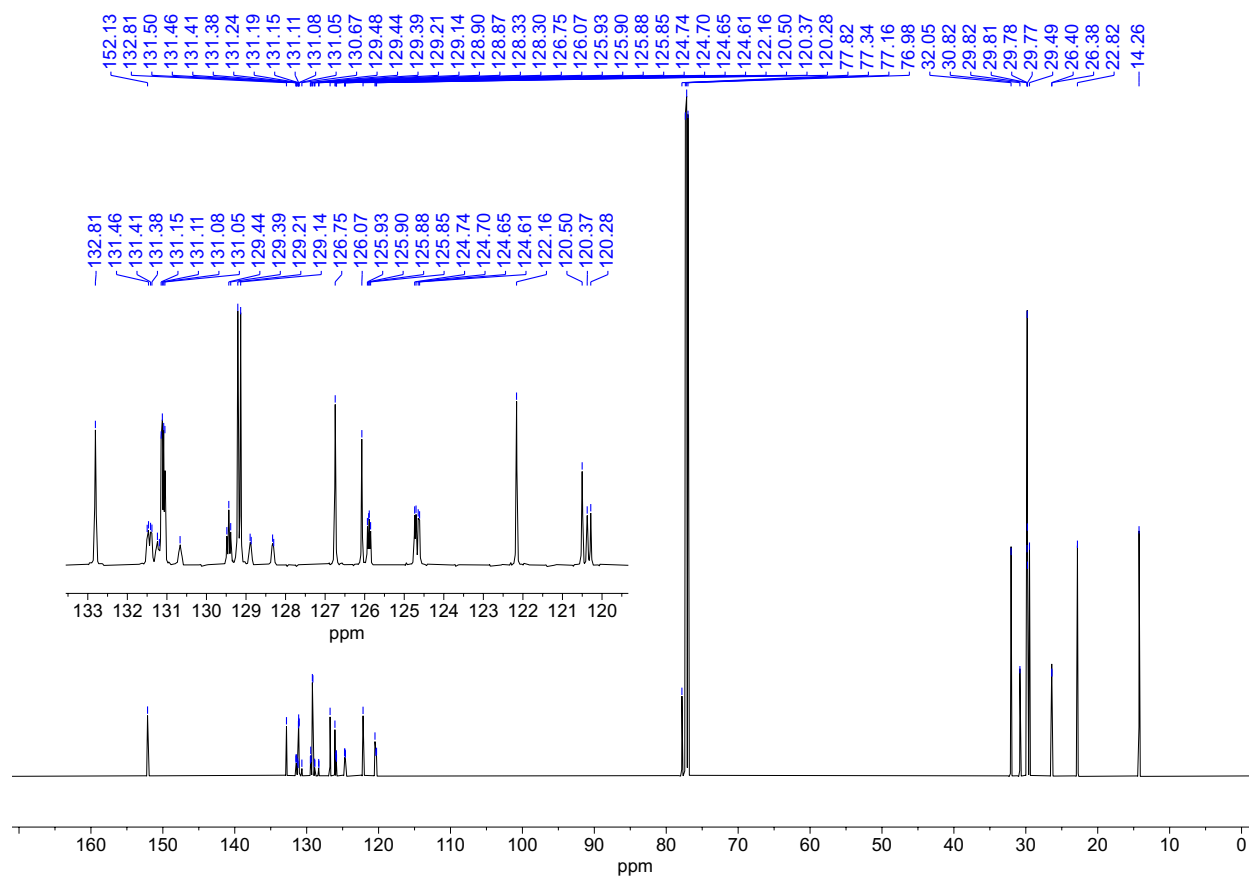


Figure S3-9. Cyclic voltammograms (oxidation) of **3-2**, **3-4-*trans***, **3-4-*cis*** run in CH₂Cl₂; scan rate: 100 mVs⁻¹, electrolyte: 0.1 M *n*-Bu₄PF₆, vs Fc/Fc⁺.

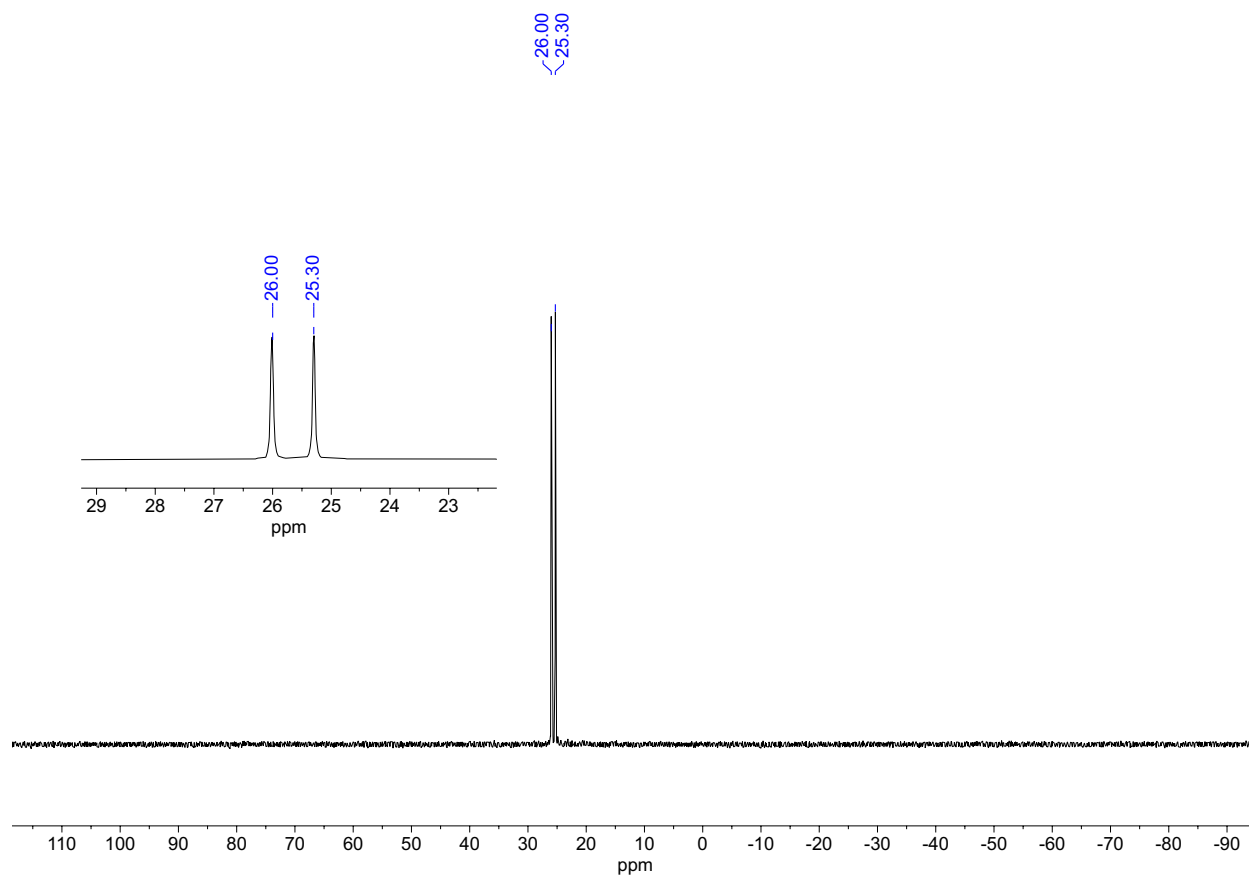
¹H NMR spectrum of **3-2** measured in CDCl₃ (300 MHz).



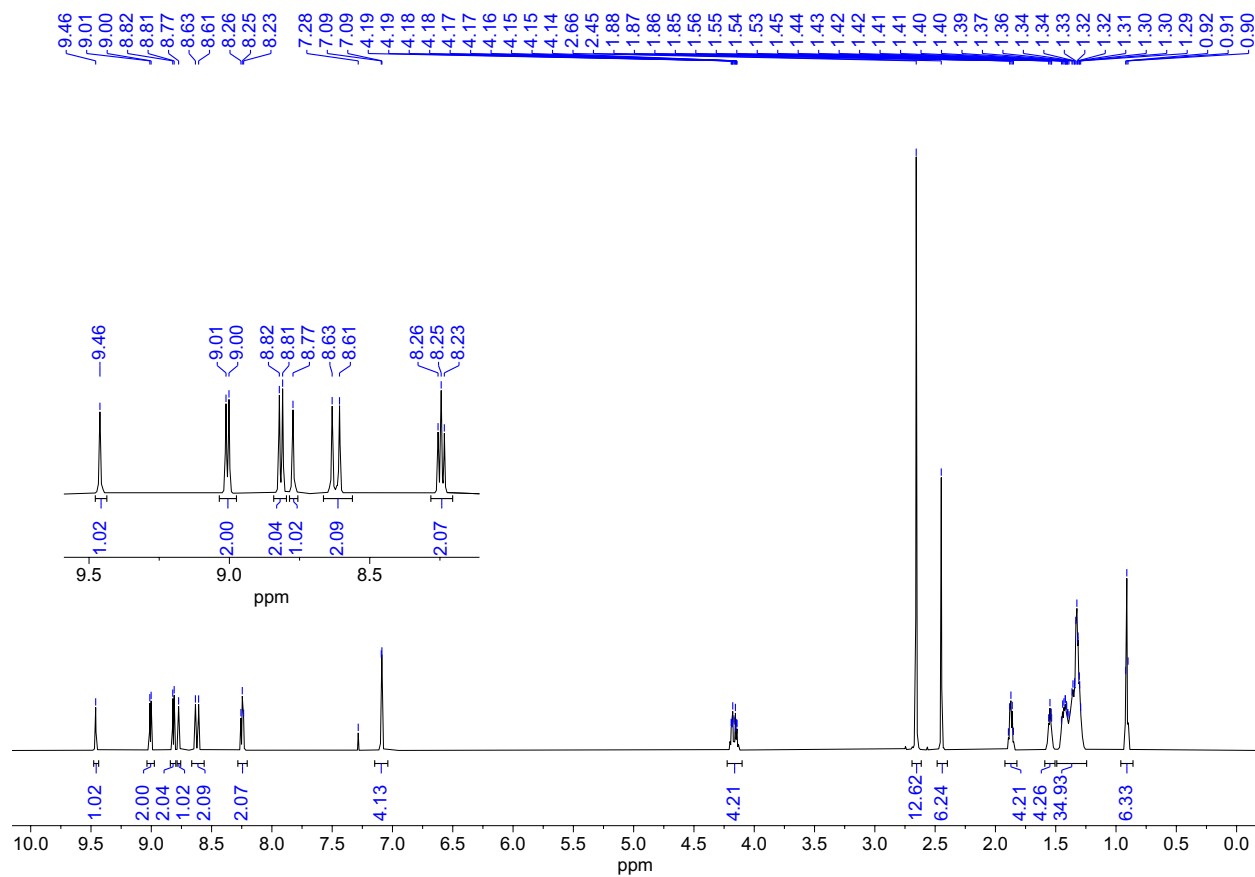
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3-2** measured in CDCl_3 (176 MHz).



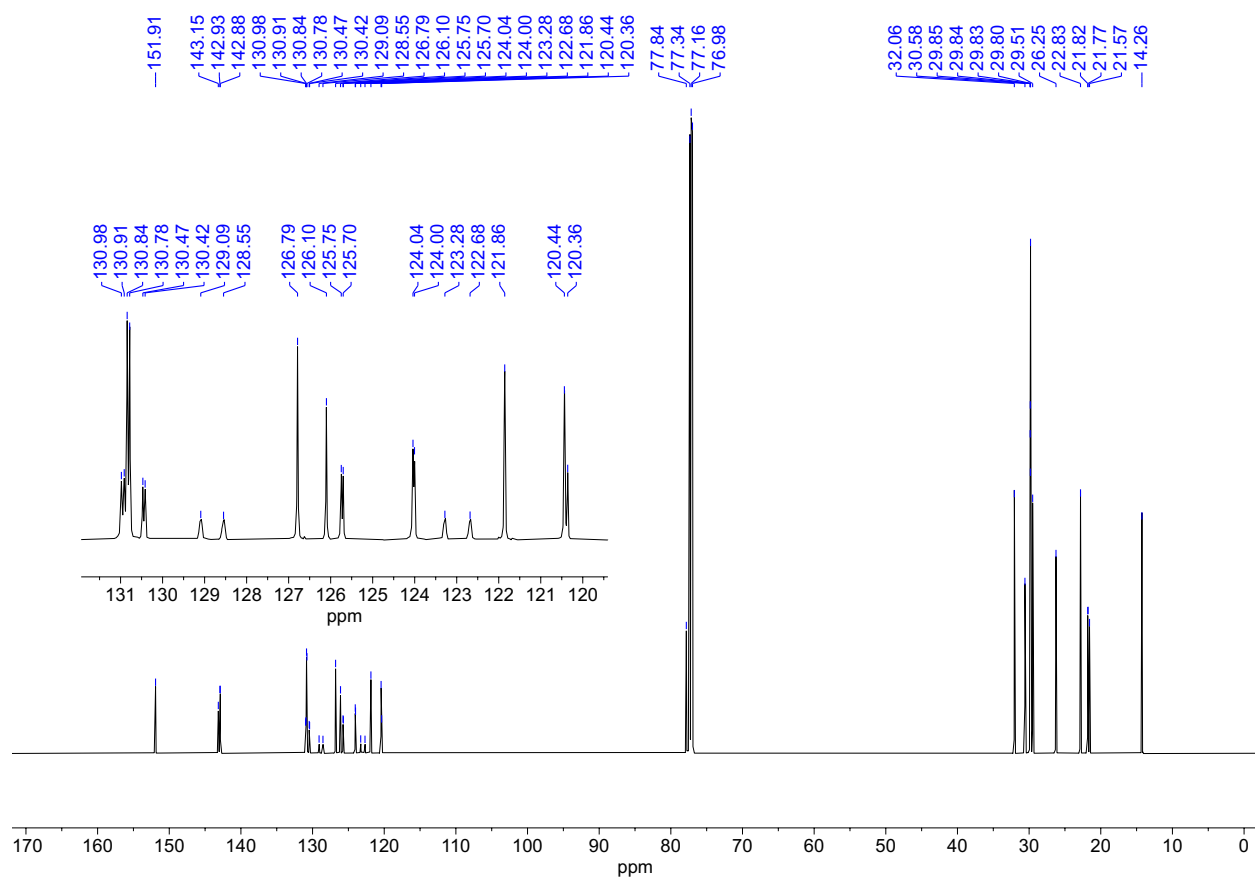
$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3-2** measured in CDCl_3 (121 MHz).



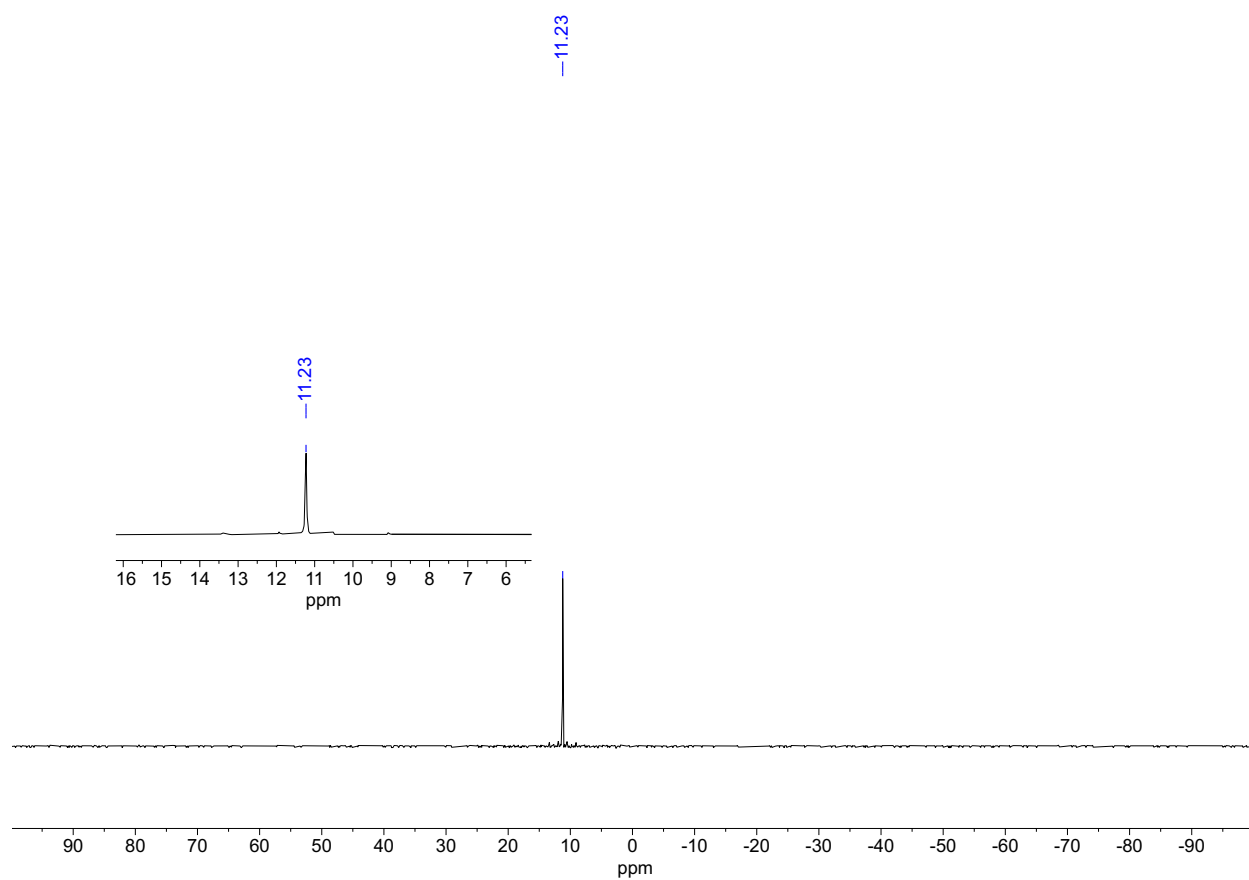
^1H NMR spectrum of **3-3a** measured in CDCl_3 (700 MHz).



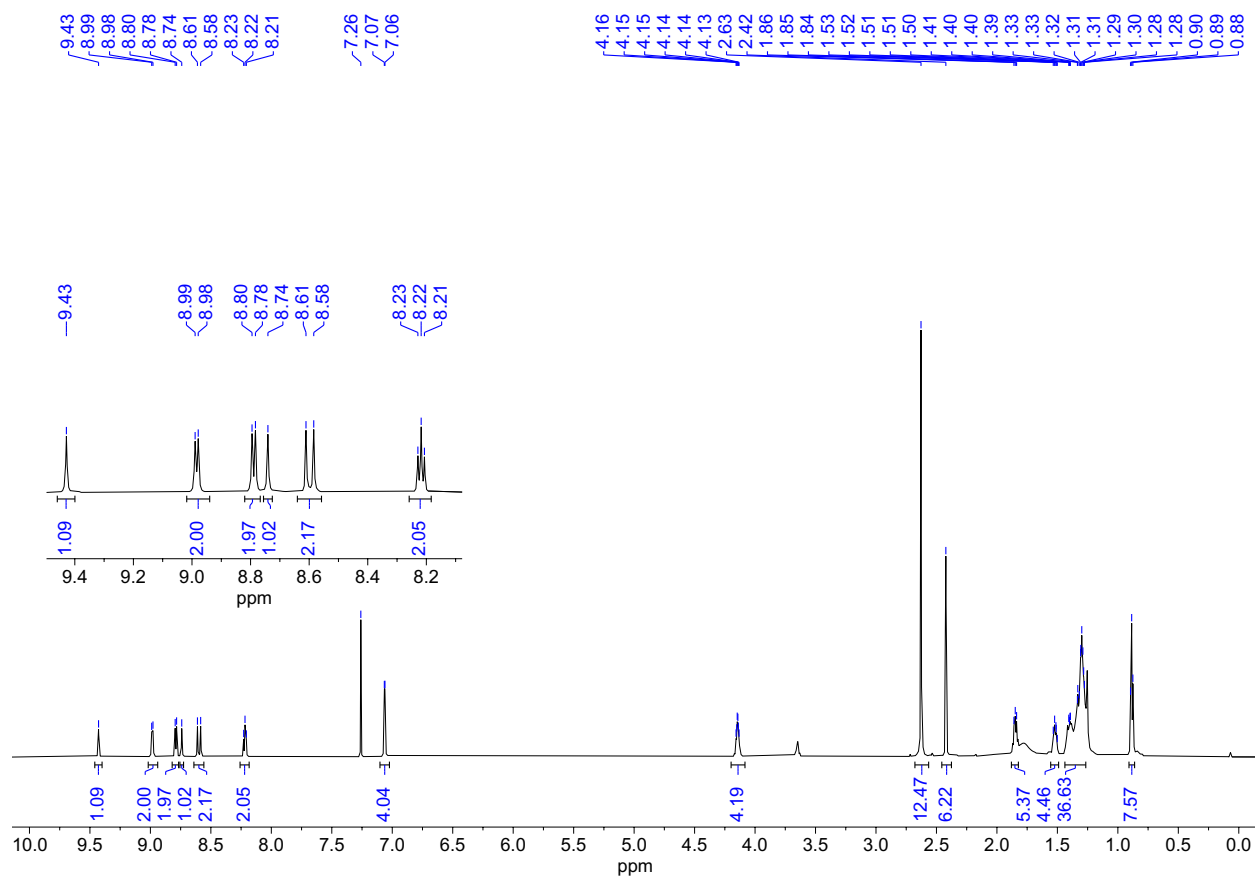
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3-3a** measured in CDCl_3 (176 MHz).



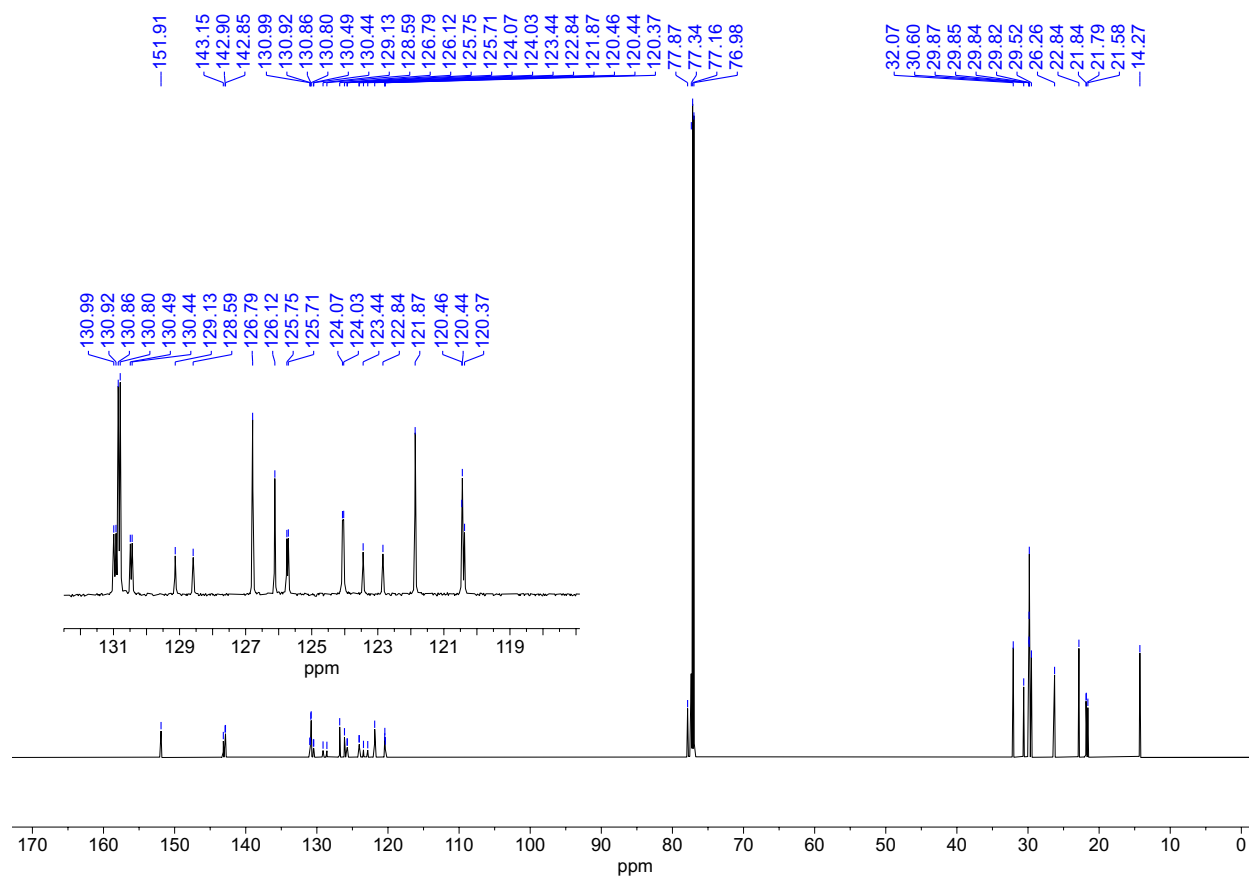
$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3-3a** measured in CDCl_3 (121 MHz).



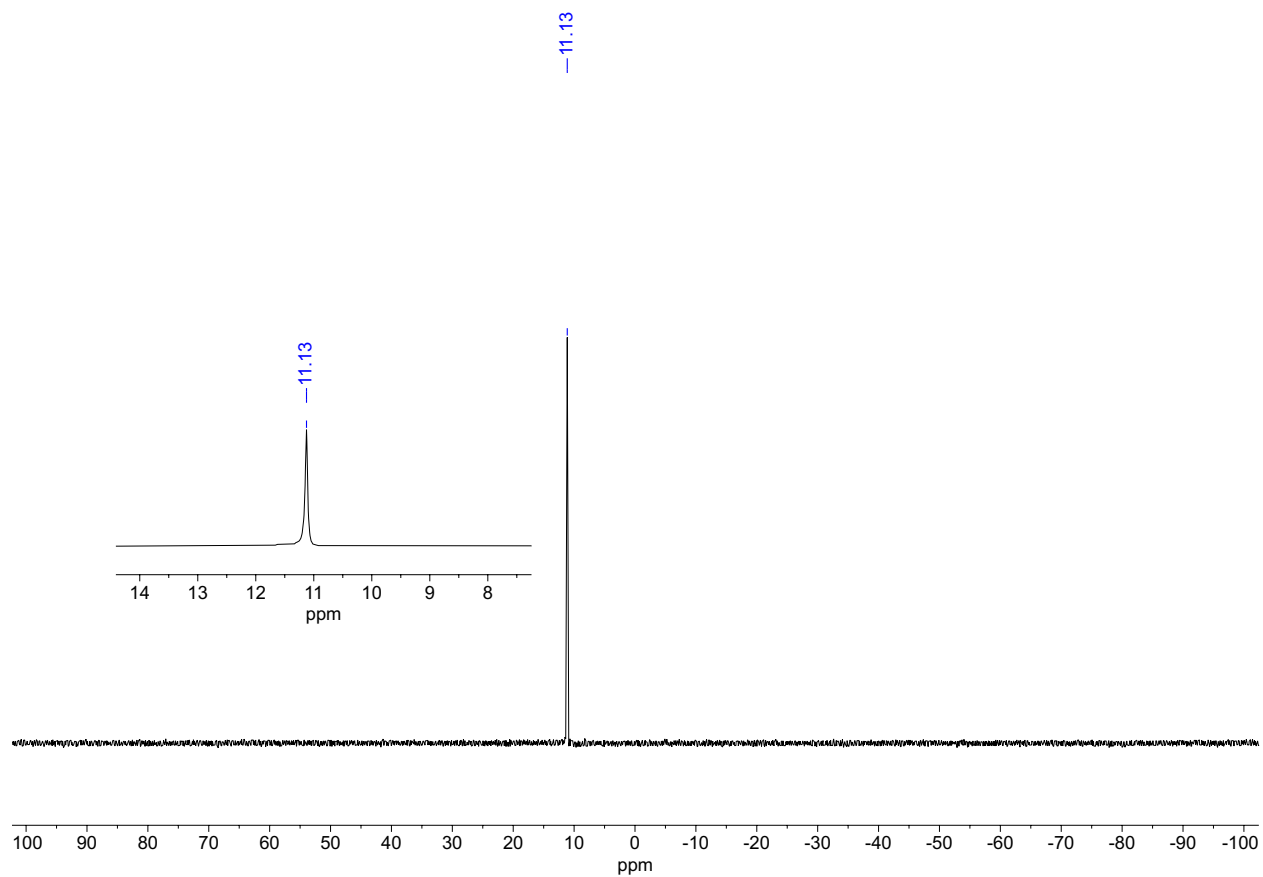
^1H NMR spectrum of **3-3b** measured in CDCl_3 (700 MHz).



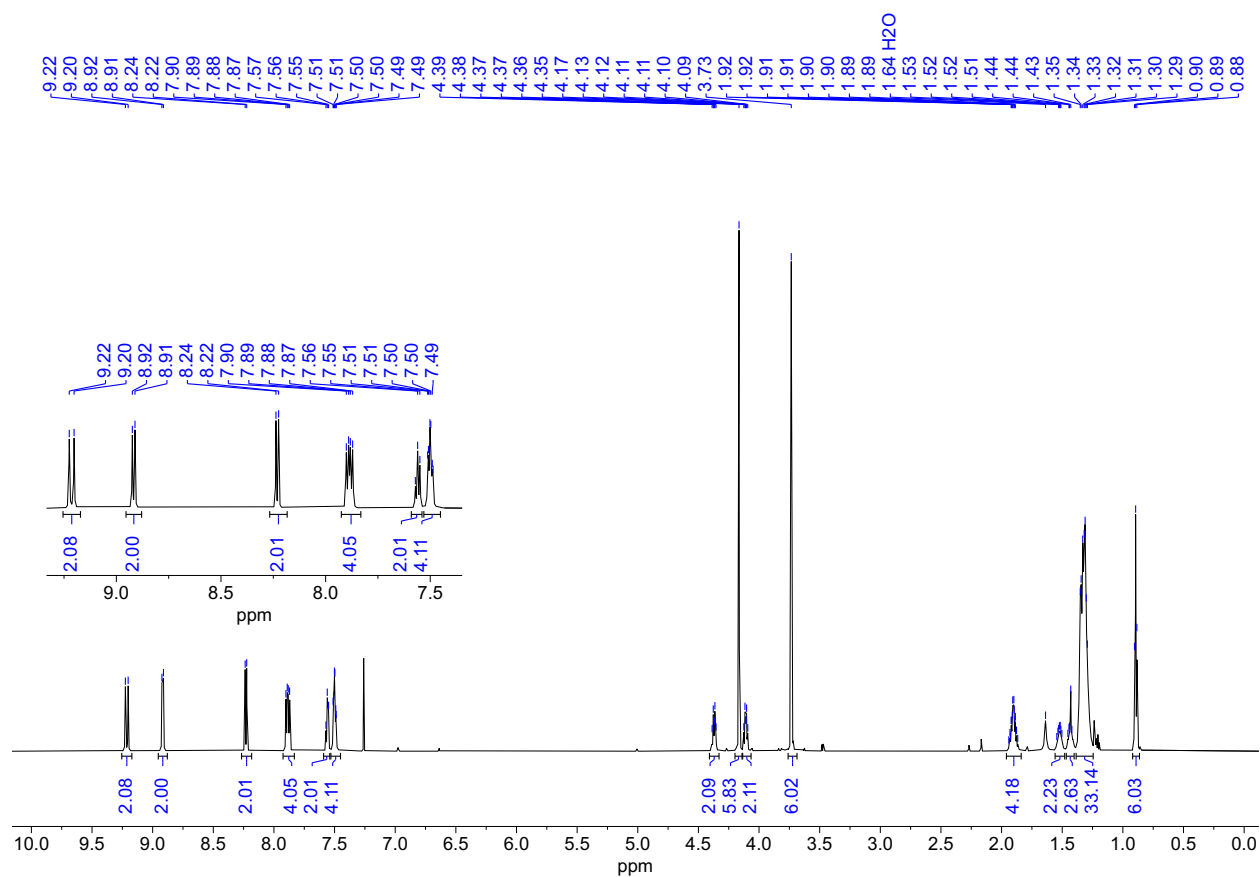
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3-3b** measured in CDCl_3 (176 MHz).



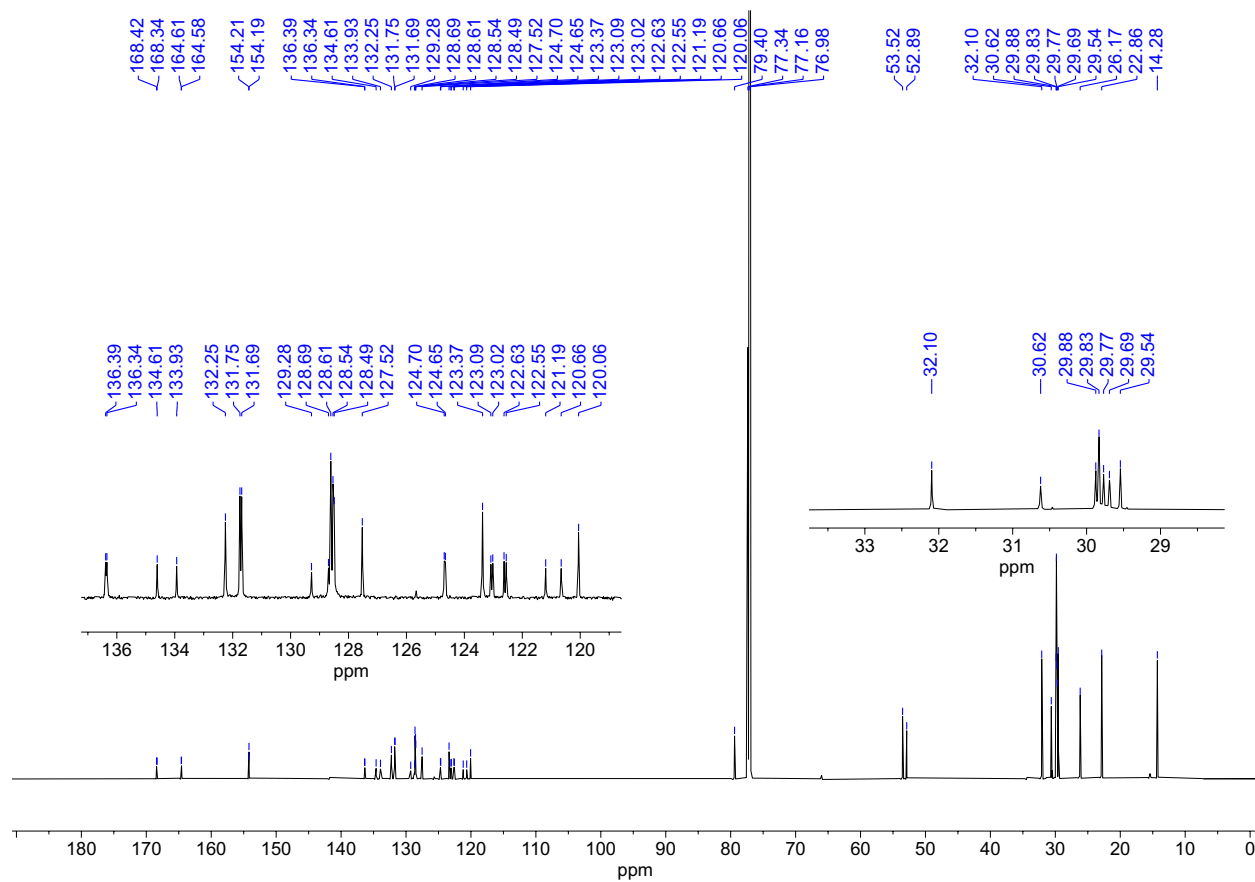
$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3-3b** measured in CDCl_3 (121 MHz).



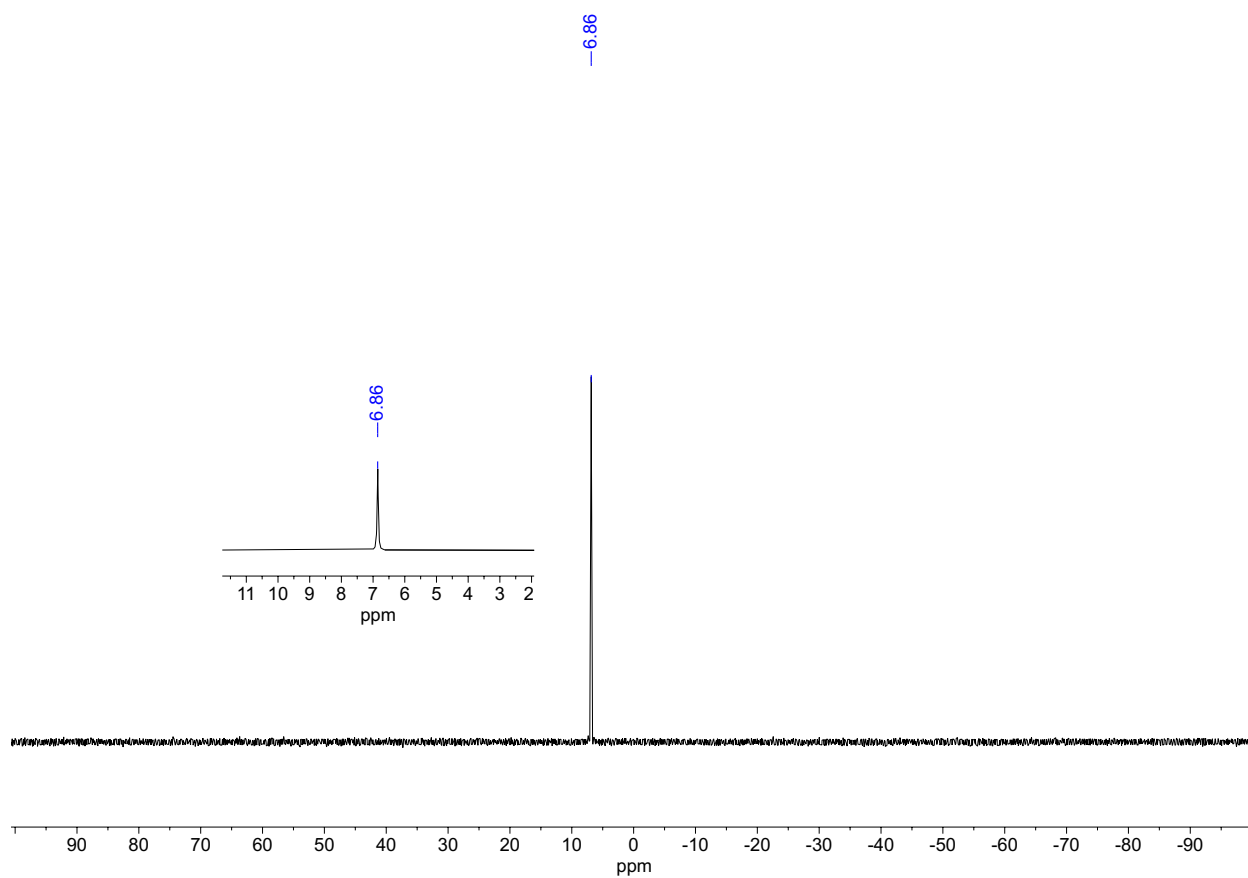
^1H NMR spectrum of **3-4-trans** measured in CDCl_3 (700 MHz).



$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3-4-trans** measured in CDCl_3 (176 MHz).



$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3-4-*trans*** measured in CDCl_3 (121 MHz).



The figure displays two ^1H NMR spectra of compound **1**. The top spectrum was recorded in CDCl_3 , and the bottom spectrum was recorded in $\text{DMSO}-d_6$. Both spectra show a complex pattern of peaks in the aromatic region (6.5–9.2 ppm) and aliphatic region (0.88–4.56 ppm). Integration values are provided for several peaks in both spectra.

Top Spectrum (CDCl_3):

- Chemical shifts (ppm): 9.22, 9.20, 8.92, 8.91, 8.23, 8.22, 7.88, 7.87, 7.86, 7.85, 7.55, 7.54, 7.53, 7.50, 7.49, 7.48, 7.47, 7.26, 4.38, 4.37, 4.17, 4.16, 4.15, 4.14, 3.73, 1.94, 1.93, 1.92, 1.92, 1.92, 1.91, 1.91, 1.43, 1.38, 1.36, 1.36, 1.35, 1.34, 1.33, 1.33, 1.32, 1.31, 1.30, 1.29, 1.29, 1.26, 1.26, 0.89, 0.88.
- Integration values: 1.99, 2.00, 1.98, 3.99, 2.23, 4.23.

Bottom Spectrum ($\text{DMSO}-d_6$):

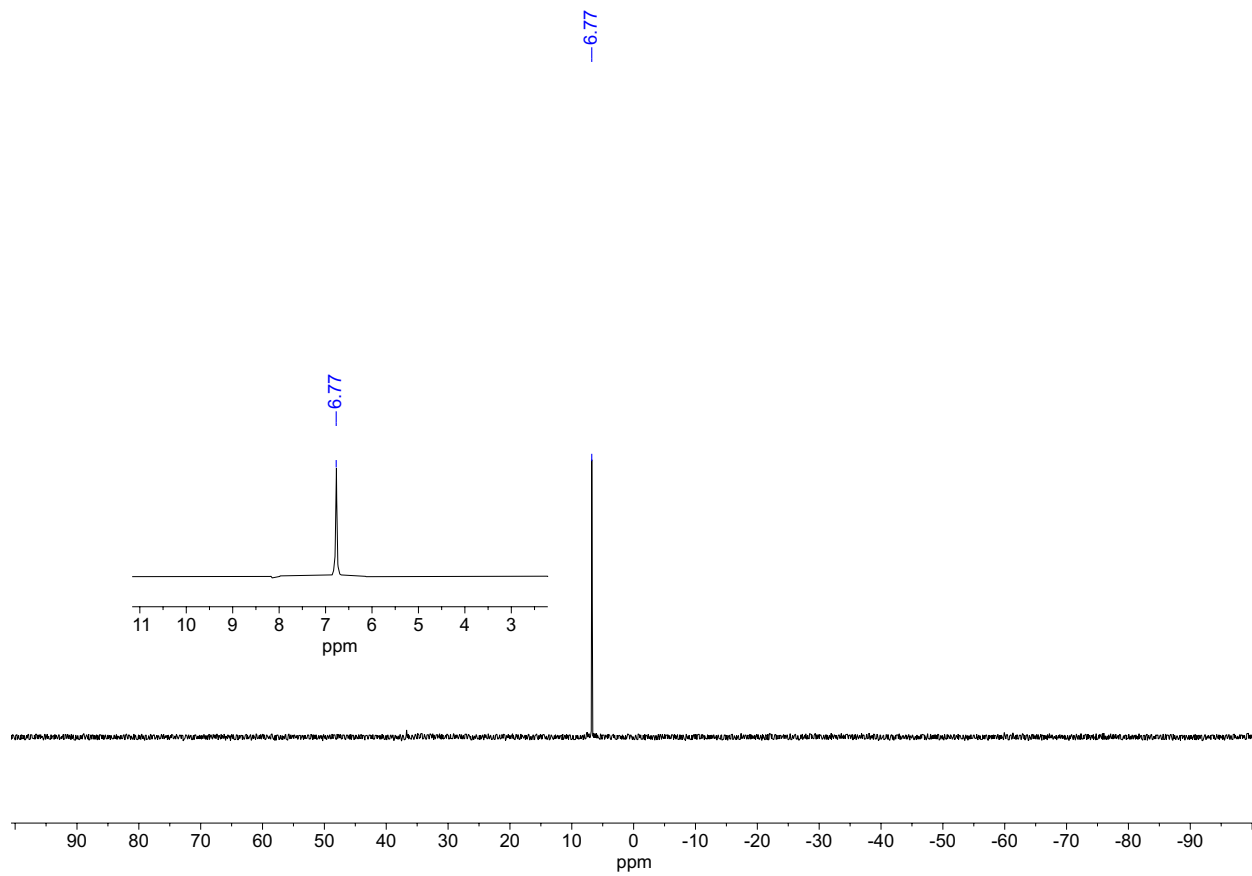
- Chemical shifts (ppm): 9.25, 9.22, 8.95, 8.94, 8.26, 8.25, 7.90, 7.89, 7.88, 7.86, 7.85, 7.55, 7.54, 7.53, 7.50, 7.49, 7.48, 7.47, 7.26, 4.38, 4.37, 4.17, 4.16, 4.15, 4.14, 3.73, 1.94, 1.93, 1.92, 1.92, 1.92, 1.91, 1.91, 1.43, 1.38, 1.36, 1.36, 1.35, 1.34, 1.33, 1.33, 1.32, 1.31, 1.30, 1.29, 1.29, 1.26, 1.26, 0.89, 0.88.
- Integration values: 1.99, 2.00, 1.98, 3.99, 2.23, 4.23, 2.00, 5.80, 2.04, 5.50, 4.56, 2.39, 2.56, 36.86, 6.63.

13C NMR Spectrum (CDCl₃) of Compound 10a

Chemical Shifts (ppm):

- 168.48, 168.39, 164.60, 164.57, 154.15, 154.14, 136.27, 136.23, 134.62, 133.95, 132.24, 132.22, 131.69, 131.63, 129.21, 128.63, 128.60, 128.55, 128.53, 128.50, 127.52, 124.69, 124.65, 123.40, 123.10, 123.04, 122.64, 122.56, 121.27, 120.74, 120.07, 79.42, 77.34, 77.16, 76.98, 53.56, 52.89, 32.09, 30.64, 29.88, 29.83, 29.77, 29.70, 29.54, 29.50, 29.44, 29.38, 29.32, 29.26, 29.20, 29.14, 29.08, 29.02, 28.96, 28.90, 28.84, 28.78, 28.72, 28.66, 28.60, 28.54, 28.48, 28.42, 28.36, 28.30, 28.24, 28.18, 28.12, 28.06, 28.00, 27.94, 27.88, 27.82, 27.76, 27.70, 27.64, 27.58, 27.52, 27.46, 27.40, 27.34, 27.28, 27.22, 27.16, 27.10, 27.04, 26.98, 26.92, 26.86, 26.80, 26.74, 26.68, 26.62, 26.56, 26.50, 26.44, 26.38, 26.32, 26.26, 26.20, 26.14, 26.08, 26.02, 25.96, 25.90, 25.84, 25.78, 25.72, 25.66, 25.60, 25.54, 25.48, 25.42, 25.36, 25.30, 25.24, 25.18, 25.12, 25.06, 25.00, 24.94, 24.88, 24.82, 24.76, 24.70, 24.64, 24.58, 24.52, 24.46, 24.40, 24.34, 24.28, 24.22, 24.16, 24.10, 24.04, 23.98, 23.92, 23.86, 23.80, 23.74, 23.68, 23.62, 23.56, 23.50, 23.44, 23.38, 23.32, 23.26, 23.20, 23.14, 23.08, 23.02, 22.96, 22.90, 22.84, 22.78, 22.72, 22.66, 22.60, 22.54, 22.48, 22.42, 22.36, 22.30, 22.24, 22.18, 22.12, 22.06, 22.00, 21.94, 21.88, 21.82, 21.76, 21.70, 21.64, 21.58, 21.52, 21.46, 21.40, 21.34, 21.28, 21.22, 21.16, 21.10, 21.04, 20.98, 20.92, 20.86, 20.80, 20.74, 20.68, 20.62, 20.56, 20.50, 20.44, 20.38, 20.32, 20.26, 20.20, 20.14, 20.08, 20.02, 19.96, 19.90, 19.84, 19.78, 19.72, 19.66, 19.60, 19.54, 19.48, 19.42, 19.36, 19.30, 19.24, 19.18, 19.12, 19.06, 19.00, 18.94, 18.88, 18.82, 18.76, 18.70, 18.64, 18.58, 18.52, 18.46, 18.40, 18.34, 18.28, 18.22, 18.16, 18.10, 18.04, 17.98, 17.92, 17.86, 17.80, 17.74, 17.68, 17.62, 17.56, 17.50, 17.44, 17.38, 17.32, 17.26, 17.20, 17.14, 17.08, 17.02, 16.96, 16.90, 16.84, 16.78, 16.72, 16.66, 16.60, 16.54, 16.48, 16.42, 16.36, 16.30, 16.24, 16.18, 16.12, 16.06, 16.00, 15.94, 15.88, 15.82, 15.76, 15.70, 15.64, 15.58, 15.52, 15.46, 15.40, 15.34, 15.28, 15.22, 15.16, 15.10, 15.04, 14.98, 14.92, 14.86, 14.80, 14.74, 14.68, 14.62, 14.56, 14.50, 14.44, 14.38, 14.32, 14.26, 14.20, 14.14, 14.08, 14.02, 13.96, 13.90, 13.84, 13.78, 13.72, 13.66, 13.60, 13.54, 13.48, 13.42, 13.36, 13.30, 13.24, 13.18, 13.12, 13.06, 13.00, 12.94, 12.88, 12.82, 12.76, 12.70, 12.64, 12.58, 12.52, 12.46, 12.40, 12.34, 12.28, 12.22, 12.16, 12.10, 12.04, 11.98, 11.92, 11.86, 11.80, 11.74, 11.68, 11.62, 11.56, 11.50, 11.44, 11.38, 11.32, 11.26, 11.20, 11.14, 11.08, 11.02, 10.96, 10.90, 10.84, 10.78, 10.72, 10.66, 10.60, 10.54, 10.48, 10.42, 10.36, 10.30, 10.24, 10.18, 10.12, 10.06, 10.00, 9.94, 9.88, 9.82, 9.76, 9.70, 9.64, 9.58, 9.52, 9.46, 9.40, 9.34, 9.28, 9.22, 9.16, 9.10, 9.04, 8.98, 8.92, 8.86, 8.80, 8.74, 8.68, 8.62, 8.56, 8.50, 8.44, 8.38, 8.32, 8.26, 8.20, 8.14, 8.08, 8.02, 7.96, 7.90, 7.84, 7.78, 7.72, 7.66, 7.60, 7.54, 7.48, 7.42, 7.36, 7.30, 7.24, 7.18, 7.12, 7.06, 7.00, 6.94, 6.88, 6.82, 6.76, 6.70, 6.64, 6.58, 6.52, 6.46, 6.40, 6.34, 6.28, 6.22, 6.16, 6.10, 6.04, 5.98, 5.92, 5.86, 5.80, 5.74, 5.68, 5.62, 5.56, 5.50, 5.44, 5.38, 5.32, 5.26, 5.20, 5.14, 5.08, 5.02, 4.96, 4.90, 4.84, 4.78, 4.72, 4.66, 4.60, 4.54, 4.48, 4.42, 4.36, 4.30, 4.24, 4.18, 4.12, 4.06, 4.00, 3.94, 3.88, 3.82, 3.76, 3.70, 3.64, 3.58, 3.52, 3.46, 3.40, 3.34, 3.28, 3.22, 3.16, 3.10, 3.04, 29.98, 29.92, 29.86, 29.80, 29.74, 29.68, 29.62, 29.56, 29.50, 29.44, 29.38, 29.32, 29.26, 29.20, 29.14, 29.08, 29.02, 28.96, 28.90, 28.84, 28.78, 28.72, 28.66, 28.60, 28.54, 28.48, 28.42, 28.36, 28.30, 28.24, 28.18, 28.12, 28.06, 28.00, 27.94, 27.88, 27.82, 27.76, 27.70, 27.64, 27.58, 27.52, 27.46, 27.40, 27.34, 27.28, 27.22, 27.16, 27.10, 27.04, 26.98, 26.92, 26.86, 26.80, 26.74, 26.68, 26.62, 26.56, 26.50, 26.44, 26.38, 26.32, 26.26, 26.20, 26.14, 26.08, 26.02, 25.96, 25.90, 25.84, 25.78, 25.72, 25.66, 25.60, 25.54, 25.48, 25.42, 25.36, 25.30, 25.24, 25.18, 25.12, 25.06, 25.00, 24.94, 24.88, 24.82, 24.76, 24.70, 24.64, 24.58, 24.52, 24.46, 24.40, 2

$^3\text{P}\{^1\text{H}\}$ NMR spectrum of **3-4-*cis*** measured in CDCl_3 (121 MHz).



3.4. X,Y,Z Coordinates of optimized geometries by DFT calculations of all the synthesized conjugated materials.

Compound 2-S1

C	-2.98785	0.97651	-0.58913
C	-3.81673	2.08315	-0.37829
C	-3.27815	3.35378	-0.11961
C	-1.90825	3.54974	-0.08535
C	-1.02523	2.46722	-0.31592
C	-1.56358	1.15984	-0.55972
H	-3.94894	4.1907	0.05324
H	-1.49803	4.53103	0.12635
C	0.39041	2.6389	-0.30422
C	-0.6853	0.06028	-0.77275
C	0.71664	0.25242	-0.73066
C	1.25576	1.56341	-0.486
C	2.68408	1.71826	-0.4266
H	3.06915	2.70732	-0.19815
C	1.59495	-0.84478	-0.95522
C	3.01903	-0.65985	-0.93144
C	3.53519	0.66799	-0.62489
C	-3.50408	-0.36255	-0.84208
C	-1.22402	-1.25027	-1.02096
C	-2.65257	-1.40987	-1.05493
H	-3.03841	-2.40236	-1.26619
C	-0.3583	-2.32203	-1.22271
C	1.05711	-2.14783	-1.22164
C	1.94033	-3.22141	-1.49087
H	1.53048	-4.19832	-1.72268
C	3.84825	-1.75292	-1.20241

C	3.30971	-3.019	-1.48306
H	3.97991	-3.84546	-1.70229
O	0.90468	3.89146	-0.05501
O	-0.87439	-3.5714	-1.48413
C	-1.03624	-4.42421	-0.33352
H	-1.42431	-5.3713	-0.71216
H	-0.07676	-4.58958	0.16894
H	-1.74966	-3.98547	0.37363
C	1.10925	4.71583	-1.22067
H	0.1665	4.87426	-1.75591
H	1.49131	5.66927	-0.852
H	1.84132	4.25616	-1.89433
H	4.92521	-1.62385	-1.2203
H	-4.8947	1.96993	-0.42154
Br	-5.376	-0.73868	-0.89229
Br	5.40505	1.01572	-0.44934

Compound 3-2

C	5.9421	0.33802	-0.2154
C	7.34395	0.35355	-0.16407
C	8.01389	1.45681	0.38921
C	7.28202	2.54726	0.88756
C	5.88011	2.53222	0.83082
C	5.22259	1.42387	0.28209
H	9.084	1.4669	0.4305
H	7.79391	3.38808	1.3085
C	5.05352	3.72417	1.36641
C	3.70003	1.38541	0.21911
C	2.95204	2.45772	0.69972
C	3.64978	3.6842	1.28653

C	2.77937	4.85288	1.77628
H	3.23782	5.72884	2.1839
C	1.42269	2.41824	0.64449
C	0.67068	3.50868	1.12165
C	1.37446	4.76855	1.68809
C	5.19095	-0.87152	-0.82442
C	3.00777	0.15695	-0.37891
C	3.77901	-0.9104	-0.87152
H	3.28784	-1.76422	-1.28858
C	1.46889	0.10454	-0.43392
C	0.71904	1.18316	0.06205
C	-0.81067	1.15676	0.0334
H	-1.33421	0.31061	-0.3601
C	-0.74016	3.47822	1.08977
C	-1.50978	2.25963	0.5308
H	-2.57997	2.26098	0.52357
O	5.71176	4.85887	1.93854
O	0.80911	-1.03633	-0.98917
C	0.59305	-0.82515	-2.38747
H	0.10347	-1.67926	-2.80686
H	-0.02005	0.04068	-2.5261
H	1.53337	-0.67817	-2.87605
C	5.88519	4.65191	3.34517
H	6.48171	3.77782	3.50645
H	6.375	5.50187	3.77383
H	4.92873	4.52102	3.80752
P	6.15131	-2.26546	-1.49393
P	0.34999	6.16565	2.24352
C	0.65532	7.61191	1.18387
C	1.56899	7.52939	0.12514
C	-0.03032	8.80943	1.42732

C	1.78972	8.64323	-0.6971
H	2.09693	6.61696	-0.05611
C	0.19053	9.92238	0.60657
H	-0.72351	8.87282	2.24047
C	1.09917	9.83878	-0.45712
H	2.48524	8.58037	-1.50766
H	-0.33443	10.83629	0.79164
H	1.26536	10.68845	-1.08605
O	-1.10327	5.78545	2.1533
C	5.70238	-2.54902	-3.23631
C	4.38053	-2.85094	-3.5917
C	6.69035	-2.46465	-4.2264
C	4.05082	-3.06894	-4.93722
H	3.62307	-2.91482	-2.83854
C	6.3607	-2.68113	-5.56939
H	7.69852	-2.23532	-3.95523
C	5.04065	-2.98436	-5.9265
H	3.04209	-3.30035	-5.20961
H	7.11671	-2.61436	-6.32253
H	4.7885	-3.15119	-6.95316
O	7.6207	-1.94878	-1.40589
H	-1.28991	4.31794	1.46146
H	7.9026	-0.47556	-0.54522
H	5.88544	-3.37476	-0.7735
H	0.65808	6.46777	3.52171

Compound **3-3a**

C	-3.03437	0.90405	-0.64822
C	-3.91334	1.95232	-0.36149
C	-3.44167	3.22634	-0.00812

C	-2.0838	3.48641	0.05314
C	-1.1481	2.46626	-0.24395
C	-1.62015	1.15532	-0.58832
H	-4.15503	4.01349	0.21953
H	-1.72364	4.46853	0.33893
C	0.25708	2.70501	-0.20202
C	-0.68581	0.12	-0.86997
C	0.70477	0.37593	-0.79579
C	1.17659	1.68931	-0.45078
C	2.5943	1.90832	-0.3656
H	2.92479	2.89647	-0.06056
C	1.63925	-0.65721	-1.08498
C	3.05336	-0.40441	-1.02925
C	3.50345	0.92283	-0.62941
C	-3.48476	-0.43382	-1.01127
C	-1.15748	-1.19296	-1.21713
C	-2.5755	-1.41639	-1.28567
H	-2.90658	-2.40928	-1.57418
C	-0.23762	-2.20459	-1.48089
C	1.16746	-1.96289	-1.44878
C	2.10307	-2.97184	-1.78242
H	1.74309	-3.94809	-2.08792
C	3.93232	-1.43871	-1.3627
C	3.46054	-2.70546	-1.74116
H	4.17325	-3.4811	-2.00709
O	0.70582	3.96042	0.14288
O	-0.68825	-3.45642	-1.8365
C	-0.82478	-4.39341	-0.7502
H	-1.15853	-5.33021	-1.19974
H	0.134	-4.54568	-0.24216
H	-1.57018	-4.04068	-0.02793

C	0.88734	4.87301	-0.95902
H	-0.05379	5.02258	-1.49966
H	1.21584	5.81587	-0.5184
H	1.65155	4.49787	-1.64913
P	-5.24836	-0.87934	-1.25285
P	5.2689	1.41504	-0.54443
C	5.75485	2.34876	-2.04835
C	5.69725	1.69803	-3.31169
C	6.23675	3.68292	-1.96706
C	6.09497	2.39611	-4.45737
C	6.61593	4.33179	-3.15111
C	6.54918	3.71697	-4.40377
H	6.05051	1.88805	-5.4186
H	6.98393	5.35355	-3.0847
O	5.65522	2.05482	0.77141
C	-6.19292	-0.65596	0.30567
C	-5.85261	-1.44747	1.43705
C	-7.28374	0.25101	0.38631
C	-6.58403	-1.29658	2.62056
C	-7.97468	0.3622	1.6014
C	-7.64284	-0.39082	2.73047
H	-6.31756	-1.90942	3.47931
H	-8.808	1.0594	1.65936
O	-5.86571	-0.25162	-2.4835
H	5.00181	-1.26798	-1.34223
H	-4.98325	1.78962	-0.40542
H	-5.11484	-2.28348	-1.34921
H	5.86549	0.14897	-0.7443
C	6.3972	4.46577	-0.67711
H	5.4616	4.56283	-0.1182
H	7.10553	3.98376	0.00228

H	6.76097	5.47285	-0.90296
C	6.93847	4.45799	-5.66079
H	6.05759	4.91386	-6.13273
H	7.64918	5.26312	-5.44723
H	7.39007	3.78528	-6.39804
C	5.23494	0.26593	-3.49389
H	5.84228	-0.44374	-2.91871
H	4.19366	0.12368	-3.18672
H	5.31069	-0.02108	-4.54658
C	-4.73657	-2.47336	1.43407
H	-4.89151	-3.25174	0.67656
H	-3.75774	-2.02264	1.24005
H	-4.68378	-2.97205	2.40609
C	-7.78496	1.10246	-0.76526
H	-7.00664	1.73555	-1.20022
H	-8.16465	0.48525	-1.58474
H	-8.59452	1.75068	-0.41604
C	-8.39121	-0.22058	4.03109
H	-7.89522	0.52161	4.67115
H	-9.4157	0.12682	3.86114
H	-8.43367	-1.15913	4.59422

Compound **3-3b**

C	-2.98785	0.97651	-0.58913
C	-3.81673	2.08315	-0.37829
C	-3.27815	3.35378	-0.11961
C	-1.90825	3.54974	-0.08535
C	-1.02523	2.46722	-0.31592
C	-1.56358	1.15984	-0.55972
H	-3.94894	4.1907	0.05324

H	-1.49803	4.53103	0.12635
C	0.39041	2.6389	-0.30422
C	-0.6853	0.06028	-0.77275
C	0.71664	0.25242	-0.73066
C	1.25576	1.56341	-0.486
C	2.68408	1.71826	-0.4266
H	3.06915	2.70732	-0.19815
C	1.59495	-0.84478	-0.95522
C	3.01903	-0.65985	-0.93144
C	3.53519	0.66799	-0.62489
C	-3.50408	-0.36255	-0.84208
C	-1.22402	-1.25027	-1.02096
C	-2.65257	-1.40987	-1.05493
H	-3.03841	-2.40236	-1.26619
C	-0.3583	-2.32203	-1.22271
C	1.05711	-2.14783	-1.22164
C	1.94033	-3.22141	-1.49087
H	1.53048	-4.19832	-1.72268
C	3.84825	-1.75292	-1.20241
C	3.30971	-3.019	-1.48306
H	3.97991	-3.84546	-1.70229
O	0.90468	3.89146	-0.05501
O	-0.87439	-3.5714	-1.48413
C	-1.03624	-4.42421	-0.33352
H	-1.42431	-5.3713	-0.71216
H	-0.07676	-4.58958	0.16894
H	-1.74966	-3.98547	0.37363
C	1.10925	4.71583	-1.22067
H	0.1665	4.87426	-1.75591
H	1.49131	5.66927	-0.852
H	1.84132	4.25616	-1.89433

P	-5.29134	-0.72167	-0.89002
P	5.32034	0.99997	-0.45729
C	5.88909	0.20153	1.08349
C	5.18504	0.35052	2.28923
C	7.07559	-0.54492	1.05804
C	5.66486	-0.24591	3.45714
C	7.55175	-1.14312	2.22888
C	6.84776	-0.99384	3.42733
H	5.11624	-0.1289	4.38783
H	8.47073	-1.72262	2.20377
O	6.18647	0.65684	-1.65016
C	-5.9311	-0.58969	0.81578
C	-5.24231	-1.14616	1.90554
C	-7.16	0.05254	1.02452
C	-5.77978	-1.05816	3.19143
C	-7.69408	0.14108	2.31377
C	-7.00546	-0.41394	3.39636
H	-5.24206	-1.48845	4.03202
H	-8.64566	0.64197	2.4705
O	-6.11308	0.06737	-1.88639
H	4.92521	-1.62385	-1.2203
H	-4.8947	1.96993	-0.42154
H	-5.25759	-2.11282	-1.14342
H	5.28755	2.37835	-0.14199
C	7.84589	-0.70148	-0.26624
H	7.23687	-1.22488	-0.97338
H	8.09049	0.2657	-0.65307
H	8.74553	-1.25405	-0.09238
C	7.37311	-1.65192	4.71672
H	7.40364	-2.71375	4.58834
H	8.3578	-1.28956	4.92645

H	6.72292	-1.40968	5.53126
C	3.8791	1.16545	2.33385
H	3.97837	2.03244	1.71467
H	3.07026	0.56283	1.97672
H	3.68128	1.4673	3.34115
C	-3.88889	-1.85002	1.69476
H	-3.92597	-2.43329	0.79848
H	-3.11453	-1.11635	1.61106
H	-3.68578	-2.48946	2.52828
C	-7.91187	0.66156	-0.17356
H	-7.32795	1.45211	-0.5966
H	-8.07729	-0.09443	-0.91249
H	-8.85278	1.05014	0.156
C	-7.59419	-0.31638	4.81603
H	-7.47518	0.68138	5.18372
H	-8.63463	-0.56463	4.78852
H	-7.08182	-0.99813	5.46225

Compound **3-4-*trans***

C	6.04851	0.2868	-0.32774
C	7.46376	0.25989	-0.181
C	8.13936	1.44605	0.1574
C	7.44127	2.63883	0.36356
C	6.05424	2.65359	0.26546
C	5.36345	1.48194	-0.0657
H	9.20279	1.43516	0.25967
H	7.97168	3.53968	0.59783
C	5.2799	3.95753	0.52571
C	3.83723	1.49913	-0.13743
C	3.13164	2.66551	0.16312

C	3.88623	3.94787	0.49016
C	3.08713	5.21265	0.78203
H	3.5953	6.13577	0.96719
C	1.59712	2.67425	0.17526
C	0.8869	3.85539	0.52684
C	1.6861	5.16557	0.81733
C	5.23051	-0.95814	-0.76248
C	3.0943	0.22716	-0.53472
C	3.82025	-0.92862	-0.86102
H	3.29721	-1.80472	-1.18225
C	1.55211	0.22643	-0.56694
C	0.85084	1.38301	-0.1919
C	-0.67045	1.3775	-0.13849
H	-1.22217	0.49948	-0.39903
C	-0.54664	3.82214	0.61169
C	-1.33077	2.53588	0.26191
H	-2.39902	2.53735	0.3264
O	5.98204	5.1684	0.81115
O	0.83535	-0.94695	-0.96813
C	0.61474	-0.91153	-2.38204
H	0.07736	-1.7867	-2.68228
H	0.04563	-0.04032	-2.63375
H	1.55626	-0.88021	-2.88891
C	6.15993	5.29897	2.22161
H	6.71841	4.46388	2.5885
H	6.69059	6.20417	2.4306
H	5.20345	5.32741	2.70191
P	6.10029	-2.49516	-1.14743
P	0.81058	6.68412	1.22345
C	-0.95112	6.31485	1.30041
C	-1.43258	5.02309	1.05167

C	1.39	7.30338	2.83124
C	2.73178	7.67911	2.99049
C	0.50143	7.40672	3.90766
C	3.18343	8.15683	4.22762
H	3.40929	7.60225	2.16672
C	0.95872	7.8712	5.14933
H	-0.52453	7.12805	3.78354
C	2.29801	8.24919	5.30922
H	4.20512	8.45069	4.34646
H	0.28444	7.93667	5.97553
H	2.64543	8.60841	6.25503
C	-1.94486	7.43501	1.64502
C	-2.94108	4.76301	1.22925
O	-3.41303	3.62029	0.99241
O	-1.52724	8.59662	1.88881
O	-3.34421	7.15254	1.68016
O	-3.80663	5.81107	1.67318
C	-5.13175	5.55982	1.20542
H	-5.4706	4.61921	1.58736
H	-5.78238	6.33778	1.54416
H	-5.13504	5.5323	0.13644
C	-4.06942	8.30698	1.25228
H	-5.11749	8.09241	1.25783
H	-3.86881	9.12252	1.91594
H	-3.76408	8.57043	0.26089
C	8.34377	-1.00926	-0.36478
C	7.85832	-2.24344	-0.82223
C	5.85413	-2.94249	-2.89942
C	6.87109	-3.6114	-3.60235
C	4.68929	-2.55038	-3.57286
C	6.69836	-3.93057	-4.95795

H	7.78053	-3.87797	-3.10434
C	4.51864	-2.86813	-4.92872
H	3.92964	-2.00625	-3.05241
C	5.51811	-3.56685	-5.61784
H	7.46834	-4.45144	-5.48943
H	3.62216	-2.57936	-5.43752
H	5.37997	-3.82161	-6.64837
C	9.84124	-0.9111	-0.0155
C	8.85038	-3.39771	-1.04531
O	10.31987	0.17802	0.39606
O	10.68014	-2.06315	-0.14963
O	10.24664	-3.19065	-0.81207
O	8.43877	-4.51945	-1.43504
C	11.68173	-2.04809	0.87251
H	12.28082	-1.16827	0.77255
H	11.21029	-2.05187	1.83297
H	12.30235	-2.91481	0.77765
C	10.998	-3.99048	-1.72642
H	10.75518	-3.70475	-2.72871
H	12.04371	-3.84143	-1.5555
H	10.7568	-5.02277	-1.58101
O	5.57646	-3.60108	-0.27356
O	1.06789	7.72886	0.16951

Compound **3-4-*cis***

C	6.04851	0.2868	-0.32774
C	7.46376	0.25989	-0.181
C	8.13936	1.44605	0.1574
C	7.44127	2.63883	0.36356
C	6.05424	2.65359	0.26546

C	5.36345	1.48194	-0.0657
H	9.20279	1.43516	0.25967
H	7.97168	3.53968	0.59783
C	5.2799	3.95753	0.52571
C	3.83723	1.49913	-0.13743
C	3.13164	2.66551	0.16312
C	3.88623	3.94787	0.49016
C	3.08713	5.21265	0.78203
H	3.5953	6.13577	0.96719
C	1.59712	2.67425	0.17526
C	0.8869	3.85539	0.52684
C	1.6861	5.16557	0.81733
C	5.23051	-0.95814	-0.76248
C	3.0943	0.22716	-0.53472
C	3.82025	-0.92862	-0.86102
H	3.29721	-1.80472	-1.18225
C	1.55211	0.22643	-0.56694
C	0.85084	1.38301	-0.1919
C	-0.67045	1.3775	-0.13849
H	-1.22217	0.49948	-0.39903
C	-0.54664	3.82214	0.61169
C	-1.33077	2.53588	0.26191
H	-2.39902	2.53735	0.3264
O	5.98204	5.1684	0.81115
O	0.83535	-0.94695	-0.96813
C	0.61474	-0.91153	-2.38204
H	0.07736	-1.7867	-2.68228
H	0.04563	-0.04032	-2.63375
H	1.55626	-0.88021	-2.88891
C	6.15993	5.29897	2.22161
H	6.71841	4.46388	2.5885

H	6.69059	6.20417	2.4306
H	5.20345	5.32741	2.70191
P	6.10029	-2.49516	-1.14743
P	0.81058	6.68412	1.22345
C	-0.95112	6.31485	1.30041
C	-1.43258	5.02309	1.05167
C	1.39	7.30338	2.83124
C	2.73178	7.67911	2.99049
C	0.50143	7.40672	3.90766
C	3.18343	8.15683	4.22762
H	3.40929	7.60225	2.16672
C	0.95872	7.8712	5.14933
H	-0.52453	7.12805	3.78354
C	2.29801	8.24919	5.30922
H	4.20512	8.45069	4.34646
H	0.28444	7.93667	5.97553
H	2.64543	8.60841	6.25503
C	-1.94486	7.43501	1.64502
C	-2.94108	4.76301	1.22925
O	-3.76704	5.3005	0.44597
O	-2.17939	7.72323	2.84714
O	-2.59489	8.1513	0.5945
O	-3.40723	3.90421	2.2732
C	-4.74208	4.26854	2.62439
H	-5.37317	4.17541	1.76503
H	-5.09575	3.62146	3.39866
H	-4.75802	5.28031	2.97012
C	-2.80642	9.50324	1.00589
H	-3.27495	10.04829	0.21349
H	-3.43611	9.52011	1.87134
H	-1.8646	9.95394	1.24118

C	8.34377	-1.00926	-0.36478
C	7.85832	-2.24344	-0.82223
C	9.84124	-0.9111	-0.0155
C	8.85038	-3.39771	-1.04531
O	10.66146	-0.50065	-0.87773
O	10.29209	-1.27646	1.29301
O	9.12047	-3.85686	-2.37311
O	9.42056	-3.94032	-0.06547
C	11.38977	-0.4402	1.6724
H	12.19337	-0.56932	0.97918
H	11.07591	0.58265	1.66877
H	11.71983	-0.70736	2.65477
C	9.38237	-5.26062	-2.33917
H	8.52611	-5.77106	-1.95
H	9.58723	-5.60981	-3.32965
H	10.22786	-5.45207	-1.71192
O	1.06789	7.72886	0.16951
C	5.46726	-3.83924	-0.09618
C	5.81204	-3.88952	1.25477
C	4.63734	-4.819	-0.64104
C	5.32753	-4.91973	2.06046
H	6.46697	-3.11737	1.68384
C	4.1518	-5.84904	0.16498
H	4.36536	-4.77943	-1.70574
C	4.49684	-5.89963	1.51551
H	5.59975	-4.95977	3.12515
H	3.49713	-6.62117	-0.26479
H	4.11489	-6.71179	2.15097
O	5.86895	-2.89249	-2.79446

3.5. References

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Chapter Four: Phosphorus-Incorporated Polycyclic Aromatic Hydrocarbons; From Quinoidal Conjugation to Doublet NIR Emission

This chapter is the result of a formal collaboration with Carlos Romero-Nieto at UCLM in Spain. I would like to thank Roberto Diaz-Rodriguez (Murugesu group, uOttawa) for performing the luminescence measurements of the PMMA films. I am also grateful of Jesse LeBlanc for performing the X-ray crystallography, and Dr. Avik Bhattacharjee for his help with DFT calculations of the paramagnetic species.

Important Note: Number **4** before every number, scheme, and figure in this chapter indicates they belong to **Chapter Four**.

4.1. Introduction

The family of polycyclic aromatic hydrocarbons (PAHs) are comprised of many structurally diverse organic frameworks that, in addition to serving as semiconductors through strong π - π interactions, possess extended conjugation responsible for their widely pursued properties in materials chemistry, as introduced in Chapter 1.^{1,2} The preparation of heteroatom-based PAHs has emerged as a robust approach towards accessing structural diversity and distinct properties once only attainable with transition metals.^{3,4} Despite the extensive literature on O-, N-, S-, and even B-incorporated systems, P-based PAHs are conspicuously underrepresented, as mentioned in Chapter 1.2 onwards.⁵⁻⁸ Overcoming this bottleneck would clearly be advantageous, as numerous smaller P-based synthons—reported by other research groups—not only exhibit tunable electronics resulting in adjustable properties, but also offer to regulate molecular organization in the solid state via versatile exocyclic substituents.⁹⁻¹²

As a subclass of PAHs, vat dyes include large, conjugated scaffolds that are consistently endowed with at least two keto groups (see Chapter 1.3).¹³ While their unique π -delocalized backbones offer a clear advantage, a major caveat is their poor solubility in organic solvents. A primary remedial strategy—employed by us and other groups—involves sacrificing the keto groups for introducing solubilizing functionalities to the core structure. Consequently, reports on vat dye-based structures featuring the original keto groups remain scarce.¹⁴⁻¹⁶

The strategic position of the keto groups in Vat Orange 3 (VO3) specifically, facilitates a quinoidal conjugation pathway that is central to its electronic core structure and can enable exceptional stability towards obtaining further electrons. Additionally, embedding carbonyl groups within a π -system is a well-known method for increasing electron acceptor character, i.e., lowering the FMO energy levels, as well as enhancing the spin-orbit coupling and activating triplet excited states.^{17,18}

Our initial study on extending the conjugation of the parent VO3 core through merging it with two phosphacycles (Chapter 2) resulted in systems with electronics that could be readily modulated by substituent variation around the phosphorus centres.¹¹ Moreover, the core modification also involved the conversion of the keto groups into -OC₁₂H₂₅ moieties to improve solubility, which simultaneously altered the character of the functional groups to electron-donating. However, restoring the keto groups in these compounds would create a particularly intriguing conjugation scenario: four tethered Clar π -sextets (benzene with six π -electrons) forming a linear tetraphenyl unit (blue) that meets a quinoidal conjugation from the two keto groups (red), precisely in the middle, while the outer rims involve the conjugation of phosphine oxide vs. keto units bridged through a butadiene linker (black; Figure 4-1). The distinct π -delocalized framework is surrounded by strong electron-withdrawing groups that should significantly increase the structural tolerance upon gaining electrons.

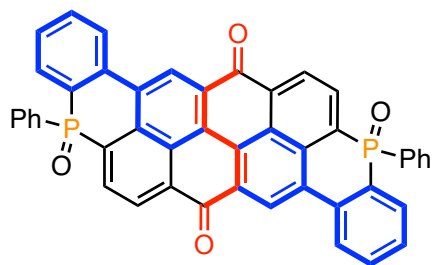


Figure 4-1. Proposed target structure containing keto groups.

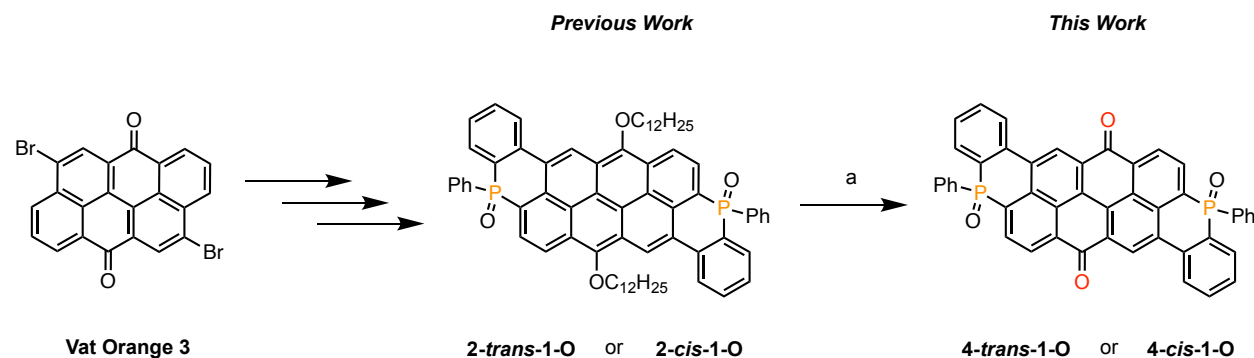
Consequently, we postulate that exploration of such system along with showcasing a novel method on liberation of the original keto group in Vat Orange 3 would be an worthwhile endeavour. It is particularly compelling to inspect the communication between the keto and phosphine oxide pairs, as well as their interaction with the tetraphenyl unit, along with their overall influence on the molecular orbitals in these systems. The electronics in the first-generation species with -OC₁₂H₂₅

side groups exhibited a great degree of tunability upon varying P-functionalities; due to the presence of major components in the conjugation of the new system, we aim to determine whether P-modification can still exert a pronounced electronic impact. Finally, the intensity and quality of light absorption and luminescence will provide valuable insights on the phosphorus-annulated scaffold incorporating the elusive native vat-dye core.

4.2. Synthesis and Characterization

The synthetic route toward isomers **4-*trans*-1-O** and **4-*cis*-1-O** (referring to P-substituents, Oxygen vs. Phenyl) is illustrated in Scheme 4-1. As mentioned in Chapter 2, by employing a few conventional synthetic steps, VO3 can be converted to the isomeric mixture of **2-*trans*-1-O** and **2-*cis*-1-O**, which are separable using column chromatography. In a different project (*unpublished*), we recently noticed that a mixture of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and triflic acid (TfOH) that is traditionally utilized for performing ring-annulation in PAHs (i.e., Scholl reaction), possesses the ability of cleaving the C₁₂H₂₅ chain to reinstate the original keto groups on the VO3 scaffold. The reaction presumably takes advantage of the high acidity of TfOH that protonates the etheric oxygen followed by elimination of the dodecyl chain and subsequent phenol generation. The next step is well-established DDQ oxidation of phenol to quinone.¹⁹ In order to test the generality of this procedure, DDQ and triflic acid mixture were reacted with the isolated pale orange isomers of **2-*trans*-1-O** and **2-*cis*-1-O**, giving rise to the clean transformation into isomerically pure **4-*trans*-1-O** and **4-*cis*-1-O** that have a dark purple colour. Both isomers were characterized by respective ³¹P{¹H} NMR shifts at 8.0 and 7.5 ppm and their corresponding ¹H NMR spectra. While **4-*trans*-1-O** and **4-*cis*-1-O** possess excellent ambient stability, their

strictly limited solubility in DCM and chloroform—particularly for the *trans* isomer—hindered the acquisition of satisfactory $^{13}\text{C}\{^1\text{H}\}$ NMR data, despite several attempts.



Scheme 4-1. Synthetic procedure toward the first-generation and current phosphacyclic structures based on Vat Orange 3. (a) DDQ, TfOH, dichloromethane, R.T. (yields: 75% - **4-*trans*-1-O**; 82% - **4-*cis*-1-O**).

Single crystals of **4-*trans*-1-O** were grown from vapour diffusion of methanol into a chloroform solution at room temperature, and the solid-state structure was determined by X-ray crystallography. Due to steric hinderance of the H-atoms in the bay region, the terminal benzene rings experience a twist with an angle of 8.3° away from the exocyclic phenyl substituent. Notably, this value is slightly larger than the torsion angle of the parent structure (**2-*trans*-1-O**) confirming the supressing effect of the long alkyl chains on the out-of-conjugated-plane distortion. In striking contrast, removal of the $-\text{OC}_{12}\text{H}_{25}$ leads to a higher degree of molecular organization for **4-*trans*-1-O** (Figure 2-2) compared to the *trans* isomer of the first-generation analogue. The conjugated units in **4-*trans*-1-O** are packed in face-to-face slipped π -stacks at a distance of $3.4 \text{ \AA}$ with effective overlap between molecular planes, indicative of strong π - π interactions. The latter is a key criterion for organic semiconductors. The same short distance, albeit with smaller overlap, is also observed

between the neighbouring exocyclic P-phenyl rings belonging to the adjacent delocalized framework.

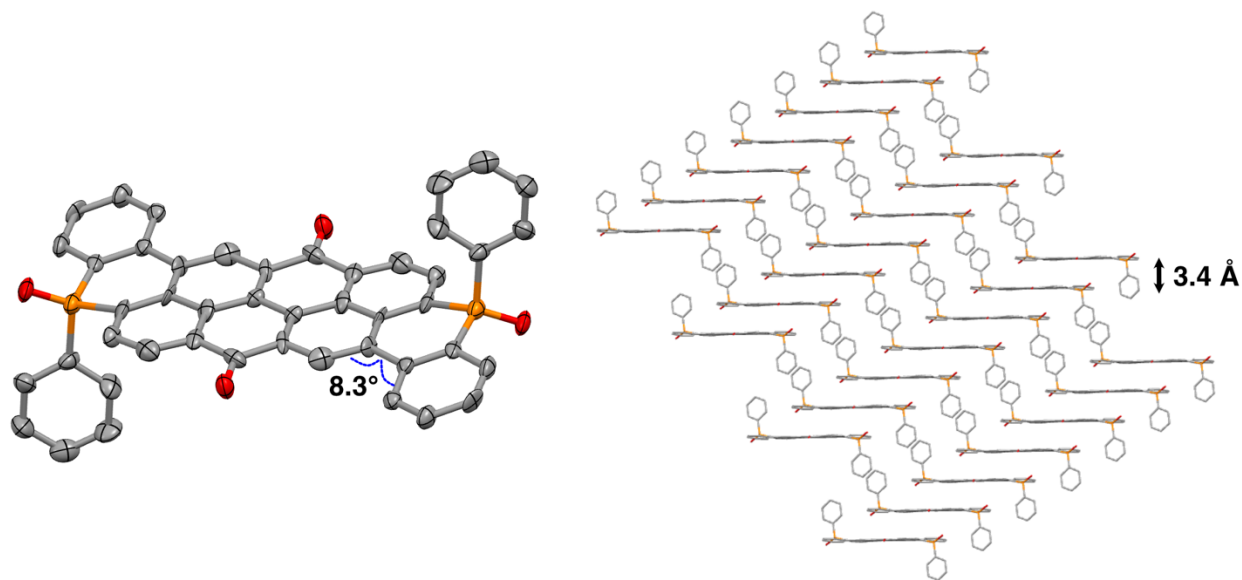
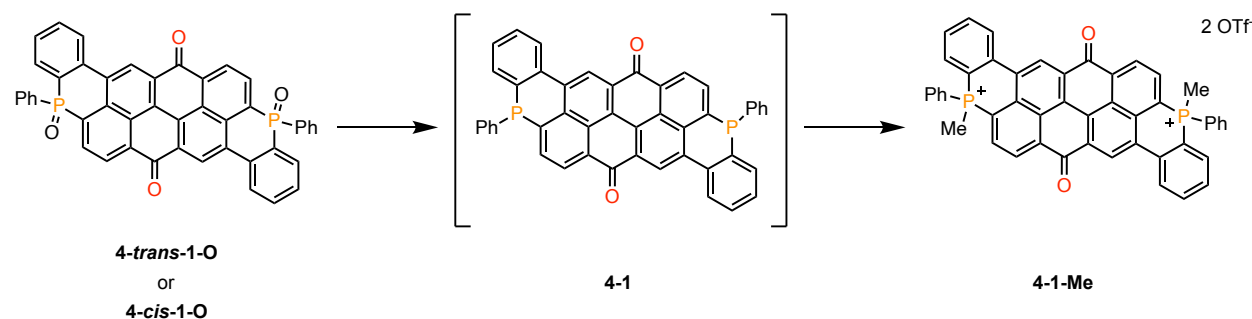


Figure 4-2. Solid-state structure (left) and molecular packing (right) in **4-*trans*-1-O** (ellipsoids at 50% probability, H atoms omitted for clarity).

With a view toward broadening the scope, methylation of the phosphorus centers was carried out based on a similar procedure elaborated in Chapter 2 (Scheme 4-2). First, the pentavalent phosphoryl P=O groups in **4-*trans*-1-O** or **4-*cis*-1-O** were reduced to the trivalent phosphines using excess of HSiCl_3 under microwave conditions at 150 °C. This again resulted in the formation of isomeric mixtures of **4-1** that could not be separated, irrespective of the nature of the pure isomer used as starting material. Moreover, due to the reactive nature of the trivalent phosphorus centres in **4-1**, it was used for the next step without further characterization. Subsequently, methyl triflate was added to complete the conversion toward the dicationic product **4-1-Me** that was also obtained as an inseparable mixture of *cis* and *trans* isomers.



Scheme 4-2. Conversion of **4-trans-1-O** or **4-cis-1-O** to **4-1-Me** using the procedure introduced in Chapter 2.

$^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy was conducted on **4-1-Me** revealing phosphorus signals at 0.4 and 0.5 ppm for the *cis* and *trans* isomers, respectively, in the expected range for methyl phosphonium centers and in good agreement with the observed shift for P-methylated analogue with $-\text{OC}_{12}\text{H}_{25}$. However, the signals also show signs of broadening, and possibly overlap with other unresolved peaks, suggestive on the presence of additional species. A comparable broadening was also observed in the ^1H NMR spectrum of the diastereomeric mixture, complicating the peak assignments.

To reveal the nature of the compounds in the mixture, high-resolution mass spectrometry (HRMS) was performed on the sample confirming the presence of the desired dicationic product **4-1-Me** – evident in a peak at 350.0862 (m/z). To our surprise, however, another peak with the mass of a monocationic (and thus likely radical) species **4-2-Me** (700.17 m/z, Figure S4-11) was also detected. This suggests that compound **4-1-Me** appears to be gaining an electron from the environment (e.g., solvent) and further studies were deemed necessary to elucidate the underlying reason (*vide infra*).

EPR spectroscopy conducted on the DCM solution of **4-1-Me** showed a weak signal confirming the presence of the monocationic radical species **4-2-Me** but also indicating that the transformation

occurs only partially. Interestingly, addition of DMSO to the methylated species induces a colour change from the original magenta to dark blue, corroborating the facile redox interaction of this species with organic solvents.

4.3. DFT Calculations and Electrochemistry

To obtain detailed information on the molecular orbitals and the energy levels of the target compounds, DFT calculations were conducted at the UB3LYP/6-31G(d) level of theory. The HOMO in **4-cis-1-O** displays excellent π -overlap with the entirety of the central aromatic tetraphenyl unit (Figure 4-3a). The perpendicular quinoidal conjugation pathway is also clearly contributing to the HOMO indicative of its stabilizing influence. Nevertheless, the LUMO is primarily localized on the quinoidal pathway, with contribution of the phosphoryl moieties present as well. Expectedly so, removal of $-\text{OC}_{12}\text{H}_{25}$ from the original structure and formation of **4-cis-1-O** has a significant stabilizing effect on the HOMO, lowering it by 0.63 eV to -6.01 eV. The stabilization of the LUMO is even stronger ($\Delta_{\text{E}} = -0.71$ eV), leading to the overall reduction of the energy gap to 2.45 eV (cf. **2-cis-1-O**: 2.53 eV). Moreover, the π -system of the P-methylated **4-1-Me** is manifested in a similar manner for both the HOMO and the LUMO. However, the cationic phosphorus centres induce yet another substantial stabilization of $\Delta_{\text{E}} = -0.74$ eV for both FMO energy levels in **4-1-Me**, validating the pronounced impact of P-modification. Interestingly, both HOMO and LUMO levels undergo identical reduction in energy, suggesting that despite the marked shift in the absolute energy levels, the energy gap remains the same. Most notably, the LUMO energy of **4-1-Me** drops to -4.30 eV, considerably lower than common electron acceptors such as PCBM- C_{60} (-3.70 eV). This value supports the pronounced tendency of **4-1-Me** for electron uptake under ambient conditions. (see SI for *trans* isomer).

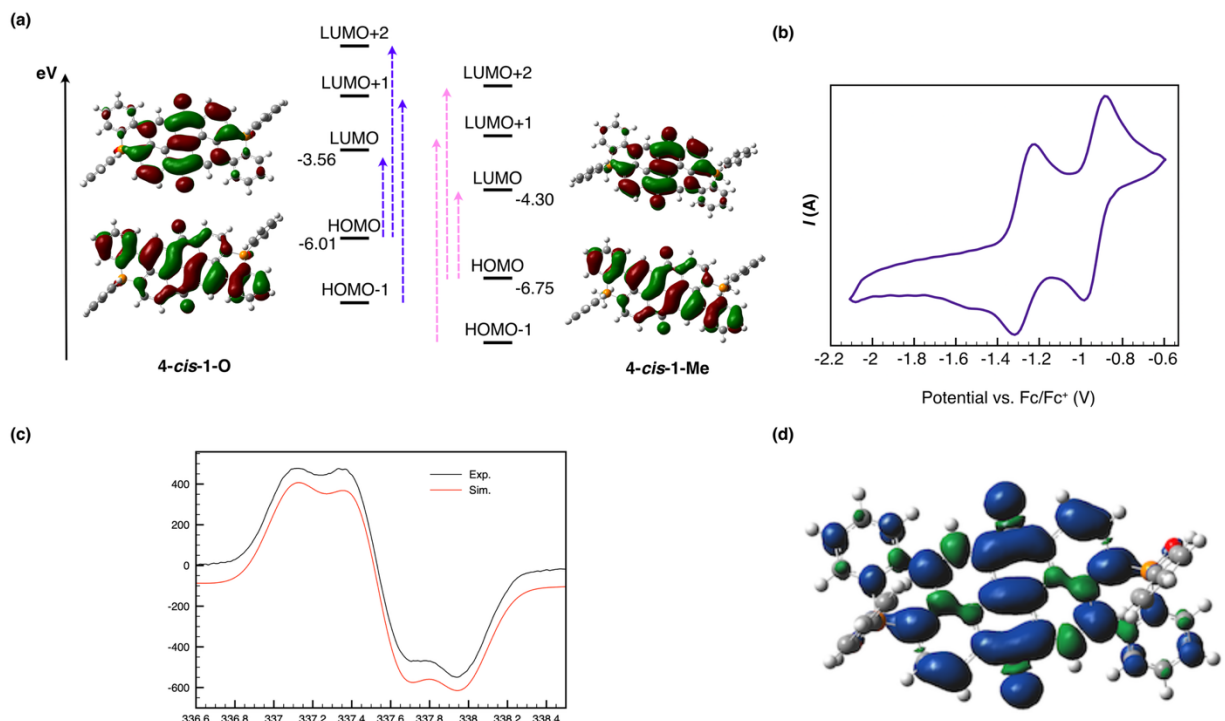


Figure 4-3. (a) FMOs of **4-cis-1-O** along with the involved electronic transitions, (b) cyclic voltammograms of **4-cis-1-O** in CH₂Cl₂; scan rate: 100 mVs⁻¹, 0.1 M *n*-Bu₄PF₆, vs. Fc/Fc⁺, (c) experimental and simulated EPR spectra of **4-cis-2-O** in CH₂Cl₂, (d) spin density map of **4-cis-2-O**.

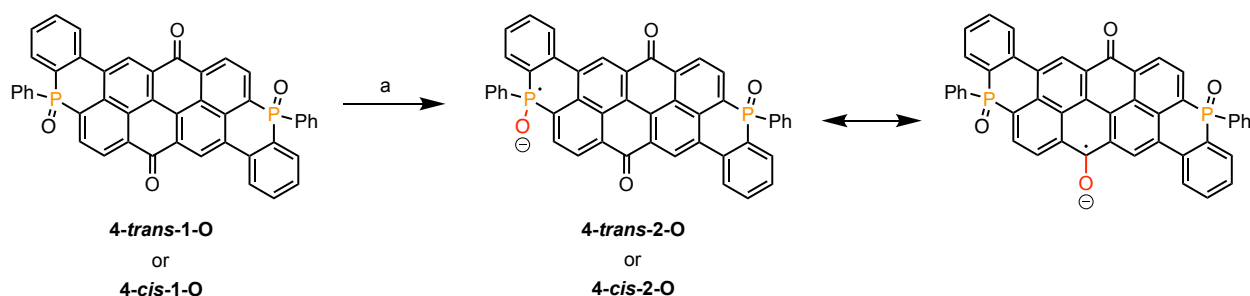
The enhanced electron-accepting character of the newly synthesized compounds prompted an evaluation of their electrochemical behaviour via cyclic voltammetry (Figure 4-3b). Compound **4-cis-1-O** possesses two reversible reduction peaks at -0.93 and -1.27 V with a similar pattern to that observed for the parent compound **2-cis-1-O** with two close equidistant reduction events at -1.64 and -1.99 V (Figure 2-9). The similar voltammogram profile suggests that the peaks originate from the sequential reduction of the phosphoryl groups in both compounds. The markedly reduced reduction thresholds by 0.7 V in **4-cis-1-O** demonstrate its more pronounced electron-acceptor character and align well with its lowered LUMO level. However, the expected reduction of the

keto groups was not observed, as it appears to lie beyond the spectral range of dichloromethane. Along similar lines, the reduction thresholds of **4-1-Me** move to remarkably low values of -0.52 and -0.75 V, as supported by DFT calculations, although with the first event becoming quasi-reversible (Figure S4-3). Further (irreversible) reduction events, presumably belonging to the keto groups, emerge at higher reduction thresholds (-1.54 and -1.90 V), demonstrating the fundamental ability of these systems for accepting multiple electrons. Akin to the *cis* isomer, **4-trans-1-O** also displays two reductions at -0.94 and -1.25 V, but the extremely limited solubility of the *trans* isomer in dichloromethane compromises the reversibility of these peaks. Notably, no reversible oxidation events were apparent for the mentioned species, which is in line with the previous generation relatives.

The robust electron-accepting properties of both **4-trans-1-O** and **4-cis-1-O** then led us to investigate the chemical reduction of these materials with sodium and 15-crown-5 (as suspension in THF) to generate **4-cis-2-O** and **4-trans-2-O**, respectively. The overnight reaction was marked by the conversion of purple to deep blue precipitates that were subsequently separated from the THF solution and redissolved in DCM. The reduced species **4-cis-2-O** (as well as **4-trans-2-O**) revealed a strong EPR signal at $g = 2.004$ with a distinct peak pattern in DCM (Figure 4-3c). The presence of two reduction peaks in the voltammogram raises the question of whether the chemical reduction involves a one- or a two-electron transfer step. There are two possible scenarios for the compound's electronic configuration upon acceptance of the second electron. The electron can either combine with the first electron in the SOMO, creating closed-shell, EPR silent species, or populate the LUMO, which results in a triplet configuration (open shell). The first scenario can be excluded from the experimental data, as the reduced species has a strong EPR signal. Formation of the triplet species, on the other hand, requires degeneracy (or near-degeneracy) of the SOMO

and LUMO levels (Figure S4-2). DFT calculations (UB3LYP/6-31G(d)) on **4-cis-2-O** and **4-trans-2-O** indicate an 1.9 eV gap between SOMO and LUMO, which renders the triplet scenario highly unlikely. More importantly, the interaction between two unpaired electrons should result in a half-field transition signal in the EPR spectrum, which was not observed for these species. Hence, the reduction with Na most likely involves only one electron. The mono-radical anion character is also corroborated by the simulated EPR spectrum that closely matches the corresponding experimental spectrum. Thus, the second reduction is likely thermodynamically unfavourable under the employed conditions and likely requires the use of stronger reducing agents.

The spin-density map of **4-cis-2-O** displays the delocalization of the single electron in the conjugated core with a strong presence in the quinoidal conjugation pathway and between the keto and the phosphoryl groups (Figure 4-3d). The corresponding resonance structures of the mono-reduced species show that the single electron can readily oscillate between the keto and phosphoryl moieties, leading to a significant stabilization of the overall radical structure. These findings align with the monitored stability of the radical anions as they remain durable in ethanol for days as evident in a continually strong EPR signal (see SI for *trans* isomer).



Scheme 4-3. Generation of **4-cis-2-O** and **4-trans-2-O** through chemical reduction, along with resonance structures arising from keto- and phosphoryl conjugation. (a) Na, 15-crown-5, THF, R.T., overnight.

Additionally, by employing the same procedure mentioned above, the chemical reduction of the mixture of P-methylated compounds yielded **4-2-Me** (as isomeric mixture). Its EPR spectrum was measured in dichloromethane and the data provided a good fit with the simulated spectrum (Figure S4-7).

4.4. Photophysical Properties and TD-DFT Calculations

To acquire more information about their interaction with light, the photophysical properties of the new-generation P-incorporated PAHs compounds were studied in dichloromethane. The absorption spectra of **4-cis-1-O** and **4-trans-1-O** exhibit a similar pattern with two main bands at 315 and 560 nm (Figure 4-4a). Compared to the first-generation relatives, the high energy bands undergo a blue-shift (40 nm), while the low energy ones experience a red-shift (50 nm) supporting a smaller optical band gap in the new system. Moreover, as predicted by the DFT calculations, the optical band gap remains unchanged for the P-methylated products **4-1-Me**. Notably, removing the long alkyl chain leads to more intense light absorption with extinction coefficients in the new-generation systems spiking from 58,600 $\rightarrow$ 71,000 for **4-cis-1-O**, 94,300 $\rightarrow$ 180,100 for **4-trans-1-O**, and 88,400 $\rightarrow$ 121,900 $\text{M}^{-1} \text{cm}^{-1}$ for **4-1-Me**.

The absorption spectra of the radical anion species **4-cis-2-O** and **4-trans-2-O** feature NIR absorption at 800 and 1100 nm that is typical for paramagnetic organic conjugated molecules, thus further validating their radical-anion nature. Additional absorption bands at 350 and 620 nm are observed, rendering the absorption profile of these radical anions quite complex. The radical cation of **4-2-Me** exhibits a similar pattern with the NIR absorption bands shifted to 938 and 1086 nm, respectively. Moreover, the extinction coefficients of all the reduced species range from 19,600 to 42,400 $\text{M}^{-1} \text{cm}^{-1}$, considerably smaller than those of their non-reduced congeners.

To learn more about the responsible transitions involved, TD-DFT calculations were carried out. The low-energy absorption bands in both **4-*cis*-1-O** and **4-*trans*-1-O** are $\pi \rightarrow \pi^*$ transitions from HOMO to LUMO with oscillator strengths of $f = 0.46$ for both isomers. On the other hand, high-energy bands in these compounds arise from multiple electronic transitions each comprised of distinct components. In **4-*cis*-1-O**, the major contribution originates from HOMO-1 to LUMO+1 and HOMO to LUMO+2 with respective f values of 0.63 and 0.66. Compound **4-*trans*-1-O** is primarily associated with a HOMO-1 to LUMO+1 transition ($f = 0.56$), along with two closely spaced transition involving HOMO to LUMO+3 as the main component, with respective oscillator strengths of 0.30 and 0.34. Similar data are also obtained for **4-1-Me** with HOMO to LUMO transition for the low-energy peak ($f = 0.47$), and HOMO-1 to LUMO+1 ($f = 0.40$) and HOMO to LUMO+2 ($f = 0.82$) for the high-energy peak. These data show a good match between the predicted and experimental absorption spectra in both intensity and wavelength range for these species.

The absorption spectra for the reduced species **4-*cis*-2-O** and **4-*trans*-2-O** exhibit a good match with the TD-DFT-predicted data from the calculations. While the first NIR-absorption band at 1100 nm originates from an electronic transition of SOMO (α spin) to LUMO (α spin) with $f = 0.23$ for both isomers, the second one at 800 nm has a main component of HOMO (β spin) to SOMO (β spin) with $f = 0.10$. The visible band around 600 nm receives a major contribution from a SOMO (α spin) to LUMO+2 (α spin) with $f = 0.29$, and the UV band around 350 nm from HOMO-1 (β spin) to LUMO (β spin) with respective f of 0.86 and 0.88 for *cis* and *trans* isomers. The strong correlation between theoretical and experimental results provides further compelling evidence for the radical anion species arising from a single-electron transfer. The involved orbitals and their f values in **4-2-Me** for the NIR and visible absorption bands display a good alignment

with those of **4-cis-2-O**. The UV band for **4-2-Me** is comprised of HOMO-1 (β spin) to LUMO (β spin) with $f = 0.46$ and HOMO (α spin) to LUMO+1 (α spin) with $f = 0.50$.

As the incorporation of carbonyl groups in the framework of π -conjugated materials is known to attenuate the fluorescence, we expected the presence of the two keto groups in **4-cis-1-O** and **4-trans-1-O** would quench the emission of these species. To our surprise, however, both conjugated materials are highly luminescent with emission maxima located around 600 nm (Figure 4-4b). A closer look at the luminescence intensities revealed that, relative to the first-generation species, the quantum yield of **4-trans-1-O** remained nearly unchanged (55 $\rightarrow$ 50%), whereas **4-cis-1-O** exhibited an even enhanced emission (37 $\rightarrow$ 54%). The excited-state lifetimes for both **4-cis-1-O** and **4-trans-1-O** are identical with 5.5 ns, and indicative of fluorescence. The pronounced emission observed in these compounds can likely be attributed to their extended π -conjugation and the established emissive character of phosphorus-based systems.²⁰ Nevertheless, it is worth noting that while **4-1-Me** is still moderately emissive, the QY value was lower than that of the OC₁₂H₂₅-substituted system (41 $\rightarrow$ 21%, $\lambda_{\text{max}} = 601$ nm).

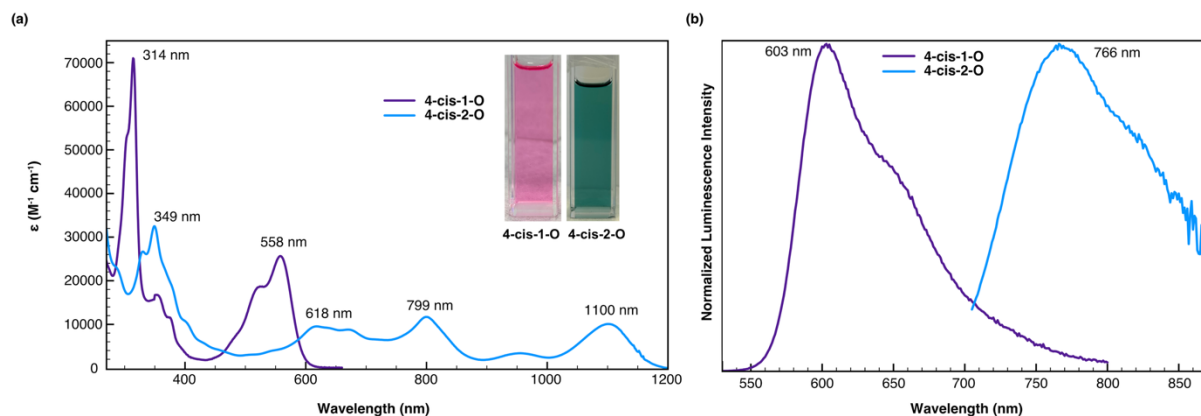


Figure 4-4. Absorption (a) and emission (b) spectra of **4-cis-1-O** and **4-cis-2-O** in CH₂Cl₂.

Despite their radical character, luminescence spectroscopy confirmed that the radical anion species **4-*cis*-2-O** and **4-*trans*-2-O** are indeed emissive, which considering their radical anion nature suggests that doublet emission is unlocked for these species (Figure 4-4b). Notably, both isomers emit in the NIR region, with maxima at 762 nm (*trans*) and 766 nm (*cis*). Moreover, the reduced P-methylated radical cation **4-2-Me** is also emissive with a maximum wavelength at 681 nm (Figure 4-5b). Occurrence of both light-emitting phosphorus-based conjugated radicals and NIR doublet luminescence (at large) is highly unusual and merits significant attention.

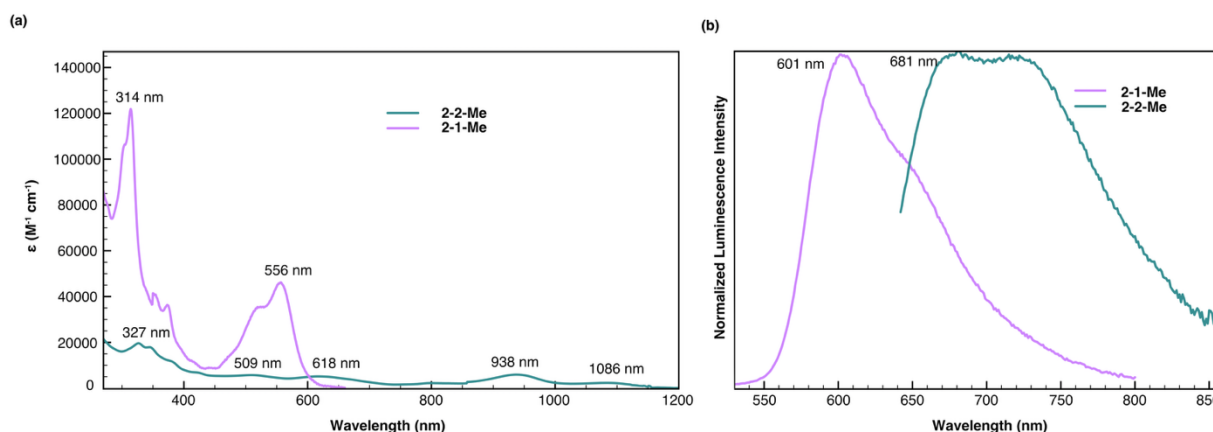


Figure 4-5. Absorption (a) and emission (b) spectra of **4-1-Me** and **4-2-Me** in CH₂Cl₂.

4.5. Solid-state Emission Properties

The intriguing photophysical properties observed in solution for the new-generation compounds prompted the subsequent examination of their solid-state emission. Following the same approach as in Chapter 2, PMMA films of **4-*cis*-1-O** and **4-*trans*-1-O** at two different concentrations (0.1 and 1 wt%; compound to polymer ratio) were prepared. Interestingly, solid-state interactions seem to give rise to a deviating behaviour between the *cis* and *trans* isomers. Compared to their emission

in solution, while 0.1 wt% film of **4-*trans*-1-O** shows a marginal blue-shift (7 nm, 601 → **594** nm), **4-*cis*-1-O** displays a red-shift (24 nm, 603 → **627** nm). Increasing the film concentration from 0.1 to 1 wt%, causes red-shifts of 14 nm for the *trans* (594 → **608** nm) and 19 nm for the *cis* isomer (627 → **646** nm). Aggregation between conjugated units in the solid-state, as seen in the first-generation relatives, appears to drive the red-shifted emission in these compounds. The removal of the -OC₁₂H₂₅ chains accentuates the structural differences between the isomers, in a way that the *cis* isomer displays stronger red-shift presumably due to stronger aggregation and tighter intermolecular π - π interactions in this isomer. Accordingly, reducing the temperature for the high-concentration film of **4-*trans*-1-O** to 10 K causes no change in the emission maxima, whereas **4-*cis*-1-O** exhibits a further 10 nm red-shift (646 → **656** nm).

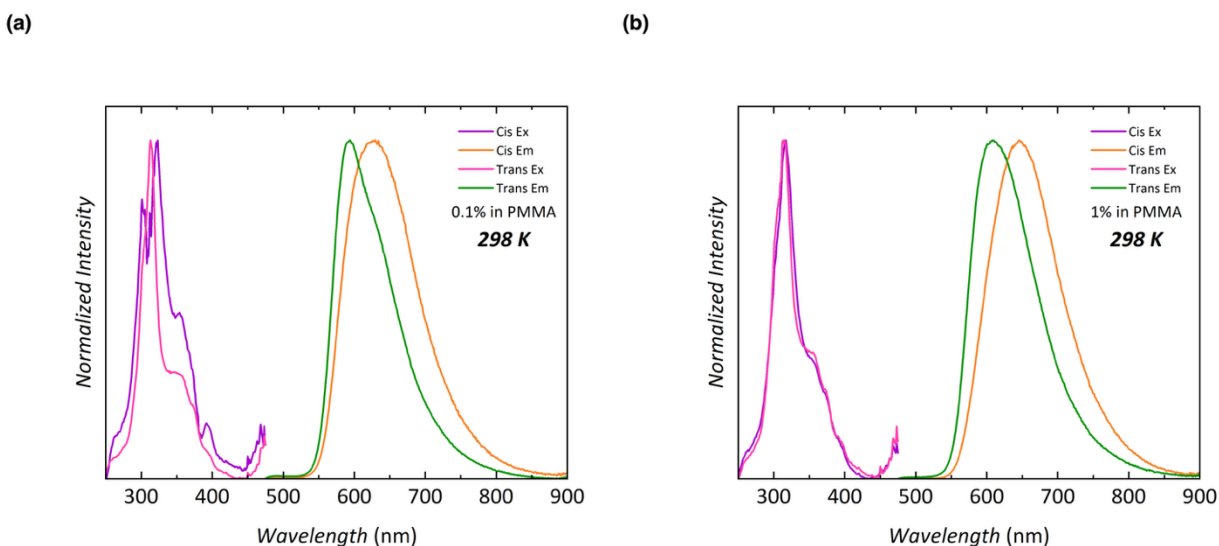


Figure 4-6. Emission spectra of the PMMA films containing (a) 0.1 wt% and (b) 1 wt% of compounds **4-*cis*-1-O** and **4-*trans*-1-O**.

Incorporation of the carbonyl group within the π -system of conjugated materials is known to enhance the intersystem crossing, thereby activating the triplet states, and to induce red-shifted

longer-lived phosphorescence emission. Therefore, time-resolved emission spectroscopy on the films of different concentration was carried out at 10 K (Figure 4-7). For the 0.1 wt% films, introducing time delays of 50-125 μ s before collection of the emission spectrum for **4-*cis*-1-O** (same for **4-*trans*-1-O**) simply led to the residual of similar emission already observed in steady-state spectrum. Similar results were repeated for 50 μ s delay of the 1 wt%, which corroborates the nature of the emission being fluorescence at low and high temperatures.

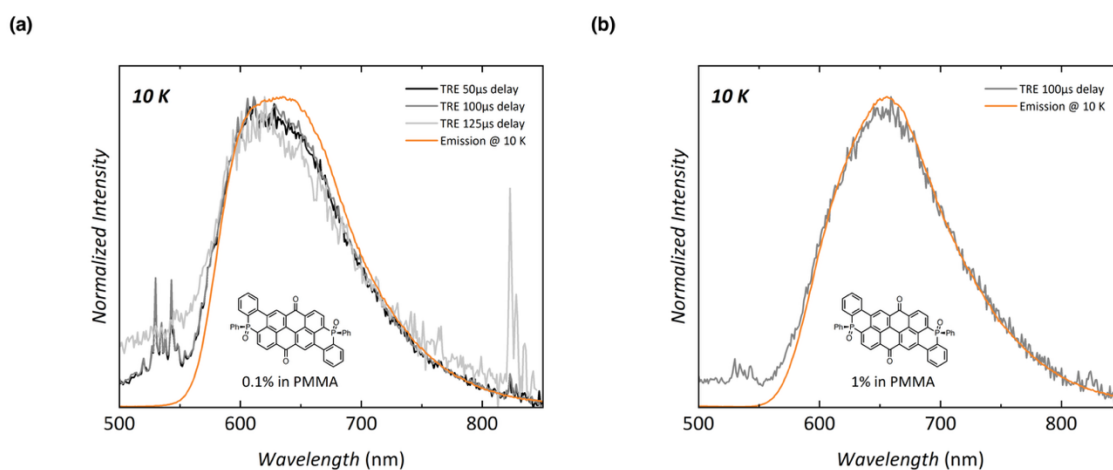


Figure 4-7. Time-resolved emission spectroscopy at 10 K for 0.1 wt% films of **4-*cis*-1-O** and **4-*trans*-1-O**.

4.6. Conclusion

In summary, a new-generation, phosphorus-based polyaromatic hydrocarbon system built on Vat Orange 3 (VO3) is reported. A novel synthetic method for regeneration of the keto groups of the native VO3 was employed. The emergence of unique conjugation features such as the quinoidal pathway and the aromatic tetraphenyl unit along with the already present phosphoryl moieties leads to a distinct level of stability for these compounds. The expectedly lowered FMO energy

levels in these species enable two reversible reduction events as low as 0.93 V for the P=O-containing systems and quasi-reversible reduction at -0.52 V for the P-Me species. The chemical reduction of these new-generation P-modified VO₃ congeners led to the formation and characterization of the respective radical anions (from P=O) and radical cations (from P-Me). The reduced species exhibit excellent stability, even in protonating solvents such as ethanol, and possess complex absorption spectra all the way into the NIR region. While the presence of the carbonyl groups in the backbone of the target compounds does not trigger the activation of triplet states, the conjugated materials nonetheless retain strong luminescence. The reduced systems with unpaired electron display a surprising NIR luminescence that is unprecedented for P-based organic compounds with extended conjugation.

4.7. References

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Appendix C: Chapter Four

Chapter Four: Phosphorus-Incorporated Polycyclic Aromatic Hydrocarbons; From Quinoidal Conjugation to Doublet NIR Emission

4.1. General section

Reactions were carried out in dry glassware and under an inert atmosphere of purified argon using Schlenk techniques. Anhydrous solvents such as CH₂Cl₂ and THF and pentane were used directly from a solvent purification system (MBraun) or, in case of reactions or column chromatography, were purchased from commercial suppliers and used as received. Standard solvents such as MeCN, chloroform (CHCl₃), CH₂Cl₂, diethyl ether, hexanes, methanol, and ethanol were purchased from commercial suppliers and used as received. Deuterated solvents such as chloroform-d were purchased from commercial suppliers and used as received. Silica gel, Celite[®], sodium sulfate (Na₂SO₄), *n*-butyllithium (*n*-BuLi) (2.5 M solution in hexanes), sodium bicarbonate (NaHCO₃), dichlorophenylphosphine PhPCl₂, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), and triflic acid (TfOH) were purchased from commercial suppliers and used as received. The synthetic procedure and spectral data of compound **2-*trans*-1-O** and **2-*cis*-1-O** can be found in Chapter 2 and its Appendix.

4.2. Experimental data

4.2.1. Synthesis and characterization

Compound **2-trans-1-O** (80 mg, 0.08 mmol) was dissolved in 20 mL of CH₂Cl₂ in a 50 ml torched Schlenk flask under argon and was treated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (70 mg, 0.31 mmol) and trifluoromethane sulfonic acid (0.40 mL, 4.6 mmol). The reaction was stirred at room temperature for 45 minutes under argon and then neutralised with addition of 20 mL of saturated solution of sodium bicarbonate. The organic layer was separated and washed with water and brine multiple times. The solvent was evaporated under reduced pressure and the purple products **4-trans-1-O** was recrystallized from acetone and CH₂Cl₂ and ether (75% yield, 40 mg, 0.06 mmol).

¹H NMR (400 MHz, CDCl₃) δ 9.42 (s, 2H), 8.91 (d, *J* = 7.4 Hz, 2H), 8.68 – 8.60 (m, 2H), 8.60 – 8.54 (m, 2H), 8.11 (dd, *J* = 13.2, 7.5 Hz, 2H), 7.83 (t, *J* = 7.8 Hz, 2H), 7.67 – 7.56 (m, 6H), 7.45 (d, *J* = 7.4 Hz, 2H), 7.38 (t, 4H).

³¹P{¹H} NMR (162 MHz, CDCl₃) δ 8.0.

HRMS (ESI, *m/z*): [M+H]⁺ calculated for: C₄₆H₂₅O₄P₂, *m/z*=703.1223; Found [M+H]⁺ *m/z*=703.1219.

Compound **2-cis-1-O** (90 mg, 0.09 mmol) was dissolved in 20 ml of CH₂Cl₂ in a 50 ml torched Schlenk flask under argon and was treated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (80 mg, 0.35 mmol) and trifluoromethane sulfonic acid (0.45 mL, 5.1 mmol). The reaction was stirred at room temperature for 45 minutes under argon. The reaction was neutralised with addition of 20 mL of saturated solution of sodium bicarbonate and the organic layer was separated and washed with water and brine multiple times. The solvent was evaporated under reduced pressure and the purple, solid **4-cis-1-O** was recrystallized from acetone and CH₂Cl₂ and ether (82% yield, 50 mg, 0.07 mmol).

¹H NMR (400 MHz, CDCl₃) δ 9.37 (s, 2H), 8.90 (d, *J* = 7.4 Hz, 2H), 8.64 (dd, *J* = 13.2, 7.4 Hz, 2H), 8.59 – 8.49 (m, 2H), 8.11 (dd, *J* = 13.2, 7.5 Hz, 2H), 7.82 (t, *J* = 7.8 Hz, 2H), 7.66 – 7.52 (m, 6H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.38 – 7.31 (m, 4H).

³¹P{¹H} NMR (162 MHz, CDCl₃) δ 7.5.

HRMS (ESI, *m/z*): [M+H]⁺ calculated for: C₄₆H₂₅O₄P₂, *m/z*=703.1223; Found [M+H]⁺ *m/z*=703.1200.

Compound **4-1-Me** was synthesized from (50 mg, 0.04 mmol) of the mixture of **2-*cis*-1-Me** and **2-*cis*-1-Me** based on the same procedure employed in chapter two (88% yield, 33 mg, 0.03 mmol).

³¹P{¹H} NMR (162 MHz, CDCl₃) δ ppm 0.4, 0.5.

HRMS (ESI, *m/z*): [M]²⁺ calculated for: C₄₈H₃₀O₂P₂, *m/z*=350.0855; Found [M+H]⁺ *m/z*=350.0862.

The generation of **4-*trans*-2-O**, **4-*cis*-2-O**, and **4-2-Me** by chemical reduction, was performed according to the following procedure:

4-*trans*-1-O (4 mg, 0.006 mmol) was added to 20 ml THF and a sodium chunk (excess, 20 eq) and 15-crown-5 (0.01 ml, 0.06 mmol) was added to the solution under argon. The mixture was stirred overnight at room temperature and the next day, sodium was removed and THF solution was

siphoned out. The dark blue solids were dried under reduced pressure and used in further characterization.

4-*trans*-2-O: $g = 2.004$. λ_{abs} : 1100 nm, 801 nm, 479 nm, 350 nm. λ_{em} : 762 nm.

4-*cis*-2-O: $g = 2.004$. λ_{abs} : 1100 nm, 799 nm, 618 nm, 349 nm. λ_{em} : 766 nm.

4-2-Me: $g = 2.004$. λ_{abs} : 1086 nm, 938 nm, 618 nm, 509 nm, 327 nm. λ_{em} : 681 nm.

4.2.2. Calculation, EPR spectroscopy, and Electrochemistry

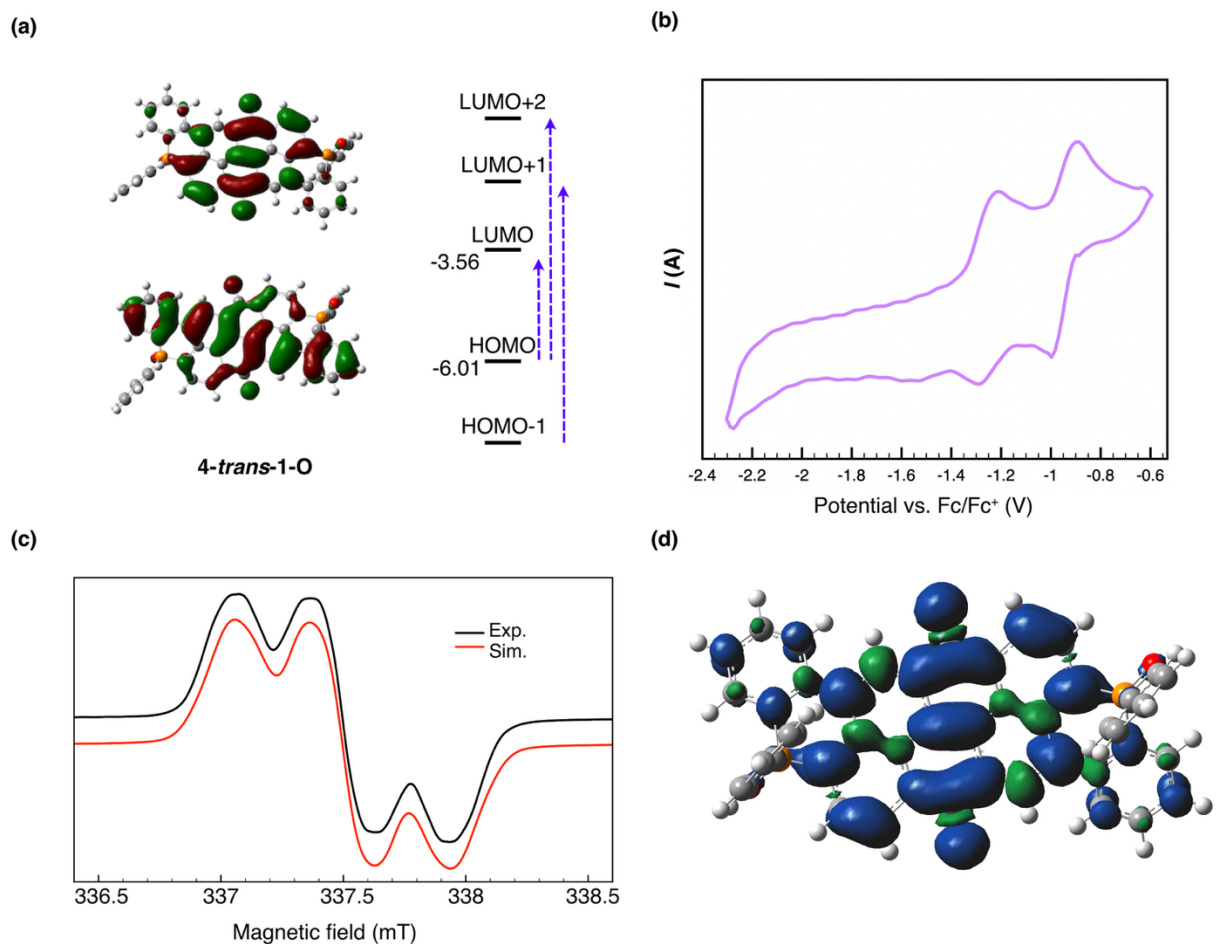


Figure S4-1. (a) FMOs of **4-*trans*-1-O** along with the involved electronic transitions, (b) Cyclic voltammograms of **4-*trans*-1-O** in CH₂Cl₂; scan rate: 100 mVs⁻¹, 0.1 M *n*-Bu₄PF₆, vs. Fc/Fc⁺, (c) experimental and simulated EPR spectra of **4-*trans*-2-O** in CH₂Cl₂, (d) spin density map of **4-*trans*-2-O**.

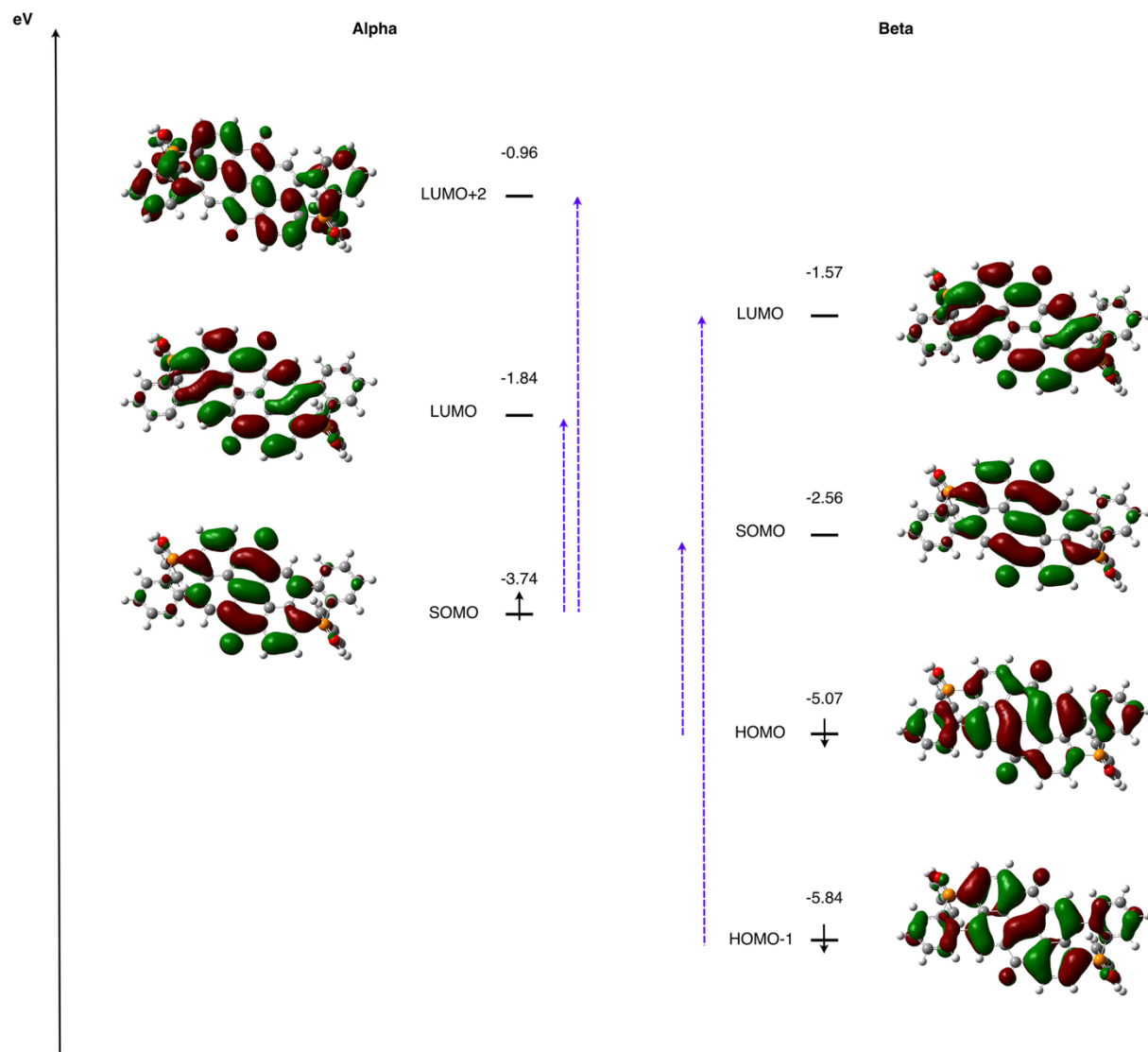


Figure S4-2. (a) FMOs of 4-*cis*-2-O along with the involved electronic transitions.

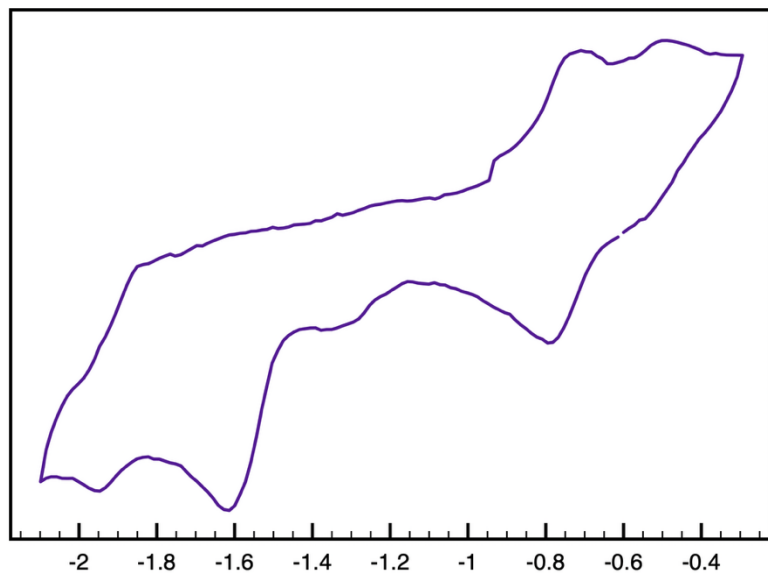


Figure S4-3. Cyclic voltammograms of **4-1-Me** in CH_2Cl_2 ; scan rate: 100 mVs^{-1} , $0.1 \text{ M } n\text{-Bu}_4\text{PF}_6$, vs. Fc/Fc^+ .

Table S4-1. Calculated and optimized hyperfine coupling constants for **4-*trans*-2-O** (displayed in Figure 4-3)

Atom	Calculated coupling (MHz)	Optimized coupling (MHz)
P	-8.13	-8.48
H ₁	-3.80	-3.61
H ₂	2.86	1.12
H ₃	-1.35	-1.25
H ₄	-1.23	-1.12
H ₅	-0.99	-1.2
H ₆	0.37	0.09
H ₇	0.35	0.26

Note: The calculated values are Fermi coupling constants taken from DFT calculations; The optimized coupling values are derived from the result of fitting the experimental EPR spectrum by EasySpin software. The value in these two columns show a good match confirming the nature of the radical.

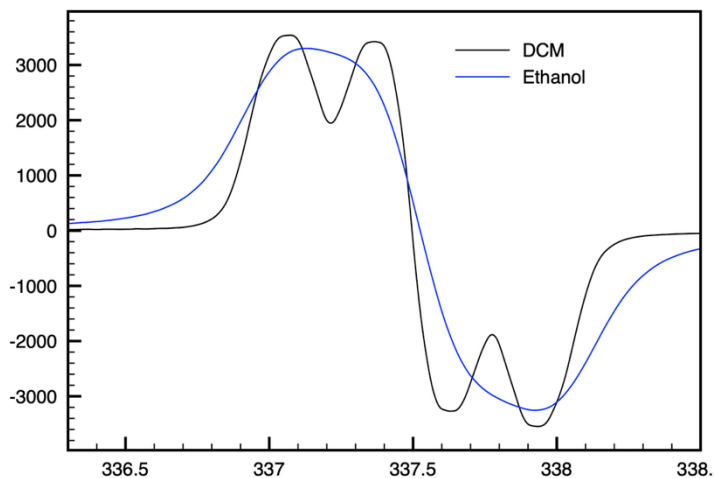


Figure S4-4. Comparative experimental EPR spectra of **4-*trans*-2-O** measured in DCM and ethanol.

Table S4-2. Calculated and optimized hyperfine coupling constants for **4-*cis*-2-O**

Atom	Calculated coupling (MHz)	Optimized coupling (MHz)
P	-8.12	-8.27
H ₁	-3.80	-3.27
H ₂	2.91	2.41
H ₃	-1.31	-1.17
H ₄	-1.22	-1.12
H ₅	-0.99	-0.92
H ₆	0.36	0.72
H ₇	0.34	0.28

Table S4-3. Calculated and optimized hyperfine coupling constants for **4-*cis*-2-Me** in DMSO

Atom	Calculated coupling (MHz)	Optimized coupling (MHz)
P	-11.30	-9.79
H ₁	-3.13	-2.15
H ₂	-2.23	-0.4
H ₃	-4.08	-3.10
H ₄	1.37	1.43

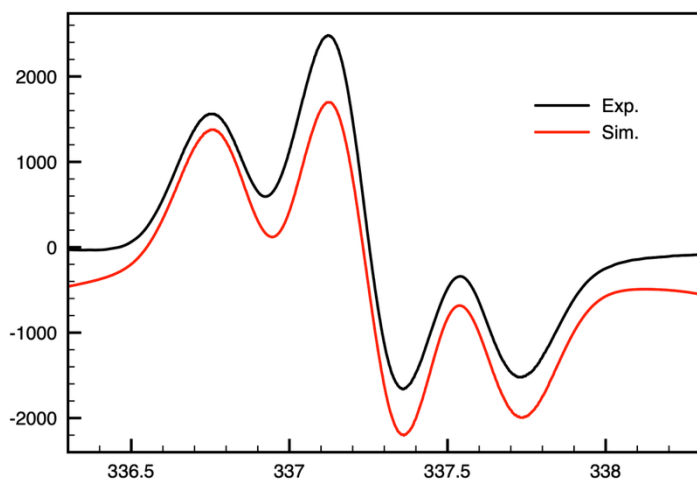


Figure S4.5. Experimental and simulated EPR spectra of **4-2-Me** in DMSO.

Table S4-4. Calculated and optimized hyperfine coupling constants for **4-2-Me** in DCM.

Atom	Calculated coupling (MHz)	Optimized coupling (MHz)
P	-11.30	-9.67
H ₁	-3.13	-2.39
H ₂	-2.23	-0.98
H ₃	-4.08	-3.12
H ₄	1.37	2.33

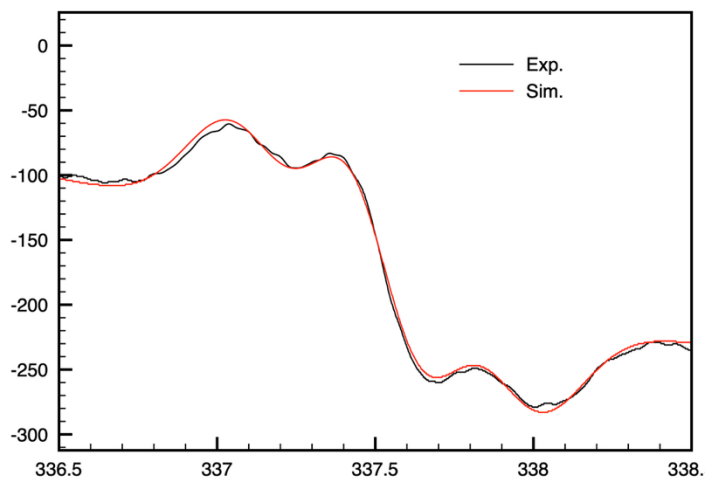


Figure S4-6. Experimental and simulated EPR spectra of **4-2-Me** in DCM.

Table S4-5. Calculated and optimized hyperfine coupling constants for **4-2-Me** in DCM reduced with Na.

Atom	Calculated coupling (MHz)	Optimized coupling (MHz)
P	-11.30	-7.30
H ₁	-3.13	-2.13
H ₂	-2.23	-2.17
H ₃	-4.08	-3.08
H ₄	1.37	2.03

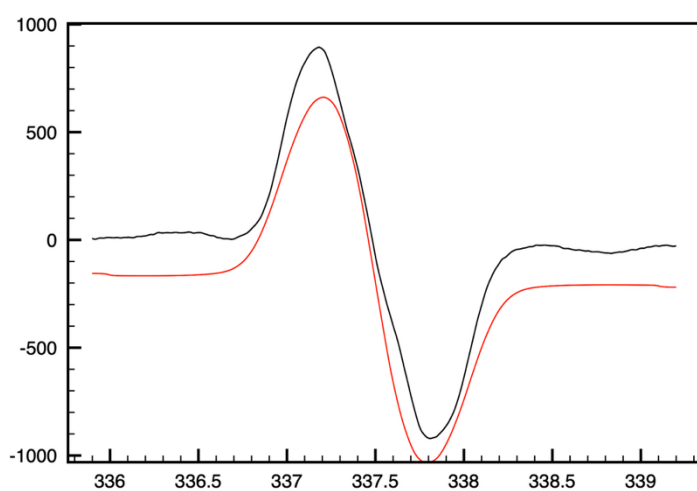


Figure S4-7. Experimental and simulated EPR spectra of **4-2-Me** reduced with sodium and measured in DCM.

4.2.3. Photophysical Properties (Solution and Solid State)

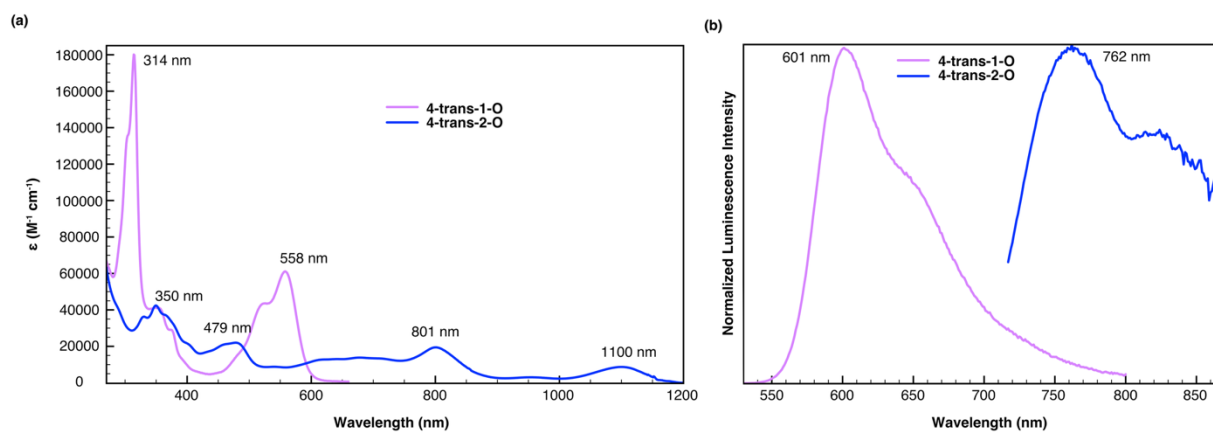


Figure S4-8. (a) Absorption, and (b) emission spectra of **4-1-Me** and **4-2-Me** in CH_2Cl_2 .

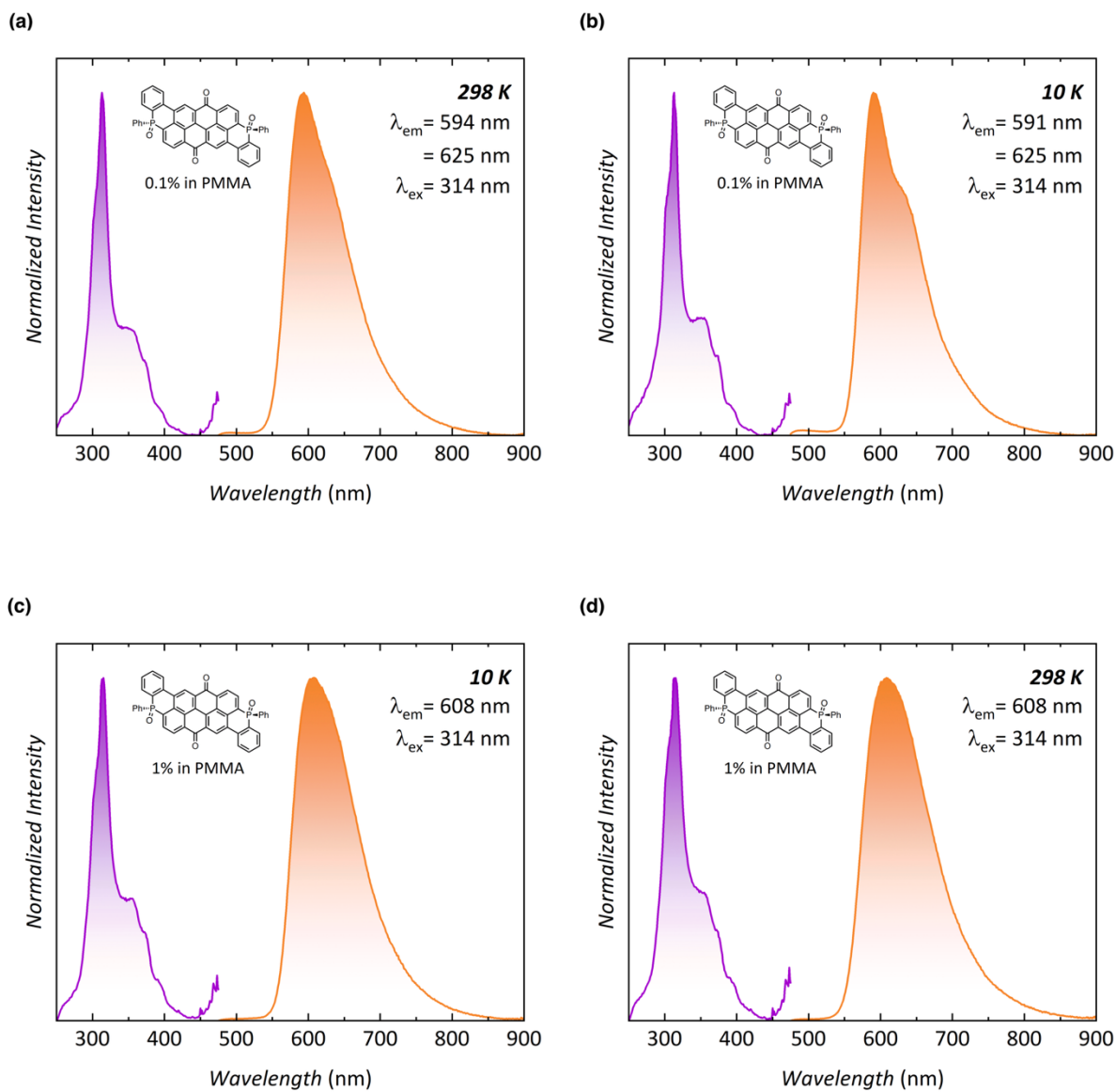


Figure S4-9. Emission spectra of the 4-*trans*-1-O PMMA film (a) 0.1 wt% at 298 K, and (b) 0.1 wt% at 10 K, (c) 1 wt% at 10 K, (d) 1 wt% at 298 K.

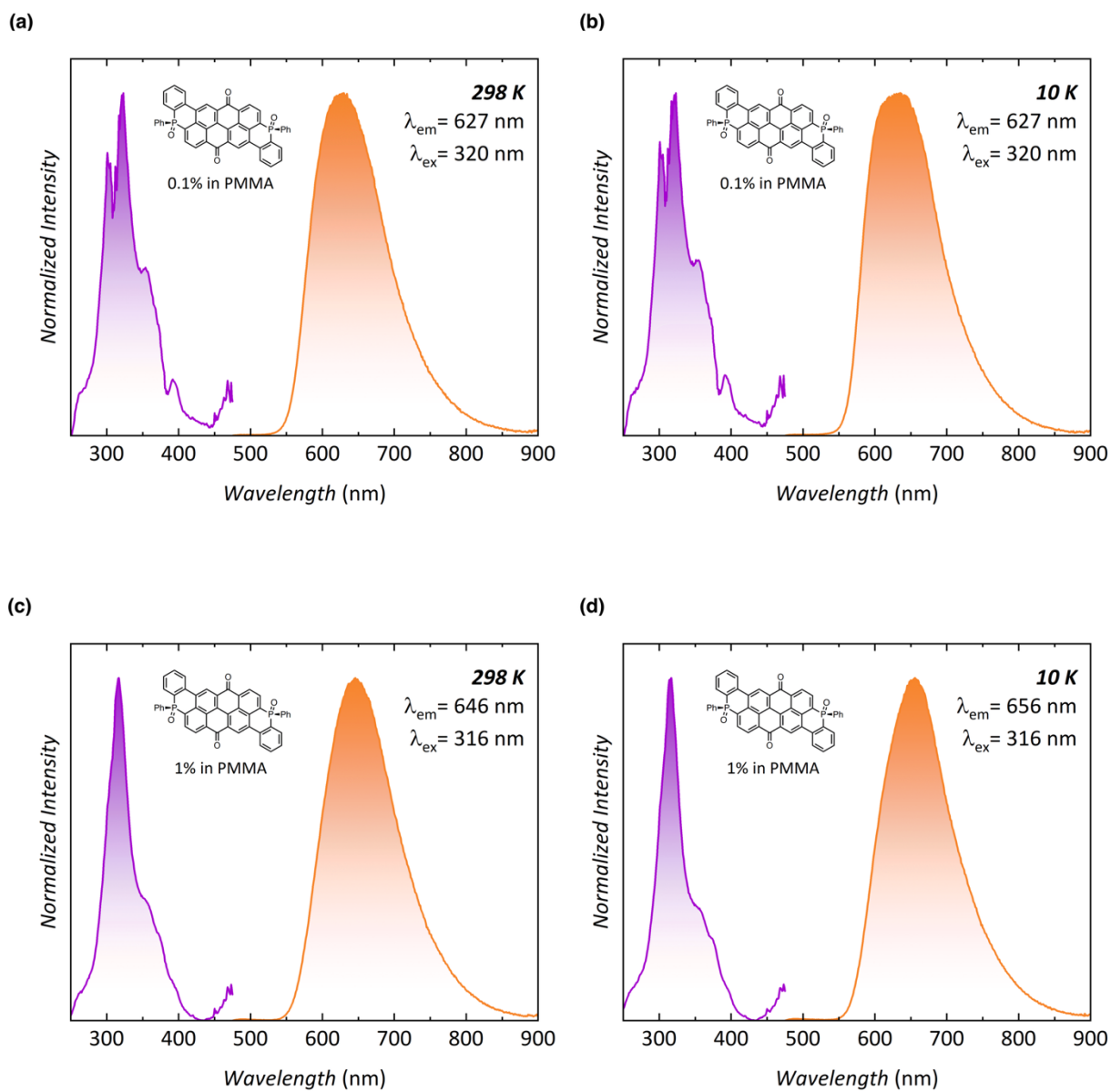


Figure S4-10. Emission spectra of the 4-*cis*-1-**O** PMMA film (a) 0.1 wt% at 298 K, and (b) 0.1 wt% at 10 K, (c) 1 wt% at 298 K, (d) 1 wt% at 10 K.

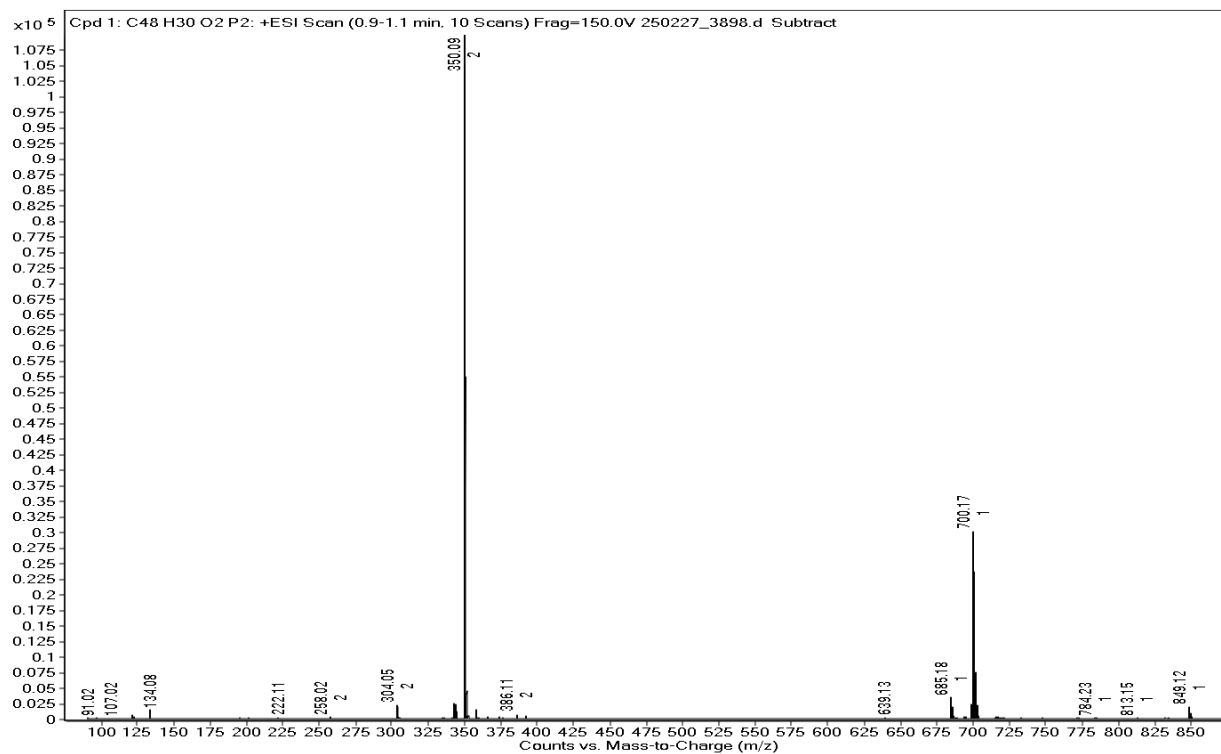
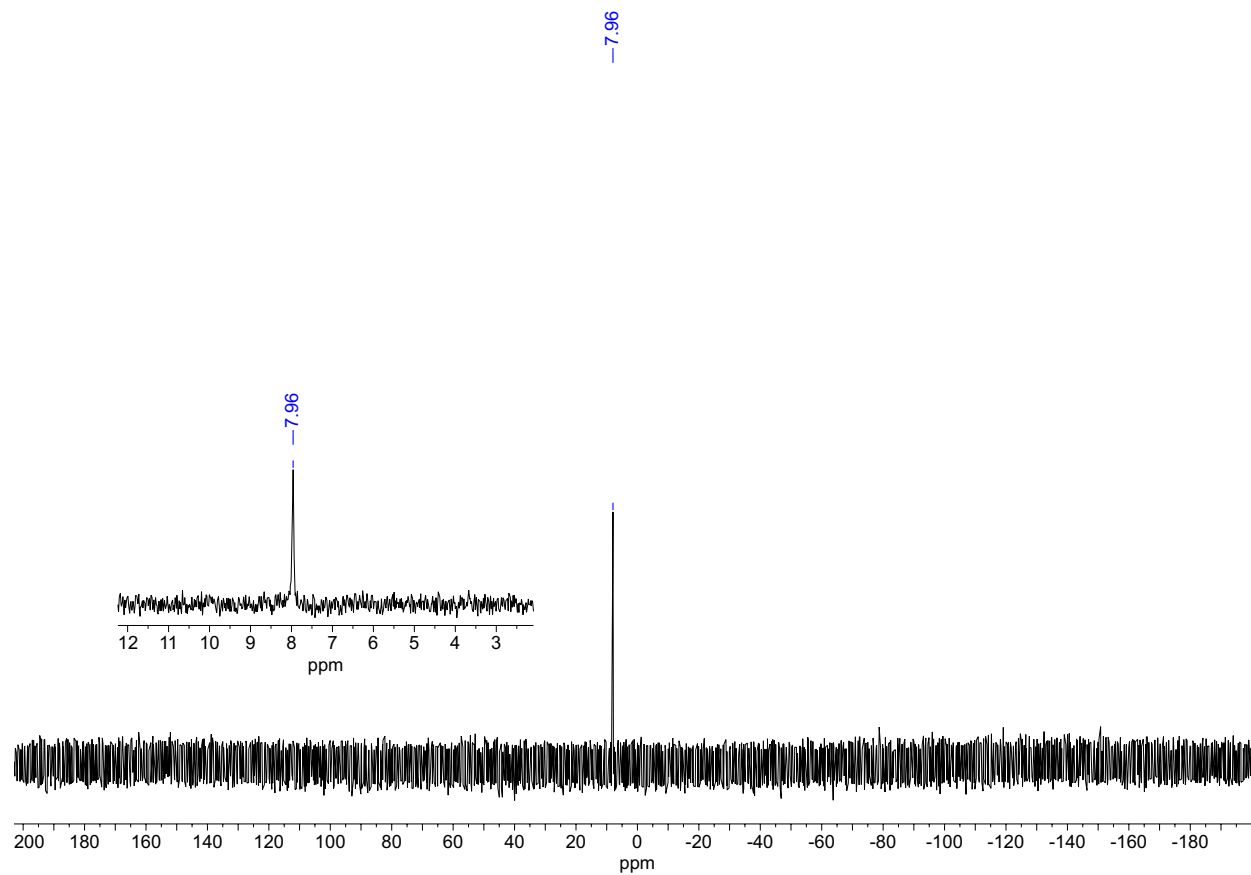


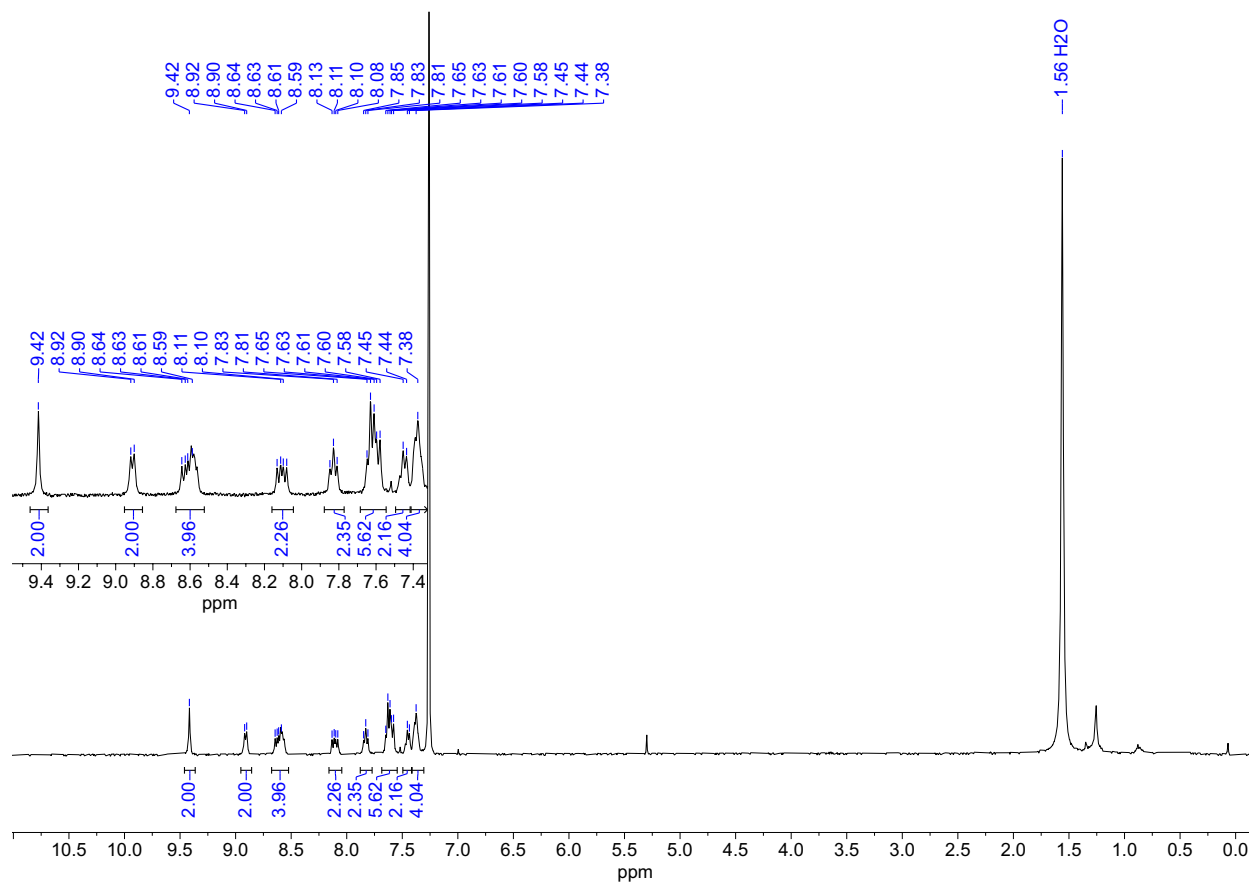
Figure S4-11. Mass spectrum of **4-1-Me** with mass/charge of 350.0862 containing the radical cation of **4-2-Me** with mass/charge of 700.17.

4.3. NMR Spectra

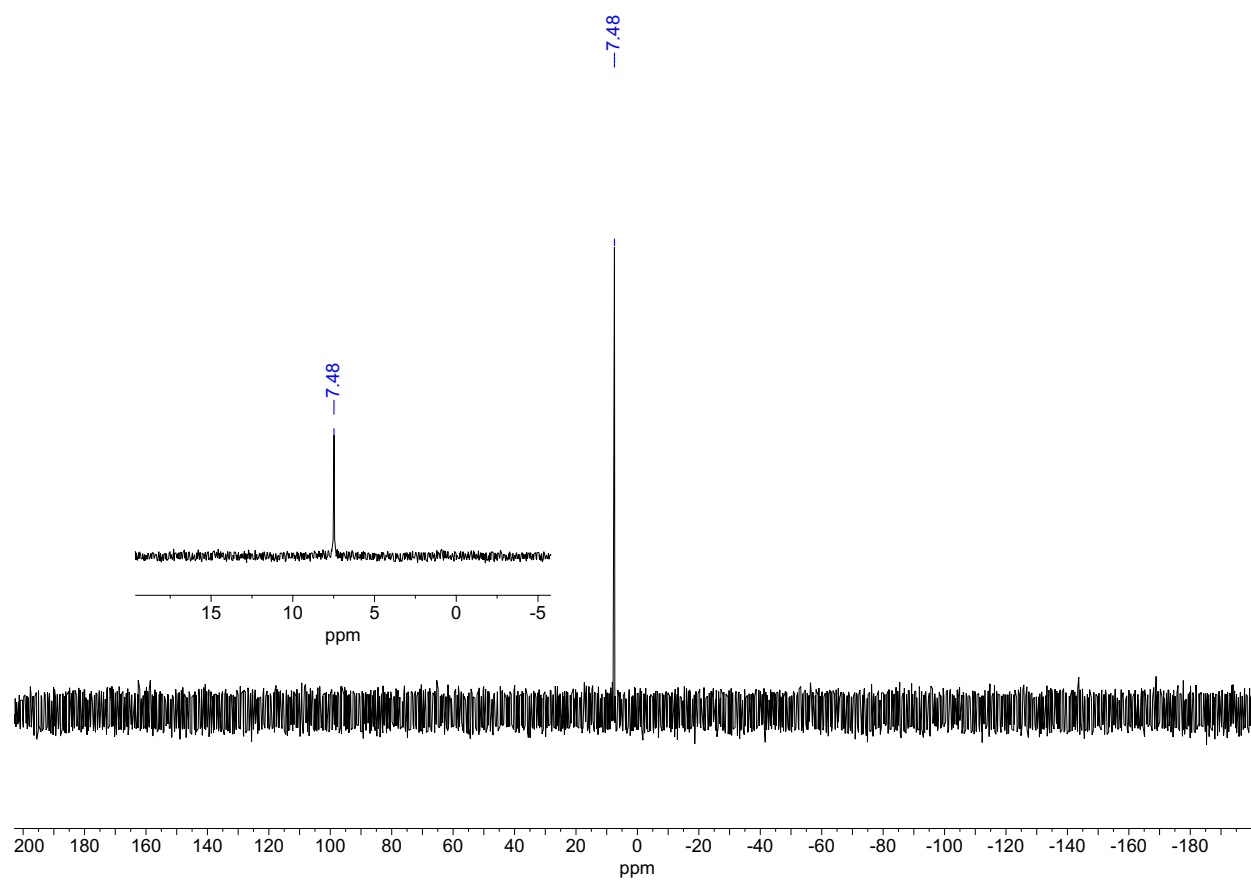
$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4-*trans*-1-O** measured in CDCl_3 (162 MHz).



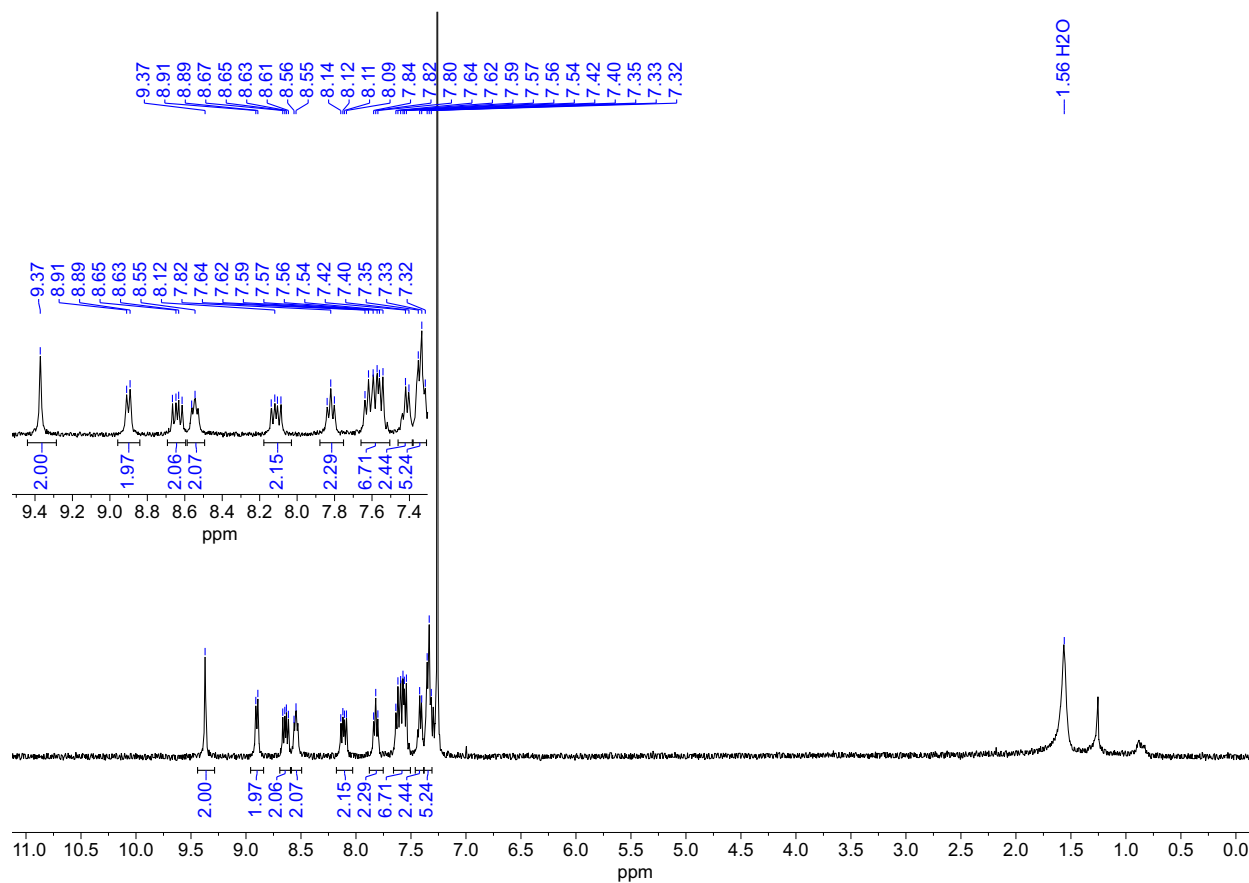
^1H NMR spectrum of **4-*trans*-1-O** measured in CDCl_3 (400 MHz).



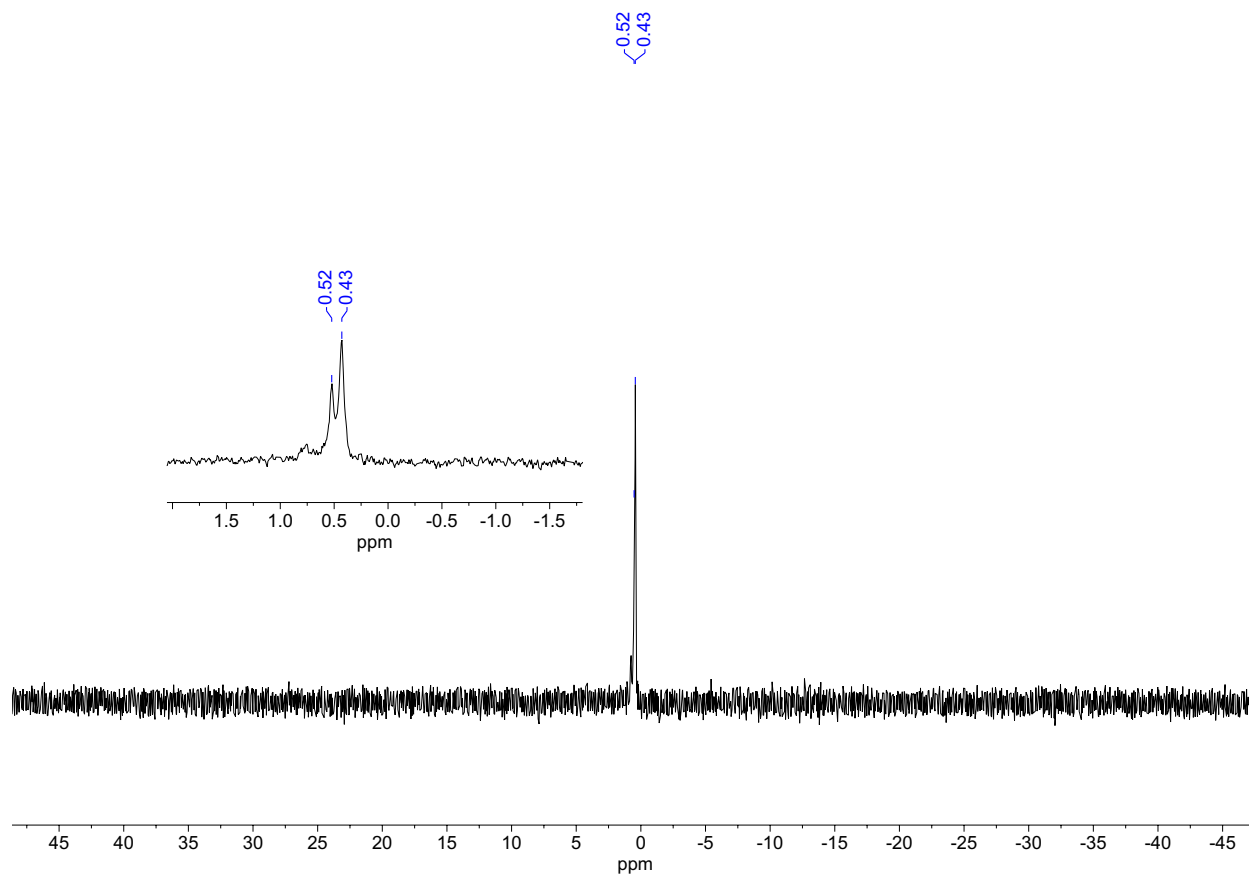
$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4-*cis*-1-O** measured in CDCl_3 (162 MHz).



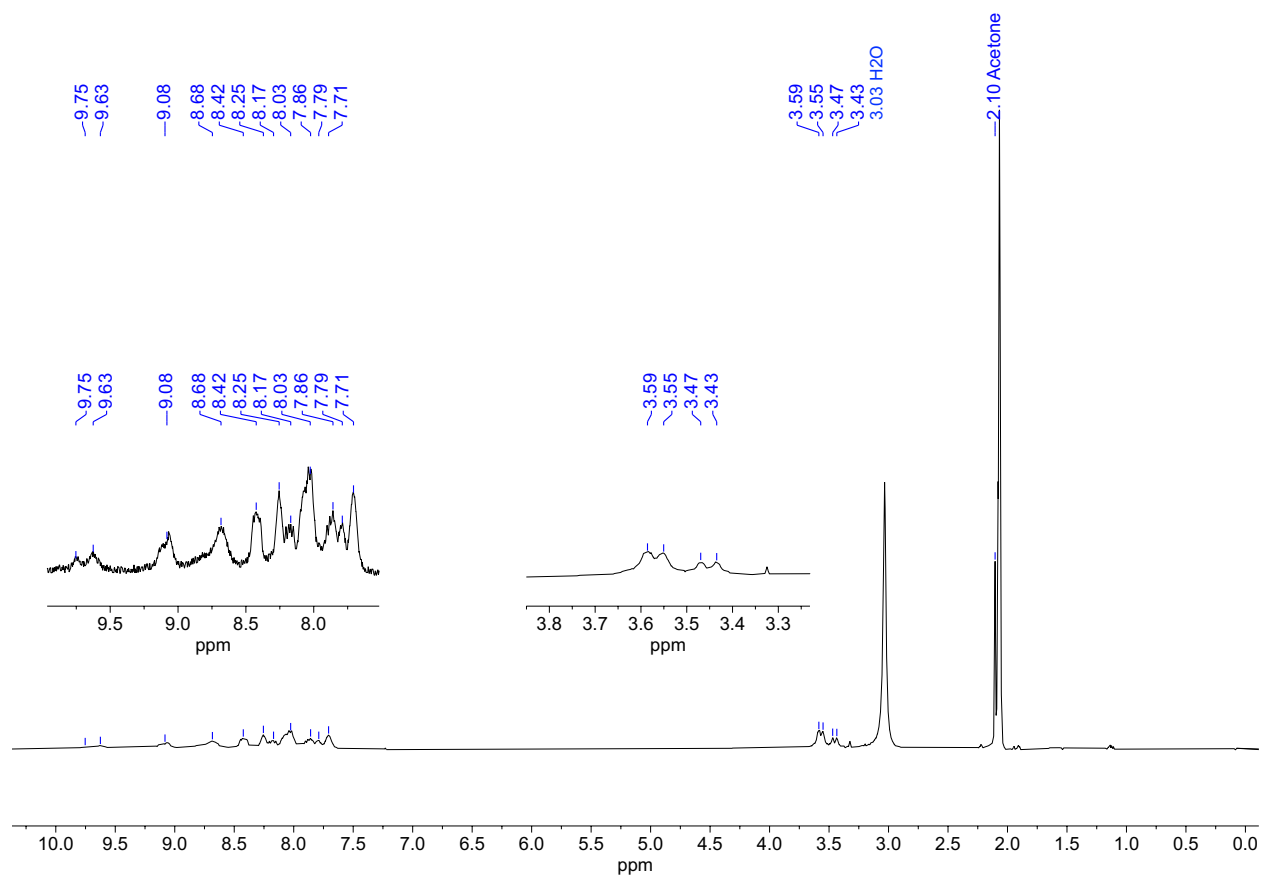
^1H NMR spectrum of **4-*cis*-1-O** measured in CDCl_3 (400 MHz).



$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4-1-Me** measured in *d*-Acetone (162 MHz).



^1H NMR spectrum of **4-1-Me** measured in *d*-Acetone (400 MHz).



Note: Despite the broadening due to the presence of paramagnetic species, the methyl peaks on the phosphorus centres at 3.57 and 3.45 ppm are distinguishable.

4.4. X,Y,Z Coordinates of optimized geometries by DFT calculations of all the synthesized conjugated materials.

4-trans-1-O

C	-3.11274	0.13421	-0.27386
C	-4.23326	-0.69145	-0.47423
C	-4.08312	-2.08811	-0.62232
C	-2.84457	-2.68717	-0.57129
C	-1.68184	-1.89677	-0.41443
C	-1.80818	-0.47336	-0.29726
H	-4.96548	-2.70093	-0.78299
H	-2.74425	-3.75953	-0.69183
C	-0.38529	-2.48487	-0.40055
C	-0.63325	0.32187	-0.23602
C	0.64642	-0.27921	-0.28209
C	0.76862	-1.70418	-0.34737
C	2.07448	-2.28463	-0.33564
H	2.11467	-3.36386	-0.39225
C	1.82147	0.51804	-0.2709
C	3.12749	-0.08795	-0.3094
C	3.22969	-1.54861	-0.26052
C	-3.21299	1.57691	-0.04299
C	-0.75729	1.74713	-0.1814
C	-2.06103	2.32073	-0.05797
H	-2.10085	3.39634	0.05135
C	0.39484	2.53086	-0.21331
C	1.69225	1.94634	-0.25052
C	2.85527	2.75098	-0.26405
H	2.75439	3.82845	-0.2066
C	4.24695	0.75924	-0.39662

C	4.09615	2.16347	-0.3594
H	4.98144	2.79134	-0.40553
O	-0.27485	-3.85333	-0.48705
O	0.29037	3.90157	-0.17102
C	5.78007	-1.6065	-0.2849
C	-5.7609	1.63428	-0.02514
C	-6.96194	2.30134	0.26606
C	-4.51303	2.24021	0.24928
C	4.53427	-2.24846	-0.09697
P	-5.8646	0.01177	-0.81342
P	5.88852	0.12037	-0.80194
C	6.98431	-2.31037	-0.11916
H	7.92771	-1.79274	-0.27042
C	4.56837	-3.60081	0.30823
H	3.64663	-4.12328	0.53372
C	5.76395	-4.29195	0.46383
H	5.74023	-5.33232	0.77544
C	6.98645	-3.65173	0.2427
H	7.92308	-4.18631	0.3687
C	-4.53826	3.50865	0.86802
H	-3.61154	3.98536	1.16487
C	-5.7316	4.16422	1.14815
H	-5.70371	5.1399	1.62492
C	-6.95702	3.5669	0.84031
H	-7.89142	4.07338	1.06243
H	-7.90803	1.81488	0.04488
O	-6.22766	0.03385	-2.28214
C	-7.06658	-0.96142	0.15714
C	-8.16312	-1.52754	-0.50651
C	-6.91875	-1.15508	1.54011
C	-9.10268	-2.27865	0.204

H	-8.27168	-1.37551	-1.57595
C	-7.85753	-1.90544	2.24659
H	-6.0721	-0.7213	2.06605
C	-8.95041	-2.46751	1.57863
H	-9.95075	-2.71487	-0.31635
H	-7.73824	-2.05231	3.31637
H	-9.68102	-3.05189	2.13118
C	6.20353	0.2396	-2.5905
C	6.61931	1.44981	-3.14637
C	6.02941	-0.87889	-3.40549
C	6.86024	1.54159	-4.51705
H	6.75575	2.33162	-2.50369
C	6.27132	-0.7875	-4.77645
H	5.70189	-1.83284	-2.96751
C	6.68655	0.42251	-5.33234
H	7.18736	2.49562	-4.95536
H	6.13435	-1.66965	-5.41873
H	6.87663	0.4951	-6.41303
O	7.09564	0.94415	0.08594

4-*cis*-1-O

C	-3.11274	0.13421	-0.27386
C	-4.23326	-0.69145	-0.47423
C	-4.08312	-2.08811	-0.62232
C	-2.84457	-2.68717	-0.57129
C	-1.68184	-1.89677	-0.41443
C	-1.80818	-0.47336	-0.29726
H	-4.96548	-2.70093	-0.78299

H	-2.74425	-3.75953	-0.69183
C	-0.38529	-2.48487	-0.40055
C	-0.63325	0.32187	-0.23602
C	0.64642	-0.27921	-0.28209
C	0.76862	-1.70418	-0.34737
C	2.07448	-2.28463	-0.33564
H	2.11467	-3.36386	-0.39225
C	1.82147	0.51804	-0.2709
C	3.12749	-0.08795	-0.3094
C	3.22969	-1.54861	-0.26052
C	-3.21299	1.57691	-0.04299
C	-0.75729	1.74713	-0.1814
C	-2.06103	2.32073	-0.05797
H	-2.10085	3.39634	0.05135
C	0.39484	2.53086	-0.21331
C	1.69225	1.94634	-0.25052
C	2.85527	2.75098	-0.26405
H	2.75439	3.82845	-0.2066
C	4.24695	0.75924	-0.39662
C	4.09615	2.16347	-0.3594
H	4.98144	2.79134	-0.40553
O	-0.27485	-3.85333	-0.48705
O	0.29037	3.90157	-0.17102
C	5.78007	-1.6065	-0.2849
C	-5.7609	1.63428	-0.02514
C	-6.96194	2.30134	0.26606
C	-4.51303	2.24021	0.24928
C	4.53427	-2.24846	-0.09697
P	-5.8646	0.01177	-0.81342
P	5.88852	0.12037	-0.80194
C	6.98431	-2.31037	-0.11916

H	7.92771	-1.79274	-0.27042
C	4.56837	-3.60081	0.30823
H	3.64663	-4.12328	0.53372
C	5.76395	-4.29195	0.46383
H	5.74023	-5.33232	0.77544
C	6.98645	-3.65173	0.2427
H	7.92308	-4.18631	0.3687
C	7.06066	0.93113	0.33942
C	8.17773	1.58364	-0.19861
C	6.87061	0.916	1.73055
C	9.09659	2.21341	0.64449
H	8.31725	1.59364	-1.27523
C	7.78867	1.54578	2.56961
H	6.0065	0.41472	2.15927
C	8.90264	2.19456	2.02673
H	9.96082	2.71774	0.2213
H	7.63662	1.53178	3.64521
H	9.61695	2.68477	2.68252
C	-4.53826	3.50865	0.86802
H	-3.61154	3.98536	1.16487
C	-5.7316	4.16422	1.14815
H	-5.70371	5.1399	1.62492
C	-6.95702	3.5669	0.84031
H	-7.89142	4.07338	1.06243
H	-7.90803	1.81488	0.04488
O	-6.22766	0.03385	-2.28214
O	6.28983	0.3316	-2.2454
C	-7.06658	-0.96142	0.15714
C	-8.16312	-1.52754	-0.50651
C	-6.91875	-1.15508	1.54011
C	-9.10268	-2.27865	0.204

H	-8.27168	-1.37551	-1.57595
C	-7.85753	-1.90544	2.24659
H	-6.0721	-0.7213	2.06605
C	-8.95041	-2.46751	1.57863
H	-9.95075	-2.71487	-0.31635
H	-7.73824	-2.05231	3.31637
H	-9.68102	-3.05189	2.13118

4-1-Me (*trans*)

C	3.13714	-0.11644	-0.2733
C	4.26414	0.75186	-0.38113
C	4.12447	2.13299	-0.41135
C	2.85376	2.71741	-0.36078
C	1.72653	1.91573	-0.31623
C	1.84009	0.49782	-0.2814
H	4.99989	2.77074	-0.48048
H	2.73591	3.79489	-0.37793
C	0.38909	2.57546	-0.30755
C	0.65913	-0.30743	-0.26882
C	-0.65915	0.3074	-0.2689
C	-0.80211	1.69118	-0.271
C	-2.07551	2.28695	-0.21391
H	-2.08872	3.36867	-0.20656
C	-1.84011	-0.49786	-0.28124
C	-3.13715	0.11641	-0.27328
C	-3.24823	1.55324	-0.16004
C	3.24822	-1.55324	-0.15968
C	0.80209	-1.69122	-0.27052

C	2.07549	-2.28696	-0.21328
H	2.08871	-3.36869	-0.20562
C	-0.3891	-2.5755	-0.3068
C	-1.72655	-1.91578	-0.31568
C	-2.85377	-2.71747	-0.36003
H	-2.73592	-3.79495	-0.37689
C	-4.26416	-0.75193	-0.38085
C	-4.12449	-2.13306	-0.41074
H	-4.99991	-2.77082	-0.47971
O	0.28048	3.79879	-0.32833
O	-0.2805	-3.79884	-0.32721
C	-5.80405	1.63962	-0.11988
C	5.80403	-1.63965	-0.11975
C	7.00222	-2.33282	0.11236
C	4.54156	-2.25422	0.06217
C	-4.54156	2.25428	0.0617
P	5.90622	0.06391	-0.66477
P	-5.90626	-0.06405	-0.66453
C	-7.00222	2.33283	0.11216
H	-7.95587	1.83187	-0.02547
C	-4.55533	3.58646	0.52199
H	-3.6253	4.09464	0.74179
C	-5.74282	4.27643	0.74244
H	-5.7011	5.30201	1.09577
C	-6.97642	3.65752	0.53233
H	-7.90355	4.19215	0.71022
C	-7.16114	-0.97093	0.26321
C	-8.21001	-1.63373	-0.39329
C	-7.07555	-0.99803	1.66732
C	-9.16713	-2.32019	0.35497
H	-8.28895	-1.62247	-1.47479

C	-8.03575	-1.68704	2.40253
H	-6.26949	-0.48473	2.18296
C	-9.08049	-2.34677	1.74743
H	-9.97817	-2.83161	-0.15349
H	-7.97029	-1.70795	3.48573
H	-9.82809	-2.88125	2.32565
C	4.55535	-3.58625	0.52289
H	3.62533	-4.09433	0.74297
C	5.74285	-4.27619	0.74342
H	5.70115	-5.30165	1.0971
C	6.97644	-3.65737	0.53295
H	7.90358	-4.19197	0.71089
H	7.95587	-1.83193	-0.02552
C	-6.25937	-0.1512	-2.45027
H	-6.24923	-1.19104	-2.78769
H	-7.23089	0.30166	-2.66466
H	-5.47858	0.4061	-2.97414
C	6.32354	0.13619	-2.4348
C	6.83686	1.31198	-2.98298
C	6.13032	-0.98388	-3.24329
C	7.15621	1.36781	-4.33949
H	6.98836	2.19509	-2.34547
C	6.45064	-0.92851	-4.60003
H	5.72592	-1.91072	-2.81137
C	6.9634	0.24712	-5.14824
H	7.56023	2.29474	-4.77176
H	6.29857	-1.81192	-5.23716
H	7.21532	0.29136	-6.21776
C	7.14637	0.96653	0.31487
H	6.93462	0.84586	1.35674
H	8.12054	0.57867	0.10164

H	7.11306	2.00573	0.06216
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4-1-Me (*cis*)

C	3.13634	-0.11124	-0.28106
C	4.27036	0.74239	-0.42244
C	4.12187	2.12289	-0.46017
C	2.85481	2.71286	-0.37923
C	1.72291	1.91744	-0.30746
C	1.8379	0.49906	-0.27241
H	4.9972	2.75686	-0.56646
H	2.73839	3.79103	-0.39833
C	0.38955	2.57642	-0.26974
C	0.65851	-0.30706	-0.24654
C	-0.65867	0.3071	-0.24654
C	-0.80204	1.69239	-0.23974
C	-2.07776	2.28433	-0.18287
H	-2.09545	3.36617	-0.16425
C	-1.83806	-0.49899	-0.27294
C	-3.13651	0.11132	-0.28157
C	-3.24964	1.54664	-0.14978
C	3.24944	-1.54659	-0.14956
C	0.80189	-1.69234	-0.24023
C	2.07761	-2.2843	-0.18323
H	2.09536	-3.36616	-0.16499
C	-0.38968	-2.57636	-0.27106
C	-1.72304	-1.91736	-0.30848
C	-2.85492	-2.71278	-0.38056
H	-2.73848	-3.79093	-0.40005
C	-4.2705	-0.74231	-0.4232
C	-4.12199	-2.1228	-0.46129

H	-4.99731	-2.75676	-0.56766
O	0.27872	3.80266	-0.26425
O	-0.27884	-3.8026	-0.26653
C	-5.79902	1.61827	-0.1705
C	5.7988	-1.6182	-0.16979
C	6.99748	-2.31361	0.04971
C	4.54928	-2.23919	0.06281
C	-4.54953	2.23928	0.06224
P	5.90638	0.05936	-0.82962
P	-5.90672	-0.05946	-0.82983
C	-6.99775	2.31378	0.04847
H	-7.94507	1.81602	-0.13939
C	-4.57155	3.55839	0.56185
H	-3.64547	4.05847	0.81787
C	-5.76419	4.24188	0.7733
H	-5.73415	5.25679	1.15882
C	-6.98951	3.62574	0.50993
H	-7.92278	4.1546	0.67718
C	-7.11658	-0.95759	0.19516
C	-8.16895	-1.62425	-0.44662
C	-7.01778	-1.00005	1.59536
C	-9.11416	-2.32709	0.30425
H	-8.23981	-1.58666	-1.52922
C	-7.9625	-1.70303	2.34117
H	-6.20716	-0.48506	2.10434
C	-9.01109	-2.36667	1.69573
H	-9.92837	-2.84175	-0.19792
H	-7.88267	-1.73333	3.42406
H	-9.74643	-2.91342	2.27947
C	4.57116	-3.55818	0.5627
H	3.64499	-4.05817	0.8186

C	5.76377	-4.2416	0.77463
H	5.73366	-5.25642	1.16037
C	6.98913	-3.62546	0.51147
H	7.92238	-4.15425	0.67912
H	7.94485	-1.81587	-0.138
C	7.11682	0.95764	0.19454
C	8.17017	1.62223	-0.44778
C	7.0177	1.00196	1.59467
C	9.11603	2.32485	0.30247
H	8.24124	1.58328	-1.53033
C	7.96307	1.70475	2.33985
H	6.20632	0.48862	2.10409
C	9.01263	2.3663	1.69387
H	9.93099	2.83792	-0.20013
H	7.88296	1.73652	3.42268
H	9.74848	2.91289	2.27712
C	-6.28428	-0.10984	-2.60952
H	-6.23576	-1.12105	-2.95594
H	-7.26755	0.27764	-2.77664
H	-5.57148	0.48428	-3.1423
C	6.28311	0.10921	-2.6095
H	6.23364	1.12022	-2.95636
H	7.26661	-0.27758	-2.77687
H	5.57054	-0.48571	-3.14169

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C	1.41441	1.69128	1.33378
C	0.0382	2.23687	1.36349
C	-0.98128	1.47205	0.64167
C	-0.66609	0.2601	-0.01027
C	0.66609	-0.25973	0.00961
C	1.70856	0.45996	0.67844
C	-2.28741	1.9874	0.56426
C	-1.70859	-0.45969	-0.67895
C	-3.0568	0.04526	-0.68083
C	-3.32139	1.35576	-0.10815
C	-4.06554	-0.77127	-1.25618
C	-3.74604	-1.97216	-1.90173
C	-2.43209	-2.41653	-1.96041
C	-1.41443	-1.691	-1.3343
C	-0.03815	-2.23637	-1.36435
C	0.98129	-1.47169	-0.64232
H	-2.43893	2.93588	1.06662
H	-2.16213	-3.34048	-2.46111
C	3.05672	-0.04512	0.68054
C	2.43202	2.41667	1.96013
C	2.28735	-1.98715	-0.56473
C	4.06544	0.77129	1.25611
C	3.74593	1.97217	1.90167
H	2.16207	3.34063	2.46081
H	2.43888	-2.93563	-1.0671
O	-0.22431	3.29775	1.9614
O	0.22418	-3.29775	-1.96148
P	-5.81578	-0.39038	-1.05306

O	-6.73314	-0.82856	-2.16491
P	5.81568	0.39024	1.05327
O	6.73289	0.82829	2.16529
C	6.32722	1.18303	-0.52867
C	7.44317	2.02877	-0.50019
C	5.65339	0.97286	-1.74075
C	7.88149	2.65645	-1.66808
H	7.95305	2.18384	0.44613
C	6.09296	1.60029	-2.90604
H	4.78331	0.32307	-1.77759
C	7.20755	2.44279	-2.87139
H	8.74786	3.31311	-1.6374
H	5.56367	1.43381	-3.84086
H	7.54714	2.93219	-3.78124
C	-6.32697	-1.18316	0.529
C	-5.65296	-0.97288	1.74096
C	-7.44285	-2.02901	0.50075
C	-6.09227	-1.6003	2.90635
H	-4.78294	-0.323	1.77763
C	-7.8809	-2.65669	1.66874
H	-7.95288	-2.18418	-0.44548
C	-7.20678	-2.44292	2.87193
H	-5.56284	-1.43373	3.84107
H	-8.74721	-3.31344	1.63822
H	-7.54617	-2.93232	3.78185
H	-4.54595	-2.5503	-2.35664
H	4.54582	2.55021	2.35676
C	4.61654	-2.05189	0.29742
C	5.78885	-1.38958	0.73572
C	4.71559	-3.44954	0.10743
C	6.98005	-2.09294	0.96466

C	5.90584	-4.1362	0.31129
H	3.83565	-4.01576	-0.17488
C	7.05254	-3.46324	0.74514
H	7.84288	-1.54556	1.33469
H	5.93165	-5.21166	0.15166
H	7.97885	-4.00322	0.92289
C	-4.61675	2.05189	-0.2975
C	-5.78907	1.38945	-0.73557
C	-4.71591	3.44954	-0.10753
C	-6.98039	2.09268	-0.96432
C	-5.90626	4.13607	-0.31121
H	-3.83598	4.01585	0.1746
C	-7.05297	3.46298	-0.74483
H	-7.84323	1.54521	-1.33418
H	-5.93215	5.21153	-0.1516
H	-7.97937	4.00286	-0.92243
C	3.32128	-1.35562	0.10787

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C	1.41156	2.15515	-0.7077
C	0.00596	2.61989	-0.7349
C	-1.02387	1.57895	-0.76836
C	-0.68389	0.20865	-0.76574
C	0.68388	-0.2086	-0.76573
C	1.73279	0.76668	-0.74037
C	-2.37514	1.96247	-0.83645
C	-1.73281	-0.76663	-0.74052
C	-3.11149	-0.35272	-0.72602
C	-3.42619	1.05999	-0.86904

C	-4.10093	-1.35986	-0.57832
C	-3.75675	-2.71715	-0.55858
C	-2.42854	-3.11206	-0.64398
C	-1.41157	-2.1551	-0.70801
C	-0.00597	-2.61984	-0.73544
C	1.02386	-1.5789	-0.76855
H	-2.55013	3.03179	-0.86823
H	-2.14086	-4.15823	-0.63651
C	3.11148	0.35277	-0.72591
C	2.42853	3.11211	-0.64362
C	2.37513	-1.96241	-0.83661
C	4.10091	1.3599	-0.57814
C	3.75674	2.71719	-0.55829
H	2.14085	4.15827	-0.63601
H	2.55013	-3.03172	-0.86856
O	-0.27423	3.83375	-0.72795
O	0.27422	-3.83369	-0.72793
P	-5.82509	-0.94625	-0.25161
O	-6.85837	-1.915	-0.76502
P	5.82508	0.94627	-0.25149
C	-5.9701	-0.78863	1.57783
C	-5.13902	0.04485	2.34069
C	-6.96212	-1.54213	2.21777
C	-5.30141	0.12191	3.72363
H	-4.36216	0.63216	1.85881
C	-7.12278	-1.46393	3.60275
H	-7.59649	-2.18441	1.61396
C	-6.2934	-0.63223	4.35653
H	-4.65173	0.76877	4.3078
H	-7.89437	-2.05347	4.09248
H	-6.41673	-0.57151	5.43532

H	-4.54894	-3.4565	-0.4758
H	4.54893	3.45654	-0.47545
C	4.80607	-1.53802	-1.12431
C	5.95095	-0.73274	-0.91052
C	5.0316	-2.82399	-1.66707
C	7.23645	-1.19758	-1.22277
C	6.31008	-3.28791	-1.95001
H	4.18748	-3.46179	-1.90234
C	7.42807	-2.47636	-1.73196
H	8.08031	-0.52918	-1.07394
H	6.43233	-4.28499	-2.36672
H	8.42684	-2.83209	-1.97099
C	-4.80608	1.53812	-1.12424
C	-5.95096	0.73282	-0.91051
C	-5.03162	2.82414	-1.66689
C	-7.23646	1.19768	-1.22271
C	-6.3101	3.28808	-1.94978
H	-4.1875	3.46195	-1.9021
C	-7.42808	2.47651	-1.73179
H	-8.08032	0.52927	-1.07392
H	-6.43235	4.28519	-2.3664
H	-8.42686	2.83226	-1.97077
C	3.42618	-1.05993	-0.86906
O	6.85836	1.91506	-0.76483
C	5.97012	0.7885	1.57794
C	5.13907	-0.04506	2.34074
C	6.96213	1.54197	2.21794
C	5.30147	-0.12223	3.72367
H	4.36221	-0.63235	1.85882
C	7.1228	1.46366	3.60291
H	7.59647	2.18432	1.61417

C	6.29345	0.63188	4.35663
H	4.65181	-0.76915	4.3078
H	7.89438	2.05318	4.09268
H	6.41679	0.57107	5.43541

4-2-Me (*cis*)

C	3.13714	-0.11644	-0.2733
C	4.26414	0.75186	-0.38113
C	4.12447	2.13299	-0.41135
C	2.85376	2.71741	-0.36078
C	1.72653	1.91573	-0.31623
C	1.84009	0.49782	-0.2814
H	4.99989	2.77074	-0.48048
H	2.73591	3.79489	-0.37793
C	0.38909	2.57546	-0.30755
C	0.65913	-0.30743	-0.26882
C	-0.65915	0.3074	-0.2689
C	-0.80211	1.69118	-0.271
C	-2.07551	2.28695	-0.21391
H	-2.08872	3.36867	-0.20656
C	-1.84011	-0.49786	-0.28124
C	-3.13715	0.11641	-0.27328
C	-3.24823	1.55324	-0.16004
C	3.24822	-1.55324	-0.15968
C	0.80209	-1.69122	-0.27052
C	2.07549	-2.28696	-0.21328
H	2.08871	-3.36869	-0.20562
C	-0.3891	-2.5755	-0.3068
C	-1.72655	-1.91578	-0.31568

C	-2.85377	-2.71747	-0.36003
H	-2.73592	-3.79495	-0.37689
C	-4.26416	-0.75193	-0.38085
C	-4.12449	-2.13306	-0.41074
H	-4.99991	-2.77082	-0.47971
O	0.28048	3.79879	-0.32833
O	-0.2805	-3.79884	-0.32721
C	-5.80405	1.63962	-0.11988
C	5.80403	-1.63965	-0.11975
C	7.00222	-2.33282	0.11236
C	4.54156	-2.25422	0.06217
C	-4.54156	2.25428	0.0617
P	5.90622	0.06391	-0.66477
P	-5.90626	-0.06405	-0.66453
C	-7.00222	2.33283	0.11216
H	-7.95587	1.83187	-0.02547
C	-4.55533	3.58646	0.52199
H	-3.6253	4.09464	0.74179
C	-5.74282	4.27643	0.74244
H	-5.7011	5.30201	1.09577
C	-6.97642	3.65752	0.53233
H	-7.90355	4.19215	0.71022
C	-7.16114	-0.97093	0.26321
C	-8.21001	-1.63373	-0.39329
C	-7.07555	-0.99803	1.66732
C	-9.16713	-2.32019	0.35497
H	-8.28895	-1.62247	-1.47479
C	-8.03575	-1.68704	2.40253
H	-6.26949	-0.48473	2.18296
C	-9.08049	-2.34677	1.74743
H	-9.97817	-2.83161	-0.15349

H	-7.97029	-1.70795	3.48573
H	-9.82809	-2.88125	2.32565
C	4.55535	-3.58625	0.52289
H	3.62533	-4.09433	0.74297
C	5.74285	-4.27619	0.74342
H	5.70115	-5.30165	1.0971
C	6.97644	-3.65737	0.53295
H	7.90358	-4.19197	0.71089
H	7.95587	-1.83193	-0.02552
C	7.16115	0.97094	0.26275
C	8.21008	1.6335	-0.3939
C	7.07556	0.99839	1.66686
C	9.16725	2.32007	0.35419
H	8.28904	1.62195	-1.47541
C	8.0358	1.68753	2.4019
H	6.26946	0.48528	2.18262
C	9.08059	2.34701	1.74664
H	9.97833	2.8313	-0.15439
H	7.97032	1.70872	3.48509
H	9.82822	2.88159	2.32473
C	-6.25937	-0.1512	-2.45027
H	-6.24923	-1.19104	-2.78769
H	-7.23089	0.30166	-2.66466
H	-5.47858	0.4061	-2.97414
C	6.25925	0.15072	-2.45054
H	6.24922	1.19051	-2.78813
H	7.23071	-0.30229	-2.66491
H	5.47837	-0.40656	-2.97429

Chapter Five: Conclusions and Future Outlook

5.1. Conclusion

In this thesis, annulation of Vat Orange 3 with phosphorus-containing heterocycles was accomplished in various ways. Extending the conjugation in Vat Orange 3 through incorporation of phosphorus centres establishes a new platform toward accessing highly sought-after properties for materials chemistry and biochemistry. Vat Orange 3 has a distinct framework among all vat dyes; the juxtaposition of core anthanthrene with halogens and keto groups give rise to an intriguingly malleable system whose electronics can be pushed to extreme cases.

While converting the keto groups to $\text{OC}_{12}\text{H}_{25}$ seems a necessary measure for addressing (in)solubility issues, it is an important method for injecting electron density into the core and setting the stage for production of electron-rich materials. Addition of trivalent phosphorus centres into the structure (similar to amines) enhances this electron-rich character; yet introduction of phosphoryl ($\text{P}=\text{O}$) or phosphonium ($\text{P}-\text{Me}$) groups reverses this effect. Notably, P-modification is not the only key parameter for property tuning, as the presence of two inherent conjugation routes in the original Vat Orange 3 scaffold and installation of substituents along them can amplify these effects. In the context of this research, we were able to demonstrate that sacrificing the keto groups is not a mandatory compromise, and their restoration represents a significant advancement in improving the electron-accepting character of these materials.

At the heart of this thesis lies the recognition of the promising synergy of “phosphorus + VO3” can offer a wealth of opportunities, but more importantly, when the concepts mentioned above are

applied to a common core, they can unlock a vast range of photophysical and electrochemical properties critical to organic electronic devices.

Finally, the results presented in Chapter 2-4 provide answers to the questions posed at the end of Chapter 1:

Despite the lower ratio of phosphorus moieties to hydrocarbon backbone in these structures, phosphorus still exerts pronounced control over the electronics. This is due to its involvement in the conjugation, as evident in the LUMO of most of the synthesized conjugated materials.

Therefore, introducing different substituents on phosphorus through P-modification can alter the optical and electrochemical properties as demonstrated by characterized materials in Chapter 2. Interestingly, when the native Vat Orange 3 structure with keto groups was present as the core, a simultaneous (significant) energy reduction for both FMOs occurs, however, with unaffected energy gap. Therefore, even though the electrochemical behaviour is adjusted, the optical properties remain largely unchanged.

The supramolecular organization of different isomers arising from phosphorus-based stereochemistry is impacted differently from the orientation of the P-substituents. The effects are large enough to dictate different packing modes in *cis* and *trans* isomers, but not sufficient to cause different optical behaviours in the solid-state (Chapter 2).¹ Notably, the -OC₁₂H₂₅ alkyl chains act as the structural equalizer between isomers. Once removed, the emissive behaviour of these isomers in the solid-state is not identical anymore and it is likely dominated by the distinct intramolecular interactions in the solid-state (Chapter 4).

5.2. Future outlook

In the following section, further structural variations to the scaffolds presented each chapter will be proposed and the specifically targeted properties for each species will be addressed. The simple placement of phosphorus into the conjugation pathway produces **5-1** (Figure 5-1), the regioisomer of the main target structure in Chapter 2. According to the DFT calculations at the B3LYP/6-31G(d) level of theory, this will cause a 0.19 eV reduction in energy gap through destabilization of HOMO (stronger) and LUMO. This is also seen in the related regioisomeric congener discussed in Chapter 3. Also, modifying the P-functionalities in **5-1** will likely have a further impact on the electronics and in turn expected properties.

As it was discussed in Chapter 1, addition of nitrogen heterocycles such as pyridine and pyrazine in smaller synthons is an established method of increasing the electron-accepting character in π -organic materials (Figure 1-8). The selection of pyridine over benzene as terminal rings in **5-2** can likely give rise to the gain of multiple electrons while improving the subsequent stability of the reduced species (Figure 5-1). Moreover, methylation of the nitrogen and phosphorus centers generate the tetracationic species **5-3** with the expectedly marked lowered reduction events that should be able to accept up to four electrons.

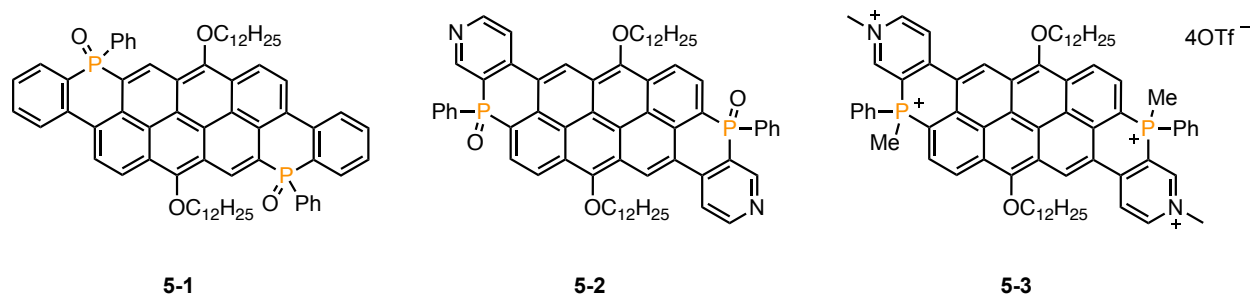


Figure 5-1. New proposed structures based on target species in Chapter 2.

As it was observed for all the synthesized conjugated materials in Chapters 2-4, the identity of all the oxidation events were found to be irreversible or indeterminate. However, the presence of both reversible oxidation and reduction processes is essential for materials intended for use in organic batteries, particularly redox-flow batteries. The conversion of the pentavalent phosphoryl group to a trivalent phosphine can remedy this issue to some extent, but the limited stability of such species under ambient condition (discussed in Chapter 2) may impede their broad application. The Morin group's work on Vat Orange 3-based scaffolds bearing TIPS-acetylene or amine groups highlights the emergence of one and two reversible oxidation events in the voltammogram of these compounds, respectively.^{2,3} Consequently, the adoption of such groups instead of $-\text{OC}_{12}\text{H}_{25}$ as suggested in compounds **5-4** and **5-5** will likely trigger controlled ambipolar behaviour that is desired in materials chemistry (Figure 5-2).

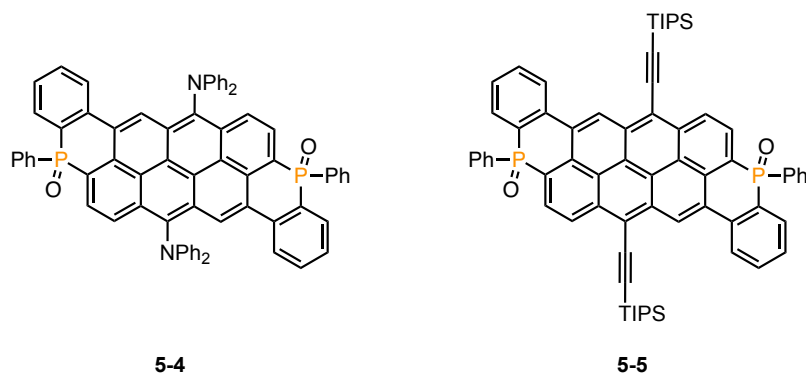


Figure 5-2. VO3-based systems with potential ambipolar property.

In the past few decades, π -organic systems with twisted backbone have attracted lots of attention.⁴ This is due to suppression of aggregation-caused quenching, better solubility, and enhanced properties such as thermally-activated delayed fluorescence (TADF). As elaborated in Chapter 2,

the examined compounds are endowed with twisted π -systems with torsion angles of up to 16.7° because of H-H repulsion of the bay region.

Increasing the steric profile of the incorporated units could thus enhance the curvature in these systems. As exemplified by the proposed structure **5-6**, the replacement of the terminal benzenes with phenanthrene units can achieve this effect while also extending the π -conjugation of this system (Figure 5-3).

Nonetheless, using common heterocycles as ring-fusion partner for phosphorus is not the only method of achieving novel compounds. For instance, employing 1,2-dichlorocyclobuten-3,4-dione with a diketo group on a cyclobutene ring can lead to the generation of **5-7**. Although **5-7** promotes the aromatic character of the 4-membered ring, reduction of the keto units can favour its antiaromaticity, presenting an intriguing system to explore. Furthermore, having 4 keto and 2 phosphoryl groups could potentially lead to acceptance of up to six electrons by this compound.

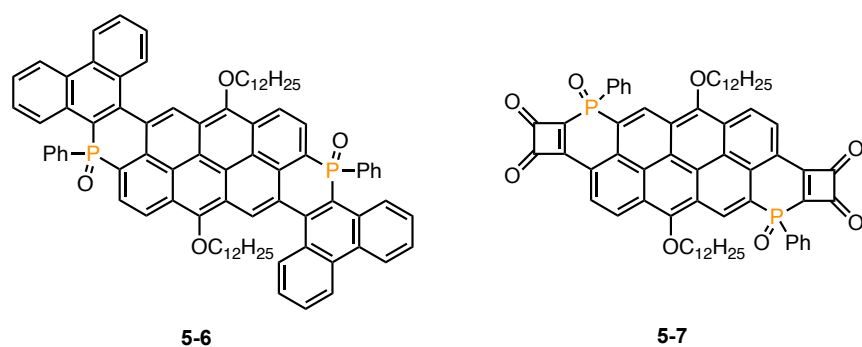


Figure 5-3. Exploiting phenanthrene and cyclobutene-based moieties for ring closure.

Conjugated materials with TADF properties have been attracting increasing attention as they are highly valuable in cutting-edge technologies.⁵ From OLEDs to photodynamic therapy and sensing, their ability to harvest their singlet and triplet excited states, makes them exceptionally valuable. The key to achieve this property in compound is the tailored separation of HOMO and LUMO in

a molecule as it reduces the energy gap between singlet and triplet state through weakening the exchange interaction. Once the ΔE_{ST} is reduced (<0.1 eV), these states can communicate effectively, and TADF is induced. Separation of HOMO and LUMO is typically accomplished through designing twisted systems (mentioned above) or orthogonal arrangement. Therefore, substitution of $-OC_{12}H_{25}$ with sterically bulky carbazole or anthracene units is anticipated to enforce an orthogonal arrangement relative to the anthanthrene core (**5-8** and **5-9**). Given their conjugated nature and strong electron-donating ability, they are promising candidates for promoting TADF in these materials (Figure 5-4).

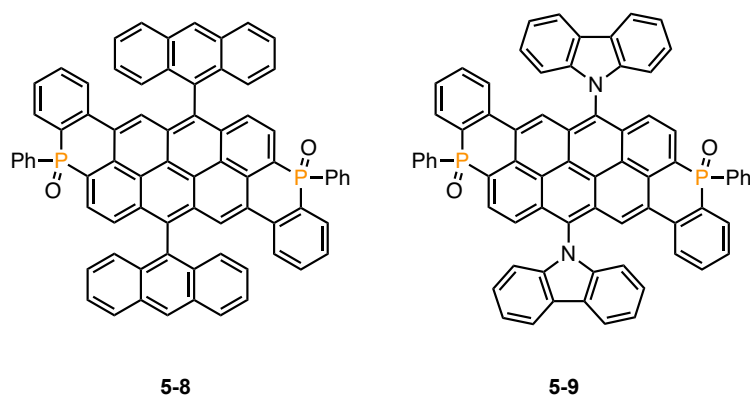


Figure 5-4. Proposed structures with potential TADF behaviour.

As the luminescence wavelength progress further into the NIR-I (700-950 nm) and NIR-II (1000-1700 nm) regions, non-invasive fluorescence imaging gets more efficient as the background fluorescence of the biological molecules present in tissues gets weaker.⁶ Consequently, although the materials synthesized in Chapter 3 exhibit emission maxima at the onset of the NIR-I region, their utility could be improved by red-shifting the emission. Accordingly, investigation of the influence of P-modification on the π -organic systems shows that installation of a second P-phenyl

group (phenylphosphonium) on the phosphorus yields an even stronger stabilization on the FMO energy levels than methyl.⁷ Corresponding DFT calculations reveal that is indeed the case for **5-10** since the energy gap is lowered to 1.93 eV (Figure 5-5). Moreover, the LUMO undergoes a pronounced down shift of 0.85 eV, to -4.57 eV, which is an impressively low value and comparable to the ultra-electron-deficient materials reported by the Mukhopadhyay group.⁸ Additionally, utilizing different acetylene reagents with potent electron-withdrawing groups such as dimethylpyridine acetylene, can give rise to hexacationic species **5-11** with likely even stronger electron accepting properties. Alternatively, the -OC₁₂H₂₅ group in **5-10** can be converted to the original keto groups, which will most likely direct the changes in a similar direction.

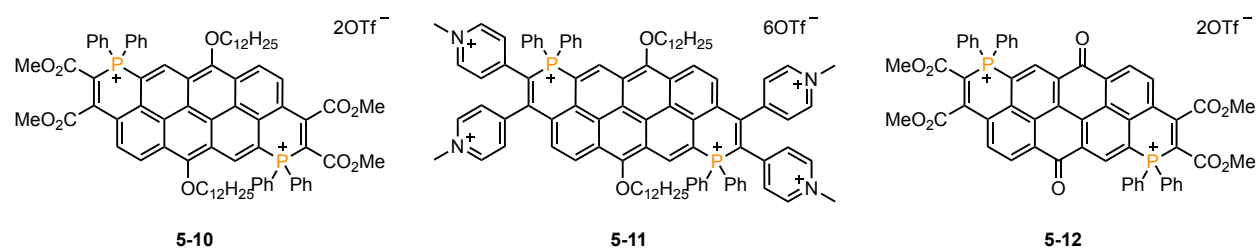


Figure 5-5. Target compounds with very strong electron-accepting characters.

Diphenyl acetylene has been widely employed in Ag-mediated oxidative coupling reactions with phosphorus. We therefore believe **5-13** lacks the high novelty we aim to achieve (Figure 5-6). However, **5-13** can open up the way to the synthesis of **5-14** with extensive conjugated nanocarbon scaffold through a Scholl reaction. It would also be interesting to explore if this procedure caused the restoration of the keto groups or compound **5-14** (or both).

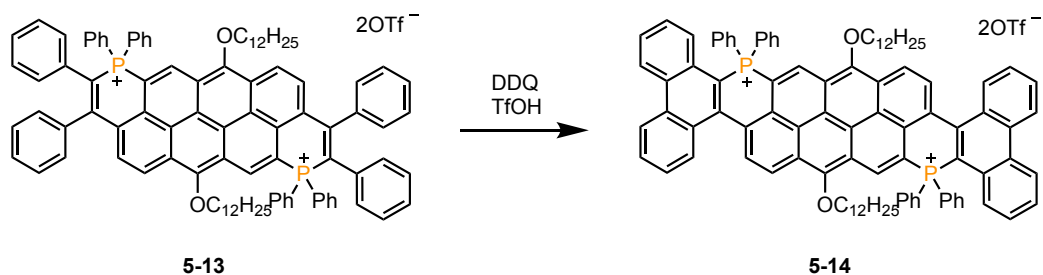


Figure 5-6. Suggested method to develop a P-containing expanded nanocarbon.

The low solubility of the conjugated materials reported in Chapter 4 is problematic for their characterization. This inherent shortcoming can be addressed by using the commercially available 1,2-dibromo-*tert*-butyl-benzene in an aim to install a coupled of *t*-butyl groups on the scaffold (**5-15**, Figure 5-7). This can however bring about the downside of diminishing π - π interactions in the solid state.

One of the challenges faced in Chapter 4, was the inseparable mixture of *cis* and *trans* species for P-methylated products, which made the characterization difficult as the properties of such isomers tend to be similar, if not identical. As suggested above, installation of the second exocyclic phenyl group only leads to formation of one possible compound. Moreover, functionalization of the second phenyl tends to have highlighted influence for tuning the properties. Compound **5-17** will more likely show even lower and more reversible reduction potentials for all the events originating from both the phosphoryl and keto groups.

As it was discussed in Chapter 4, the inclusion of carbonyl groups in the synthesized species alone was not successful in imposing the effective intersystem crossing and activation of phosphorescence. We believe the heavy atom effect coming from the addition of two bromine or iodine atoms in structures such as **5-18** can intensify the spin-orbit coupling and hopefully induce phosphorescence in these systems.⁹

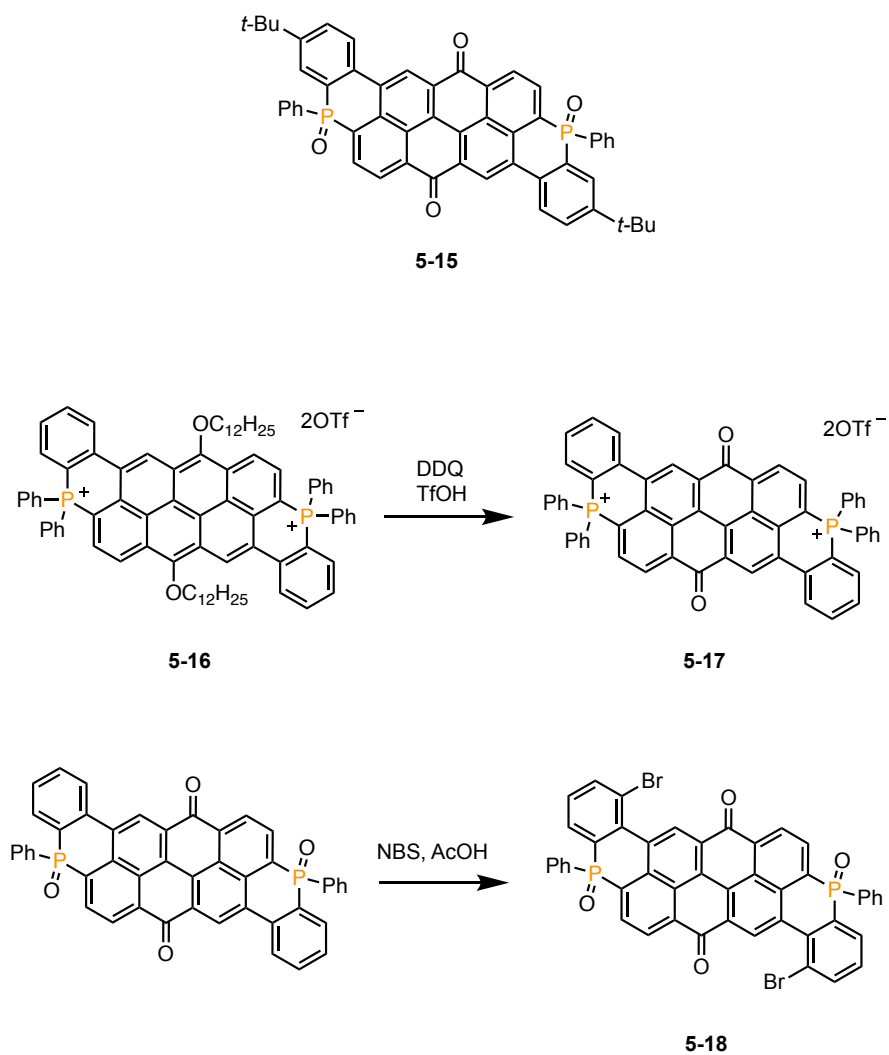


Figure 5-7. Proposed structures to solve the challenges faced in Chapter Four. **5-15** (better solubility), **5-17** (only one isomer with potentially enhanced properties), **5-18** (targeted phosphorescence).

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